THE
SCIENCE OF PETROLEUM

VOLUME III

THE SCIENCE OF PETROLEUM

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

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ADSORPTION

By **ALEXANDER KING, M.Sc., A.R.C.S., D.I.C.**

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THE phenomenon of adsorption was first remarked by Scheele in 1773 and received the attention of most of the masters of chemical science of the time At the beginning of the nineteenth century de Saussure carried out a quantitative investigation which established the fact that all porous substances such as wood, charcoal, asbestos, meerschaum, &c , take up various gases, heat being evolved in the process Adsorption was defined as the concentration or retention of substances at surfaces The decolorizing and deodorizing properties of charcoal were early applied in industry while knowledge of adsorption was in a still very rudimentary state At present adsorption is receiving very intensive study, some 3,000 papers on the subject having appeared during the last decade

Adsorption is a universal phenomenon occurring at every solid and liquid surface, its extent depends on surface area and is, therefore, small on liquids and crystalline solids, where its influence is not usually of primary importance Adsorption may take place by many different types of mechanism, no one theory being capable of explaining all the different manifestations of the phenomenon

Sorption has been proposed as a general term to cover the various processes by means of which molecules may be removed from a gas or a liquid by a surface, especially if the nature of the process is not specified When a gas is put into contact with an adsorbent such as charcoal there is a rapid decrease in the volume or pressure of the gas, which is completed within a few seconds, this is usually a physical process since it can be carried out with the inert gases, and consists in the condensation or *adsorption* of molecules on the surface of the adsorbent After this rapid intake of gas by the solid, there is a slow sorption of gas which may continue for long periods and is due to diffusion of the molecules along cracks or capillaries, or to *absorption* or solid solution in the interior of the adsorbent The initial fixation may also be chemical in nature and lead to the formation of a surface compound, in which case it is known as *chemisorption* It has long been realized that adsorption and catalysis are intimately related, hence many adsorbent surfaces are efficient catalysts, the adsorption cum catalytic effect of many surfaces is effective in industrial purification processes

The Liquid Surface

In the interior of a liquid or solid, each molecule or ion is, on the average, symmetrically surrounded by other molecules, and there is thus no residual attraction in any particular direction If the surface layer only is considered different conditions are found to prevail, each surface molecule or ion is attracted inwards and to each side by its neighbours, but there is no compensating outward force to balance the inward pull, and so every surface possesses a strong inward attraction perpendicular to the surface In liquids, where there is complete molecular mobility, this force tends to reduce the surface and gives rise to all the forces associated with surface tension The surface of a liquid is thus a seat of energy, and work must be done if its area is to be extended

The surface energy of any system will tend to reduce to a minimum, if, therefore, a substance is dissolved in a liquid, the molecules of solute and solvent will distribute themselves in such a manner that the surface tension is as low as possible Now if solvent molecules attract one another less strongly than they do solute molecules, the presence of the latter at the surface will increase the surface tension and, owing to the mobility of the system solute, will tend to be pulled into the liquid and accumulate in it away from the surface If, on the other hand, solute molecules have smaller fields of forces than solvent molecules, they will be subjected to a smaller inward attraction from the surface, and will thus tend to accumulate there with a resultant lowering of the surface tension In other words, a dissolved substance will be adsorbed at the surface of a liquid if it can thereby bring about a lowering of the surface tension, if it raises the surface tension the solute will collect in the bulk of the liquid away from the surface layer—will be negatively adsorbed This fundamental relationship is expressed quantitatively by the Gibbs equation

$$U = -\frac{C}{RT}\frac{d\sigma}{dC},$$

where U is the excess of substance at the interface, C its concentration in the volume of liquid, σ the surface tension, R the gas constant, and T the absolute temperature

Generally, minute concentrations of suitable materials are sufficient to bring about a finite reduction in surface tension, this being easily understood when it is realized that a unimolecular layer adsorbed at the surface is sufficient to bring it about

The concept of the unimolecular layer is fundamental in all adsorption studies The reality of monomolecular films on liquid and solid surfaces has been demonstrated by optical, thermal, electrical, and chemical methods Especially interesting in this connexion is the work of N K Adam and others [1] on films of organic materials, which has yielded evidence of the state as well of the existence of unimolecular films It appears that the molecules of the unimolecular layer are always orientated in the same direction, thus with a good aqueous surface tension depresser such as soap, it is found that the molecules are arranged with their main carbon atom axes perpendicular to the surface, the polar end of the molecule being submerged and the hydrocarbon chain projecting out of the water It is noticed that the groups which tend to pull molecules into the water are normally those which confer solubility to organic compounds Monomolecular films on liquids may exist in different physical states, corresponding to the solid, liquid, or gaseous states of ordinary three-dimensional physics, there being definite energies of transformation between the states There is evidence that unimolecular films on solids are also orientated

The Solid Surface

The properties of the solid surface, although governed essentially by the same factors, are profoundly modified by the rigidity of the surface atoms, which prevents the manifestation of surface-tension effects The surface energy of a solid, however, also strives to reduce itself and this is accompanied just as in the case of liquids, by adsorption The study of energy relationships at the solid interface is difficult owing to the enormous complexity of the surface, which in the case of highly porous substances such as charcoal may be so great that no two adjacent atoms possess the same energy Unfortunately the large proportion of the work on adsorption has been carried out with complex commercial adsorbents of this type which can fix large and thus easily measurable amounts of material Owing to surface complexity such results are seldom of use in discovering the mechanisms of the processes involved and indeed it is almost impossible to obtain reproducible results, probably no two samples of charcoal surfaces with properties quantitatively and qualitatively identical have ever been prepared Information of more theorical importance is obtained from studies of adsorption on the surfaces of metals and polar crystals

Surface energy is reduced by adsorption a system such as that represented in Fig 1, for example, must possess at its surface, strong cohesional forces similar to those which hold the metal together in the interior of the lattice Such forces are chemical in nature and suggest that surface energy would be reduced by combination of the surface atoms with some readily accessible gas with which the metal is normally capable of reacting, and it is, in practice, very difficult to free many surfaces from oxygen Initial proof of the existence of surface compounds—unimolecular chemisorbed layers—came from Langmuir's work [11, 1913–16], on the tungsten filament At low pressures a unimolecular film of oxygen was adsorbed on the metal, which was stable even at 2,000° The presence of this film could be demonstrated by its effect in lowering the electron emission of the filament, in inhibiting the dissociation of hydrogen, and in combining with further amounts of oxygen to form the normal oxide which remained as a visible layer on the surface below 1,000° C yet distilled off at higher temperatures These and other properties could only be explained by assuming that the oxygen in the form of atoms was bound to the surface by ordinary chemical forces as is represented in Fig 2

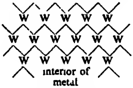


FIG 1

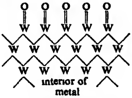


FIG 2

When carbon monoxide is allowed to react with a tungsten filament at low temperatures, a unimolecular layer is chemically attracted, presumably with the formation of a surface carbonyl as indicated in Fig 3 On raising the temperature, $W = C = O$, distils off showing that the chemical linkage between the carbon monoxide and the metal is stronger than that which holds the atoms of tungsten together

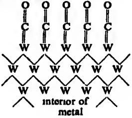


FIG 3

In a similar manner many other surfaces may be covered with unimolecular layers of chemically held atoms or radicals, that of carbon, for example, being normally covered by an oxide film At low temperatures charcoal adsorbs oxygen by physical forces and on evacuating the adsorbent the gas can be recovered in the elementary condition At higher temperatures the oxygen becomes chemically attached and cannot be recovered by lowering the pressure, on heating the charcoal the oxygen is finally obtained but in the form of oxides of carbon [17, 1912, 18, 1929] Surface compounds are of special significance in the study of specific adsorption and catalysis at surfaces

Surface energy can be reduced by retention of molecules by physical as well as by chemical forces, true *ad*sorption being a more widespread phenomenon than its chemical counterpart Physical adsorption is due to the same cohesional force that causes, for example, the liquefication of the inert gases and is, therefore, often referred to as van der Waals adsorption While chemisorption is an irreversible process, physical adsorption is reversible

Van der Waals forces are little affected by the presence of other molecules, thus the first layer of adsorbed molecules will thus still have van der Waals forces emanating from them and should be able to adsorb further layers of adsorbate Such forces, however, only become appreciable at pressures near the saturated vapour pressure, since they are of the same order as those operating between the molecules of a gas, in which condensation can only take place when the concentration is sufficiently high

It has long been known that the vapour pressure above the meniscus of a liquid in a narrow capillary is lower than that of the free liquid at the same temperature, in other words, a vapour will condense at a lower pressure in a porous solid composed of minute capillaries than it would at a plane surface, a fact which is obviously connected with the phenomenon of adsorption Assuming that the typical adsorbent consists of an inert rigid aggregate of cylindrical micropores in which the adsorbate is held in the form of liquid with a concave meniscus, then the pressure (p') above the meniscus is less than that (p) above a plane surface at the same temperature The quantitative relationship is given by the Kelvin equation

$$\log_e \frac{p'}{p} = \frac{2v\sigma}{RTr},$$

where v is the volume of the liquid, σ its surface tension, and r the radius of the capillary Thus if a vapour below its critical temperature is brought into contact with the porous adsorbent, it should condense as a liquid in all pores which have a radius smaller than that calculated for the particular value of p from the above equation Assuming this *capillary condensation* mechanism to be operative, it is possible by combination of the adsorption isotherm with the Kelvin equation to obtain a structural analysis of the adsorbent.

Attempts have been made to apply capillary condensation as a general theory of adsorption, but in illustration of the arguments against this may be mentioned the fact that the magnitude of pore radii, as calculated above, is often of the same order or even less than that of the adsorbed molecules and also that there is little difference in the adsorption of a gas above and below its critical temperature From the great mass of available data on the adsorption of vapours by porous adsorbents we may conclude that capillary condensation must undoubtedly occur and is probably the most important factor when the pressure of the vapour is approaching saturation, for gases above their critical temperature and for vapours at low relative pressures it is certainly inoperative

It is a well-known fact that the amount of substance adsorbed at a given pressure decreases with rise in temperature as must be the case since the heat of adsorption is always positive A typical isobar is represented by Fig 4, curve *A* A few systems have recently been investigated [5, 1930, 13, 1932], in which the isobar has the anomalous shape of Fig 4 *B* and *C*), indicating that adsorption is actually increasing with temperature on one part of the curve In these instances it is invariably found that the time required for equilibrium is short on the low temperature part of the curve and much longer on the higher temperature part It thus seems as if two processes, a fast one and a slow, are taking place side by side at the higher temperature In some cases it is possible actually to estimate the quantities taken up in each way The heat of adsorption in the low temperature range indicates a normal van der Waals adsorption, while that for the higher temperatures is of a higher order Further, the slow, high temperature process possesses a temperature coefficient, so that from the velocity coefficients at two temperatures an energy of activation can be calculated In order to explain these facts Taylor [20, 1931] postulates a further type of adsorption which he terms *Activated adsorption*, which will proceed at an immeasurably slow rate at low temperatures, but which, on raising the temperature, ultimately becomes very fast In the actual isobar, curve *B* represents the van der Waals adsorption while *C* shows that of the activated adsorption which in the dotted region before the point of inflection *X* of the experimental curve is immeasurably slow As might be predicted, an enhanced equilibrium value at a given low temperature can be obtained by allowing the system to attain equilibrium at a high temperature and then cooling down In activated adsorption the adhesion forces are probably chemical in nature, the process consisting in the conversion of a unimolecular layer of physically held molecules to the chemisorbed condition It should be noted here that many of the experimental facts of activated adsorption can be interpretated by other means, viz displacement of impurities from the surface [3, 1932] and diffusion into the interior [22, 1931]

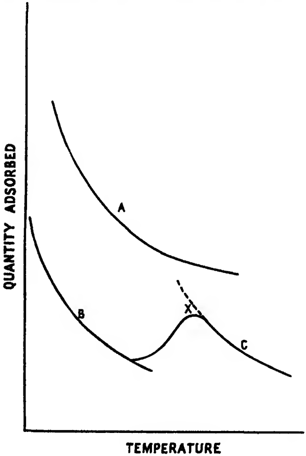


Fig 4

In concluding this section, mention should be made of a process of *electroadsorption*, which is effective in the many purification processes in which the impurities are particles of colloidal dimensions Silica gel which is negatively charged will remove positive colloidal particles, whereas positively charged adsorbents such as alumina will remove the more common negative colloids All commercial adsorbents are charged colloids of the solid foam type and precipitate, in the normal way, particles charged in the opposite sense, the coagulated impurities being retained within the pores This important process is thus to be regarded as an example of mutual precipitation of colloids rather than of true adsorption

The Adsorption Isotherm

For most practical purposes it is necessary to express the relationship between the weight (x) of substance adsorbed by a given weight (m) of adsorbent and the concentration (or in the case of a gas, the pressure) of adsorbate (p) This function

$$\frac{x}{m}=f(p),$$

or its graphical representation at a given temperature is known as the adsorption isotherm As adsorption can be regarded as the distribution of a substance between two phases, it might be supposed that the amount adsorbed per unit weight of adsorbent would be directly proportional to the equilibrium concentration in analogous manner to the Henry's law relationship for the solubility of gases in liquids As a result of numerous investigations it may be stated that, while at low pressures or concentrations this is generally the case, deviations become considerable as soon as medium concentrations are reached, the amount adsorbed at a given concentration being much less than it would be if Henry's law were still valid That the adsorption isotherm is, as a rule, concave to the pressure axis is shown in Fig 5, where a number of isotherms for systems of widely different type are represented.

The first attempt at a quantitative formulation of adsorption led to the employment of the empirical relationship known as the Freundlich isotherm.

$$\frac{x}{m}=kp^{1/n},$$

k and n are constants for a given system at a given temperature and have no physical significance This equation does not reduce, at low values of x and p, to the Henry's law relationship characteristic of adsorption at low pressures, but it does hold fairly well over restricted pressure ranges and for systems of widely different character On plotting $\log x$ against $\log p$, a curve, rectilinear over small distances but nearly always slightly concave to the $\log p$ axis is obtained Owing to its versatility the Freundlich isotherm offers a useful and widely used method of expressing and comparing adsorption results As a means of elucidating the mechanism of the adsorption process it is useless owing to its empirical nature and consequently numerous other attempts have been made to devise an equation based on theoretical considerations Langmuir, assuming that adsorption results in the formation of unimolecular surface films, and regarding the process as being essentially kinetic in nature, arrives at the expression

$$\frac{x}{m}=\frac{abp}{1+ap}$$

for adsorption at a homogeneous, plane surface [12, 1915–18] It will be noticed that this equation reduces to the Henry's law relationship for low values of p, while for high pressures $x/m = b =$ a constant, the adsorption tending to a maximum, saturation value

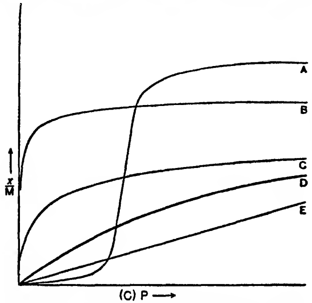


FIG 5 Some typical adsorption isotherms on charcoal A Water, B Toluene, C Benzoic acid (in water), D Nitrogen at 0° C, E Krypton at 0° C Curve B is the most typical

The Langmuir equation is, in general, somewhat more satisfactory than that of Freundlich but the constants are still empirical and incapable of deduction from the mechanism postulated The most important contribution of Langmuir is that of the unimolecular layer, which, as we have already seen, is now supported by direct experimental evidence and may be taken as the generally accepted view

Probably the most significant feature of the experimentally obtained isotherm is the large amount of adsorption at exceedingly low pressures or concentrations (cf initial part of curve *B*, Fig. 5) It is this which enables small amounts of impurities to be removed by the adsorbent from dilute solution in a liquid or a gas and thus makes possible its practical application.

Until recently it has always been assumed that the amount of material adsorbed is a continuous function of the pressure, but evidence has accumulated within the last few years which suggests that the adsorption isotherm may be discontinuous, being composed of a series of intersecting curves, so small that one continuous curve is generally drawn with the individual points lying somewhat irregularly about it In some cases, as in that of the adsorption of carbon tetrachloride on silica gel (Fig 6), the isotherms seem to consist of a series of rectangular steps [2, 1931, 6, 1933] The experimental technique on which these results are based seems to be sufficiently sensitive but no satisfactory explanation has yet been proposed

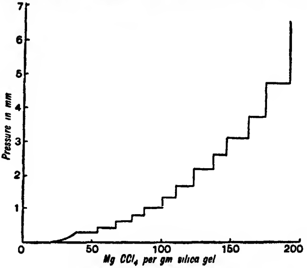


FIG 6 Adsorption of carbon tetrachloride on silica gel (Allmand and Burrage)

Complex Nature of the Solid Surface—Active Centres

The limited mobility of the atoms of a solid causes the surface structure to remain in the state in which it was formed unless very drastic measures (such as polishing) are taken to modify it When the bright surface of a metal is examined microscopically it is seen to consist of numerous pits and elevations, and there is every reason to suppose that the submicroscopic structure is even more irregular; even in the case of optically perfect crystals, the existence of deep fissures—so called Smeckal cracks—has been proved The surface of a piece of bright nickel may be represented diagramatically thus

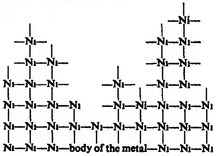


FIG 7

It is immediately obvious that even in the relatively simple case of a metal there is a considerable variation in the position and manner of linkage of the surface atoms and that physical and chemical properties must vary from atom to atom on the surface, edge, peak and corner atoms being especially active When more complicated surfaces such as charcoal or activated earths, which have been formed quickly by disruptive action, are considered, it is clear that there are infinite possibilities for the formation of pits and cavities resulting in variability of surface properties

The extreme activity of a small portion of a surface is very marked in catalytic reactions in which the intermediate formation of adsorption complexes is an important mechanism In some cases surface heterogeneity is itself necessary for catalysis Thus while chemically reduced copper is an excellent oxidizing catalyst, the metal deposited by electrolysis from aqueous solution is quite inactive [15, 1924]

By far the weightiest evidence for the existence of active centres, that is to say the small portions of the surface which possess a greater activity for adsorption and catalysis than the rest, comes from a study of catalyst poisoning In many instances catalytic activity may be diminished or even completely inhibited by tenacious adsorption of some foreign substance, in quantity greatly insufficient to form a unimolecular layer over the whole surface [19, 1925, 4, 1925] An impressive illustration of this emerges from the work of Vavon and Husson [21, 1922] on the effect of poisons on the hydrogenation of organic compounds in the presence of platinum black The clean catalyst, for example, was able to facilitate the reduction of dipropyl ketone, after adsorption of a mere trace of carbon disulphide the surface became inert for this reaction, but was still capable of reducing piperonal On the admission of a further small quantity of the poison, piperonal was no longer reduced but nitrobenzene was still attacked It is thus clear that platinum black must contain at least three levels of surface of varying activity In a similar manner it has been shown that the charcoal surface contains portions of great, of medium, and of low activity The high activity of the active centres is also proved by the fact that the heat of adsorption of a clean charcoal surface for the first traces of oxygen, sufficient to cover only a small fraction of it, is 224,000 cal For comparison it should be stated that the heat of combustion of solid carbon is 97,000 cal and of gaseous carbon 380,000 cal [14, 1927] It would thus seem that the atoms forming the active centres of carbon are in a state intermediate between that of gas and solid, which is exactly the state of affairs envisaged in Fig 7 for the peak atoms of a solid surface

The enhanced activity contributed to a surface by its active centres is often its most conspicuous characteristic, any correlation between surface properties and structure must, therefore, be made with the utmost caution as the small proportion of active surface may not be recognized by physical methods of exploration such as electron diffraction, and the properties of the active centres thus erroneously related to the structure of the larger, inert surface

Specific Adsorption

The fact that a substance is capable of retaining on its surface relatively large amounts of other compounds is not in itself sufficient to make the process of adsorption useful for purification purposes The adsorbent must be capable of removing from a mixture of compounds, small amounts of impurities—it must display selective action Preferential adsorption is largely a matter of the chemical relationship between adsorbent and adsorbate. An excellent illustration of this is offered by the contrasting properties of silica gel and charcoal The former substance is strongly hydrophilic and is thus continually striving to become hydrated, in the presence of water vapour therefore, other substances adsorbed on the gel surface will tend to be displaced by the water Silica gel is thus the adsorbent par excellence for drying purposes, but its use as a refining adsorbent for mixtures, which may contain moisture, is limited for the same reason Apart from its predilection for water, silica gel is remarkably unspecific in action Charcoal, on the other hand, is usually hydrophobic and adsorbed water is immediately displaced by hydrocarbon or other organic vapours, thus this substance will act as an efficient gas mask adsorbent even in an atmosphere saturated with water vapour The charcoal surface is rich in active centres which favour specific retention by chemisorption and consequently catalytic action

The nature of the adsorbate is of importance even with an inert adsorbate and, as is mentioned in Stagner's paper on acid treated clays, p 1699, practically all adsorbents will extract from a mixture of organic compounds, first those with unsaturated linkages, then amines and other nitrogen, sulphur and oxygen containing molecules, with saturated hydrocarbons last of all In general we may conclude that the specific action of an adsorbent is closely related to the chemical nature of its surface and especially of its active centres

Activation of Adsorbents

In order to produce adsorbents in an efficient condition they have generally to be activated by either chemical or heat treatment Thus silica gel has to be treated to rid it of water and in a similar manner bauxite must be roasted to produce the porous adsorbent gel The acid treatment of clays is a further important example of activation, which is treated elsewhere by Stagner in his article on Acid-treated Clays The activation of charcoal is a somewhat more complicated matter, but illustrates well the general processes involved in the production of an effective adsorbent Charcoal as normally prepared by the combustion of organic materials is a porous aggregate consisting of microcrystals of the graphite type together with numerous hydrocarbon chains which are residues of the original compounds employed This initial material is a relatively poor adsorbent, containing a great deal of combined hydrogen some of which is stable at 2,000° C The activity of a charcoal is roughly inversely proportional to its hydrogen content On heating such a material in a stream of air, oxygen, steam or carbon dioxide, the hydrogen is gradually removed and the carbon partially oxidized with the formation of a product which is highly active as an adsorbent The processes effecting this improvement appear to be threefold

1 Cleansing of the surface by removal of surface hydrocarbons and other impurities
2 Extension of the surface area by oxidation which results in the opening up of new pores
3 Exposure of free valency bonds and creation of active centres

If the treatment is too intensive, over-oxidation will result in a lowering of the surface area and burning away of active centres, and if the temperature employed is too high an orientation of the crystals—graphitization—may occur with a consequent loss in activity

It should be realized here that the normal charcoal surface is covered by a unimolecular film of chemisorbed oxygen which can only be removed at a high temperature as oxides of carbon Adsorption on active charcoal is thus due either to a van der Waals retention on the surface oxide or else chemical combination with or displacement of this compound That charcoal is a useful oxidizing catalyst is not difficult to understand Recent work [9, 1934, 8, 1936] has shown that the actual nature of the surface oxide depends essentially on its temperature of formation and that many of the specific properties of the substance can be explained on this basis

Evaluation of Adsorbents

General comparison of the properties of adsorbents is a matter of great difficulty and if possible, tests should always be carried out under the actual conditions under which the substance is to be employed Adsorption of substances such as methylene blue, phenol, iodine, &c , have been proposed as general measures of adsorption capacity or surface area [10], but owing to the specific nature of the adsorption process, information of this type is of little use For example, one charcoal may be an excellent adsorbent for bases and poor for acids, while another may efficiently remove acids from solution but totally ignore bases [9, 1934, 8, 1936] Consequently, if even a superficial knowledge of the properties of a given adsorbent is required, a considerable number of tests have to be carried out

A further complication may arise as a result of steric difficulties The ultrapores of charcoal, for example, may be small compared with the dimensions of a large molecule such as congo red, so that although the surface may be capable of retaining this substance, there will be no apparent adsorption On enlarging the pore diameter without changing the nature of the surface, however, the large molecules may obtain access to the pores and be adsorbed to a considerable extent It has indeed been found [7, 1934] that, on progressive oxidation of a surface, a time comes when molecules of a given size, which have been completely excluded, suddenly become adsorbed to a considerable extent The apparent surface area of an adsorbent as measured by the adsorption of various substances on it thus varies with the size of the molecules of adsorbate [16, 1924]

Adsorption and Catalysis

The development of modern adsorption theory justifies the statement made by Faraday a century ago, that the seat of chemical change is the film of adsorbed material All adsorbents are more or less efficient catalysts and their catalytic action is often of great use in refining methods such as the Gray process (Mandelbaum, p 1693) in which gum-forming unsaturated hydrocarbons are polymerized on a fuller's earth surface

It is found that the law of mass action may be applied to such heterogeneous reactions but that the term 'active mass' refers to the amount adsorbed and no longer to the concentration of material in the homogeneous phase which merely acts as a reservoir to replace molecules removed from the adsorbed layer on reaction The adsorption equilibrium is usually quickly attained and is rapid compared to the subsequent reaction, except where activated adsorption is the controlling factor, when this is so, the simple generalizations given below have to be modified

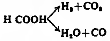
Two extreme cases have to be considered, both are known in practice as are numerous intermediate cases Firstly, if the amount of adsorption is small, the amount adsorbed will be directly proportional to the pressure

If the surface change involves only one molecule of gas, then the rate of change is proportional to the number of adsorbed molecules and hence to the pressure of the reacting gas, thus the ordinary unimolecular law applies In a similar way, if two molecules are involved, the rate of reaction is proportional to the square of the surface concentration and hence of the pressure, the reaction is bimolecular

If, on the other hand, the amount of adsorption is great, removal of a few molecules by reaction and their immediate replacement from the homogeneous phase does not appreciably affect the surface 'active mass,' and so the reaction is independent of the concentration in the homogeneous phase, i e is of zero order

When one of the products of reaction is capable of being adsorbed on the catalytic surface, it competes with the reactant molecules for room on the surface and leads to a decreased rate of reaction or even to complete inhibition

At first sight it might seem as if the increased concentration in the adsorbed film might bring about increased reaction velocity merely by a 'mass action' effect That this is not the case is demonstrated by results of Sabatier from the study of the decomposition of compounds which can split up in more than one way Thus with formic acid the two following reactions may occur



$$H\,COOH \begin{cases} \nearrow H_2 + CO_2 \\ \searrow H_2O + CO \end{cases}$$

Now, using different surfaces as catalysts, either reaction may be accelerated at the expense of the other This highly specific type of catalytic reaction, which is very common, is due to chemisorption, usually associated with active centres

Although catalysis is most common on surfaces where one of the reactants is capable of being chemisorbed, it is highly probable that molecules adsorbed by physical forces are often more reactive than in the free state It has been suggested that the very fact of one type of molecule being anchored to a surface should render a higher proportion of collisions with a second type more fruitful of reaction than in the gaseous condition, or that the possibility of two reactant molecules occupying adjacent places on a surface and thus being in contact for a finite time renders reaction probable

Although the general mechanism by means of which adsorbed molecules are enabled to catalyse a reaction is still obscure, two methods of influencing the reaction emerge—the catalyst may lower the heat of activation of the reaction and may also facilitate it by allowing it to proceed along a path impossible for a homogeneous change

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TREATING MINERAL OILS BY PERCOLATION AND CONTACT FILTRATION

By E. R. LEDERER, Ph.D., M. Inst. P.T., and E W ZUBLIN

I. INTRODUCTION

In the processing of mineral oils, treatment with adsorptive substances, such as clays, is usually one of the most important steps Owing to the relative simplicity of this operation and its far-reaching effects, it is applied wherever practical Not only does clay treating yield products of improved colour, but it also improves stability towards storage, oxidation and breakdown, and improves demulsibility The treating can be carried out with the oil in liquid or vapour phase

In the following pages, discussion will be limited to treatment in the liquid phase only, and of oils not including gasoline Methods, commercial applications, difficulties, relative advantages and cost will be reviewed

A review of the history of treating oils with clay reveals that this art was known to the Chinese more than a thousand years ago for improving colour, odour, and taste of fatty oils The first authentic description of the use of clay in the purification of oils appears to be the British Provisional specification No 1211 by Benjamin Fulwood of 28 May 1855 [5, 1927] This antedates Colonel Drake's discovery oil-well in the United States by 4 years In the early days of the Pennsylvanian oil industry, gravity filtration through relatively coarse clay was taken up Spasmodic methods involving mixing of fine clay with oil were experimented with, but it was not until 1920 that this latter method was successfully applied on a large scale

Activated and synthetic clays became known in the last few years of the nineteenth century In 1910 acid-activated clays were produced commercially in Germany

To-day coarse fuller's earths and powdered contacting clays are used side by side Each has its field and its advantages Two distinct methods of application have been built around them, each of which takes reasonable advantage of their physical and chemical characteristics, although there is much room for improvements These methods are known as percolation and contact filtration

II. TREATING METHODS

1. Percolation

By percolation is understood the passage of oil through a stationary bed of granular relatively coarse clay of considerable depth The direction of flow is relatively unimportant, in special cases vertical flow is used quite universally, either downward by gravity or upward by pumping Anti-gravity flow is particularly suited for non-viscous oils [29, 1928]

Percolation filters consist of cylindrical shells, 6 to 12 ft wide, mostly with cone bottoms, and with manholes for introducing and removing clay, and suitable lines for directing the oil The clay in the shell rests on a perforated plate or screen

The depth of the clay bed is limited for practical purposes to 30 ft [3, 1923], chiefly because the tendency towards channelling increases with depth

Channelling—one of the greatest evils of percolation—may be defined as the preponderance of flow through certain portions of the clay bed Channelling sometimes can be overcome by applying fluctuating pressure on the oil to break down temporary resistances that may have built up in some areas If that is of no avail, the filter must be repacked Results of channelling are relatively low yields of material treated to specifications The depth of the filter bed varies usually from 10 to 20 ft, depending on the properties of oil to be filtered, the character of suspended materials, the kind of dissolved materials, and the final colour desired Greater depth of clay means, of course, longer running cycles for a given diameter clay filter. This in turn results in greater throughput per time unit

Percolation is usually carried out at temperatures ranging from 100 to 200° F Some filters are fitted with steam coils, others with steam jackets As a rule better colours are obtained at higher temperature, and high temperature is essential when percolating highly viscous oils, or oils containing tarry materials or wax

The rate of filtration depends on the mesh of the clay and on the viscosity of the oil

Clays of 20 to 90 mesh size can be used It is of advantage to separate by particle size within close limits Not only are certain sizes of greatest advantage for certain oils, but the elimination of relatively fine material greatly improves the rate of filtration

Considerable progress has been made in late years in the matter of better utilization of percolating equipment It has been stated [19, 1934] that in 1934 40% less filtering capacity was required on the basis of similar results as compared with 10 or 15 years ago Much improvement can be made by developing continuous countercurrent methods in which the clay also is continuously fed at one end and withdrawn at the other

Bell [3, 1923] gives the following filtering rates as being typical

TABLE I

	Bbl per sq ft per day
Cylinder stocks	0 6
South Texas lubricants	0 7
Pressed neutrals	0 8
Wax	4 to 6

There is no doubt that by careful control of the vital factors, such as mesh of clay, temperatures, pressure, &c, higher rates can be obtained than indicated in the above table

Funsten [19, 1934] recommends the following general filtering conditions that have proved satisfactory in practice.

A complete filtering cycle consists of
- Charging the filter with clay
- Bringing oil and clay to temperature
- Filtering oil through clay to specifications
- Washing with naphtha
- Blowing with steam
- Removing clay and restoring (or dumping) it.

TABLE I *A*

Stock	*Saybolt Viscosity*	*Temp of filtration °F*	*Rate of filtration bbl per hr for 1,000 cu ft filt*	*Pressure* filtration lb per sq in*
Light spindles	up to 200/100	80–100	5–25	0–25
Heavy spindles	200–500/100	100–140	5–15	0–25
Overhead or residual cylinder stock	100–160/210	160–200	2–10	15–50
Naphtha solution of cylinder stock		100–130	30–50	5–15
Petrolatums	100–160 M P	25 over M P	5–20	0–15
Waxes	100–160 M P	25 over M P	5–20	0–15

* Pressures in the higher range are required where 60–90 mesh earth are used

The naphtha wash is fractionated Recovered oil is added to unfiltered stock and naphtha is recycled

Filter yields are affected by moisture content of the oil Moisture in excess of 0 1% reduces the clay efficiency considerably [19, 1934]

Oils manufactured by percolation processes generally are of high quality The degree of quality naturally depends largely on the effectiveness of the clay

It is possible to make many kinds of special products by percolation By separating various cuts during a run, oils from water-white to practically no improvement in colour over the charging stock can be secured

The most recent development is that of filtering in solution of propane Due to the low viscosities propane imparts to even the heaviest lubricating oils, high filter-rates are developed, coupled with increased bleaching efficiencies (see article on Propane Refining)

2. Contact Filtration

In contact filtration finely divided adsorbent is mixed with oil, the mixture is heated to the desired temperatures, and the clay is separated from the oil by filtration

As previously mentioned, attempts to carry out this seemingly simple process were made early They all failed because of lack of means to heat the mixture quickly Not until the advent of the pipe-still was commercial success of the method secured

As compared with percolation, contacting lacks flexibility In a single-contact cycle only one finished product can be obtained as against the many from the percolation cycle Clays are not spent to the same degree, for percolation, being a semi-countercurrent process, will exhaust the clays farther Attempts to contact oil first with spent clay and then with successively fresher clays, or to filter the treating stock through a filter cake of spent clay, prior to contacting with fresh clay [24, 1932], or to introduce the clay in several batches with and without intermediary filtration, have met with little success Many of the suggestions were quite ingenious, however, the extra expense involved in their execution invariably frustrated their commercial feasibility

There are two main reasons why contacting grew to its present importance Because it enables the application of activated clays of efficiencies better than twice that of the best percolation clays, and because it enables neutralization and decolorization of acidic oil in one step

There are other reasons for or against contacting, however, they are of minor importance as compared with those mentioned, save the problem of revivification. That will be discussed later

Activated clays are not applicable to percolation, because during the process of activation they disintegrate or are forcibly disintegrated to a fine powder The most important type of clay activation employed commercially to-day is that of digesting it with strong mineral acids, either sulphuric or hydrochloric This leaves the activated clay in the form of a pulp, and immediately the problem arises, when, where, and how it is most economical to eliminate the water Two methods have evolved The 'dry' contact method, in which clay freed from water by settling, filtration, and drying methods is mixed with oil, the mixture is heated to the desired temperature, cooled, and filtered, and the 'pulp' contact method, in which the clay pulp is mixed with oil, the mixture heated, the water flashed off, and the dehydrated mixture is further heated to be eventually cooled and filtered

Choice of methods is merely one of economical considerations Activated clays are commercially available in dry powdered form Where the price of raw clay and availability of acid are favourable, savings can be effected by the pulp method over the application of dry activated clays

Contact-filtration plants vary in size from 5-gal batch oil-reclaiming apparatus to several 1,000 bbl a day continuous equipment Operations are quite simple, although the application of clay in the pulp form complicates them somewhat

The 'dry method' is applicable to batch and continuous processing In batch processing, which is usually done on small scale for the reclaiming of used lube oils, the dry clay and oil are introduced into a suitable vessel, provided with necessary covers, lines, and heating devices The temperature is raised while steam is blown through the mixture, and when the required point is reached the mass is released through a cooler and filtered

In the continuous large-scale 'dry' method, the clay is suspended in oil to form a slurry This slurry is fed and proportioned continuously to be mixed with a stream of oil, which is subsequently passed through a pipe-still, an optional reaction chamber, a cooler, and a filter-press To facilitate filtering, dilution with naphtha is usually resorted to

The 'wet' or 'pulp' method differs from the above, as it is suitable only for continuous methods because of excessive foaming during the period of evaporation of the water The 'pulp' and oil are proportioned and mixed as before, but instead of passing directly through a pipe-still the mixture enters first into a flash tower or separator, in which a high liquid-level is maintained From its bottom a continuous stream is withdrawn, which circulates through a pipe-still and back into the flash tower, thereby providing heat for the vaporization of the water As the ratio of freshly introduced wet oil to that of hot oil in the flash tower is quite small at any given moment, excessive foaming never occurs From the separator a portion equivalent to the one freshly introduced is continuously withdrawn, to be cooled and filtered, if necessary in dilution with naphtha

A flow diagram of a typical pulp-contact plant is shown in Fig 1. This plant was designed to handle long residuum, having an open cup flash-point of 420 to 440° F. Temperatures at the most important points are indicated, but it should be remembered that these temperatures can vary within wide limits, depending on general practices, nature of oil and clay, and particular type of equipment.

Contacting temperatures, for instance, may range from slightly above 200 to 750° F In the early days, relatively low temperatures close to 200° F were employed Later, operations were carried out at incipient distillation, until Prutzman [42] showed that temperatures above normal evaporation but below cracking produced oils of greatly improved 'cast' or 'outer tone'

Typical results of contacting Ranger long residuum, which had been treated with 35 lb per bbl 98% sulphuric acid, and 25 lb per bbl activated Woodite clay [30, 1932] under identical conditions except for variations in the temperature are shown below

TABLE II

Temperature	*Tag-Robinson colour*
420° F	2
470° F	2½
530° F	3½

Time of contact must be considered in conjunction with temperature Kalichevsky and Ramsay [27, 1933] have shown that colour intensity of oils during the early stages of contacting decreases rapidly As time progresses decolorization slows down, comes to a standstill, and finally is reversed The higher the temperature, the less time is required for the above to happen In other words, to obtain the best results in a given continuous equipment, for which variations as to time are limited, temperature variations are limited also

Kalichevsky and Ramsay [27, 1933] present the following highly instructive figures

TABLE III

Effect of Time and Temperature on Colour of Oil in Contacting Acid-treated Mid-Continent Cylinder Stock with Adsorbent Clays

	*Activated Clay A**		*Activated Clay B†*		*Natural Clay‡*	
Treating temp ° F (° C)	*Time at max temp Min*	*Colour intensity*	*Time at max temp Min*	*Colour intensity*	*Time at max temp Min*	*Colour intensity*
500 (260)	0	322	0	440	0	255
	5	260	5	320	10	180
	10	205	10	280	30	165
	20	192	20	285	60	165
	30	170	30	260	200	185
	45	165	60	210		
	75	137	120	192		
	120	125	200	165		
	200	125				
600 (315 6)	0	163	0	245	0	160
	5	135	5	170	10	136
	10	112	10	153	20	125
	20	98	20	130	30	125
	30	91	30	130	45	125
	60	84	120	92	90	108
	120	76	200	94	120	105
	200	76			200	108
700 (371 1)	0	108	0	145	0	146
	5	82	5	113	5	136
	10	77	10	95	20	119
	20	66	20	95	30	119
	30	66	30	86	60	132
	90	68	90	84	90	119
					130	112

* 3% by weight † 4% by weight. ‡ 8% by weight

In handling acid-treated oils and earths, special attention must be paid to the problem of corrosion Where sulphuric acid has been used, duriron, monel metal, bronze, &c , and in many locations cast iron, have proved satisfactory metals for construction.

Besides corrosion, erosion sometimes must be contended with Some clays contain considerable proportions of silica sand or volcanic ash Clay grinders being adjusted for rather soft materials do not pulverize sand, and relatively coarse hard particles cause considerable wear on conduits and pumps This condition is particularly bad after the clay has been thoroughly dried

Very recent developments in air-operated 'separating tables' [47] enable the removal of sand from ground clay without appreciable loss of fines through dusting This results in practically complete elimination of erosion

The effect of contacting oils with suitable clays as described is not only that of removing chromophores but acid constituents as well The removal of the latter is so complete that clay contacting makes caustic treatment subsequent to acid treating altogether unnecessary Neutralization numbers of freshly contacted oils run commonly around 0 01 mg KOH per gram of oil Weak acids are not as readily removed by clays as strong acids.

Davis [12, 1928] points out that the control of neutralization by clay-contacting methods is accurate and positive Above all, contacting overcomes emulsion troubles experienced in neutralization with chemicals and the oil is of superior quality, more so than if neutralized with alkalis

In many instances contacting is used solely for the purpose of neutralization, no attempt being made to improve colour at the same time In other instances it has been found possible greatly to improve the decolorizing power of clays on neutral reacting oils by mixing a very small percentage, say between ½ and 2% of acid to the oil, and contacting it with clay without settling the sludge

3. Contact Distillation

A special application of contact filtration is contact distillation Although not very widely used at present, it has such a field of advantageous application that in the future its application is likely to grow considerably

It consists of distilling oils in the presence of clays, condensing overhead streams, and separating the solids from the bottom stream by filtration When considering the data by Kalichevsky and Ramsay presented in Table III, it becomes evident that batch treatment is not likely to be as suitable as continuous treatment for this process, because of the excessive length of time the clay remains in contact with hot still bottoms in the former

In its proper execution clay is mixed with oil to form a slurry The slurry is proportioned and mixed continuously with a stream of oil, which passes through a pipestill and into a flash tower The flash tower may be of the atmospheric or vacuum type, depending upon the results to be achieved Vaporized fractions are taken overhead and the unvaporized portion leaves as a bottom stream, as in any other continuous distillation Bottoms are filtered in any convenient manner to separate clay from oil A flow sheet of the process is shown in Fig 2

Contact distillation is of particular advantage in processes in which the contacting is the final step The oil resulting therefrom is in a highly saturated condition and shows excellent storage stability Filtration in this case cannot very well be carried out in dilution, because dilution requires reheating and redistillation, which partly offsets the advantages gained by the process So-called 'hot' filtration must be employed

In the chain of processing steps, contacting distillation takes a position similar to that of percolating to obtain good colour The main difference between the two is that

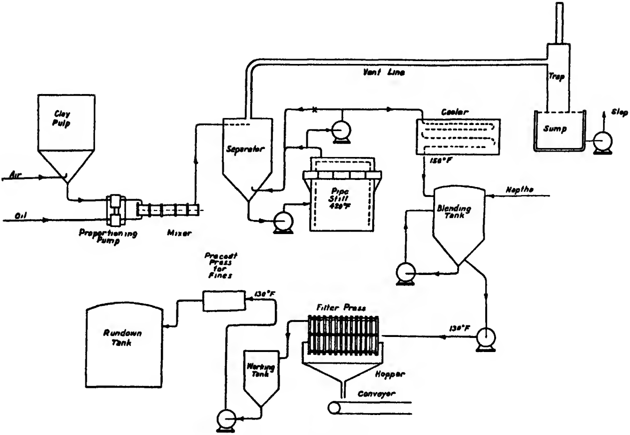


FIG 1 Pulp contact plant

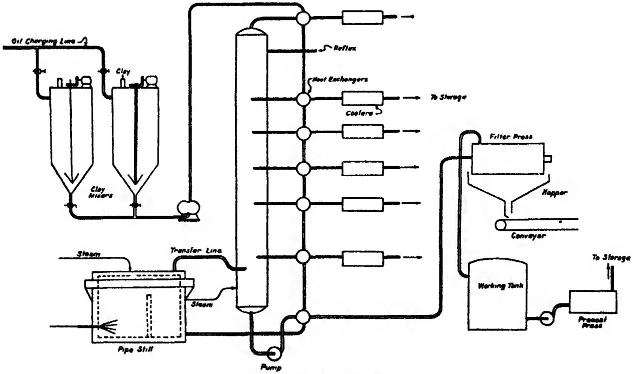


FIG 2 Atmospheric contact distillation unit.

percolation permits fractionation by degrees of colour, while contact distillation fractionates by boiling-range, producing only one colour for each fraction

There is promise that contact distillation will play an important role in the recently developed solvent extraction processes By employing contact distillation to solvent extracted oils, considerable savings in clay are claimed [16, 1933] over the application of ordinary contacting

A special application known as 'Filtrol' Fractionation [15, 1932] is concerned with contact distillation in the presence of activated clays Due to the relatively high efficiencies of such clays the potential uses and effects of the process are quite remarkable

4. Combination Methods

In many instances it is found advantageous to clay-treat oils more than once

The choice of the number of steps involved in a complete manufacturing process is, of course, largely guided by economic considerations Where cheap clays of intermediate decolorization efficiency are available, multiple clay-treating is usually considered good practice [12, 1928]

The first clay treatment is usually that of contacting the acid-treated oil, mainly for the purpose of neutralization The oil is then dewaxed and topped to the desired viscosity, either by ordinary or contact distillation In the first case the oil is finished by percolation

Another procedure which has been suggested, but which to the writers' knowledge is not in actual use at present, is that of contact distilling the crude oil, subsequently acid-treating the filtered residuum if necessary, dewaxing, distilling, and percolating, or contact distilling and filtering

III. TYPES OF OILS

1. Kerosine

Marketable kerosine must have a colour better than 21 on the Saybolt colorimeter, and also possess good burning qualities without depositing carbon or soot on wick and chimney, and without clogging the wick

Gurwitsch [22, 1927] points out the detrimental effects on burning quality of carbures, soft asphalts, and soaps Clay-treating of kerosine has largely the purpose, besides stabilizing the colour, of either preventing the formation of these compounds, or, if they are present, of eliminating them It follows that the type of clay treatment resorted to depends entirely on the nature of crude from which the kerosine is prepared and on the treatment it has received

It is accepted that kerosine from paraffinic crudes is the best However, many mixed base and asphaltic crudes yield fine kerosines, provided they receive the proper treatment Kerosines from sweet, paraffinic crudes frequently receive only an alkali or sodium plumbite treatment ('Doctor'-treatment)

Such kerosines as a rule do not readily respond to clay treatment. Only a few selected clays of the Floridin type or Bauxite improve such kerosines sufficiently to warrant the extra expense

Bowen [6, 1933] suggests the addition of clay to the still charge before distilling the kerosine, chiefly to improve colour stability in cases in which light treatments only are used for finishing This amounts to contact distillation

Kerosines that have received acid treatment are most advantageously neutralized with clays by contacting Formation of harmful soaps can in this manner completely be suppressed The proper choice of the clay is of importance, as it must be free from a tendency of liberating calcium or magnesium ions in contact with the acid constituents of the kerosine Soaps of these metals greatly depress the burning qualities It has been found good practice in many instances to wash the acid-treated kerosine with water prior to clay contacting This not only saves clay, but also minimizes the danger of soap formation due to liberation of ions

Whereas clay treatment may be of importance to improve colour stability and burning time, it has practically no effect on illuminating power [11, 1932]

Allibone's [1, 1933] experiments on colour stabilization by percolation through Bauxite led to the conclusion that fractions boiling up to 280° C (536° F) were well stabilized, from 280 to 300° C (572° F) partly stabilized, and above 300° C (572° F) not at all stabilized

The stabilizing effect of Bauxite is greatly enhanced by a pre-treatment with liquid sulphur dioxide

2. Neutrals

The expression 'neutral oils' or 'neutrals' is commonly used by the trade as indicating distilled lubricants of Saybolt Universal Viscosities from 70 sec to as high as 2,000 sec at 100° F, regardless of whether or not such oils have been acid-treated

Considering oils from the point of view of clay treating, it is the viscosity that sets limitations for the practical application of various methods, and therefore the lighter neutrals only will be discussed in this article

Neutral oils containing no free mineral acids are particularly suited for percolation treatment Their relatively low viscosity permits good rates of filtration without the necessity of adding diluents This is particularly useful in processes in which dewaxing precedes treating to obtain good colour Not only is the finished oil well stabilized and brilliant, but this procedure also enables the simplified manufacture of a number of special products

Acid-treated neutrals have in the past been neutralized most commonly by means of caustic soda This is being replaced almost entirely by contacting with a good grade of neutralizing clay For this operation clays can successfully be applied that have little or no colour-removing ability The concentration of chromophores in distilled oils is low, and most of the objectional remaining colouring material is removed by the acid itself For that reason further improvement of colour with clay is frequently unnecessary

The writers have observed the phenomenon, that on some distilled acid-treated oils practically the same colour is obtained, whether this oil is contacted with poor or highly efficient decolorizing clays, and with varying quantities thereof Thus a 300 vis at 100° F neutral obtained by atmospheric steam distillation from a Mid-Continent crude, which was treated with 9 lb per bbl of 93% sulphuric acid, was contacted with a natural South Texas clay in percentages ranging from 1½ to 5% by weight The colour was 2 A S T M on all samples The same oil was then contact-treated under the same conditions with an activated clay, which on bright stocks was about 3 times as efficient as the natural clay The colour of the resulting oil was again 2, and only slightly better when higher percentages of activated clay were used

In the so-called long residuum process of lubricating oil manufacture, neutrals are treated jointly with the bright stocks, and are separated from the latter in the final distillation Contact distillation is very applicable to this manner of processing

White oils, particularly medicinal oils, are not usually prepared by ordinary acid and clay treating Nugey [35, 1934] reports a simplified and practical method of their production, which consists of the following steps

(1) 2% of 93% sulphuric acid
(2) 50% of 20% fuming sulphuric acid, slowly added and agitated
(3) Settle and remove sludge
(4) Neutralize with caustic soda solution and separate
(5) Extract soaps with methyl alcohol
(6) Wash with water and blow to dryness
(7) Contact with ground fuller's earth and filter

Other methods of preparation include repeated acid treating, neutralization, distillation, and percolation or contacting

3. Bright Stocks

The two most common methods of clay-treating bright stocks are

(*a*) Percolation in dilution
(*b*) Contacting without dilution at elevated temperatures
(*c*) In comparatively few cases are bright stocks percolated without dilution, or contacted with clays in the presence of diluents

Percolation in dilution is resorted to in order to reduce the viscosity of the oil and thereby increase the speed and volume of oil through the filters Disadvantages are loss of solvent-naphtha by evaporation and necessity of distillation after treatment Where dewaxing succeeds clay treatment, the latter need not be considered, as dewaxing is carried out in dilution with some medium also

Kauffman [29, 1928] reports data on percolation treatment as shown in Table IV

TABLE IV

	Original stock	*First through clay*	*Stream after yields of* *10 bbl*	*23 bbl*	*75 bbl*	*148 4 bbl*	*294 6 bbl*	*500 4 bbl*	*589 4 bbl*
Temperature of filter stream, ° F		106	136	118	106	84	68	68	68
Gravity, ° Bé	41 6	49 0	48 3	46 2	43 2	42 4	41 9	41 8	41 5
Sulphur, %	0 134	0 011	0 020	0 045	0 080	0 128	0 125	0 133	0 129
				After reducing					
Gravity, ° Bé	23 0	30 7	29 7	27 7	25 4	23 9	24 1	22 9	23 3
Flash, ° F	430	460	480	440	420	435	470	440	440
Fire, ° F	540	535	540	540	525	540	545	540	535
Viscosity, 100° F	3,122	819	892	1,148	1,937	2,291	2,662	2,722	2,798
Viscosity, 210° F	156	90	87	95	125	135	160	140	140
*Viscosity index	83	105	103	95	92	88	82	80	77
Pour-point	60	55	55	55	65	65	65	65	65
Iodine value	18 0	0 61	1 2	4 3	12 1	14 8	16 4	17 4	18 1
A S T M carbon residue, %	2 25	0-008	0 027	0 115	0 546	0 932	1 49	1 61	1 79

* Calculated by writers

The change of gravity, viscosity, viscosity index, carbon residue, iodine number, and sulphur should be noted The changes are greatest for all properties at the beginning of the filtration process and gradually diminish as more oil comes through This lack of uniformity, which in the case of neutral oils can be of advantage, as it permits the simple production of special products, is undesirable for bright stocks and has been contributory to the development of the contact process

At the present time the most important application of percolation for heavy stocks is in conjunction with contacting

As pointed out before, percolation produces oils of somewhat greater stability, brilliancy, and demulsibility On the other hand, contacting produces uniform products and serves as the best means for the removal of acids Many plants therefore have adopted combination methods Davis [12, 1928] points out the economical advantages of combinations The methods evolved vary from simple neutralizing by contacting without improving colour and decolorizing entirely by percolation, to neutralizing and decolorizing by contacting and percolating through small quantities of clay to improve demulsibility, stability, and brilliancy This permits the interchangeable use of clay, in various stages of revivification by burning in special furnaces, for filtering different products for which it might be best suited

Staley [45, 1931] describes a combination method applied to Bradford, Pennsylvania, oils Long residuum of 85 to 90 sec Saybolt Universal Viscosity is contacted with a raw powdered California clay at temperatures of 600 to 650° F The hot oil is cooled against incoming oil in heat exchangers and is diluted thereafter with an equal volume of a narrow cut naphtha The bulk of clay is removed in filter-presses and fines are retained in a blotter-press

The contacted oil now proceeds to the dewaxing plant, and after wax removal the solvent naphtha is distilled off, using steam in the still at a temperature of about 350° F The oil leaving the still has a colour of 6–7 A S T M As a final step it is percolated through a filter containing about 12 tons of 15 to 30 mesh fuller's earth One charge of clay will treat several thousand barrels of oil, as no attempt is made to improve the colour

At the Texas Pacific Coal and Oil Company, Fort Worth, Texas, long residuum of 90–95 S U viscosity at 210° F from Ranger crude is treated with 30 to 40 lb of 98% sulphuric acid per barrel in two dumps After removal of the bulk of the sludge, 'pepper' sludge is thrown out by passage through De Laval centrifuges The acid oil having an acidity averaging about 6 mg KOH per gram of oil is mixed with clay pulp produced in the activation of the clay (see under 'Types of Clays') so as to result in a mixture containing about ¾ lb. of dry clay per gallon of oil. This is introduced into a separator (see Fig 1) from which a stream of oil is continuously withdrawn and circulated through a pipe-still in which the temperature is raised to about 440° F The larger part of the stream returns to the separator to cause evaporation of the water contained in the fresh incoming mixture A smaller part of the circulating stream equivalent to the fresh mixture introduced into the separator is continuously withdrawn at a point in the return line between the pipe-still and the separator This fraction is cooled, diluted, and filtered as shown in Fig 1

After filtration the oil is dewaxed and the diluent is removed in a continuous pipe-still Neutral oils are separated from heavy bright stock in the same distilling operation After removal of last traces of moisture, both the neutral and bright stocks are finished and receive no further treatment

Processes in which the crude oil is acid-treated, or in which the lubricating stock is diluted with naphtha before receiving the acid treatment, are best given their clay treatment by the contact distillation method This is of particular interest in processes in which the wax is removed prior to or simultaneously with acid treating Overhead streams including the neutrals are finished except for drying, as are the bottoms after clay removal by filtration

Petty [39] contends that lower temperatures are permissible, when contacting in dilution This may be the case with some clays, however, with others, better clay efficiency is secured at higher temperatures (400 to 650° F)

An important phase in the economy of clay treating viscous oils is the removal of oil retained in the filter or cake It is generally conceded that a light, narrow-cut naphtha is the best means to displace the oil, it can be separated from the extracted lube oil by subsequent distillation In some particular cases, oils of the gas-oil range or even heavier are recommended as being more efficient in their displacing action [37] Hot naphtha or kerosine is advocated by Stratford [46]

In most plants warm naphtha is employed for the purpose Its application results in relatively low losses by evaporation and it is easily separated from the recovered oil

4. Wax and Petrolatum

Waxes and petrolatums are almost exclusively decolorized by percolation, except those which are treated in conjunction with oils, from which they are separated subsequently In the latter case they receive whatever treatment is given to the oil with which they are combined

White waxes must almost invariably be filtered Fuller's earth that is no longer suitable for oil treatment can still be used for wax decolorization, and the only cost involved in this process is that of moving the clay to the wax percolators Bell [4, 1923] states that apparently this accounts for the popularity of percolation as applied to waxes

Truesdell [49, 1928] describes the manufacture of various grades of petrolatum at L Sonneborn & Sons, Inc , refinery at Petrolia, Pa The crude is produced in the Butler, Pa , area, and is said to be particularly suited for the purpose The petrolatum, once separated, is filtered through fuller's earth and bone black, the latter for decolorizing The grades and the number of times each is filtered are as follows

TABLE V

Colour Trade name	*Approx A S T M*	*Times filtered*
Alba		10
Snow		8
Lilly	1	6
Cream	1½	4
Golden	2½	3
Extra Amber	3½	2
Amber	4½	1

5. Used Lubricating Oils

The reclamation of used lubricants, particularly crankcase oils, is a business of growing importance The fact that the treating stock is spread in small batches over the country has given rise to the development of a number of reclaiming processes The machines used to carry these out are invariably of the batch type and range from about 5 to 100 gal capacity In the more successful processes the oil is contacted at elevated temperatures (400 to 650° F), using live steam for agitation Volatile portions are distilled off and condensed The oil and clay are then released through a cooler to lower the temperature to that of safe filtering operation Clay is usually removed by filtering through blotting-paper, using steam pressure on the treating vessel to move the charge

IV. TYPES OF ADSORBENTS

The list of adsorbents commonly applied in the petroleum industry includes the following

1 Fuller's earth, natural or impregnated
2 Contact clays, raw
3 Contact clays, activated
4 Bauxite
5 Silica gel
6 Activated carbon

From a practical point of view adsorbents are divided into two main groups, depending upon whether they are suitable for percolation or contacting In subdividing the main groups consideration is given as to whether adsorbents have particular decolorizing, neutralizing, desulphurizing, stabilizing, or other qualities

1. Fuller's Earth

Fuller's earth is almost synonymous with percolation clay

A good grade of fuller's earth is naturally active, has considerable compressive strength and hardness, and is not disintegrated by water

In practice the clay is dried after mining, often receiving a slight acid-treatment, and is then ground and screened to various particle sizes In the percolation of viscous oils 16–30 mesh clay is usually required Non-viscous or diluted oils may be percolated advantageously through 60–90 mesh, or 20–90 mesh clay The latter results in somewhat better rates of filtration and apparently less channelling

Brockway [7, 1927] states that a 30–60 mesh clay has an efficiency about 20% greater than a 20–30 mesh, and 60–90 mesh clay is 10–15% better than one of 30–60 mesh This relation is graphically illustrated in Fig 3 The slope of the curve indicates that the gain in efficiency will not greatly increase with clays finer than 60–90 mesh

Funsten [19, 1934] contradicts the above, stating that the importance of mesh size is overrated Part of the improved results when employing smaller-size clay is due to increased time of contact

Good percolating clays must be able to withstand temperatures of the order of 1,000° F without losing too much of their efficiency and without disintegrating excessively to fines This is important in their recovery, as will be shown later

Percolation clays are chiefly applied to remove chromophores, carbures, and small quantities of sulphur compounds of the sulphone or sulphonic-acid type In order to raise the sulphur-removing properties, impregnation with various metals, oxides, and salts have been suggested Thus Cross [10, 1932] makes claims for desulphurizing oil with clay containing copper or compounds thereof In particular the sulphides of copper [26, 1932] and lead have been found to absorb sulphur compounds Heavy metal sulphides can be precipitated on clays No practical process, however, has developed employing impregnated earth

An important property of fuller's earth and, for that matter, of all clays, is their tendency to retain oil Oil retention is very undesirable, as it causes losses and difficulties in restoration of the clay Haseman [25, 1929], who has investigated this property, concludes that it is largely a matter of porosity and can be reduced by 'filling in the pores without impairing efficiency' Lederer and Zublin report oil retention to be a function of the fineness particularly in the case of fine contact clays They recommend carrying out grinding in the presence of 10 to 15% moisture to avoid excessive fine formation

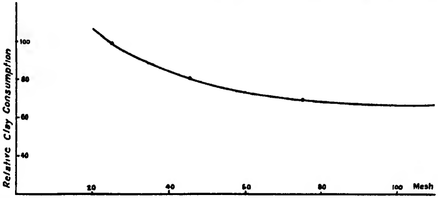


FIG 3

2. Raw Contact Clays

The main application of raw clay by the contact method is for the purpose of neutralization In a few specialized cases powdered fuller's earth is used for decolorizing as well

Deposits of clays suitable for neutralization are wide-spread Mining is cheap and freight rates usually are low Handling and application are simple and free of danger Thus raw clays make an almost ideal material for neutralization Advantages are enhanced in places where the clay is used for percolation prior to powdering, for purposes of contact neutralization The only cost, then, is that of burning, regrinding, and moving the clay

Some few raw contact clays have bleaching efficiencies of the order of that of good fuller's earths However, they are not suitable for percolation because of their softness and because they disintegrate upon moistening

It has been previously stated (see article on 'Contact Filtration') that weak organic acids are not readily removed by clays It is appreciated that different clays vary a great deal in this respect, and particularly acid-activated clays are in general poorer than raw clays This may in part be due to the fact that raw clays contain small quantities of loosely attached bases which may be available for the neutralization of such acids

In some instances it is necessary to neutralize the oil with caustic or lime, separate as much as possible of the excess chemical, and then follow up with clay contacting Soaps of the acids contained in the oil are reasonably well removed thereby [50, 1927]

It has been suggested to add metal oxides or hydroxides to the clay, which are capable of reacting with weak acids but which do not affect the silicic acid [30, 1932] Suitable oxides or hydroxides most easily available are those of iron, aluminium, and magnesium (Brucite) Thus cotton-seed oil having an acid number of higher than 0 5 mg KOH per gram of oil was contacted with activated Woodite clay to which various additions of the character pointed out were made The effect of the addition over the straight clay was that the neutralization number was greatly reduced, while the colour suffered relatively little

Clays high in magnesium, calcium, and aluminium are considered undesirable as they promote sludge formation in the oil treated by them Magnesium and aluminium soaps are soluble and conducive to sludge and emulsion troubles Pollock [41, 1932] adds sodium silicate to oils containing magnesium and calcium soap in order to precipitate them.

3. Activated Contact Clays

Decolorizing ability of some clays is greatly increased by leaching with strong mineral acids, either hydrochloric or sulphuric Efficiencies better than twice of those of the best percolating clays can be obtained quite commonly

The methods for activation vary with the clays, some requiring only the addition of 5% acid [34, 1932], while others must be treated with as much as twice their own weight [25, 1932, 36, 1933] of sulphuric acid Most clays responding to such treatment require from 25 to 60% their own weight of sulphuric acid The choice between hydrochloric and sulphuric acids is largely a matter of price, although in a few instances hydrochloric acid may result in higher efficiencies due to its greater solvent action on calcium

During the leaching with acid, acid soluble parts are removed This results in a loss of weight which varies from about 5% to as high as 50% Some of the best-known activated clays, such as California Palex or Oklahoma Woodite, lose 20% by weight on activation

The economy of activated clays depends upon several factors, which include final efficiency of the clay, acid consumption, handling, cost of cooking and washing, and loss of weight

Acid cost can be minimized by using recovered acid [40, 1931] from acid sludge of lubricating oils

Plant procedures of activation have been described in the literature [30, 1932, 40, 1931] An excerpt follows

The raw clay, which has preferably been dried to a suitable moisture content, is ground to 80–90% passing through 200-mesh sieve It is dumped into a lead-lined cone-bottom cooker fitted with steam coils and open steam lines, and containing the predetermined volume of a 10 to 20% solution of sulphuric acid The mixture is digested at temperatures of 160 to 200° F under slight agitation for 8 to 10 hours The thick pulp is transferred to wash tanks, which may consist of huge wooden settling vats or which may be of the Dorr thickener type The clay is washed with water until a sample of water, when titrated with phenolphthalein, shows an acidity of well below 1% sulphuric acid If preferred, washing can also be carried out on filters

The washed pulp is either vacuum-dried and sacked ('Filtrol'), or is directly mixed with the oil to be treated

Control of the acidity is important for two reasons Many oils, including most acid-treated ones, are unstable if treated with clays of too high an acid content This instability is reflected in loss of colour, sludging, and poor demulsibility Some investigators blame the aluminium and magnesium salts that are associated with clays of high acidity The facts are that oils of greater stability are produced by the same clay, provided it is washed more thoroughly

On the other hand, certain types of non-acid oils, including used oils, do not respond readily to activated, well-washed clays In order to obtain the desired bleaching effect, a small amount of acid must be added to the clay, which all goes to show that there is no universal clay for all purposes Differences as great as the following are encountered

(*a*) One of the activated clays most highly efficient on acid-treated Mid-Continent oils had practically no bleaching effect on a semi-naphthenic, vacuum-distilled neutral heavy stock The overhead stock was very effectively bleached by an acidulated clay, which showed a comparative efficiency of less than 40% on the same acid-treated Mid-Continent oil

(*b*) A special clay for re-treating used oils had practically no bleaching effect on a Mid-Continent acid-treated oil, while on used oils the special clay gave considerably better results than the activated clay which was so highly efficient on Mid-Continent acid-treated oils

Corrosion in the process of activation is, of course, a big factor and problems are best solved by the application of special metals

4 **Bauxite, Silica gel, Activated Carbon** are discussed separately by other authors

V. SPENT CLAY

1. Regeneration

All methods for regenerating spent clays consist of two principal steps

(*a*) removal of excess oil, naphtha, or solvents, &c , this may be called the 'drying' step,

(*b*) removal of adsorbed matter, this may be called the 'surface-cleaning' step

(*a*) **Removing Excess Oil** The usual procedure for removing excess oil consists of washing the clay with naphtha and subsequently steaming

In the case of percolation clays this is always carried out in the percolation filter without difficulties Fine clays may be handled similarly in the filter-press, the cake may be also removed from the filter, agitated with wash naphtha in a suitable vessel, refiltered, and steamed Difficulties are numerous incomplete washing due to channelling and cracking of the cake, plugging of the filter-leaves during steaming, dust formation of the steamed clay with consequent losses, &c

Olson [37] recovers entrained heavy lubricating oil by displacing it with gas oil or light spindle oil, thereby reducing channelling a great deal Stratford [46] flushes the filter cake with hot naphtha or kerosine and under pressure sufficient to maintain the liquid state Cannon [8] adds pulverized solids to washing liquid for the purpose of filling cracks that form on shrinkage of the cake, due to extraction. **Dunham** [13] 'de-oils' spent clay by treatment with an optimum amount of water, the quantity to be determined experimentally for each batch, while Hall [23] achieves similar results with hot water Lowry [33] employs alkaline solution at elevated temperatures

When working with naphtha solution for washing filter cakes, the completeness of oil removal depends a great deal on time and temperature Examples [53, 1932] are shown in Fig 4 and Table VI

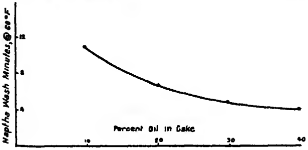


FIG 4

TABLE VI

Temperature of naphtha	*Time of wash*	*Per cent oil in cake*
125° F	10 min	1 1
130° F	15 „	0 2
132° F	8 „	1 0
136° F	7 „	0 8
140° F	8 ,	0 5

Steaming of filter cakes composed of fine clays often results in plugging of screens, particularly so when metal screens are used Clays used for neutralizing release enough acid constituents on steaming to make the application of duck for filtering impracticable Monel-metal screens are most frequently employed in such cases

Clogging may be due to release of asphaltic organic matter and to disintegration of clay to excessively fine particles The mixture of the two forms a viscous slime that resists removal by mechanical and chemical means Formation of this slime can at times be prevented by using dry superheated steam, or partly removing some asphaltic substances by thorough agitation with hot naphtha or other solvents

Lemmon and Brown [31] suggest removal of adhering oil and naphtha by blowing with inert gas, such as refinery 'high line' Flue gases have been used repeatedly, but are apt to give trouble due to their content of soot

(*b*) **Removing Adsorbed Matter** This step can be carried out in two radically different ways by burning (roasting, oxidation) or by extraction with solvents.

Burning is the older and more obvious method It has been applied to coarse clays for more than 50 years

A good percolation clay can be burned as many as 40 times before finally being discarded During each roasting the efficiency drops, and a considerable proportion of the charge may go to fines

Fines should be separated Some are blown out through the stack during burning They can either be collected and used for contacting or else are discarded

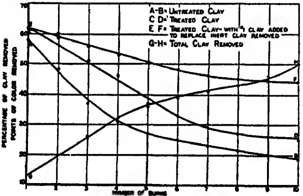
The number of burns to which a clay is actually subjected depends on a combination of factors price of raw clay, loss of fines, drop in efficiency, cost of burning, &c

The degradation of a typical percolation clay due to burning is reported by Shepard [44, 1934] On the basis of fresh clay which has a decolorizing value of 100 points, the following table is obtained

TABLE VII

Number of burns	*Decolorizing value*
1	58 points
2	40 "
3	37 "
4	31 "
5	27 "
6	25 "
7	23 "
8	21½ "
9	20 "
10	18½ "

Shepard [44, 1934] observed that during each burn a slight amount of sintering takes place, and that the particles thus affected become inert and increase in specific gravity By means of 'concentrating' tables it has been possible to remove the inert material, thereby maintaining an average efficiency of close to 50 points, as shown in Fig 5



POINTS OF COLOR REMOVED
BY CLAY AT DIFFERENT STAGES OF BURNS

FIG 5

The practice of keeping many grades of clay in as many storage bins is greatly simplified by this concentration method If desired, not more than 2 or 3 grades need be kept

Roasting is carried out in rotary kilns or multiple hearth-type furnaces at temperatures ranging from 700 to 1,400° F Each clay has an optimum roasting temperature, which should strictly be adhered to Heat is usually supplied by passing hot gases carrying excess oxygen through the spent material

Wilson [51] suggests providing heat by burning residual oil in the clay and controlling the temperature by diluting the air with inert gases

Lewers [32] heats clays in an atmosphere deficient of oxygen to achieve distillation The so-treated clay is then exposed to air to remove remaining carbonaceous matter by oxidation The Petro-Met Engineering Company [38] has devised a furnace in which to carry out Lewers' [32] invention Higher efficiencies and smaller losses of fines are claimed over ordinary roasting methods

Fine clays must be roasted in specially designed furnaces in which a low velocity of combustion gases passing through the clay is maintained Removal of hydrocarbons to not more than 2% previous to burning is important, as otherwise evaporation and combustion of the oil content is likely to cause excessive dust losses

While practically all percolation clays can be roasted to yield recovered products of high efficiencies, this is not so with all contact clays Some of them begin to lose their adsorptive power when heated to 400° F Others can safely be heated to 1,100° F As roasting below 700° F is impracticable, clays deteriorating at temperatures below that are automatically eliminated

Some contact clays can be burned a great many times without appreciable loss in efficiency This was shown in semi-plant and laboratory tests by various investigators [28, 1933, 43, 1929] Other clays of similar nature gave efficiencies of not better than 75% of the original upon roasting In many instances results were even lower, in spite of carefully regulated conditions, which gave rise to the belief that factors not directly connected with the burning enter the problem [30, 1932]

Extraction methods for regeneration were suggested some time ago, but for various reasons have not found great public favour In 1931 a pilot plant designed by Goslin-Birmingham Manufacturing Company [20] using solvents furnished by the Commercial Solvents Corporation [9] was operated successfully Recovery cost per ton of clay was said to be between $6 00 and $8 00 Efficiencies of recovered clays ranged from 60 to 80% of the original Flow diagrams of a complete extraction plant are shown in Fig 6

The efficiency of the solvent-regenerated clay not only depends on the nature of solvent and clay but also on the nature and age of the adsorbed matter It is well known that much of the colouring matter is unstable and subject to oxidation and polymerization, particularly when in contact with clays If adsorbed matter is allowed to age it becomes less and less soluble even in the most powerful solvents, and solvent regeneration results in reduced efficiencies

Solvents amenable to clay regeneration must answer three requirements

they must be capable of displacing adsorbed matter,
they must be good solvents for the adsorbed matter,
they must be fairly volatile to facilitate their reclamation by distillation

Kalichevsky and Stagner [28, 1933, p 218] give a list of solvents suggested for the purpose To mention a few

Mixture of hydrocarbons and oxygenated solvents, such as alcohols, aldehydes, esters, &c , coal-tar products, including pyridine, chlorinated compounds, carbon bisulphide, liquid sulphur dioxide, &c

Gurwitsch [21, 1926] points out that the heat of wetting of a liquid when brought in contact with clay is a measure of its ability to displace other adsorbed matter His tests terminate in the conclusion that mixtures of alcohol and benzene, or acetone and benzene, represent about as active a solvent for clay extraction as can be found

Trescott [48, 1934] gives a comprehensive outline of solvent reactivation of spent contact clay He points out the effect of time and temperature on the process Raising the temperature in general is conducive to more rapid extraction Several hours, however, may be required completely to remove the colouring matter Particular attention is paid to the use of water as a reactant

2. Uses and Disposal

Clays not fit for regeneration must be disposed of. Attempts to utilize them for a practical purpose have been quite successful Spent contact clays when incorporated into Portland cement result in a combination of improved

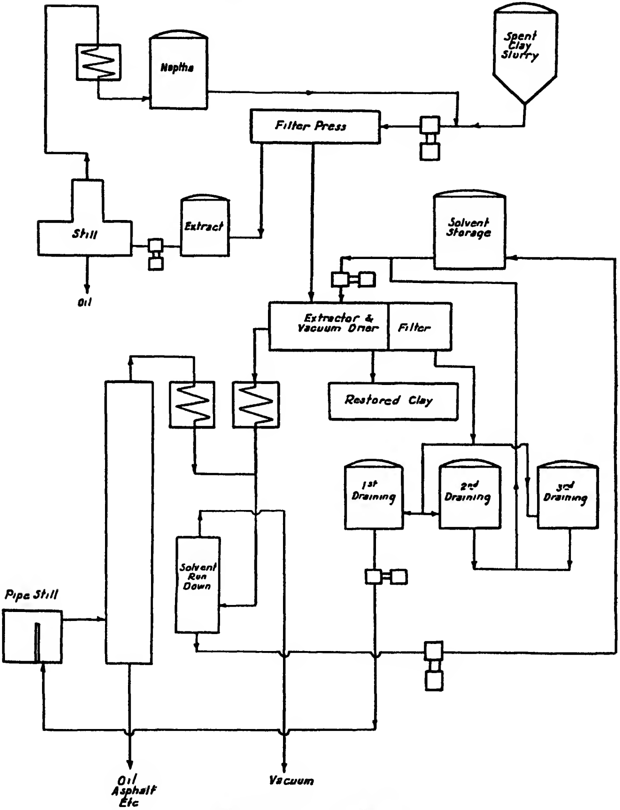


Fig 6 Solvent extraction of spent clay

tensile and compressive strength as well as water-proofness The process is controlled by the Evans Process Company [14, 1932]

Spent fine clays can easily be pumped or conveyed in a stream of water to whatever location is desired Coarse clays must be handled by conveyor or truck and dumped

VI. FILTER PROBLEMS

Difficulties occurring in the separation of oil and clay vary from the problem of retaining 'fines' to temperature considerations in hot filtration, plugging of screens in steaming, dusting in the drying operation, &c

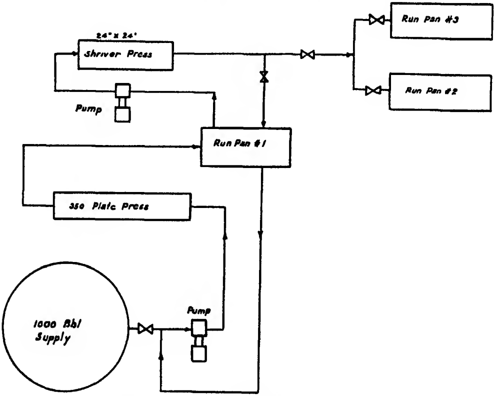


FIG 7 Clarification-filtration

Percolation offers no serious problem The only item worth mentioning is that upon repeated burning the percentage of relatively fine material increases, which results in loss of filtering rate Screening, or the more recently introduced separation of inert material by means of concentrating tables [47, 1934], greatly reduces the content of fines

Fines of contact clays tend to pass through the filter screen at the beginning of each filter cycle Once the cake is built up to a certain extent, even the finest material is retained Fines in the oil are liable to cause trouble in subsequent processing and are generally objectionable They are most easily removed by refiltering the oil through a blotter-press or a press precoated with a filter-aid Such secondary presses need be cleaned at long intervals only and the cost of filter-paper or filter-aid is therefore negligible The outlay as shown in the flow diagram of Fig. 7 is used at the Sand Springs Refinery of the Sinclair Refining Company [18, 1932]

'Hot' filtration is employed advantageously where contacting is the last step in the process

Special precautions must be taken because of the fire hazard involved in this operation Fires are particularly apt to start if the cake is dumped while at elevated temperatures Closed-type presses, in which the cake is dropped into containers forming an integral part of the press, equipped with screw conveyors to move the clay, are recommended for this purpose, although leaf and rotary vacuum presses have been used.

The choice of proper screen material is important Not only are rates of filtration and passage of fines greatly affected by it, but wear and life of the screens as well Whenever corrosion is a major problem, or where high temperatures are involved, monel-metal screens have proven satisfactory Plugging of screens is often serious It is usually due to a combination of asphalt-like matter containing an inorganic filler of clay This combination is highly resistant to mechanical and chemical action, and it is next to impossible to remove it from screens Steaming of the clay on the press is usually responsible for it, and where it is encountered filtering procedure may have to be changed to eliminate its formation Steaming should be eliminated and replaced by vacuum of gas drying Air drying can safely be employed where low temperatures are involved

If the spent clay is reduced to a dry powder, dusting is likely to cause a major problem In order to protect workers from its effects, either closed-type presses as mentioned above, or ventilating systems connected to dust separators, should be used

VII. COST

In the course of the development the relative costs of percolating and contacting have varied with the progress in each method

In the past decade contacting was somewhat favoured, and percolation was in some circles considered antiquated.

Most recent developments, however, particularly the discovery of means to remove inert materials from burnt percolation clays [44, 1934], have changed the sentiment in favour of percolation

Davis [12, 1928] comes to the conclusion in a comparison of costs that, as long as there are no commercial methods for reclaiming fine contact clays, contacting will be considerably more expensive Quoting Davis 'The contact process, however, fills an important role in the production of high-quality lubricants (neutralization without alkali) which cannot be performed by the percolation filters, and it therefore seems that a combination of the two is the correct solution '

The following table presented by Davis shows the relative cost of decolorizing oil to 1 Tag-Robinson colour by

I Single contact (1½ T R colour because of subsequent darkening in dewaxing and distilling)

II Double contact (½ T R during neutralization and 1 T R in final contact)

III Contact and percolation (contact to ½ T R colour)

The cost of neutralization and decolorization to ½ T R is not included in any of the above methods

TABLE VIII

	I Single contact	II Double contact	III Percolation
Clay used per bbl (lb)	44	46	133
Clay cost per ton	$14	$14	$20
Net cost per ton	$14	$14	$0 50
Times used	1	1	40
Cost burning			$0 85
Clay cost per bbl of charge	$0 308	$0 322	$0 090
Cost per bbl direct operation	$0 050	$0 196	$0 270
Total cost per bbl charge	$0 358	$0 518	$0 360
Yield finished bright stock	80%	98%	98%
Cost of decolorizing 1-bbl finished bright stock	$0 448	$0 528	$0 367

The cost of percolation and restoring percolating clays is reported by Funsten [19, 1934], who made a thorough analysis Parts of his data are shown in Tables IX and X

Cost of percolation clays can be further reduced by removing the inert matter, formed during burning, by means of separating tables [44, 1934]

Activated contact clays are by far the highest priced, and their economy lies entirely in their high efficiency Factors in their cost calculations are price of raw clay, grinding and drying, acid consumption, steam, water, labour, recovery, and final efficiency

The following figures are typical

TABLE IX

Filter-turnover Costs (per 1,000 Cu -ft Filter)

Note Applicable to the percolation decolorization of an acid-treated, neutralized Mid-Continent cylinder stock processed as follows 1, solution percolated, 2, dewaxed and reduced and 3, straight filter finished

Type of Filter *Average Clay No*	*Solution* *5–12*	*Straight* *1–4*
A *Labour and general expense items —$0 5446 per 1,000 lb	$17 97	$17 97
B Steam for washing (25,000 lb at $0 30 per 1,000 lb)	7 50	7 50
C Naphtha loss filter washing—1 8% at 5 cents per gal	4 50 (100 bbl used)	13 50 (300 bbl used)
D †Fuel—clay burning	2 48	2 48
E ‡Reducing filter wash	0 59	26 06
F Clay cost (see Table X)	29 46 (5–12 clay at $0 864 per 1,000 lb)	43 64 (1–4 clay at $1 417 per 1,000)
Total filter turnover cost	$62 50	$111 15

Notes

*A This item computed from costs allocated on a basis of clay throughput

†D 50 lb fuel per 1,000 lb clay at $1 50 per 1,000 lb fuel

‡E As follows

1 Solution filters, reducing only 5% of wash (158 2 bbl per filter), balance to fresh solution make-up

2 Reducing all straight filter wash (354 6 bbl per filter)

TABLE X

Standard Cost of Clays by Clay Numbers

Column *Clay No*	*A* *Original weight*	*B* *Burning loss (1 5%)*	*C* Net weight *Pounds*	*D* Net weight *% of total*	*E* *Efficiency (%)*	*F* *Product (E× C)*	*G* Clay costs ($ per 1,000 lb) *'M'*	*G* Clay costs ($ per 1,000 lb) *'N'*	*H* Clay costs (Per 1,000 lb) *'M'*	*H* Clay costs (Per 1,000 lb) *'N'*
1	1,000	150	850	9 045	100	850	1 450	1 595	1 708	1 879
2	850	13	837	8 907	86	720	1 230	1 353	1 469	1 616
3	837	13	824	8 768	77	634	1 083	1 191	1 316	1 447
4	824	12	812	8 640	69	560	0 957	1 053	1 178	1 297
5	812	12	800	8 513	64	512	0 875	0 963	1 093	1 203
6	800	12	788	8 385	58	457	0 781	0 859	0 991	1 090
7	788	12	776	8 257	54	419	0 716	0 787	0 922	1 015
8	776	12	764	8 130	51	389	0 665	0 732	0 871	0 958
9	764	11	753	8 013	48	361	0 617	0 679	0 820	0 902
10	753	11	742	7 899	45	334	0 571	0 628	0 769	0 846
11	742	11	731	7 781	43	314	0 536	0 590	0 735	0 808
12	731	11	720	7 662	42	302	0 519	0 570	0 718	0 789
Total	9,677	280	9,397			5,853	$10 000	$11 000		

	Initial cost of clay $ per ton *'M'*	*Initial cost of clay $ per ton* *'N'*
Clay cost	$12 50	$12 50
Freight	7 00	9 00
Handle and burn	0 50	0 50
Total	$20 00	$22 00
Clay cost $ per 1,000 lb	$10 00	$11 00

Unit clay cost by numbers (column 'H') =

$$\frac{\text{Clay weight } (C) \text{ times efficiency } (E)}{F \text{ (Total)}} \text{ times } \frac{\text{Initial clay cost (\$ per 1,000 lb)}}{\text{Clay weight } (C)} \text{ times } 1{,}000$$

TABLE XI

Acid activated clay	$27·00 per ton
Clay (0 6 lb per gal acid oil)	34 cents per bbl acid oil
Mixing	3 cents " "
Pipe-still operation	5 cents " "
Filter-press	4 5 cents per bbl solution (60% oil and 40% naphtha)
	7 5 cents per bbl acid oil
Solution naphtha	5 cents per bbl charge
	8 3 cents per bbl acid oil
Total operating cost	57 8 cents per bbl acid oil

Losses 50–50 oil-naphtha, 8% of filter charge at 5 5 cents per gal
= 30 8 cents per bbl acid oil

Total clay treating cost = 88 6 cents " "
– 93 cents " finished oil
2 2 cents per gal finished oil

Note 1 bbl – 42 U S gal

VIII. CONTROL AND TESTING

Percolating as well as contacting are usually controlled by colour For practical purposes the Tag-Robinson colorimeter is sufficient For exacting laboratory investigations the Lovibond instrument or the method for measuring the true colour densities [17, 1934] are required

Solvent refined oils that frequently are of sufficient colour to need no further improvement are 'stabilized' with clay In this case means of control are sludging, oxidation, and emulsion tests

In order to arrive at reasonable cost figures and for control purposes the efficiencies of clays are important It is quite common practice to rate the efficiency in weight of clay per gallon of oil required to obtain a certain approximate result, and compare this with the weight of a standard clay which produces the same result

Davis [12, 1932] discusses the fallacy of the above method, pointing out that different relative quantities of various clays may be needed for different duties and, whereas one clay may be cheapest for low colours, another clay may be cheaper than the first for high colours In order to obtain a true picture of clay efficiency, curves should be plotted for colour (or its equivalent in another property) versus clay requirement

Furthermore, a curve determined for one type of oil is not applicable to another type of oil Different oils behave very differently towards various clays, and the history of the oil should in all cases be known when judging the efficiencies of clays

The actual tests to establish the efficiency of a clay or for plant control are performed in small laboratory apparatus reproducing plant equipment and operations

When investigating clays to be activated, the type and quantity of acid to be used, digesting time and temperature and treating losses must be determined Once these factors are established, plant control becomes simplified to control of the final acidity of the clay Oils contacted with clays having neutralization numbers of more than 5 mg KOH per gram are likely to be quite unstable

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FULLER'S EARTH TREATMENT OF CRACKED GASOLINE

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When the treatment of cracked gasoline achieved importance following the first commercial production of pressure distillate from the Burton cracking stills, sulphuric acid, which had long been used by the petroleum industry to refine kerosine and naphtha, was the reagent first employed Since the purpose was to mask the presence of cracked products in marketed blends, and the profits of cracking were so high that treating losses were comparatively unimportant, it was sufficiently satisfactory that cracking plants installed in the period 1914–24 almost invariably carried with them installations for acid treating and redistilling the cracked product It was not until nearly the end of that period that refiners became aware of the needlessly large losses incurred by the costly processing then in vogue While rational treating methods now in use reduce the gum-forming tendencies of cracked gasoline at the expense of treating losses averaging in the neighbourhood of 1%, the older method involved consumption in the form of solution, polymer and rerun losses, of from 4 to 5% of the cracked gasoline being refined Moreover, due to their higher reactivity with sulphuric acid, the losses were greater proportionally for those classes of hydrocarbons responsible for the superior anti-knock characteristics of cracked motor fuel Depreciation equivalent to two or three points on the present octane number scale were the rule due to acid treating, and even higher losses were experienced on highly cracked gasoline

Among the processes for treating cracked gasoline to produce a commercially satisfactory product with minimum costs and losses, fuller's earth treatment is most widely used, with installed capacity aggregating more than 200,000 barrels of cracked gasoline per day, apportioned among the Gray, Osterstrom, and Stratford processes as shown in Table I While these processes differ in technique, they all have as their main feature the selective polymerization, by fuller's earth or a similar treating agent, of the objectionable unstable constituents of the cracked spirit

The use of adsorbents to decolorize and deodorize petroleum oils is as old as the industry itself, having been taken over from much earlier practice in the purification of animal and vegetable oils Although the commercial applications which survived were liquid phase processes, early workers in the field (Parsons [10, 1869], Steedman [12, 1874], Baynes, Fearenside, and Thompson [1, 1884], and others) passed certain vaporized oils through charcoal, earths, and other substances

Commercial Application of Fuller's Earth Treatment of Cracked Gasoline in 1937 (bbl per day)

	United States	*Other countries*
Gray process	150,000	25,000
Osterstrom process	16,000	600
Stratford process		30,000
Total	176,000	55,600

Fuller's earth was widely adopted for the decolorization of lubricating and other heavy oils, and its effect was regarded as purely physical until Gurwitsch [5] in 1912 announced the low-temperature polymerizing action of porous materials, and followed this in 1915 with the observation [6] that floridin (a type of fuller's earth) brings about polymerization when used to decolorize petroleum oils, as evidenced by the formation of highly coloured substances

In the earliest days of commercial cracking Gray in the United States and Hall in England had independently found that fuller's earth could be used to purify cracked gasoline vapours But although Gray's first patent [3] was issued on an application filed in 1914, it was not until 1924 that the first commercial unit of the Gray process was installed at Barnsdall, Oklahoma

(The petroleum industry uses the terms 'fuller's earth' and 'clay' as being loosely synonymous The terms will be used interchangeably in what follows)

The development of the processes is evident from the various patents taken out by Gray [4, 1930, 1933]

As now operated, these processes include a preliminary step of separating a fraction comprising gasoline from the heavier products of cracking, a second step, frequently coincident with the first, in which the fraction to be treated is brought to the desired temperature and pressure conditions, then the polymerizing step, wherein the gasoline is subjected to the action of fuller's earth or similar material capable of causing the selective polymerization of unstable hydrocarbons, and finally one or more steps to separate the treated gasoline from polymers formed by the fuller's earth and from any other hydrocarbons boiling outside the desired range The Gray [8, 1933] and R K Stratford [14, 1930, 15, 1933] processes operate on cracked gasoline in vapour phase In the former, vapours are passed through one or more beds of 30–60 mesh clay under conditions which bring about condensation of part of the vapours, this serving as a solvent for the polymers formed While the bulk of polymerized hydrocarbons readily separate from the treated vapours by reason of their higher boiling-point, a final fractionating step is usually provided to complete the separation In the Stratford process, the cracked gasoline vapours are contacted with clay by passing them up through a bubble tower of conventional design countercurrent to a descending slurry of fine clay in a suitable carrier such as previously treated naphtha Treated gasoline is taken off as vapour from the top of the tower, while the polymers are dissolved in the slurry naphtha, and withdrawn, with the spent clay, from the bottom of the tower While the above-described vapour-phase processes can be operated in connexion with a cracking or rerun distillation unit, most Gray plants are worked in the former way (and consequently under superatmospheric pressure) while the Stratford plants in commercial use almost always treat rerun gasoline at or near atmospheric pressure

The Osterstrom process differs from those described in being essentially a liquid phase process The distillate to be treated is heated to 500–600° F under a pressure (about 1,000 lb per sq in) sufficient to maintain it in liquid phase and passed in that form through a bed of coarse clay

Polymers are dissolved in the gasoline being treated, and separated from it in a flash distillation step following the clay treatment

These clay-treating processes produce a refined gasoline of improved colour and odour with a minimum amount of gum, and having sufficient stability as regards colour and gum content to meet the usual requirements of storage and distribution These results are obtained at lower costs than are required by acid treating the same type of cracked gasoline and with lower losses of material being treated There is, moreover, usually no loss of knock rating due to earth treatment These facts account for the widespread adoption of clay treating

Fuller's earth treated cracked gasoline is ready for the American market after being alkali washed or doctor sweetened Doctor sweetening usually improves colour stability and gum stability of the gasoline on storage, but reduces stability as regards exposure to light In some cases, where rigorous conditions of storage and distribution are encountered, oxidation inhibitors or anti-oxidants are added to the clay-treated gasoline It has been reported by Steininger [13, 1934] that clay-treated cracked gasolines are extremely responsive to inhibitors

The compounds removed by clay treating are the less stable unsaturated hydrocarbons This has been determined by experiments conducted on pure compounds, analyses of polymers formed, and so on Under ordinary (commercial) conditions of treatment of cracked gasoline with fuller's earth alone, little change is brought about in the sulphur content of the material being treated, so that clay treating without an accompanying desulphurizing step is not adapted to cracked products from charging stocks of high sulphur content, when low sulphur content gasoline is required

The gum-forming unsaturated hydrocarbons are not uniformly distributed in cracked gasoline, and samples examined show peak concentrations in the middle boiling fractions The fractions highest in gum yield the greatest amount of polymers on treatment and require high clay/gasoline ratios The off-colour fractions are not associated with the gum-forming bodies, and are most frequently found in the highest boiling fractions The degumming and decolorizing reactions of fuller's earth on cracked gasoline are not the same, and treating material quite spent as regards one of these effects may have considerable life remaining as regards the other

Specifications of the fuller's earth or other clay used in these processes are not critical except as regards mesh dimension In some cases, native clays which are not really fuller's earth and which could not be adapted to the refining of lubricating oils by percolation can be used in the polymerization treatment of cracked gasoline Moreover, the clays used in these processes need not be dehydrated before use This, of course, can be explained by the high temperature of treatment, whereby the gasoline first passing through a fresh charge of clay acts as a drying agent The most important requirement is that the treating agent must have the selective polymerizing action described It is due chiefly to the low cost of fuller's earth and its selectivity of action that it has been the most widely used treating agent

In the processes employing coarse fuller's earth, the treating material can be revivified after use by roasting in multiple hearth type furnaces [9, 1926] Thus, clay from Gray tower installations is completely revivified by roasting at temperatures somewhat lower than those required for recovering clays used in the percolation of lubricating oils In view of the low cost of treating material, however, this recovery step is not practised except in plants using large amounts of clay for treating lubricating oil Clay has been reburned and reused as many as 20 times in the Gray towers at one plant, and can also be used in lubricating oil percolation after reburning In one installation of the Stratford process fine clay, spent as regards contact treatment of lubricating oils, is made into a slurry without revivification and used in the Stratford process with good effect Throughputs per ton of clay are so large and amounts of clay used in any plant so small that there has been no work done on the commercial revivification of clay from the Osterstrom process Where spent clay is not reburned, it is discarded, frequently being used as fuel

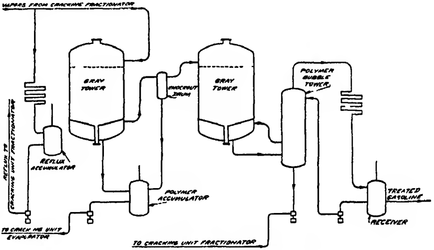

Fig 1 Flow diagram, the Gray process

Detailed discussions of the processes, the manner of working them, and results obtained are given below

The Gray Process

A flow diagram, showing the important features of a modern two-stage (series) installation, is given in Fig 1 Cracked gasoline vapours from the fractionating tower of the cracking plant are separated into two portions One of these is condensed without treatment and the condensate used as reflux in the fractionating tower The other portion passes downward through a bed of fuller's earth supported on a screen in the first Gray tower (or 'polymerizer') In most plants the equilibrium boiling temperature at the pressure conditions maintained is utilized, and a portion of the vapours condense in the clay bed Where the condensate so produced is insufficient in amount to fulfil its function, provision is made to introduce from an external source, or by additional cooling, the required amount of solvent, usually condensate of the treated vapours Polymers, produced by the reaction of the unstable unsaturated hydrocarbons in the presence of the clay, are

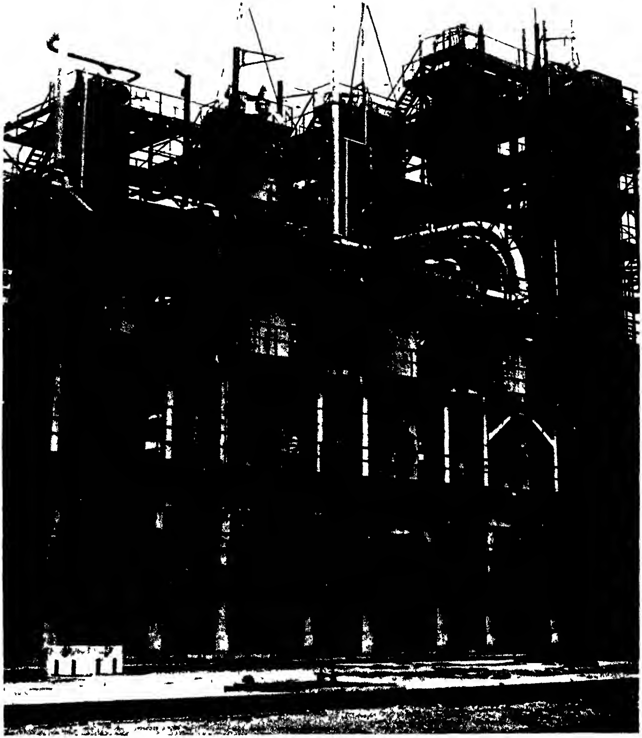

FIG. 2 Gray towers connected to combination unit, Texas City

largely dissolved in the condensate and drain from the clay with the aid of the vapour stream Partly refined vapours, and the solution of polymers in condensate, pass through the screen into the separating zone beneath Here the vapour velocity is maintained at a point sufficiently low to cause the bulk of liquid particles to drop out A further separation of vapours from entrained liquid is effected in a mist separator or 'knockout drum' of conventional design built into the vapour line connecting the two towers The partially refined vapours pass next through the second polymerizer, where they experience further refinement (In most plants using series flow, the bulk of the purification, expressed in terms of percentage, gum removal, or by any other index, takes place in the first clay tower The second tower is used to 'finish', or bring the treated gasoline up to high specification standards [8, 1933] In this way, a much greater throughput of treated gasoline per ton of adsorbent is obtained than can be effected by single or parallel flow The connexions between the towers are so arranged that the order of flow can be reversed, so that the clay need be changed in only one tower at a time and the vessel containing the fresh clay can always be the second one in the series After the utility of a charge of earth as 'finishing stage' is spent, it still has considerable useful life in the first stage The reason may perhaps be found in the higher reactivity of the more readily removed unsaturates) Vapours from the final treating stage pass through a final fractionating tower, called the 'polymer bubble tower', where they are completely separated from polymers and adjusted to the desired final boiling-point This is especially important in cases where the main bubble tower produces naphtha of a higher boiling range than that permitted by the gasoline specifications Such a condition may be brought about when it is desired to present the vapours for treatment at a higher temperature than would be possible if an end-point gasoline were maintained at or near its equilibrium boiling-point The most convenient way to accomplish this end without superheating the vapours or increasing the pressure on the system is to adjust the operation of the fractionating column so as to produce a fraction having a correspondingly higher end-point, relying on the polymer bubble tower for the final adjustment In such cases a side stream may be cut from this last tower, having furnace oil or distillate boiling range and refined as regards colour, carbon content, &c , although containing products of polymerization of the gasoline fraction

Polymer solutions from the two clay towers may be kept separate or combined The underflow from the second tower in series is usually, in any event, mixed with the bottoms from the polymer bubble tower for disposal While the total amount of 'polymer fractions' (polymers dissolved in gasoline condensates) ranges from 8 to 15% and more, based on the gasoline treated, the major portion of this material is condensed gasoline, the total amount of true polymers produced ranging from ½ to 1½% (These figures do not apply to highly cracked 'vapour-phase' gasolines, which give much higher polymer production) In order to avoid any loss of constituents in the gasoline range, the polymer fraction is recirculated to selected points in the system, depending on the type of distillation unit and the operations conducted in it Where the clay towers are connected with a cracking unit of conventional type, the polymer fraction from the first tower may be pumped to the evaporator, while that from the second tower and polymer bubble tower bottoms are returned to the main bubble tower In this way, the gasoline finds its way back into the vapour stream, lighter polymers are recycled for cracking and the heaviest polymers, which most operators prefer to keep out of the cracking tubes, are removed with the tar

The true polymers produced by the process have been found by elementary analysis to be hydrocarbons with a high carbon/hydrogen ratio, denoting a complex structure Their molecular weight indicates that they probably range from di- and tri-polymers to heavier compounds They lend themselves readily to oxidation, possess drying properties, and have in some cases found industrial application Although of high viscosity, their viscosity-temperature characteristics are poor

The polymerization reaction is exothermic, and when the vapours of cracked gasoline are turned into a chamber filled with fresh fuller's earth a rise of 30° F in temperature is not at all unusual This temperature differential gradually decreases during the first week of operation until it finally settles down to 5 or 10° F , in which range it usually remains for the duration of the clay cycle During the period when the temperature of the outlet vapours is 15–30° F higher than the inlet vapours, an increase in the end-point of the gasoline is observed, due to carrying over of polymers This is corrected in the polymer bubble tower

Although some plants are being operated at substantially atmospheric pressure, the largest proportion of Gray process operations is carried out in the 50–100 lb per sq in range, with some installations working under pressures as high as 400 lb The higher pressures result in more effective polymerization and greater operating economy from the standpoint of higher throughputs per ton of adsorbent, although this is usually accompanied by somewhat higher polymer losses than those obtained from lower pressure operation Treating temperatures range from 280 to 500° F

The optimum rate of treatment varies with the distillate to be refined and the specification desired in the finished product In most plants, treating rates are in the range from 1 to 4 barrels per ton of fuller's earth per hour, but lower and higher rates are also observed, the upper limit of commercial operation being about 6 bbl per ton per hour The higher rates, however, are not advisable where low copper dish gum tests are required on the finished products, and are employed in plants using anti-oxidants after the fuller's earth treatment One such plant, with a high treating rate, is being operated in connexion with the large Combination Unit of the Pan American Refining Company at Texas City, Texas As shown in the photograph Fig 2 and described by Price and Brandt [11, 1935], it has four Gray towers in parallel, followed by a single polymer bubble tower Some authorities [13, 1934] consider the time of contact an important factor, although differences in temperature and pressure of treatment make time of contact less significant than might appear to be the case Contact times of as little as twenty seconds and as high as fifteen minutes have been observed There seems to be no danger of over-treatment, there being no loss in octane number even after prolonged treatment, and only small differences are observed in the amount of polymer formation Consequently, high treating rates (short time of contact) are justified only when the cost of equipment increases rapidly with its size, as is the case in installations for high working pressure

Treating time, however expressed, depends only on the cubical contents of the clay bed, and not on its shape, but vapour velocity depends on the dimensions of the treating zone With downward flow of vapours, which has been found desirable, high vapour velocities are preferred because they help to drain the polymers out of the clay Contrariwise, deep beds of small diameter cause increased pressure differential, and the operation of the distillation unit limits the pressure drop allowable for a given treating system (It has been found that the pressure drop through the clay follows the relationship developed by Fancher and Lewis [2, 1933] for the flow of fluids through sand beds) There is, however, considerable flexibility allowed the designer of clay treating equipment, as evidenced by the fact that in the refineries of a single company there are towers in commercial operation having clay beds 8 ft high by 25 ft diameter and 28 ft high by 6 ft diameter, respectively The fuller's earth capacity of Gray towers in commercial use has ranged from 4 to 100 tons

The Gray process is in extensive use in the United States, Canada, the Argentine, Roumania, and Japan It is treating cracked gasoline produced by the Cross, Dubbs, Holmes-Manley, Tank and Tube, Combination and other types of cracking units operating on gas oil and fuel oil charging stocks from many types of crude and also reformed and polymer gasolines One ton of fuller's earth treats from 1,000 to 30,000 barrels of cracked gasoline, depending on the type of cracking plant, the oil charged to it, and the refinery specifications for treated cracked gasoline In general, highly cracked products require more clay than those more moderately heat treated, products of fuel oil charging stocks more than those from distillates, and naphthenic products more than those of higher paraffinicity Table II summarizes operating conditions and results at a representative plant More complete data on single versus series operation, results on different gasolines, effect on octane number, costs and the like can be found in the paper presented by the writer [8] to the World Petroleum Congress in July, 1933

TABLE II

Results from Gray Process Operations

Type cracking unit Holmes Manley
Charging stock 28° API Reduced Crude
Cracking temperature 965–70° F
Gray towers Two (series) followed by polymer bubble tower
Bbl per ton per hour 1 21
Clay treating temperature 415–35° F
Clay treating pressure 150–75 lb per sq in
Throughout per ton of fuller s earth 3,700 bbl.
Polymers produced 1 15%
Tests on treated gasoline after doctor sweetening

Gravity	58–60°
I B P	80° F
F B P	392° F
Octane no	70
Colour (Saybolt)	30 (after 90 days' storage 28)
Induction period	2 5–3 5 hours
Gum (copper dish)	2 mg (after 90 days' storage 3 mg)

The Osterstrom Process

The flow diagram given in Fig 3 shows a typical installation of the Osterstrom process Raw distillate to the treating unit is obtained by condensing the cracked product, which in most commercial installations is Gyro gasoline This material is heated to the required temperature, usually between 500 and 600° F, in the pipe-still and then passed through the bed of clay in a small treating vessel The vessels used are 24 to 36 in in diameter and contain a charge of from 2 to 4 tons of 30–60 mesh fuller's earth Such a charge is sufficient to treat as much as 2,500 barrels of cracked gasoline per day A pressure of the order of 1,000 lb per sq in is maintained in the treating chamber and is released through a manually controlled valve at the chamber outlet Polymerization takes place in the pipe-still as well as in the clay chamber and the polymers formed are removed by solution in the treated liquid The products leaving the treating chamber are flashed at a lower pressure (25 lb per sq in) and the gasoline separated from higher boiling constituents in a fractionating tower When the contained heat is not sufficient to effect this separation, additional heat is supplied either by recirculating the fractionating tower bottoms through a coil in the convection section of the pipe-still or by other means

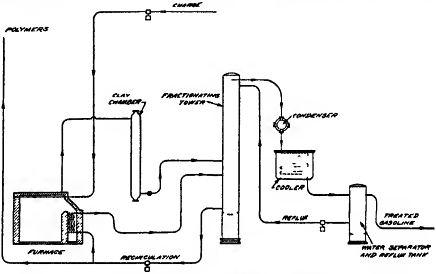

FIG 3 Flow diagram, Osterstrom process

In the case of the Osterstrom process, as in the Gray process already discussed, the treating reaction is exothermic and a rise in temperature of from 5 to 40° F is noted as the liquids pass through the treating chamber Pressure drop through the apparatus ranges from 25 lb when the clay is fresh to upwards of 100 lb as the clay becomes clogged with insoluble impurities This does not occur, however, until large quantities of gasoline have been refined In some cases as much as 70,000 barrels of Gyro gasoline have been treated per ton of fuller's earth. When applied to Gyro gasoline, polymer losses of 5–7% have been reported They are said to be very much lower on less highly cracked products, but the exact figures are not available

In most plants where this process is used colour better than 17–20 Saybolt is not required and operating conditions are maintained so as to produce this gum content of the treated spirits, for the yields indicated above are invariably below 10 mg per 100 c c and usually under 5. If desired, a gasoline having better colour characteristics can be obtained at the expense of increased fractionation capacity in the polymer separating tower

TABLE III

Representative Osterstrom High-pressure Clay-treating Data

Gyro distillate from Mid-Continent and Michigan Reduced Crude Oils

Operating data	
Throughput, barrels per day	2,500–4,000
Pressure, pounds	1,000
Temp tube still outlet	550–80
Temp clay chamber outlet	580–630
Total charge, barrels	166,342
Clay yield, 71,947 barrels of finished gasoline per ton of clay	

Note One charge of clay was used for approximately 4½ months

Tests on products

	Charging stock	*Finished Gyro gasoline*	*Polymers*
Grav	54 4	54 7	23 9
I B P	87	90	416
10%	136	129	438
20%	165	166	448
50%	263	265	
90%	387	393	
E P	435	417	
% at 500° F			49%
Colour		16–22	
*Gum		2 mg	

The finished Gyro gasoline showed an induction period of 4 hours plus, by the oxygen bomb method

* (Preformed)

The Osterstrom process is used in the United States and Japan Although developed especially to treat high octane number gasoline prepared by Gyro and similar cracking processes, where it is desirable to separate the highly reactive fixed gas from the gasoline before treatment, the Osterstrom process is also used to refine Cross cracked gasoline and reformed naphtha

Table III gives operating conditions and results of an application of the Osterstrom process

The R. K. Stratford Process

The flow diagram of the R K Stratford process is shown in Fig 4 Virtually all the commercial installations of this process in operation at the time of writing are on the rerun basis Cracked distillate is washed with alkali and is then charged to the rerun unit (which may, of course, be a pipe still although a shell still is shown in the figure) where it is vaporized and the vapours passed to a conventional fractionating column The vapours removed overhead from this column have an end-point higher than those of the desired gasoline since a temperature drop of 10–20° F is experienced in the treating tower Vapours to be treated are introduced at the bottom of the treating tower and pass upwards counter-current to a descending slurry of clay in treated gasoline, which is introduced just below the top plate The clay slurry mixture is prepared in a mixing tank, where it is kept in agitation by paddles driven at about 30 r p m The slurry is pumped from this tank by means of a triplex reciprocating pump to the treating tower

Treated vapours leaving the top of the treating tower are passed through heat exchangers and condensers in the conventional manner The slurry passing out of the bottom

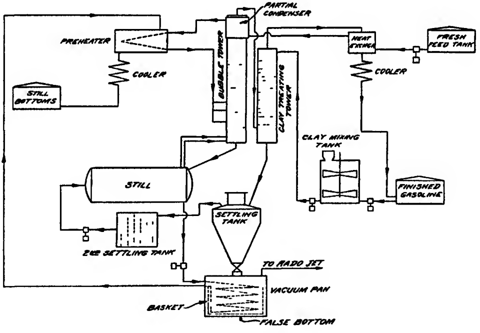

FIG 4 Flow diagram, R K Stratford process

of the treating tower is collected in a settling tank, where a preliminary separation of part of the liquid is effected, and the oil so separated is pumped to the middle of the fractionating column These separators are supplied in pairs, so that when one fills up the other is used, while the remainder of the oil from the clay mixture in the first separator is removed *in vacuo* by heat exchange with still bottoms

A typical plant having a treating capacity of 2,400 barrels per day comprises a 7½-ft diameter treating tower approximately 30 ft high with 12 bubble trays These trays are equipped with 5½-in weirs so that the depth of slurry on each tray is at least this height

About 200–250 gal of slurry containing approximately 250 lb of fine fuller's earth (200 mesh) is charged to the treating tower per hour, the concentration of clay depending on the type of gasoline being treated and the results desired

The clay is maintained in suspension during the passage of the slurry down the tower by means of agitation due to vapours bubbling through the pool on each plate Samples taken at intermediate points show the percentage of clay in the slurry to be substantially uniform, and inspection of the treating tower after 90 days of continuous operation showed no clogging of the bubble trays due to clay This process is in use at 6 refineries in Canada and Peru with a total treating capacity of approximately 30,000 barrels of cracked gasoline per day A summary of operating conditions and results is given in Table IV

The outstanding characteristic of the Stratford process is its extreme flexibility, as both the proportion of clay in the slurry and the rate with which the slurry is pumped into the tower may be varied Since fine clay is used, it is possible to utilize activated clays of the acid-treated type Another advantage is the uniformity of the product, since this is actually a continuous process Comparatively small amounts of cracked gasoline are treated per ton of clay used, optimum results in most cases being obtained at ratios in the range of 800–1,000 barrels of gasoline per ton of adsorbent

TABLE IV

Summary of R K Stratford Clay Treating Operations

	Charge to stills	*Overhead stream*
Still temp ° F		405
Vapour temp ° F		300
Gravity ° API	52 1	55 5
I B P ° F	178	180
Per cent off at 140° F		
158° F		
212° F	7	12
257° F	33	47
284° F	48	63
302° F	57	75
356° F	83	96
374° F	91	
392° F	96	
400° F	97	
End-point, ° F	424	372
Per cent recovery	98	98
Colour		30
Gum (A S T M Mg /100 c c)		nil
Sulphur		0 085
Octane number		58
Acid heat test		40
Vapour pressure (Reid)		2 3

Summary

Charged to still	125–30 bbl per hour
Colour-rundown tank	30
Vapour temp top of bubble tower	295° F
Pounds of clay per in of slurry	21
Vapour temp top of clay tower	280–5° F
Pumping rate of slurry	12 in (240 gal) per hour

In addition to the processes described above, others have been suggested. Some have reached the stage of commercial application although not in widespread use Of these perhaps the most important is another process [7, 1931] developed by Osterstrom and his associates at The Pure Oil Company in which the gasoline to be treated is mixed with fine clay and then passed to a heating zone where it is raised to polymerization conditions of temperature and pressure The mixture of clay and oil is then removed from the heating zone, the clay separated from the oil and the latter flashed to remove polymers This process was in commercial use several years ago but was replaced by the liquid phase process already described, which was found to be much more economical

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ACID-TREATED CLAYS

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CERTAIN kinds of clays when brought into intimate contact with unrefined or partly refined petroleum products possess the property of selectively removing undesirable constituents from the oil In their natural state some of these clays, such as fuller's earths and some of the Death Valley clays, are efficient adsorbents and require only drying and milling to prepare them for use There are other clays which have no, or very little, selective power of adsorption in their natural state, but which, when properly treated with acid, become far more efficient than the naturally active clays

The fuller's earth can be milled to a fine powder, 200 mesh or finer, and then intimately commingled with the oil and filtered therefrom in 'contact' refining, or it can be crushed to grains of 16 to 90 mesh and packed firmly in deep beds in towers, and the oil passed through the packed material in 'percolation' refining Powdered clay cannot be used commercially in percolators because it quickly becomes impervious to the flow of the oil In the activation of a clay with acid, the clay either crumbles or is reduced to a fine state of division, and consequently the activated clay is available only for contact and not for percolation processes This article, therefore, deals only with the activated clays in the contact refining of mineral oils The acid-activated clays are for the most part employed in the contact refining in substantially the same manner as the naturally active clays A discussion of contact refining is presented elsewhere in this treatise

Origin of Bleaching Clays

The naturally active clays and those activated by acid treatment are all degradation products of igneous rock, particularly of volcanic ash, and practically all such clays in America now exist as sedimentary deposits

Some of the best-known naturally active clays or fuller's earths are those of Georgia, Florida, Death Valley, England, and Japan Those in the south eastern part of the United States and in the Death Valley region of California are highly efficient, but the cost of shipment of the Death Valley clay prevents an extensive market outside California.

The fuller's earths have become activated by weathering and water leaching under favourable natural conditions

P G Nutting [22, 23, 1933] thinks it is possible that the clays, such as bentonites, glauconites, &c, which can be activated by acid occupy an intermediate degradation stage between an original igneous rock, such as volcanic ash or volcanic tuff, and the active fuller's earths in that they have been decomposed under conditions of thorough weathering, but of even more limited water-leaching than the active fuller's earths The fuller's earths have thus been leached under very special conditions much farther with pure water or more probably with weakly acidic water Neither of these two types of clay has in its disintegration process gone so far as to become inactive clay or soil

Of the clays that are naturally inactive but susceptible to activation, bentonite is the best representative because of its abundance and ease of handling For a discussion of bentonite, see the works of Raymond B Ladoo [12, 1921, 13, 1925], H S Spence [28, 1924], C W Davis and H C Vacher [5, 1928], and J W Mellor [16, 1925]

Bentonites are deposited widely over the world They occur in North America in Canada, British Columbia, Wyoming, Nevada, California, Texas, Arizona (the highly activated adsorbent Filtrol is produced from the deposits in the vicinity of Chambers, Arizona), and in several other States Many of the deposits are too thin for economical mining and may contain impurities that cannot be activated

Montmorillonite, beidellite, indianaite, halloysite, &c, are included in the general classification of bentonite However, other types of earths are found that can be activated as well as the bentonites, but they are not so accessible nor easily handled Among these are the marine secondary mineral glauconite and certain partly decomposed igneous rocks low in silicate and high in bases (see Table II and comments)

The bentonites consist mainly of hydrous aluminium silicate and usually contain from 5 to 15% of alkalis or alkaline earth oxides They have no narrowly fixed chemical composition, and their physical properties are not constant

C S Ross and E V Shannon [26, 1926] have assumed that a formula $R''OR'''_2O_3 5SiO_2 5-7H_2O$ can be used to represent fairly accurately the molecule of pure bentonite, the symbol R'' representing divalent Ca or Mg atoms, and R''' trivalent Al or Fe atoms

The basic elements sodium, potassium, calcium and magnesium, &c, in the bentonite molecule are subject to exchange or displacement by other bases, a property commercialized in the well-known zeolite for water softening Consequently, bentonitic clays from different deposits, or from different sections of the same deposit, may show marked variations in their composition from this one cause alone In this base exchange, perhaps all the bentonites permit the easy replacement of the alkaline and alkaline earth oxides, one with another Thus the sodium and potassium atoms are exchangeable with the calcium and magnesium atoms, as illustrated in the reversible equation

$$2NaCl+CaO\ Al_2O_3\ 5SiO_2 \rightleftharpoons CaCl_2+Na_2O\ Al_2O_3\ 5SiO_2$$

The base exchange may well account for the high content of magnesium in much of the naturally active clays found in and near Death Valley

C W Davis and L R Messer [4, 1929] show the analyses of some adsorbents and clays in Table I. They point out that samples *A* and *B* of Table I are both good adsorbents and differ markedly from each other, whereas clay *C*, quite similar to *B*, has no bleaching action and cannot be activated In a general way the composition of active fuller's earths is informative, however, for their ratio of silica to alumina is much higher than that of kaolin, ranging in fuller's earth from about 4–6 to 1

The raw bentonites suitable for activation usually have a silica to alumina ratio of from 2–3 to 1 (samples *E* and *F*, Table I), which ratio is intermediate between active fuller's earths and kaolin. The acid treatment of the bentonite (sample *F*) raises its ratio of silica to alumina to 5 or more to 1 (sample *G*), which equals or even exceeds the ratio in fuller's earth

TABLE I

Analyses of Adsorbents and Clays

	A	*B*	*C*	*D*	*E*	*F*	*G*
SiO_2, %	72 95	58 10	58 72	57 95	58 04	47 38	59 30
Al_2O_3, %	12 65	15 43	16 01	1 57	15 81	15 38	9 53
Fe_2O_3, %	3 56	4 95	2 12	0 85	3 10	2 57	1 70
FeO, %	0 47	0 30					
MgO, %	0 57	2 44	3 30	19 71	4 12	4 24	3 20
CaO, %	1 00	1 75	1 05	4 17	1 19	2 25	1 13
Na_2O, %	0 20	0 27	2 11	1 84	1 62	0 59	0 40
K_2O, %	0 68	0 66	1 50	0 43	0 75		
CO_2, %		0 84		1 22		none	none
(loss below 105° C) %	5 77	4 59	6 21	4 82	4 92	20 50	15 10
(loss above 105° C) %	1 25	9 45	8 61	8 11	10 03	7 10	8 79

A Commercial fuller's earth from Florida
B Commercial fuller s earth from Florida
C Typical clay from Nevada with no bleaching action
D Commercial high-magnesia earth from Nevada
E Earth (bentonite) from which commercial acid treated adsorbents are prepared
F Earth (bentonite) from which commercial acid-treated adsorbents are prepared
G Commercial adsorbent prepared from earth *F*

Sample *D* of Table I is of special interest It is typical of the naturally active magnesium silicate clays of the Death Valley region Its low content of aluminium and high content of magnesium differentiate it from the bentonite clays, although P G Nutting [20, 21, 1933] thinks it is possible that this clay comes from a bentonite that has undergone much base exchange and become activated through natural processes

In the fuller's earths and the bentonites the amount of moisture driven from the clay between 50 and 200° C is higher than in a kaolin type of clay, and Nutting [23, 1933] suggests that this characteristic may be common to all types of efficient hydrous adsorbents except the Death Valley clays that have the high percentage of magnesium The rise of adsorbent power with this characteristic loss of water of constitution is used by Nutting in support of the 'open bond' theory for adsorbent activity, which is later discussed briefly

Bentonite when wetted may absorb several times its volume of water and expand six- or eightfold, but all samples do not show this behaviour, nor is it an indication that the clay can be activated

Activation of Clays with Acid

V Salmi [27, 1926], in a fairly representative laboratory activation process, boiled a kilo of bentonite, sample *F* of Table I, with 2,000 ml of sulphuric acid of 17% strength for 3 hours, filtered out the clay, and washed it with distilled water until acid could no longer be detected in the filtrate The clay was then dried to a moisture content of about 15% and ground to pass through a 200-mesh screen In actual practice the washing is usually continued until the wash water contains about 0 2 to 0 5% acid Should the clay be washed with hard water after the acid is neutralized, the clay is injured by absorbing basic ions from the water

O Burghardt [2, 1931] describes the activation of a German hydrous aluminium silicate, called 'Isartone', doubtless a bentonite, and shows a detailed schematic arrangement for the mechanical operations, the principal steps of which are

1 Mixing the raw clay with water to form a thick slime
2 Adding acid to the clay-water slime, heating and agitating with live steam, and digesting at 105° C (220° F)
3 Filter-pressing and washing the clay in the press with fresh water to remove free acid and dissolved salts
4 Drying the clay in a rotary kiln with gentle heating
5 Milling the clay so that 85–90% passes through 180-mesh screen

He states that he uses 0 28–0 30 lb actual hydrogen chloride per pound of raw clay, but does not give its concentration He finds that the clay activates equally well with hydrochloric and sulphuric acids, but the sulphuric acid requires more time for the digestion, 5 or 6 hours instead of 2 or 3, and the clay after contact with an oil gives more trouble in the filtering process

For further details of plant practice in the activation of clay with acid, the reader should consult the publication of E R Lederer and E W Zublin [14, 1932] and patents issued to P W Prutzman and C J Von Bibra [25, 1923], to M L Chappell, R F Davis, and M M Moore [3, 1927], to W S Baylis [1, 1930], and to M J Welsh [29, 1915]

P G Nutting [20, 21, 22, 23, 1933] has made an extensive study of the acid activation of different types of clays and the influence on the activation of the kind and concentration of acid, the amount of clay leached away, &c He determined the bleaching activity of the clay after it was ground to 150 mesh and dried for 1 hour at 160–200° C by supporting a 1-in layer of the clay in a vertical glass test-tube and filtering oil through the layer at normal temperatures The oil used for this purpose was a black California crude, having about the same resistance to bleaching as a Pennsylvania cylinder stock (not acid-treated) diluted with an equal volume of naphtha The volumes of the oil were read that filtered through water-white, green, yellow, and red The ratio of the volume of the bleached oil to the volume of the clay was taken as the measure of the decolorizing power of the clay The best clay completely decolorized about 2 volumes of oil, and its efficiency was therefore rated as 2

Some of the data derived from the more important earths are shown in Table II The bleach-rating data in this table refer to the volume of oil bleached water-white at normal temperatures

Concerning the method of determining the comparative efficiencies of the clays in this somewhat arbitrary manner, it may be said that no one method of evaluating a clay can be relied on when the clay is applied to a different oil or to the same oil under appreciably different conditions Nutting found in these experiments that the bleach ratings were about twice as high when the oil was filtered at 200–350° C instead of at normal temperatures Obviously the laboratory tests and the refinery operations should be closely correlated

The first of the two columns under 'Bleach Rating' in Table II shows the efficiency of the raw clays based on the volume of water-white oil filtered The next column shows the maximum efficiency obtainable by the acid activation of the raw clay Some of the naturally active clays are shown to be degraded by the acid treatment. Column 3 shows the total percentage of clay that is extracted by the acid at the time the clay is given its maximum activity. The next 4 columns show separately the relative proportions of iron, aluminium, calcium, and magnesium extracted

TABLE II

Acid Activation of Various Types of Clays

	Bleach rating		Clay extracted, %	Soluble (scale of 10)				Weight loss, %	
	Raw	Ac ttd		Fe	Al	Ca	Mg	25–160° C	160–800° C
1 Attapulgus	0 8	0 5	18 6	4	4	1	1	3 2	9 6
2 Quincy	0 7	0 6	25 6	4	3	3	*	4 6	10 5
3 San Antonio	0 7	1 1	11 1	6	3	1	*	1 5	5 2
4 Olmstead	0 6	0 3	23 3	7	3	0	*	2 3	5 1
5 Death Valley	1 8	1 2	24 9	*	1	1	8	3 2	6 2
6 Tehachapi	1 1	1 1	13 1	4	4	*	2	5 6	7 0
7 Chambers	0 6	2 0	22 6	5	4	1	*	6 8	8 1
8 English earth	1 2	2 0	19 9	5	4	1	*	9 0	5 7
9 Japanese	1 0	1 1	14 2	3	6	1	0	9 1	5 3
10 N C dunite	1 2	1 2	40 0	5	0	0	5	4 1	9 2
11 Otay, Calif, bentonite	0 5	1 8	31 3	2	8	*	0	11 3	5 2
12 Silver Cliff	0 8	2 0	30 7	1	7	1	1	14 4	5 6
13 Westcliffe	1 3	1 9	31 5	0	7	2	1	16 1	4 8
14 Santa Rita	0 8	1 5	21 7	1	8	1	*	12 2	6 5
15 Laurel	0 7	2 0	41 4	4	4	2	0	16 8	6 2
16 Evansville	0 4	1 3	4 7	4	3	3	0	3 7	6 4
17 W Tenn	1 0	1 9	27 9	4	5	1	*	6 9	5 6
18 Midway	0 7	0 8	33 0	2	2	6	*	6 6	13 3
19 Commercial fuller's earth	1 3	1 6	26 3	3	2	3	2	6 8	10 0
20 Halloysite	1 0	1 4	42 9	0	10	*	0	9 4	14 2
21 Woodward	0 6	1 7	41 0	5	4	1	*	13 1	11 2
22 Saline	0 8	1 6	29 5	3	5	2	0	14 6	6 9
23 Cordele	1 3	1 3	15 1	4	5	1	*	2 0	8 8
24 Musselwhite	0 9	1 8	30 6	5	4	1	*	5 4	8 6
25 Fort Gaines	1 3	1 4	4 5	5	4	1	*	4 3	6 0
26 Chickamauga	1 0	1 9	20 7	3	5	2	*	2 7	7 2
27 Wyoming bentonite	0 7	1 3	19 7	3	5	2	*	6 3	5 9
28 N J glauconite	1 2	1 5	43 3	9	1	0	0	1 9	5 1
29 Md glauconite	1 2	1 7	38 3	10	0	*	*	3 5	5 9
30 Bavarian bentonite	0 7	2 0	21 9	3	4	3	0	11 0	5 5

* Trace

Nutting makes the following comments on the samples of clay in Table II

'Clays 1–9, 11, and 18 are well-known commercial clays, 10 is a decomposed olivine rock from near Webster, N C , 12 and 13 are pink bentonites from Colorado, 14 is a similar bentonite from Santa Rita, N Mex , 15 is a brown waxy bentonite from near Laurel, Miss , 16 is a green bentonite from eastern Tennessee, 17 is a sedimentary clay, possibly a reworked bentonite from a bank of the Tennessee River sent in by Prof Walter H Bucher of Cincinnati, 19 is a "fuller's earth" supplied by a chemical supply house, 20, horny white halloysite from near Rome, Ga , 21 is from the 5-foot deposit being worked near Woodward, Okla , apparently an impure bentonite, 22, bentonite from Saline County, central Arkansas, submitted by State Geologist J C Branner, 23, 24, and 25 are central Georgia clays submitted by Poole Maynard, Atlanta, Ga , 26 is an Ordovician bentonite, greenish grey, very like shale in texture'

Optimum Leaching in Acid Activation

From the data obtained in the acid activation of several clays, Nutting [22, 1933] plotted the decolorizing efficiencies against the per cent of clay leached out by the acid One of the typical figures, that of a bentonite clay from Laurel, Miss , is reproduced here (Fig 1) This clay is inactive until treated with acid

The four curves in the plot refer, respectively, to the appearance first of green, then of yellow, red, and finally black, as the oil filters through the clay Up to the lowest curve (*G*) the oil comes through white, but here it begins to show a tinge of green The second curve (*Y*) shows the beginning of the yellow, &c

In all the clays that can be activated, the adsorbent power increases to a maximum with increasing amounts of acid used in leaching, and then decreases with further increments of the acid, as illustrated by the curves in this plot (Fig 1)

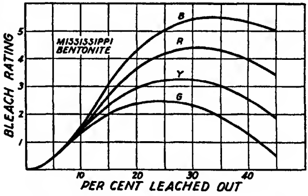


FIG 1 Activation of a typical bentonite by acid leaching

The efficiency figure is, of course, higher when it is based on the volume of oil bleached, for example, to a red colour rather than to the white, and, as to be expected, the ratios of the volumes bleached white to the volumes bleached red are not constant for the different clays In other words, some of the clays, after failing to bleach the oil to a water-white colour, continued to bleach the oil to a green, yellow, or red colour in relatively much larger amounts than other clays Each sample of oil and each sample of clay manifests its own individualities in the bleaching processes This sample of activated bentonite was found to be most efficient in bleaching cotton-seed oil when 18–32% of its weight had been leached away by the acid, whereas for petroleum oil, it was most efficient when 27–42% had been leached away

Nutting [22, 1933] finds, as a rule, that the bentonites which can be highly activated have low bleaching power before treatment, and that if the bentonite has already been partially activated in nature by water or weak acid, it cannot be converted by the normal acid-leaching process into a highly active clay Such clays go over to nearly pure silica, even though efforts are made to prevent this action by controlling the time, temperature, and concentration of the acid Some of the grains of the clay consistently leach more readily than others He found, however, that he could equalize the leaching effect on the grains by first adding to the acid certain soluble salts, such as the chlorides of iron, aluminium, and magnesium to hydrochloric acid, or the sulphates of these metals to sulphuric acid

TABLE III

Salt-acid Solution in Clay Activation

	Not treated	*Acid leached*	*Salt and acid solution*
Florida clay	0 7	0 6	1 8
Bentonite	0 5	1 5–2 0	2 0
Glauconite	1 2	1 0–1 7	2 0
English earth	1 2	1 6–2 0	2 0
Death Valley	1 8	1 2	2 0

Table III shows the influence of the salt-acid solution on some typical earths The Death Valley clay, for example, a naturally highly efficient adsorbent which was degraded by the normal acid leaching, was materially improved by the salt-acid combined treatment The process [24, 1935] may be found applicable to earths in which certain components are unfavourably affected by the acid or to clays that are seriously degraded by too much acid

H L Kauffman [11, 1927] investigated the possibility of increasing the efficiency of powdered Georgia fuller's earth by treatment with acid and was able to increase it by only 20–40% for the oils used in his tests He found that similar acid treatment of a bentonite clay made it several times as efficient as the natural fuller's earth under investigation

In the activation of earths with acid, the soluble magnesium, aluminium, and other metallic elements are converted into salts of the acid Much of the alumina, however, is not attacked by the acid, but remains permanently associated with the silica in the approximate ratio of 1 to 5–6, as stated above

Concentration of the Acid used for Clay Activation

In the activation of non-active clays the optimum concentration of the acid employed usually ranges from about 15 to 20% The amount of the dilute acid varies for different clays and must be determined experimentally

P G Nutting's tests on many samples of clays confirm the usual observation that hydrochloric and sulphuric acids of about 20% concentration give equal activation Even with clay high in calcium, he found no measurable differences in the bleaching effects

C W. Davis and L. R. Messer [4, 1929] reported more in detail the effect of the concentration of sulphuric acid in activating clay The clay after activation was ground to 200 mesh and commingled with the oil at temperatures ranging from 80 to 190° C The colour of the filtered oil was determined by an Ives tint photometer reading from 0 to 100, the reading of 100 indicating a colourless oil The optimum concentration of the acid usually fell in the range of 15 to 20%, although for one sample of lubricating oil the clay was equally well activated over a range of acid concentration from 20 to 50% This last effect is shown by the curve *A* in Fig 2 The colour is plotted against the concentration of the acid employed in activating the clay

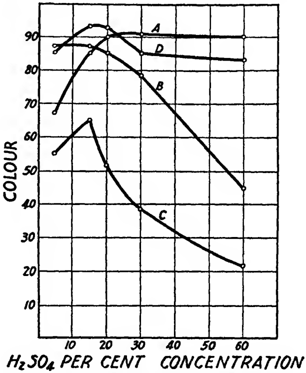


FIG 2 Optimum concentration of acid for clay activation
A Texas oil
B Oklahoma oil
C California oil
D Soya-bean oil

J D Haseman [9, 1929], in a discussion of the theory of bleaching actions of clays, states that the average bentonite can be activated with an equal weight of boiling dilute sulphuric acid of 33% strength, but that halloysite, often classed as a bentonite, containing 3 times as much aluminium, requires much more acid for activation

P G Nutting [22, 1933] has compared the use of different amounts of hydrochloric acid of 1% concentration and of 10% concentration for the activation of a Texas bentonite, which he considered typical of the bentonite clays, and has plotted the bleach rating of the treated samples in the two series against the corresponding percentage of material extracted from the clay (Fig 3) The maximum activity of the clay treated with the 10% acid was about twice that of the clay treated with the 1% acid, although the maximum activity produced in each occurred when from 20 to 30% of the clay was leached away.

Joe E Meyer [17, 1930] has studied the activation of the bentonite near San Diego, California (Otaylite from near the town Otay), and found that ½ lb of 20% sulphuric acid per pound of dry raw clay gave the clay its maximum adsorptive power for mineral oils Later and more extensive development of the Otaylite has confirmed Meyer's data, although some parts of this practically limitless deposit of clay require considerably more of the weak acid than found by Meyer

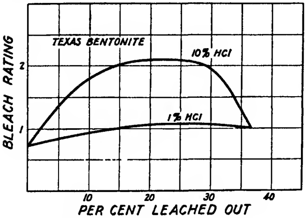


Fig 3 Influence of acid strength on maximum activity of a clay

Meyer reports the bleaching power of this activated earth to be from 4 to 6 times that of the best fuller's earth This figure, however, requires elaboration In certain cases, as in bleaching a lubricating oil to a specially light colour, the activated clay may be from 4 to 6 times as effective as the best natural earths, whereas for bleaching the oils to medium colours, a well-activated clay is usually from 2 to 3 times as effective as the best natural earths

Although the principal object in the application of clay is that of bleaching the oil, nevertheless other effects are usually considered, such as the shade and stability of the colour, removal of resins, removal of acids, both organic and inorganic, resistance of the oil to oxidation, to sludge formation, and to emulsification with water, &c , and these factors must be weighed in evaluating the clay

Temperature of Contacting Clay and Oil

No specific temperature can be prescribed for contacting adsorbents with oil, the optimum temperature for each individual oil and clay must be determined experimentally The acid-activated clay is not different in this respect from the naturally active clays Refiners often neglect to determine the most economical temperatures and fail to provide facilities for treating at these temperatures

Temperatures of 121–260° C (250–500° F) are commonly used This temperature may give a better initial colour to a naphthene-base lubricating oil than a higher temperature, but the oil may soon darken to an undesirable blue or purple colour On the other hand, a temperature of 370° C (700° F) may not produce so light an initial colour, but the colour may be more stable, and in a month of storage the latter oil may change but little and then actually have a better colour than the oil treated at a lower temperature When the colour of an oil treated at higher temperatures does change, it may become green rather than blue, and thus have a much more pleasing appearance or 'outer tone' than an oil treated at lower temperatures However, bleaching at 370° C (700° F) an acid-treated transformer oil from California petroleum yielded a much better initial colour than bleaching at 121–260° C. (250–500° F), but the oil was much less resistant to oxidation and to sludge formation in long oxidation tests

Obviously, air must be completely excluded from the mixture of hot oil and clay Live steam is commonly used for this purpose, as well as for agitation It is usually economical to use some type of mechanical agitation for thorough commingling (e g , energetic flow through a pipe still) and to use only enough steam to exclude air After the heating, the oil is filtered, preferably through Monel metal leaves, or if cloth filters are used, the oil is first cooled to about 120° C (250° F) so that the heat will not injure the cloth After being filtered, the oil is cooled to a non-oxidizing temperature before it is permitted to come into contact with air The oil from the main filter-press may carry an almost negligible amount of very fine clay, which is often most economically removed by filtering the oil through a special filter-paper or 'blotting'-paper.

V A Kalichevsky and J W Ramsay [10, 1933] investigated the influence of temperature and time in bleaching a sample of acid-treated Mid-Continent cylinder stock with two different activated earths and an untreated but efficient natural earth The temperature range investigated was from 260 to 371° C (500–700° F), and the time of contact from an instant up to 200 min at the indicated temperatures

Their tabulated data show that with the activated clays the best initial colours were attained at 371° C (700° F) and in about 20 min At 315° C (600° F) the maximum bleaching effect with the activated earths was not attained in less than 2 hours, and the oil was then not bleached so light as at 371° C (700° F) in 20 min The lightest colour produced by the naturally active earth was obtained at 315° C (600° F) and in 2 hours' time If the bleaching power of the clays is based alone on the initial colours, the better of the two activated clays was considerably more than 3 times as efficient as the natural earth Other qualities of the bleached oils were not described

It is often found advisable to heat a lubricating oil and clay to a temperature at which the distillation loss begins to become excessive However, under any condition the oil can be condensed and returned to the main charge or used for other purposes

Optimum Amount of Moisture in Clay

Whether the clay requires drying before use depends on how it is to be used in bleaching If the oil and clay mixture is not heated to a temperature sufficient to dehydrate the clay and to develop its maximum adsorbent power, the clay must first be suitably dried However, if the bleaching is conducted at an elevated temperature, preliminary drying is not necessary Refiners of lubricating oils who activate their own clay usually find it uneconomical to dry the clay after activating it, and apply it wet or in the state of a slurry or mud The clay in this way automatically passes through its optimum state of dehydration in actual contact with the oil and thus develops its maximum bleaching action.

The method of application of the water and clay pulp is described in the patent of P W Prutzman and C J Von Bibra [25, 1923], and more recently in a report of E R Lederer and E W. Zublin [14, 1932]

L Gurwitsch [8, 1926] states that a sample of Floridin (fuller's earth) used in bleaching oil at normal temperatures was most efficient when the moisture content had been reduced to about 11 %, and that 'silica gel' is most efficient with about 7% moisture content, but he recognizes that the amount for the various clays is not a sharply fixed factor In the same discussion Gurwitsch points out that a clay dried to 8 or 9% water content by brief heating to 350–60° C decolorizes better than if dried to 5 or 6% by prolonged heating at 200–50° C Gurwitsch thinks the injury comes from the sintering of the clay at the long period of heating, but there is a possible explanation in the excessive dehydration characterized by closing of the free valences or open bonds, as assumed by Nutting

Experience in general indicates that if a clay, whether a naturally active fuller's earth or an acid-activated clay, is to be used at a normal, or a relatively low, temperature, it has the greatest bleaching power if previously heated for a short time at 160–200° C This temperature usually leaves 4–12% water of constitution At 600–800° C the moisture is expelled almost completely and with substantial loss in the bleaching action of the clay, especially for lubricating oils This behaviour is common to the naturally active clays and to the acid-activated clays, as well as to the adsorbents produced synthetically, such as 'silica gel' and aluminium hydroxide.

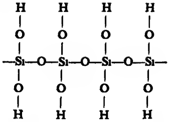
Theory of Adsorption

Although adsorption, particularly the decolorizing power of charcoal, has been known for much more than a century, no theory of the phenomenon has thus far been advanced that is entirely satisfactory The theories applying to naturally active clays and to acid-activated clays are considered to be substantially identical The phenomenon is certainly made up of several factors and is both physical and chemical, although the chemical manifestation is often secondary

Forces affecting adsorption are the attraction of opposite electrical charges on the adsorbent and the substance adsorbed and greater coherence between similar molecules of the pure liquid (or oil) than between those of the liquid and the impurities, the effect of which is to crowd the impurities to the outer surface of the liquid and to lower its surface tension, whether the surface is bounded by a solid, a liquid, or a gaseous material An adsorbent brought into contact with such a liquid adsorbs the outer layer of the liquid which is rich in the impurities, and, further, if the adsorbent manifests a greater attraction for the impurities than for the pure liquid, and ample time is provided, its surface is taken by the impurities, which crowd out the pure liquid

An adsorbent manifests some chemical aspects in adsorbing from an oil the organic compounds which are most active chemically, whether or not these compounds have any influence on the surface tension of the oil Active clays adsorb first the unsaturated compounds and next in order those that contain oxygen, nitrogen, and sulphur The petroleum resins are strongly adsorbed and are characterized by unsaturation and a high content of oxygen

P G Nutting [18, 19, 1928] points out that in the acid activation of clays not only the porosity of the grains is increased by the etching of the acid and removal of certain soluble constituents, but the basic atoms, calcium, magnesium, sodium, &c , of the clay are displaced by hydrogen atoms from the acid These hydrogen atoms are joined indirectly to the silicon (or aluminium) through oxygen atoms, as illustrated for simplicity in a section of a hydrosilicon chain, which contains about 23% of water of composition



$$\begin{array}{ccccccc} H & & H & & H & & H \\ | & & | & & | & & | \\ O & & O & & O & & O \\ | & & | & & | & & | \\ -Si & -O- & Si & -O- & Si & -O- & Si- \\ | & & | & & | & & | \\ O & & O & & O & & O \\ | & & | & & | & & | \\ H & & H & & H & & H \end{array}$$

The two OH groups attached to a silicon atom are unstable, and with mild heating, one of the hydroxyl groups readily unites with the hydrogen of the other, yielding a molecule of water, the oxygen of the second hydroxyl group remaining attached to the silicon atom After the heating, many of the atoms of silicon in the chain can be represented in the following manner

$$\begin{array}{c} -Si- \\ | \\ O \end{array}$$

The two actual or potential open bonds represented by the vertical dotted lines extending from the silicon and the oxygen atoms are ready, with varying degrees of activity, to become attached to certain alkyl or weakly basic radicals, causing either adhesion or a surface action producing insoluble silicates Nutting points out that these compounds may be as stable as certain well-known loosely combined substances, and the union cannot be severed by extracting the adsorbent with any simple solvent

The water associated with the clay which can be driven off by heating to 50° C is so loosely held that it opens no bonds useful in bleaching, but, on the other hand, the heating to 160–200° C is sufficient to develop the maximum bleaching power Nutting assumes that heating the clay to above 200° C opens additional bonds, but it, nevertheless, closes some that were already open

When the hydrous silica (or any active clay) is heated to 800–1,000° C, it loses its total content of water and is then without power again to absorb moisture The latter theory is in agreement with the fact that the clay is injured if heated out of contact with the oil to as high a temperature as can be advantageously employed if the clay is first mixed with the oil The latter process may be considered as a 'fixation' of the open bonds by the adsorbed material as fast as they are opened by the rising temperature

E R Lederer and E W Zublin [14, 1932] lend credence to the open-bond theory, but point out that it cannot apply to a revivified adsorbent which after use has been ignited at 425–85° C (800–900° F) and still possesses 75% of its original adsorptive properties when re-used under conditions precluding any addition of OH groups or formation of open bonds

An extensive review of the theories of adsorption is not attempted here, and if further information is desired, the reader is referred to the works of L Gurwitsch [8, 1926], R O Meador [15, 1928], M E Fogle and H L Olin [7, 1933], J D Haseman [9, 1929], Otto Eckart [6, 1934], P G Nutting [18, 23, 1933], and E R Lederer and E W. Zublin [14, 1932]

Generalizations Applicable to Activated Clays

In many parts of the world deposits of different types of clays exist which can be converted by treatment with acid into highly active adsorbents for refining petroleum products. The clays are reduced to a powder in the activation, and are then applicable only to contact refining.

The highest adsorbent activity is usually imparted to clays that have little or no activity in their natural state.

The maximum activity is developed when only part of the total extractable material is leached from the clay by the acid The optimum concentration of the acid is from 15 to 20%, a higher or lower concentration usually imparts less activity.

Sulphuric and hydrochloric acids are the most economical acids to use, in North America sulphuric acid is commonly used.

In bleaching oils at normal temperatures the activated clay is used only in a dry condition, but in bleaching at elevated temperatures the clay can be used either dry or as a wet slurry or pulp

The optimum temperature of contact is a characteristic of the clay and of the oil and must be determined experimentally

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SECTION 27

REFINING PROCESSES: CHEMICAL

THE CHEMISTRY OF THE REFINING OF LIGHT DISTILLATES

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I. INTRODUCTION

LIGHT petroleum distillates, whether straight or cracked, are rarely if ever obtained in a condition suitable for the purpose for which they are ultimately intended Almost without exception the former in the unrefined state possess an unpleasant odour and are corrosive to such metals as copper and zinc, while the latter in addition either contain gummy substances or produce them on storage While colour in itself is of little consequence it frequently denotes that gum or gum-forming compounds are present To eliminate these objectionable qualities, the raw distillates must be submitted to one or more refining operations, consisting of treatments with chemical reagents or, less frequently, with adsorbent materials capable of altering chemically or removing the substances responsible The more commonly employed processes were originally developed in the early days of the petroleum industry by purely empirical methods largely based upon common practice in the still older coal-tar and shale industries These relied almost entirely upon acid and soda and it is indeed remarkable that to-day they are still the most widely employed, although the manner of their application has been considerably improved, particularly in the more up-to-date refineries

Although the chemical processes involved in refining differ very much amongst themselves, they have actually a common object, the production of a satisfactory and saleable product The method by which this object is achieved depends upon whether the constituents responsible for the undesirable properties are hydrocarbon or non-hydrocarbon The latter can, in a way, be regarded as impurities and treated as such, they are in quite a different category to the hydrocarbons, which help to constitute the fuel itself and must be conserved as much as possible to avoid loss of saleable material Frequently, as will be shown later, the hydrocarbons which possess objectionable properties, possess valuable ones as well, for example, a high anti-knock value, because, however, of the readiness with which they oxidize or polymerize to form resinous substances, their removal or conversion into less troublesome derivatives is essential

Refining methods are available which are capable of dealing with the 'impurities', the troublesome hydrocarbons or both together For a complete understanding of the chemical reactions involved in these processes, some knowledge of the chemical nature and properties of the various constituents of the lighter distillates together with the objects of these treatments is essential While both of these subjects are treated more fully elsewhere, a brief account will not be out of place here

The Constituents of Light Distillates

With very few exceptions, the lighter fractions from the straight distillation of crude petroleum consist of hydrocarbons with only traces of oxygen, sulphur, or nitrogen compounds The exceptions include a few nitrogenous or sulphurous distillates, but even in these the hydrocarbon content forms 90% or more of the whole

The non-hydrocarbon content of a cracked distillate is always lower than that of the feed stock from which it is derived owing to the tendency for these compounds to break down under cracking conditions and so become eliminated as hydrogen sulphide, ammonia, or water The extent to which this elimination occurs is naturally determined by the cracking conditions employed, vapour-phase operation at elevated temperatures being the most drastic and consequently the most effective With this type of cracking there is also less tendency for recombination to take place

In spite of the low concentrations in which the non-hydrocarbon constituents occur, particularly the sulphur compounds, they are of great concern to the refiner, and an enormous sum is spent yearly in eliminating them

The hydrocarbons themselves form an extremely complex mixture of which comparatively little is known Perhaps this is hardly surprising when the vast number of possible hydrocarbons falling within the range of the lighter distillates is considered The number of isomeric forms in which even hydrocarbons of comparatively low molecular weight can exist is amazing, as is apparent from the following table in which the theoretically possible number of isomers for some paraffins and the corresponding olefines is given

Theoretical Number of Isomers for Hydrocarbons of Fixed Carbon Content

Number of carbon atoms in molecule	*Theoretical number of isomers*	
	Paraffin	*Olefine*
1	1	—
2	1	1
3	1	1
4	2	3
5	3	5
6	5	13
7	9	27
8	18	66
9	35	—
10	75	—

The effect of introducing a single ethylenic linkage upon the number of possible isomers is very striking There seems to be no reason for supposing that only a limited number of these isomers is present in a normal distillate

Broadly the hydrocarbons can be divided into four main classes, paraffins, naphthenes, aromatics, and olefines Of these only the first three are to be found in straight-run distillates, although all four occur in cracked products. The molecular linkages characteristic of the four main classes are not, however, limited to the one class Consequently hydrocarbons exist which possess two or more of such groupings and their classification into one of the four main classes becomes very difficult. Such hydrocarbons can only be classified according to the grouping which exerts the greatest effect upon its general behaviour For example, any hydrocarbon possessing a benzene nucleus in its structure is treated as aromatic because it is largely upon the presence of this nucleus that its chemical behaviour rests. While there are obviously many weaknesses in such a classification, it is very useful when considering the lower hydrocarbons which constitute the gasoline and naphtha fractions

While the lighter straight distillates are for the most part paraffinic in nature, naphthenes and aromatic hydrocarbons are invariably present Occasionally, as for example in certain Borneo distillates, aromatic hydrocarbons preponderate, while in others from Russian and Venezuelan sources a much higher content of naphthenes than is usual occurs

Both paraffins and naphthenes are on the whole very resistant to the usual refining agents as well as to oxidation at ordinary temperatures The paraffins are, however, not nearly so resistant to chemical reagents in general as has been supposed in the past While the gaseous members are extremely stable this is by no means true of all paraffins Some of the branched-chain members are surprisingly reactive and together with certain naphthenes have been shown to be capable of reactions hitherto considered to be confined to aromatic hydrocarbons, e g nitration The resistance of the paraffins towards the usual chemical reagents decreases with increasing molecular weight The branched-chain members containing a tertiary carbon atom, i e a carbon attached to three other carbon atoms, exhibit a considerable tendency to react, but those possessing a quaternary carbon atom are remarkably stable The reactivity of paraffins containing a tertiary carbon atom is well illustrated by the action of chlorsulphonic acid, nitric acid, acetyl chloride, and ethylene, the two last in the presence of suitable catalysts

While the atmospheric oxidation of paraffins and naphthenes only takes place to any considerable extent at elevated temperatures, certain naphthenes, e g 1, 4-dimethyl*cyclo*hexane and 1, 3-dimethyl*cyclo*pentane absorb oxygen readily at ordinary temperatures in bright light (Chavanne and Bode [39, 1930]) Even so, though most paraffins and naphthenes are practically unaffected by air at ordinary temperatures, a rancid odour soon becomes distinguishable in strong sunlight in the presence of air As a general rule, the resistance to oxidizing agents decreases rapidly with increase in temperature This is particularly noticeable with sulphur, which only reacts with paraffins to give traces of hydrogen sulphide at ordinary temperatures in strong sunlight On heating, however, hydrogen sulphide formation becomes very marked, so much so that the heating of sulphur with paraffin wax has actually been suggested as a convenient laboratory method for its preparation The reaction of sulphur with hydrocarbons is of great interest to the refiner in connexion with the distillation of gasolines or naphthas containing elemental sulphur and will be discussed at greater length later

Although the paraffins are chemically very stable at comparatively low temperatures, at higher temperatures their thermodynamic stability is considerably decreased At elevated temperatures they are, with the exception of the first few members of the series, much less stable than other hydrocarbons Their instability in this respect compared with that of the olefines and aromatic hydrocarbons is most marked. The mechanism of the thermal decomposition of hydrocarbons is treated under 'Cracking' and we are only concerned with it at this stage because distillation, which forms an important adjunct to certain chemical processes, may lead to a small but definite amount of cracking unless carefully carried out Traces of unsaturated hydrocarbons formed in this way may have a very adverse effect upon the stability of straight distillates The tendency to decompose on distillation is quite marked with the higher paraffins boiling at the upper end of the gasoline range Thus *n*-dodecane, boiling at 215° C shows unmistakable signs of decomposition when the pure compound is distilled in the laboratory at atmospheric pressure Time of heating is an important factor in this connexion, and paraffins which are normally stable at their boiling-point show evidence of decomposition on prolonged heating Paraffins possess no power of polymerization, a property which is confined to the unsaturated hydrocarbons Recently Ipatiev and Grosse [74, 1935] have shown that in the presence of suitable catalysts secondary paraffins are capable of reaction with olefines to form higher paraffins

Although the 3- and 4-membered ring naphthenes appear to be very reactive towards chemical reagents, the 5- and 6-membered rings closely resemble paraffins *Cyclo*pentane and its derivatives appear to be especially resistant On heating with sulphur, the *cyclo*hexanes form aromatic hydrocarbons

The aromatic hydrocarbons, although much more stable to heat than the paraffins or naphthenes, are much less resistant to chemical reagents and in many instances to oxidation Benzene itself is extremely stable, but derivatives possessing side-chains are noticeably less resistant Thus although potassium permanganate is extremely effective in oxidizing sulphur compounds, attempts to use it in the desulphurizing of gasoline impart to the latter the unmistakable odour of benzaldehyde formed as a result of the oxidation of toluene

Most aromatic hydrocarbons are particularly valuable on account of their high octane number Long side-chains, however, have a very adverse effect and lower the anti-knock value considerably

Besides the three classes of saturated hydrocarbons which form the straight distillates, there is another vast and important class occurring in the cracked distillates, namely, the unsaturated hydrocarbons or olefines These hydrocarbons are formed as a result of the thermal decomposition of saturated hydrocarbons, the extent to which they are formed and the degree of unsaturation being determined by cracking conditions. While originally cracking stock consisted of the heavy residues extending above the gas-oil range, to-day light distillates such as the heavier portion of the gasoline fraction are cracked as well The reason for this is that whereas cracking was originally employed to increase the gasoline yield, it is now also used to improve the anti-knock value of low octane fuels Cracking conditions vary over a wide range Normally operation at high temperatures and low pressures (vapour-phase operation) gives highly unsaturated products of high anti-knock value while comparatively low temperatures and high pressures (liquid-phase operation) yield much more saturated products As the anti-knock value is dependent very largely upon the olefine content and this, as well as the losses in the form of gas, increase with the temperature of the cracking operation, conditions are carefully chosen, consistent with the material to be cracked, to give the most desirable compromise between knock rating and gas loss While cracking is generally regarded as degradation of high to low molecular weight hydrocarbons, it also includes the reverse process, synthesis or polymerization Polymerization takes place in many ways and may result in the formation of extremely valuable products, e g di*iso*butene from *iso*butene

As a result of these various reactions, a very complex mixture of hydrocarbons is formed, both saturated and unsaturated, and, at the present time, practically nothing is known of the composition of any but the lightest fractions Mono- and di-olefines, both aliphatic and alicyclic have been identified and it is highly probable that aromatic hydrocarbons with unsaturated side-chains or rings such as styrene and indene are also present The unsaturation takes the form of ethenoid (olefinic) linkages, no evidence having so far been obtained pointing to the presence of ethinoid (acetylenic) compounds

Unsaturated hydrocarbons generally, since they have a higher knock rating than the corresponding saturated derivatives, are of much greater value as motor fuels As a general rule they possess a much lower response to tetraethyl lead, but their higher initial anti-knock value largely offsets this disadvantage Their increased reactivity both to aerial oxidation and towards chemical reagents is a further drawback, for the former results in gum-formation while the latter often entails heavy losses on refining and a consequent fall in octane rating Cracking, however, provides such a convenient source of gasoline of high anti-knock value that unsaturated hydrocarbons form a very considerable part of the automotive fuels in use to-day Recent developments in catalytic polymerization bid fair to increase the ratio of unsaturated to saturated hydrocarbons in gasolines even further, in fact it does not seem improbable that a time will come when deep-seated cracking followed by catalytic polymerization will be a normal refinery process A strong tendency towards gum-formation does not appear to be so generally a property of olefines as was once supposed Only certain olefines, e g conjugated aliphatic and cyclic diolefines, styrene derivatives, &c, possess it to a very marked degree The extent to which these are able to initiate chain reactions is unknown, but their removal certainly produces a reasonably gum-stable material Modern refining processes, therefore, aim only at removing the hydrocarbons which may prove troublesome in the final product, while the use of inhibitors to reduce gum-formation has made it possible to market certain distillates after little if any treatment

In considering the unsaturated hydrocarbons it is convenient to subdivide them into four classes (*a*) mono-olefines, (*b*) diolefines, (*c*) cyclic olefines including both those possessing an ethenoid linkage in the ring and in any side-chain, and (*d*) aromatic hydrocarbons with unsaturated side-chains

The mono-olefines vary very considerably in their properties and general behaviour according to the position of the double bond Under the influence of heat there is a tendency for isomerization to occur and the double bond to pass to a more stable position, that is to say, away from the end of the chain This results in an improvement in knock-rating Many of the olefines present in cracked distillates appear, however, to have the double bond in the 1- or 2-position

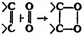
Chemically they are highly active and readily undergo additive reactions with such compounds as halogens, halogen acids, ozone, thiocyanogen, and certain non-metallic chlorides, e g sulphur chlorides, arsenic chlorides, &c Certain of these reactions, i e halogen and thiocyanogen addition, interest the petroleum chemist in that they provide a convenient method for the quantitative estimation of olefines On hydrogenation in the presence of suitable catalysts olefines form paraffins; whether this results in an improvement in knock rating is dependent upon the actual olefine All but certain olefines having complex-branched chains, e g di*iso*butene, decrease in knock rating Hydrogenation has also been employed by Waterman and others as a means of estimating the olefine content, while the method is less convenient than those using halogens, the results are more reliable

At elevated temperatures olefines polymerize to form higher boiling hydrocarbons The reaction is complex and the products include olefines and paraffins, normal olefines give considerable quantities of both iso-derivatives and naphthenes, aromatic hydrocarbons too being formed if the temperature is sufficiently high Certain substances, e g activated charcoal, are capable of catalysing this reaction without seriously affecting the products, but others such as acid catalysts apparently alter the course of the reaction with the result that the mixture of polymers formed has different properties Thus heat polymerization of the lower olefines alone invariably gives a product of lower anti-knock value than that obtained by the use of phosphoric acid catalysts

Polymerization can also be effected by α-particles, light, or the silent electric discharge, and the products formed may vary from low-boiling hydrocarbons to viscous liquids resembling lubricating oils

To-day the lighter polymers are becoming increasingly important to the refiner, on account of their high knock-rating Chemically they are more reactive than even vapour-phase cracked distillates, largely because they contain a very much higher proportion of olefines The difficulty originally experienced in refining on this account has been overcome by blending them with normal cracked distillates for treatment or by the use of inhibitors

Under suitable conditions all olefines absorb oxygen to form high-boiling and resinous products, normal primary and secondary olefines and those in which the double bond is remote from the point of branching being more susceptible than the others The actual mechanism of the reaction by which the resinous products are formed is by no means clear although two plausible theories have been advanced The first supposes that peroxides are first formed by the addition of a molecule of oxygen



which subsequently decomposes or undergoes rearrangement This theory is supported by the presence of peroxides which can usually be detected in unsaturated products after exposure to light in the presence of air The second theory due to Wagner and Hyman [148, 1930] while admitting the formation of peroxides, postulates that these merely catalyse gum-formation. This theory has not, however, been generally accepted although it finds support in the work of Cassar [37, 1931] who showed that while olefine peroxides catalysed the formation of gum in an unstable gasoline, diolefines do not in the absence of peroxides Cassar also showed that no relation existed between gum-formation and boiling-point or sulphur content. Tests carried out upon various pure olefines in 20% solution in a straight gasoline showed that even after oxidation at 100° C for 4 hr with oxygen at 100 lb per sq in. pressure under conditions when most cracked gasolines form gum, they did not. Only after 24 hr. did oxidation proceed to any considerable extent. On the other hand, diolefines gave gum on mere evaporation.

The formation of resinous compounds or gums in gasolines from unsaturated hydrocarbons is the cause of much trouble and expense to the refiner. Not only does it invariably result in a drop in the octane rating but the gum formed causes trouble in use in the engine, such as sticky valves and excessive carbon deposition. While a small amount of gum does not appear to be harmful, it is obviously desirable to prevent its formation as far as possible.

To-day two classes of gum are recognized, actual or preformed and potential gum. The first actually exists in the gasoline and is left on evaporation even under the mildest conditions, while the second is not present but only formed in use or on storage.

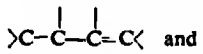
As mentioned above, gum-formation is dependent upon conditions and while all olefines are no doubt potential sources of gum, under normal conditions of storage and use, only certain hydrocarbons give trouble.

Apart from their role in gum-formation peroxides possess intensely pro-knock properties. Thus *cyclo*-hexene after a comparatively short exposure to sunlight and air can be shown to contain peroxides which very definitely decrease its knock rating. On redistillation the latter is restored to its original value. While normally the peroxides are very unstable and explode on warming, some are remarkably stable and can even be steam-distilled without decomposition. In view of the ease with which these compounds are formed and their extreme potency, it is not surprising that cracked distillates frequently decrease in knock rating when stored under adverse conditions. Redistillation of stale cracked distillates has frequently lead to violent explosions owing to the peroxide content. Qualitatively peroxides can be detected by acid potassium iodide and in higher concentration by plumbite. They are said to be destroyed by alkali washing or treatment with such reducing agents as ferrous sulphate.

The diolefines have the general formula C_nH_{2n-2} and contain two ethenoid linkages. Three isomeric types exist depending upon the position of the double bonds and these possess somewhat different properties. The three types are

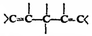
(1) allenes with the structure $>C{=}C{=}C<$,

(2) conjugated diolefines or butadiene type, e g



$>C{-}\overset{|}{C}{-}\overset{|}{C}{=}C<$ and

(3) diolefines in which the two points of unsaturation are separated by one or more carbon atoms, e g



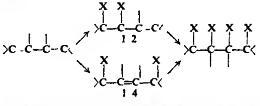
$>C{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}{-}\overset{|}{C}{=}C<$

Of these only the second class need be considered here for the allenes do not appear to be present in cracked distillates, while the diolefines of type 3 behave as normal olefines excepting that they are doubly unsaturated.

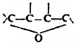
Drastic cracking conditions such as those employed in vapour-phase operation favour the formation of conjugated diolefines. Rice and Rice [130, 1935] explain their formation on the assumption that the higher members of the olefine series decompose on heating according to a chain mechanism with the production of a paraffin molecule plus a molecule of the butadiene type of structure. Certainly the lower fractions from vapour-phase cracked distillates are particularly rich in these hydrocarbons.

In their properties the diolefines in many ways resemble the mono-olefines. The simpler conjugated members are highly refractive liquids with a pungent odour and high anti-knock value. Many polymerize and undergo autoxidation when exposed to air and light although a few such as 3-methyl-1, 3-pentadiene show no tendency to do so (Fischer and Crittenden [56, 1930]).

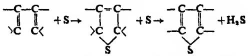
While the non-conjugated diolefines behave very similarly to mono-olefines in their addition reactions which take place at each ethenoid linkage quite normally, in the conjugated diolefines the unsaturation appears to be much intensified. Addition takes place in two stages, the first being mainly 1 4 although some 1 2 addition also occurs.



Chemically the conjugated diolefines are extremely active, and the readiness with which they polymerize and oxidize is probably responsible for most of the gum-formation in cracked distillates. According to Kogermann [86, 1930] each molecule of diolefine can absorb one atom of oxygen, the product closely resembling the gum formed from cracked gasolines. The addition of this oxygen probably takes place in the 1 4 position giving a furan derivative.

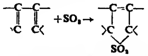


Both mono- and di-ozonides are also formed, but the latter only slowly. They are extremely explosive. Sulphur reacts at elevated temperatures with the formation of thiophen derivatives, the reaction resembling in the first stage that which occurs with oxygen.

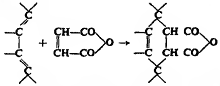


Recently it has been found that diolefines are capable of reacting with hydrogen sulphide. Thus Bockseken and Linde [21, 1935] have shown that isoprene heated under pressure with hydrogen sulphide to 96° C in the presence of iron oxide or sulphide as catalyst yields a mixture of 2-thiol-2-methyl-butene-3 and (probably) 2, 3-dithiol-2-methylbutane.

Another interesting reaction of the conjugated diolefines is the formation of addition compounds with sulphur dioxide. The product, in which addition as usual takes place in the 1 4 position, is an unsaturated cyclic sulphone of the type



They are well-defined crystalline compounds which exist in mono- and in certain circumstances polymeric forms. The former on heating readily decompose to give the parent substances, a reaction which provides an excellent method for the preparation of pure diolefines. A further interesting action common to all substances possessing conjugated linkages is the formation of an addition compound with maleic anhydride, a reaction which takes place with extraordinary ease



The compounds formed are tetrahydrophthalic acid derivatives and have been used by Birch and Scott [19, 1932] to identify the diolefines present in the lower fractions from cracked distillates, Brooks has suggested their use for the preparation of glyptal type resins It has actually been proposed to use maleic anhydride as a refining agent, and the use of maleic anhydride in the refining of coal-tar benzole and cracked gasoline (cf Carleton Ellis, U S P 2,068,850 (1 Sept 1932)) has been covered Unlike the sulphur dioxide addition compounds, they are not dissociated into their original components on heating

Conjugated diolefines polymerize to form high-molecular weight polymers many of which resemble rubber Peroxides have been shown to be extremely active catalysts in this polymerization, once again emphasizing the important role which these compounds play in gum-formation

Both mono- and di-olefines form compounds with certain metallic salts, particularly those of copper, silver, and mercury, the majority of these compounds are loosely combined molecular compounds readily resolved into their components The cuprous salts find application in the separation of olefines and diolefines from admixed saturated hydrocarbons

Cyclic olefines do not appear to have been identified in normal cracked distillates, although there is little doubt of their presence They can be subdivided into two classes, one with the ethenoid linkage in the ring and the other in which it is present in a side-chain Both resemble the aliphatic mono-olefines in their behaviour excepting that perhaps the former are somewhat more reactive *Cyclo*hexene, a typical member of this class, readily absorbs oxygen to form a peroxide which decomposes to produce a viscous gum much of which is acidic in nature In the engine *cyclo*hexene shows a tendency to pre-ignite presumably owing to this ready peroxide formation.

At least one cyclic conjugated diolefine, *cyclo*pentadiene, is a common constituent of cracked distillates and pyrolysis products generally Its extreme reactivity, particularly towards maleic anhydride, has made it possible to detect it even in comparatively low concentrations Attempts to identify the corresponding six-membered ring compound $\Delta^{1\,3}$-*cyclo*hexadiene have not proved so successful

Conjugated cyclic diolefines closely resemble the open-chain derivatives in their chemical reactivity and general behaviour and in having high anti-knock values They are even more prone to oxidation and polymerization, in fact, so great is their tendency to polymerize that it is practically impossible to distil them at atmospheric pressure without considerable polymerization taking place So marked is this tendency with certain of the higher members that polymerization occurs with explosive violence. Thus $\Delta^{1\,3}$-*cyclo*octadiene is stated to polymerize at 130–140° C with explosive violence to form a resinous material Heat is not essential to bring about polymerization for it is rapid at normal temperatures, particularly if air is present, no doubt owing to the formation of peroxides. *Cyclo*pentadiene itself furnishes an excellent example, for at 20° C. it is almost completely polymerized to the di- and trimeride In the presence of air the extremely explosive di*cyclo*pentadiene peroxide is formed and eventually a sticky brown substance separates Depolymerization of di*cyclo*pentadiene can be effected by slow distillation, iron acting as a catalyst This tendency to depolymerize is, however, by no means general, for the dimeride of $\Delta^{1\,3}$-*cyclo*hexadiene is not decomposed at its boiling-point at atmospheric pressure

Polymerization which occurs with such readiness in pure substances is less marked in hydrocarbon solution, particularly if the diluent itself is incapable of polymerization The possibility of the polymerization initiating chain reactions involving other unsaturated hydrocarbons should not be overlooked

The remaining class, the aromatic hydrocarbons with ethenoid linkages in side-chains or attached cyclic structures, can be dismissed in a few words No members of this class have been detected in normal cracked distillates but there is little doubt of their presence, particularly in the higher fractions from vapour-phase distillates Two typical members, styrene and indene, have been isolated from the products obtained during the pyrolysis of natural gases (cf Birch and Hague [12, 1934]) and, in view of the interest taken by the petroleum industry in the utilization of such gases, are likely to interest the petroleum chemist Both styrene and indene are chemically extremely reactive They polymerize slowly on standing but extremely rapidly under the influence of heat to give resinous products The styrene polymer is in considerable demand in the plastics and paint industry, a fact which would undoubtedly influence a refiner called upon to refine any material rich in styrene Chemically both styrene and indene resemble olefines They readily hydrogenate in the side-chain or unsaturated ring in the presence of mild catalysts and add on halogens quite normally

Hydrocarbons with ethinoid, i e acetylenic linkages, have not been detected in normal cracking operations, or even those carried out at comparatively high temperatures They therefore need not be considered here

The Non-hydrocarbon Constituents of Light Distillates

Sulphur Compounds.

Sulphur in the form of its compounds generally occurs to a greater or lesser extent in all crude oils Its presence in the distillates, particularly the lighter distillates, is a matter of considerable concern to the whole petroleum industry Not only do certain sulphur compounds impart an unpleasant odour to products containing them, but they are corrosive, affect the light stability, and in gasolines exert a considerable effect upon the lead response Even those sulphur compounds, which in gasolines and similar fuels are not directly objectionable, are potentially corrosive since on combustion they become converted into sulphuric or sulphurous acid. While under ordinary conditions most of the products of combustion pass out through the exhaust system (which being above the temperature of condensation for water is unaffected) part finds its way past the piston into the crank-case. Here, where owing to the lower temperature water vapour can condense, corrosion occurs

Although the objection to gasolines possessing a sour odour is not as strong as it was, automobile drivers do not like to have the odour of unrefined gasoline in their cars, and while manufacturers have to a large extent overcome gasoline vapour finding its way into the vehicle, it is almost impossible at times to prevent it entirely since the odour of the sulphur compounds is particularly penetrating and tends to linger for a considerable time, the refiner must either remove them or convert them into others less obnoxious.

Another good reason for the removal of sulphur compounds is their corrosive nature. Sulphur itself is known to be extremely corrosive towards copper and other metals, forming sulphides, while hydrogen sulphide is not only readily oxidized to free sulphur but is corrosive in itself, attacking such metals as zinc, copper, and iron. Other sulphur compounds, e.g. the mercaptans, also possess corrosive properties. The corrosion products cause trouble in several ways, particularly in flaking and choking narrow tubes, &c.

The part played by sulphur compounds in promoting 'hazing' and gum-formation in gasolines and naphthas is not entirely understood but has recently been the subject of investigation; it will be discussed later. The ready oxidation of certain compounds containing sulphur to acidic products, such as sulphuric acid, is undoubtedly partly responsible for gum-formation in cracked distillates.

More recently attention has been directed to the effect produced by sulphur compounds upon the lead response of gasolines. While certain compounds exert a much greater effect than others, it is surprising that sulphur itself is one of the least effective. Polysulphides, particularly the trisulphides, are extremely potent and possess definite pro-knock tendencies as well. It would thus appear that in spite of the outcry against unnecessary expense in reducing the sulphur content of gasolines that possibly a useful purpose may be served in doing so after all.

The presence of free or combined sulphur in kerosine for lamps leads to charring of the wick, presumably on account of sulphuric acid formation. Lamp-glasses are also clouded. The absence of sulphur from special naphthas such as painter's naphtha (white spirit) is essential, for a tendency to decompose in the presence of light or heat would adversely affect any lead-containing colour.

The need for the removal or conversion of sulphur compounds into harmless compounds thus appears to be very general over the range of lighter distillates, and much of the refining is undertaken for this reason.

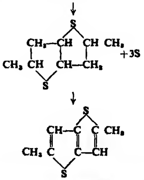
The unrefined light distillates, comprising gasoline, special naphthas, and kerosine, usually contain sulphur, not infrequently in the elemental form, but more generally combined either as hydrogen sulphide or organic sulphur bodies. These may include thio-ethers both aliphatic and cyclic (the so-called 'thiophanes'), di- and higher polysulphides, mercaptans and thiophens. Most of these compounds appear to be degradation compounds of complex sulphur-containing bodies present in the crude oil, the extent to which they are present in the lighter distillates being largely determined by distillation or cracking conditions. Hydrogen sulphide itself is a common constituent of natural gas and may form 10% or more of the dry gas. Whether the lower-boiling sulphur compounds are always degradation products is by no means sure, although in certain instances it appears to be so. Thus Iranian crude oil freed from hydrogen sulphide at a low temperature, when distilled under very mild conditions, i.e. under reduced pressure in a stream of inert gas, gives a gasoline distillate substantially free from sulphur and negative to the doctor test. Under ordinary conditions, a distillate is obtained containing 0·08–0·10% sulphur chiefly in the form of hydrogen sulphide, mercaptans, sulphides, and polysulphides. In fact it can be shown that in the neighbourhood of 130° C., a very definite decomposition takes place in the crude oil and sulphur makes its appearance in the distillate. A further striking proof is that crude oil which has been given an acid treatment sufficient to throw all the asphaltic compounds out of solution, gives distillates noticeably lower in sulphur content.

Elementary sulphur and the polysulphides are largely secondary products formed by side reactions occurring during distillation or on storage. The presence of elemental sulphur can usually be traced to aerial oxidation of hydrogen sulphide, a reaction taking place with great readiness in the presence of moisture. As a result, unless hydrogen sulphide-containing distillates are treated at a very early stage for its removal, they are invariably found to contain free sulphur.

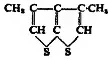
While disulphides are normal constituents of the lighter distillates, they are also formed as a result of the oxidation of mercaptans by air or sulphur, a reaction which only proceeds slowly at ordinary, but rapidly at higher temperatures. Sour distillates stored for a considerable period in the presence of air become sweetened in this way.

We have seen that oxygen is capable of reacting with many hydrocarbons under suitable conditions. Sulphur too is capable of reaction. At ordinary temperatures the action of sulphur upon the hydrocarbons occurring in light distillates is negligible, although in strong sunlight traces of hydrogen sulphide can sometimes be detected. The tendency to react increases with increasing temperature and molecular weight to such an extent that, as mentioned above, it has been suggested that heating a mixture of paraffin wax and sulphur might provide a convenient laboratory method for producing hydrogen sulphide. Even at the comparatively low temperature of 175–200° C. the action of sulphur on the higher gasoline fractions or kerosine gives hydrogen sulphide in appreciable amounts, part of the sulphur also entering into combination with the hydrocarbons. Some light has been thrown on these reactions by Friedmann, who found that sulphur heated with *n*-octane [57, 1916] at 270–280° C. under pressure gave a liquid thiophen homologue and a compound probably dimethylthiophthen which readily formed a red picrate. The formation of the thiophthen derivative probably occurs as follows:

$CH_3\,CH_2\,CH_2\,CH_2\,CH_2\,CH_2\,CH_2\,CH_3+4S$



although Friedmann suggests a rearrangement of the octane first to give 2, 3, 4-trimethylpentane which then reacts to yield



The former mechanism is regarded by the author as more likely in view of Challenger and Harrison's work [38, 1935] The thiophen homologue obtained in many respects resembled diethylthiophen

From an unsaturated hydrocarbon, hexene, Friedman obtained under similar conditions several volatile sulphur-containing compounds, $C_6H_{12}S$, $C_{12}H_{14}S$, and $C_{12}H_{26}S$, together with an asphaltic compound, the composition of which corresponded to $C_{24}H_{20}S_2$ When, however, naphthenes containing six-membered rings are heated with sulphur dehydrogenation occurs, and Markovnikov and Spady [105, 1887] and Friedmann [58, 1916] suggest that the reaction takes place in steps, the formation of sulphur compounds taking place intermediately Thus examination of the products from the action of sulphur on *cyclo*hexane proved the presence of both thiophenol and phenylsulphide The reaction is represented by Friedmann as follows

$$C_6H_{12}+S \rightarrow C_6H_{11}SH \rightarrow H_2S+C_6H_{10}$$
$$C_6H_{10}+S \rightarrow C_6H_9SH \rightarrow H_2S+C_6H_8$$

The formation of thiophenol from the *cyclo*hexadiene then takes place as follows

$$C_6H_8+2S+2H_2S \rightarrow C_6H_{12}S_4$$
$$C_6H_{12}S_4 \rightarrow 3H_2S+C_6H_5SH$$

To what extent such reactions, however, take place during the distillation of gasolines and kerosines containing free sulphur is unknown, that reaction does occur to at least a small extent is certain

Chemically the sulphur bodies present in the lighter distillates may be divided into two groups, those possessing weakly acid properties and those which are neutral in behaviour The first group comprises hydrogen sulphide and the mercaptans, the latter being derived from hydrogen sulphide by the replacement of one hydrogen with an organic radical, the remaining hydrogen atom is responsible for the weakly acid properties Most of the refiner's troubles can be traced to free sulphur, hydrogen sulphide, or mercaptans The second group which includes the thio-ethers, disulphides, and thiophens causes little concern excepting when these bodies are present in such large amounts that it is necessary to remove them in order to reduce the total sulphur content

Hydrogen sulphide possesses strongly acid characteristics and can be easily and completely removed from distillates by alkali washing When it is required to remove it from natural gas, it is usual to employ some process in which the scrubbing liquid can be regenerated cheaply and easily, e g triethanolamine, alanine, sodium phenate, and so on

Apart from its objectionable qualities in gasoline hydrogen sulphide is frequently the cause of trouble on account of its extremely poisonous nature, workmen being overpowered by leakage or accidental release of gases containing it Mercaptans are considerably less acidic than hydrogen sulphide, the relative acidity varying with the attached group Thus acidity decreases with increasing molecular weight in the aliphatic series, secondary mercaptans being more acid than the corresponding primary isomers Thiophenol is a comparatively strong acid

The lower molecular weight mercaptans possess an extremely disagreeable odour, but the higher members are odourless All those occurring in the gasoline and kerosine range are obnoxious So penetrating, in fact, is ethyl mercaptan in odour that its use as a stench for indicating leakage in gas mains has been advocated, a concentration of only 4 g per 1,000 cu ft gas being sufficient

Mercaptans are completely miscible with hydrocarbons in all proportions, but their solubility in water is low and decreases with increasing molecular weight, the higher members are practically insoluble The solubility in water, as will be seen later, has an important bearing on mercaptan removal by alkali washing

Both hydrogen sulphide and mercaptans are characterized by their behaviour with oxidizing agents Mild oxidizing agents such as iodine convert them quantitatively into sulphur and the corresponding disulphides respectively, a reaction which is used for their estimation The oxidation of mercaptans by such mild reagents as air or sulphur forms the basis for the sweetening reactions to be discussed later More vigorous oxidation, for example, with nitric acid, permanganates, or hypochlorites results in their conversion into sulphonic acids

While the alkali and alkaline metal mercaptides are readily hydrolysable, the heavy metal mercaptides are insoluble in water Lead mercaptides are somewhat soluble in benzene and other aromatic hydrocarbons The volumetric titration of gasolines containing mercaptans with copper oleate in benzene results in the quantitative precipitation of copper mercaptides, giving an excellent method for their estimation [22, 1933] Although the heavy metal mercaptides are unaffected by alkalis, they are decomposed by even comparatively weak acids

In spite of their weakly acidic nature mercaptans are capable of attacking metals such as zinc, copper, and even iron Ferrous mercaptide, like ferrous sulphide, oxidizes so rapidly on exposure to air that it becomes red hot—a fact to which may be attributed the fires that so frequently occur when lines employed for carrying sulphurous raw gasoline distillates are broken or when air is admitted to unrefined distillate storage tanks

In the second group of sulphur compounds, the sulphur is combined either with two radicals or in a ring and therefore, lacking a replaceable hydrogen atom, does not possess acidic properties, The simplest members of this group, the sulphides or thio-ethers, closely resemble the analogous oxygen compounds, the ethers, in their behaviour Physically the lower members are colourless liquids, completely miscible with hydrocarbons but practically insoluble in water, possessing a sweet if nauseating odour somewhat resembling halogen compounds, the higher members are almost odourless In dilute solution the odour is comparatively pleasant so that the presence of these substances in gasoline is not normally considered objectionable Chemically they are very unreactive Such reactions as do occur generally involve the sulphur atom alone, the C—S linkage being so strong that very drastic treatment is required for fission

The property of thio-ethers of forming addition compounds with certain metallic halides, particularly mercuric chloride, while of little direct interest to the refiner, has proved of great value in aiding investigators to isolate and identify them In the compounds formed the metallic salts are attached to the sulphur and regeneration can be accomplished by means of hydrogen sulphide or steam distillation in the presence of alkali, &c Similar compounds, in which addition to the sulphur takes place, are formed by bromine and alkyl halides, the insolubility of the benzyl sulphonium chlorides forming the basis for a desulphurizing process in a recent patent.

Oxidation occurs much less readily than with the mercaptans and can be made to take place in two stages Thus hydrogen peroxide converts alkyl sulphides into the corresponding sulphoxide,

$$R_2S \rightarrow R_2SO$$

while more drastic reagents such as permanganates or hypochlorites form sulphones

$$R_2S \rightarrow R_2SO_2$$

The oxidation of sulphoxides to the corresponding sulphones is also readily effected The greater solubility of the lower sulphones (and possibly sulphoxides) in water as distinct from petroleum hydrocarbons is responsible for the desulphurization which certain oxidizing agents effect on gasoline distillate, e g permanganate and hypochlorite

The relative stabilities of the sulphides and their oxidation products, the sulphones (the sulphoxides do not apparently share this property to the same extent, but their formation in refining operations is doubtful) account for their non-corrosive nature Their presence in the lighter internal combustion engine fuels is objectionable in comparatively high concentrations only because on combustion they furnish sulphur dioxide The cyclic sulphides, the so-called 'thiophanes' of Mabery, apparently behave as normal thio-ethers

Disulphides can be regarded as being formed from two mercaptan molecules by elimination of hydrogen and linkage of the residues thus

$$RSH + HSR \rightarrow RS\ SR + H_2$$

Unlike the sulphides, disulphides, in which two dissimilar radicals occur, do not normally appear to exist Certain higher members containing aliphatic and aromatic groups have, however, been synthesized

Physically the disulphides resemble the sulphides, they are colourless liquids, completely miscible with hydrocarbons and insoluble in water The lower members when pure possess a decidedly nauseating sweet odour which is particularly clinging and penetrating In dilute solution, however, the odour is not unpleasant

Chemically they are far more reactive than the sulphides, the S—S linkage proving an easy point of attack Thus reduction with comparatively mild reducing agents such as zinc dust and acetic acid forms two molecules of mercaptan

$$R_2S_2 + H_2 = 2RSH$$

while oxidation gives the corresponding sulphonic acid

$$R_2S_2 \rightarrow 2RSO_3H$$

As the latter, particularly those of low molecular weight, are relatively strong acids which not only are themselves readily soluble in water but also form water soluble salts with most metals, oxidation forms an excellent method for removing disulphides from the lighter petroleum distillates. As they are preferentially dissolved by concentrated sulphuric acid, acid treatment also can be employed for their removal Very little action apparently occurs between the disulphide and the acid, the solution being largely physical

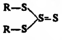
The greater chemical reactivity of the disulphides renders them less desirable constituents of light distillates than the corresponding sulphides They do not appear normally to be corrosive, but in strong sunlight in the presence of air they are responsible for haze formation (Morrell, Benedict, and Egloff [116, 1936]) This is due to the formation of sulphonic and sulphuric acids, which is particularly undesirable in cracked distillates, rendering them unstable In this connexion an observation made by the author some years ago is of interest, it was found that the precipitate formed when gasoline containing tetraethyl lead is exposed to strong sunlight consists mainly of lead sulphate, no doubt the result of sulphuric acid formation

While the higher polysulphides can be produced by heating alkyl disulphides with sulphur [68, 1910], their presence in petroleum distillates can be traced to the oxidation of mercaptans under certain conditions (Birch and Norris [16, 1929]) They are, therefore, apparently secondary products formed mainly in refining treatment, and there is no evidence to show that they ever occur as normal constituents

While the constitution of the trisulphides appears to be normal R S S S R—on reduction two molecules of mercaptan and one of hydrogen sulphide are formed

$$R_2S_3 \rightarrow 2RSH + H_2S$$

—some doubt exists concerning that of the higher polysulphides That these are formed under the same conditions as those favouring the formation of the trisulphide, there is little doubt Attempts to isolate them have not proved very satisfactory, for although they appear stable in dilute hydrocarbon solutions, on distillation even at low pressure they decompose and form elemental sulphur This behaviour indicates a loose structure which may be due to some such configuration as



This possibility is to some extent borne out by the fact that there are indications that sulphur and alkyl disulphides react in sunlight to form unstable compounds

The ease with which the polysulphides decompose to give sulphur makes their presence in such products as gasoline undesirable Fortunately they do not appear to be formed to any great extent, but even the small quantities which are formed can have a very adverse effect upon the lead response (see Plumbite Treatment) There is little doubt that the positive results obtained in the copper strip test for elementary sulphur is frequently due to the presence of polysulphides

The presence of thiophen in light petroleum distillates has been reported by a number of investigators. The parent hydrocarbon thiophen, C_4H_4S, possesses a structure similar to that of benzene, which it closely resembles in its chemical and physical properties The thiophens are colourless, highly refractive liquids, miscible with petroleum hydrocarbons in all proportions and insoluble in water They possess a pleasant benzene-like odour In their chemical properties they resemble benzene much more than the thio-ethers or thiophanes With nitric and sulphuric acids they form nitro-compounds and sulphonic acids respectively, while halogens form substitution products Unlike the thio-ethers which form mercuric chloride addition compounds of the type $R_2S\ HgCl_2$ in which the mercury is attached to the sulphur, thiophens form substitution products with the elimination of hydrogen chloride

$$C_4H_4S + HgCl_2 = C_4H_3S\ HgCl + HCl$$

These compounds readily break down on distillation with hydrochloric acid to regenerate the original components, a reaction employed by McKetterick [107, 1929] to isolate and identify the thiophens present in a cracked distillate from a Californian fuel oil

The thiophens are extremely stable substances and other than forming sulphur dioxide on complete combustion are not regarded in any way as objectionable in gasoline or other similar products

Oxygen Compounds.

Oxygen compounds occur in relatively large amounts in some asphaltic residues and as naphthenic acids in the higher-boiling fractions from certain crude oils, particularly those of Russian origin Only traces of oxygenated bodies have been reported in the lighter distillates, though possibly the difficulty which their detection affords when highly diluted with hydrocarbons may account for this Apart from naphthenic acids which have been isolated in small amounts from certain kerosine fractions, the oxygen compounds present in straight distillates apparently consist of phenols Certainly considerable quantities of phenols have been isolated from cracked distillates, from various cracking stocks, and these undoubtedly play an important part in inhibiting gum-formation, although they must be largely removed in the refining treatment The examination of the acid constituents from a West Texas pressure distillate by Williams and Richter [155, 1935] showed that these consisted largely of phenols, phenol itself, *o*-, *m*-, and *p*-cresols, 1, 3, 5-xylenol and 1, 4, 2-xylenol being isolated and identified Curiously enough the 'naphthenic acids' present proved to be aliphatic and to consist of *iso*valeric, *n*-heptylic, *n*-octylic, and *n*-nonylic acids That the phenol content of certain distillates is relatively high is shown by the large quantities of these bodies which can be isolated from spent alkali and plumbite wastes (see Plumbite Recovery)

Nitrogen Compounds.

The nitrogen content of most petroleum oils is rather low, generally less than 0 1% Certain crude oils, however, particularly those from California, Japan, and S America have considerable nitrogen contents, Mabery [98, 1900] reporting one Californian crude oil having as much as 2 39% Like the sulphur compounds, the nitrogen bases which have been isolated from the distillates, do not appear to be present as such in the crude oil, for Bailey [3, 1928] points out that dilute acid extracts practically nothing from them before distillation The bases themselves are therefore also degradation products of complex bodies present in the crude oil Comparatively little is known of their structure, Bailey and his co-workers being responsible for most of the information available. They appear to possess a hydro-aromatic structure and are closely allied to the pyridine and quinoline alkaloids Mabery claimed to have isolated nitrogen bases boiling as low as 130° C, but generally they boil at much higher temperatures and are therefore not present to any considerable extent in the lighter distillates Traces are, however, present in certain gasoline and kerosine distillates, certain of which, although water-white when freshly distilled, rapidly develop a reddish colour on exposure to air, due to the oxidation of the nitrogen compounds Unless present in sufficiently high concentrations to impart an unpleasant odour, they do not appear objectionable They are readily removed by acids and can be recovered by neutralization

II. THE OBJECT OF REFINING

We have seen that the need for refining treatment is occasioned by the presence in the untreated distillates of compounds imparting to it certain undesirable properties such as an unpleasant odour, a corrosive action upon metals, or a tendency to produce gum or resinous substances on storage or in use The object of the treatment is, therefore, to eliminate such compounds or convert them into others comparatively or completely innocuous, so producing a finished product not only conforming to any standards which may exist for it but also satisfactory to the consumer Obviously the amount of refining required must be determined by the product as well as the purpose for which it is ultimately required A product considered to be satisfactorily purified for one purpose may prove quite inadequately refined for another In this connexion it should be remembered that whereas in certain parts of the world products pass from the refinery to the consumer within a few days, in others months may elapse A product which under ordinary circumstances would be stable for weeks or even months may prove unstable if stored under adverse conditions for a prolonged period

The main objects to be achieved in refining can be summarized as follows (1) improvement of odour and colour, (2) removal or alteration of objectionable sulphur compounds, and (3) reduction or prevention of gum-formation While the improvement of odour and colour is largely to satisfy an aesthetic demand, as a rule an objectionable odour can be taken to indicate the presence of undesirable sulphur compounds, so that any treatment for the removal or conversion into other less noxious bodies would have the effect of improving the odour at the same time Colour is to-day regarded with less mistrust than formerly, particularly in gasolines, largely because it was found that the excessive treatment required to give a water-white product invariably resulted in loss in volume and valuable anti-knock rating The colour, which was rarely deeper than a pale yellow, was however very noticeable, particularly as at the time visible bowl pumps were in general use, and was assumed by the consumer to be a sign of incomplete refining The introduction of intentionally coloured gasolines made possible the use of dyes which successfully cloaked any yellow colour possessed by the gasoline itself The possibility of red dyes reducing the deterioration of cracked gasolines by absorption the actinic light has been suggested but does not appear to have been proved It is, however, claimed by Egloff and others that certain dyestuffs possess a definite inhibitory action upon gum-formation and that their presence in a cracked gasoline is therefore beneficial The introduction of a blue dye having the effect of neutralizing the yellow colour and so producing an apparently colourless product is of interest

While originally the demand for products of low-sulphur content more or less resulted from the discovery of relatively sulphur-free crude oils, the objectionable odour and corrosive nature of the more highly sulphurous products to a large extent justified this demand

The sulphur content of gasoline has been a vexed question for many years It should be, it has been held by one body of opinion, as low as possible because during combustion the sulphur becomes converted into sulphur dioxide and sulphuric acid, both of which are highly corrosive Another body of opinion has maintained that so long as the sulphur is not present in the form of obnoxious compounds, the actual sulphur content is immaterial It has been pointed out that only certain parts of the engine are cool enough for condensation and therefore liable to corrosion The enormous cost of desulphurization to the petroleum industry has been emphasized over and over again

For many years the advocates of desulphurization had their way and gasolines were to be found on the European markets containing as little as 0 02% sulphur With the demand for higher octane gasolines came, however, increased sulphur contents, not only was it found, particularly with cracked distillates in the States, that the heavy acid treatments necessary to desulphurize destroyed a part of the valuable anti-knock value, but in Europe the use of coal-tar benzole, with its high sulphur content, as a blending material rendered low-sulphur contents impossible Since then the tendency has been towards higher limits still, the recent discovery of the adverse effect of sulphur upon the lead response may check this to some extent

As mentioned before, many of the refiner's troubles can be traced to sulphur in one form or another While the conversion of the malodorous and somewhat corrosive mercaptans into the comparatively harmless disulphides goes a long way to overcoming these troubles, the product may still not be entirely satisfactory The recent work of Egloff and others on the question of haze formation when gasolines are exposed to light has shown that disulphides and sulphur are responsible, apparently being particularly reactive in the presence of each other The identification of some of the products formed during haze formation, which included sulphuric acid, throws a considerable amount of light on the cause of colour instability and gum-formation in cracked distillates under certain conditions The remarkable depressing action that disulphides and particularly trisulphides have upon lead response has already been mentioned

While in gasoline only certain groups of sulphur compounds are undesirable, in other products sulphur in any form may be considered objectionable This is particularly true of such special naphtha cuts as those required for dry cleaning or turpentine substitute The former in use must undergo frequent distillation and any sulphur bodies present tend to decompose, thereby imparting an unpleasant odour to the next batch of articles cleaned With the latter, exposure to strong sunlight may bring about decomposition of the sulphur compounds and result in discoloration of lead pigments It is probable that here again in both instances this trouble is due to the presence of disulphides, for sulphides and thiophenes are unlikely to decompose even under such drastic conditions Disulphides are known to decompose both on heating and on exposure to light to a very slight extent which, although normally unnoticeable, would be sufficient to be troublesome Possibly still other sources of trouble in other products can be traced to disulphides or to the traces of mercaptans formed when these compounds decompose

No mention has yet been made of compounds unavoidably formed during refining operations which may possess objectionable properties Such substances include sulphur dioxide, dialkyl sulphates, and chlorides, and of course sulphur itself While the removal of sulphur dioxide is easily and completely effected by an alkali wash, dialkyl sulphates and acid chlorides are not so easily destroyed and may even survive distillation Both classes of compounds hydrolyse slowly and generate acid products which catalyse gum-formation or are corrosive As, however, these substances are products of the refining processes themselves, they can hardly be considered with those the formation of which can hardly be avoided Even so, a finished product containing such substances generally leads to many complaints. Sulphur actually also comes under this category, for by due care its formation can usually be avoided Once formed, little short of re-running or mixing with unrefined material and re-treating can give a satisfactory product Its presence in a finished product renders the latter extremely corrosive and unstable to light and storage, particularly if cracked

The need for the removal of the resinous bodies generally referred to as 'gum' is obvious It is now recognized that these bodies may be preformed, i e already present in solution, or potentially present, which is to say that compounds are present capable of forming them under certain conditions While under suitably drastic conditions most hydrocarbons form resinous or high-boiling compounds, unsaturated hydrocarbons, especially certain conjugated diolefines, are particularly prone to do so Gum-formation is, therefore, almost entirely limited to cracked distillates with the possible exception of certain straight kerosine and naphtha distillates

What is actually meant by the term 'gum' is somewhat indefinite Theoretically the tests devised to measure the gum content or gum-forming propensities of a cracked gasoline are intended to indicate how these products would behave under actual conditions in use in an engine Attempts at correlation are, however, not always entirely satisfactory because, apart from other considerations, conditions vary from one engine to another All that is possible, therefore, is a test which enables products to be compared under definite standard conditions, and this is not completely reliable as there have been instances when the laboratory test has failed to agree with behaviour in practice Most tests for actual gum content merely involve evaporation of a known volume under standard conditions and weighing the residue Potential gum is either indicated by oxygen absorption or by repeating the evaporation test after the sample has been exposed in an oxidizing atmosphere

There are many objections to gum in automotive fuels Throughout the entire intake system evaporation occurs and resinous matter is deposited causing movable carburettor parts and valves to stick, under the influence of heat the gummy deposit decomposes, becoming less soluble and eventually carbonizing, as a result of which hard masses form under the valve head, prevent it from closing completely and so cause pitting or burning of the metal seatings In the combustion space gum merely increases carbon formation, thus materially reducing the effective running periods between decarbonizations So great has the risk of engine trouble through sticking valves been considered that even to-day, although gum-formation can be almost entirely prevented, the use of cracked gasolines for aircraft is by no means generally approved

Gum-formation, consequent as it is upon oxidation, is almost invariably accompanied by decrease in octane rating Peroxides, which possess intense pro-knock properties, have been shown to play an important part in gum-formation and are undoubtedly the main cause of the fall in the anti-knock value

The introduction of inhibitors, such as catechol or *p*-benzylaminophenol, which are capable of preventing gum-formation, has had a marked effect upon the refining of cracked gasolines With their aid a stable cracked gasoline can be produced with very much less drastic refining than without it Treatment can be so reduced that refining losses both in octane rating and yield are little more than normal handling losses To what extent the phenols present in most raw cracked distillates survive refining treatments and aid in the stabilization of the finished product is uncertain. Certainly unsaturated materials produced under conditions precluding the formation of phenolic compounds are generally extremely unstable and require immediate inhibiting

Numerous processes have been devised for the refining of light distillates both straight and cracked. Some of these have become generally adopted while others have not As a general rule those which have been universally adopted are easy to adapt to various stocks, cheap to operate, requiring little in the way of special equipment or materials, and do not need too close control

Undoubtedly for the most effective and efficient operation of a process close control is essential Many processes, e g the hypochlorite process, can only be successfully worked under such conditions Continuous operation, which invariably makes for efficient operation, requires less control than batch operation provided once set the conditions are maintained In a refinery receiving different crude oils in varying proportions, this is impossible because the feed and therefore the conditions must be changed every few hours unless it is possible to segregate each crude oil and handle it separately Usually it is more convenient to use a batch or semi-continuous process However, when continuous countercurrent treatment can be employed labour and chemical costs can be reduced to an astonishing extent

Only refining processes requiring cheap chemicals can be successful The effluent should be as nearly valueless as possible and easy to dispose of While recovery processes for waste chemicals are practical and are in everyday use, if they can be avoided so much the better Frequently they are adopted as much to solve the disposal problem as for any other reason The possibility of isolating marketable chemicals from refinery waste, e g plumbite, seems to be attracting a certain amount of attention Whether the markets could absorb the enormous amounts of these substances which could be recovered is a debatable question

In the following pages the chemistry of the more commonly adopted processes is discussed Certain other treatments which have a bearing on these processes or which are considered to be promising or of interest, e g the brucite process, have also been included

III. TREATMENT WITH ALKALI. THE PRELIMINARY CAUSTIC WASH

We have seen that in general the distillation of crude oils furnishes light distillates which, apart from their hydrocarbon content, contain varying amounts of sulphur, oxygen, and nitrogen compounds together, frequently with traces of hydrogen chloride Certain of these, such as hydrogen sulphide and chloride, are strong acids, while others, the mercaptans and phenols, are much less markedly acidic in their properties Whereas the former can be easily and completely removed from the distillates in which they occur by alkali washing, the latter are only incompletely removed in this way, the extent of removal depending upon the relative acidities of the compounds themselves and the conditions obtaining Even under the most favourable conditions mercaptan removal is far from complete and other methods must be employed Many methods with this object in view have been devised, but only a limited few have been generally adopted and these will be discussed later under 'Sweetening and Desulphurizing Processes' As such processes almost invariably involve the consumption of some chemical other than alkali, for example litharge, chlorine and so on, it follows that the more effectively the initial alkali washing is carried out the lower will be the actual chemical requirements The preliminary alkali wash generally consists in treatment with an aqueous solution of a caustic alkali either freshly prepared for the purpose or in the form of a spent chemical wash which still contains free alkali

The two major factors governing the choice of caustic alkali for the preliminary alkali wash are cheapness and effectiveness Of the four caustic alkalis readily available, caustic soda and potash, lime and ammonia, only the sodium and calcium compounds are sufficiently cheap for general use The use of caustic potash has been advocated for special purposes when possibly it may possess some advantage over caustic soda or lime, but its high cost is against its general adoption Ammonia finds a definite application because as a gas it can often be injected into a distillation system at a point most suited to combat corrosion, particularly that resulting from the presence of traces of hydrogen chloride The quantity required is relatively so small that the high cost is not of such great importance Both caustic soda or lime are widely used, particularly the former, which possesses certain definite advantages over the latter Lime is, however, very much cheaper, so that the choice rests upon such conditions as availability, equipment, and so on As it is really the hydroxyl group which concerns the refiner, he naturally purchases it in the cheapest and most convenient form The chief disadvantage of lime is the low solubility in water which renders it necessary to handle large bulks of solution, and where water is not too plentiful this alone is sufficient to preclude its use The solubility of slaked lime (calcium hydroxide) in water at various temperatures is given in the following table (Mellor [110, 1923])

Temperature, ° C	*Calcium hydroxide g per 100 g solution*
0	0 185
10	0 176
20	0 165
40	0 141
60	0 116
80	0 094
100	0 077

As calcium hydroxide is generally obtained by slaking quicklime, Lamy's observation that the temperature of preparation of the anhydrous oxide effects the solubility is of interest

The drop in solubility with rising temperature is very marked and offers a very definite disadvantage in the use of lime-water in certain operations, such as, for example, in a condensing system, where the temperature of the lime-water is raised during use This difficulty can be overcome by using more dilute lime-water than is usual, but this involves an even higher water consumption. For ordinary operations saturated lime-water is conveniently used, prepared by diluting lime slurry and settling out the insoluble material. The slurry is most conveniently prepared by slaking quicklime, an operation which on a large scale requires care owing to the heat evolved. Calcium hydroxide can of course be purchased as such, but as it already contains combined water, relatively more is consumed.

The refiner in considering the use of lime in place of caustic soda must consider the advantage it offers in cheapness against its disadvantages. The low solubility renders it necessary to handle large volumes of lime-water with resultant increased pumping and storage costs. Where water is scarce, the water requirements may weigh against the use of lime, a method for overcoming this difficulty is described below, for even where water is cheap it is desirable to use as little as conveniently possible.

Caustic soda, although comparatively cheap, is more costly than lime. While it is usually shipped in drums in solid form, where refineries are conveniently situated it can be purchased as a concentrated solution in railcars. The solution which is obtained directly from the electrolytic cells contains sodium chloride, but this offers no disadvantage. On a sodium hydroxide basis, the solution is considerably cheaper than the solid, as it does not have to bear the cost of evaporation or of containers. The greater bulk which has to be transported by rail is offset by the fact that subsequent handling charges are minimized.

Sodium hydroxide is readily soluble in water, as shown in the following table (Mellor [109, 1923]).

Temperature, ° C	*Sodium hydroxide, g per 100 g solution*
−20	16.0
0	29.6
20	52.2
40	56.3
80	75.8
110	78.5
192	83.9

The solubility increases quite normally with increase in temperature. In practice, high concentrations such as those present in saturated solutions are seldom if ever employed in the treatment of light distillates, the usual concentration varying from 5–15% (10–20° Bé.) according to the operation involved. Since more highly concentrated solutions are occasionally obtained during the preparation of caustic soda solutions which on cooling tend to crystallize in lines, &c., where re-solution may prove difficult, care should be taken to ensure that dilution is carried out before this can occur. Ordinary water invariably contains calcium and magnesium salts, and caustic soda solutions generally are cloudy, due to the presence of suspended matter.

Hydrogen Sulphide Removal

Hydrogen sulphide, unlike certain of the sulphur compounds present in the lighter petroleum distillates, occurs as such in crude oil and natural gas. Even though this can be conveniently removed by stabilization, more is invariably formed during the primary distillation and this must be removed by chemical methods.

One of the chief objections to the presence of hydrogen sulphide in the lighter distillates is the ease with which oxidation to sulphur and water takes place and, in spite of the fact that for certain treatments the presence of sulphur is actually advantageous, as a general rule it is desirable that it should be removed as soon after formation as possible. This is particularly true of distillates which are to receive hypochlorite treatment at a later stage, for the success of the process is largely dependent upon the absence of free sulphur.

If aerial oxidation can be successfully avoided the urgency is not so great, but the ingress of air into a condensing system or storage tank is sometimes difficult to prevent. Although the oxidation does not appear to take place when both air and hydrogen sulphide are dry, this is unlikely to occur during a distillation of crude oil, which, even if steam is not employed, invariably contains a little water. Moisture greatly facilitates the reaction, a fact which can be observed during the distillation of a hydrogen-sulphide-bearing material in glass apparatus, the formation of free sulphur occurring at the point at which condensation of the vapours takes place. It is for this reason that the condensers of distillation units are generally found to be corroded at this point—the corrosive action being increased by the temperature. Elemental sulphur formed under such conditions is amorphous in form and very much less soluble in petroleum hydrocarbons than the crystalline form. Even when oxidation can be avoided in the condensers by using a closed system—and it should be remembered that crude oils and water contain dissolved air—oxidation may take place in storage tanks, and the sulphur is then crystalline in form and relatively soluble. Before the introduction of suitable devices to prevent breathing losses, &c., crystals of sulphur were frequently to be found in the vapour space above the liquid which invariably contained relatively large amounts in solution. Even when there is no objection to the presence of sulphur in the distillate for other reasons, both it and hydrogen sulphide are highly corrosive, attacking iron with the formation of ferrous sulphide, the latter oxidizes so readily in contact with air that fires frequently result.

Undoubtedly the most convenient stage for hydrogen sulphide removal is in the condensing system, that is to say, as soon after formation as possible. This can be effectively carried out by injecting caustic alkali solution into the condensers at some point ensuring intimate contact. This procedure also serves to remove any hydrogen chloride which may be present and may dispense with the need for ammonia injection.

Compared with the mercaptans, hydrogen sulphide is a strong acid and being dibasic is capable of forming two series of salts, the sulphides and hydrosulphides. When caustic soda is used, the reaction takes place in two stages as follows:

$$2NaOH+H_2S = Na_2S+2H_2O$$

$$Na_2S+H_2S = 2NaSH$$

Both products are readily soluble in water although somewhat less so than the hydroxide. While the normal sulphide is stable and crystallizes from solution in large colourless crystals containing nine molecules of water of crystallization, the hydrosulphide is unstable and decomposes into the normal sulphide and hydrogen sulphide if an attempt is made to isolate it by evaporation. The instability of the hydrosulphide is so marked that hydrogen sulphide is disengaged when a stream of an inert gas or steam is passed through the solution, with eventual complete conversion into sulphide. Advantage has been taken by Meyer of the ease with which the sulphide can be regenerated from solutions of the hydrosulphide in a process for removing hydrogen sulphide from natural gas. The latter is scrubbed with caustic soda in a countercurrent system until saturated with hydrogen sulphide and a solution largely composed of the hydrosulphide leaves the plant. This is regenerated externally by blowing with steam, or preferably flue gas, which removes the hydrogen sulphide. The solution of the sulphide left is then used for scrubbing the gas and the cycle of operations repeated. The reactions involved are:

$$NaOH+H_2S = NaSH+H_2O$$

$$2NaSH = Na_2S+H_2S$$

$$Na_2S+H_2S = 2NaSH$$

Provided that sodium sulphide forms the main product of the reaction any concentration of caustic soda can be used for hydrogen sulphide removal The efficiency obviously falls with increasing hydrosulphide concentration so that counter-current operation gives the most economical soda consumption In practice, however, alkali washing also involves mercaptan removal, which for reasons to be discussed later requires the presence of an excess of soda, so that the question of hydrosulphide formation does not need consideration

In spite of the fact that calcium sulphides are much less definite chemically in aqueous solutions than the sodium salts, lime-water can be effectively used in hydrogen-sulphide removal Even though the solubility of calcium sulphide in water is low (Riesenfeld and Fled [129, 1921]), there is no separation as reaction with the water occurs and calcium hydroxy-hydrosulphide is formed

$$CaS+H_2O = Ca(SH)(OH)$$

If sufficient hydrogen sulphide is present, the reaction goes a stage farther and the hydroxy-hydrosulphide is converted into the hydrosulphide

$$Ca(SH)(OH)+H_2S = Ca(SH)_2+H_2O$$

Calcium hydrosulphide is considerably less stable than the corresponding sodium salt, and can only be obtained in any degree of purity in the presence of an excess of hydrogen sulphide Under ordinary conditions it readily loses hydrogen sulphide and precipitates calcium sulphide, so that it is undesirable to go farther than the hydroxy-hydrosulphide for hydrogen sulphide removal

Lime-water, used in a condensing system, is likely to give trouble unless precautions are taken to avoid the separation of lime which occurs owing to the decreased solubility at the higher temperature This lime not only tends to cause emulsification with the distillate but it is deposited on the condensing surfaces, thereby considerably lowering their efficiency The trouble can be avoided by using instead of saturated lime-water a weaker solution which will enable the lime to remain in solution, i.e. 0.02 N instead of 0.04 N A sufficient volume is used to remove all the hydrogen sulphide and yet maintain an excess of lime A considerable saving in water can be effected by mixing the spent lime-water, after the separation of the distillate, with sufficient lime slurry to bring the concentration back to 0.02 N and, after settling to remove suspended matter, recirculating the solution to the condensing system The operation can be repeated for some time before the calcium hydroxy-hydrosulphide—which is comparatively soluble—reaches saturation The recovery of the spent lime-water, while theoretically possible by steam blowing, is not economical

The recycling of lime-water in this way for scrubbing the distillate vapours is limited to hydrogen sulphide removal When employed for washing distillates, a saturated solution is used, preferably in counter-current Under these conditions a certain amount of mercaptan removal (*vide infra*) also takes place and recycling is not, therefore, possible and the spent lime-water is discarded Naturally a very much larger wash is required when lime is used, roughly 60 vol. of lime-water being equivalent to one of 10% caustic soda; this necessitates a considerable increase in equipment size

Mercaptan Removal.

The second function of the preliminary alkali wash is to reduce the mercaptan content as far as possible, thereby effecting a considerable saving in the chemical required in the sweetening process

Sodium and calcium mercaptides, with which we are here concerned, are readily soluble in water but insoluble in petroleum distillates Mercaptans are weak acids, so that in aqueous solution the salts are very largely hydrolysed and the solutions possess a strong odour of the mercaptan As a result, when a solvent which is immiscible with water is present, such as, for example, gasoline, the mercaptan—itself almost insoluble in water—passes into the solvent layer A state of equilibrium is thus set up and the mercaptan distributed between the aqueous and solvent layer The relative amounts of mercaptan in the two layers is determined by the degree of hydrolysis, itself dependent upon the relative acidity of the mercaptan as well as certain other conditions In the aliphatic series with which we are largely concerned the relative acidity decreases with molecular weight, the acidic properties, as shown by the amount extracted from petroleum ether solution under standard conditions by 10% sodium hydroxide solution, falling off very rapidly as shown in the following table (Birch and Norris [13, 1925])

Mercaptan	*% removed*
Hydrogen sulphide	100.0
Ethyl	97.1
n-Propyl	88.8
*iso*Propyl	87.2
n-Butyl	63.2
*iso*Butyl	62.8
*iso*Amyl	33.0

Hydrogen sulphide is included for comparison, it is actually a much stronger acid than even the most acidic mercaptan Apart from the obvious decrease in relative acidities with increasing molecular weight, it can be seen that the normal mercaptans are slightly more acidic than the corresponding isomers

The decrease in mercaptan removal by soda with increasing molecular weight is of considerable importance Not only is more required to effect a definite measure of mercaptan removal with the higher members, but it is obviously impossible to remove the heavier mercaptans occurring on the gasoline boiling-range completely without an infinite number of soda washes

The whole question of mercaptan removal by alkali washing has been very thoroughly treated by Meyer [112, 1931] From the above it can be seen that, with batch operation, mercaptan removal is only partial A quantity of free mercaptan remains in the oil layer in equilibrium with the alkaline layer and is not affected by further agitation, the actual amount is determined by the quantity originally present, the relative acidity, the concentration of the soda employed, the temperature, and other factors At first sight it would appear that as the hydrolysis of the alkali mercaptides increases with dilution, liberating the free acid, a given weight of caustic alkali would be more effectively employed in high concentration than if diluted In actual practice, however, the mercaptan present in the oil is generally present only at great dilution and it can then be shown that the more dilute the soda the more effectively it is employed. This is explained by Meyer as follows The equilibrium obtained is the resultant of a large number of reversible reactions occurring simultaneously and is governed by the law of mass action. In removing mercaptans from gasoline or naphtha solution by means of aqueous caustic soda, the aqueous layer will contain

Free mercaptan in solution [RSH],
undissociated sodium mercaptide [RSNa], and
mercaptide ions [RS]′

The equilibrium reactions involved are then as follows

(1) The mercaptan tends to distribute itself between the oil and aqueous layer by simple solution

$$[\mathrm{RSH\ oil}] \rightleftharpoons [\mathrm{RSH\ aq}]$$

$$\frac{[\mathrm{RSH\ oil}]}{[\mathrm{RSH\ aq}]} = C_1 \tag{1}$$

(2) Sodium mercaptide is formed

$$[\mathrm{NaOH}]+[\mathrm{RSH\ aq}] \rightleftharpoons [\mathrm{RSNa}]+\mathrm{H_2O}$$

$$\frac{[\mathrm{NaOH}][\mathrm{RSH\ aq}]}{[\mathrm{RSNa}][\mathrm{H_2O}]} = C_2 \tag{2}$$

(3) The free mercaptan in the aqueous layer is partially ionized

$$[\mathrm{RSH\ aq}] \rightleftharpoons [\mathrm{H}]+[\mathrm{RS}]$$

$$\frac{[\mathrm{RSH\ aq}]}{[\mathrm{H}]\,[\mathrm{RS}]'} = C_3 \tag{3}$$

(4) The sodium hydroxide present is partially ionized

$$[\mathrm{NaOH}] \rightleftharpoons [\mathrm{Na}]+[\mathrm{OH}]$$

$$\frac{[\mathrm{NaOH}]}{[\mathrm{Na}]\,[\mathrm{OH}]} = C_4 \tag{4}$$

(5) The sodium mercaptide is partially ionized

$$[\mathrm{RSNa}] \rightleftharpoons [\mathrm{Na}]+[\mathrm{RS}]$$

$$\frac{[\mathrm{RSNa}]}{[\mathrm{Na}]\,[\mathrm{RS}]} = C_5 \tag{5}$$

(6) The hydrogen and hydroxyl ions are in equilibrium

$$\frac{[\mathrm{H}]\,[\mathrm{OH}]}{[\mathrm{H_2O}]} = C_6 \tag{6}$$

If now the sodium mercaptide solution is concentrated, the conditions are represented mainly by (2) above The effect of dilution is mainly hydrolytic and results in the liberation of free mercaptan

In gasoline or naphtha distillates only small amounts of mercaptan are normally present (equivalent to say 0 1–0 2% mercaptan sulphur) and the soda solution obtained is only partially 'spent', consisting of a dilute solution of sodium mercaptide with a large excess of free alkali In such a case ionic dissociation as distinct from hydrolytic dissociation is the major factor

Combination of equations 1, 2, 4, and 5 gives

$$[\mathrm{RS}]' = \frac{C_4[\mathrm{RSH\ oil}][\mathrm{OH}]'}{C_1C_2C_5[\mathrm{H_2O}]} \tag{7}$$

and similar from 1, 3, 6

$$[\mathrm{RS}]' = \frac{[\mathrm{RSH\ oil}][\mathrm{OH}]'}{C_1C_3C_6[\mathrm{H_2O}]} \tag{8}$$

Now the mercaptan removed by the soda is present in three forms free [RSH aq], [RSNa], and [RS]′ As the solubility of mercaptan (with the exception of the lighter members) in water is negligibly small, the amount removed by water alone from the oil layer would be negligible Hence the first term [RSH aq] expressed in grammes per millilitre is so small that it can be neglected Moreover, at the dilution under consideration most of the sodium mercaptide would be ionized It follows, therefore, that the mercaptan or mercaptan radical, removed by the soda, is removed mainly as mercaptan ion [RS]′.

From equations 7 and 8 above, it can be seen that other factors being constant the [RS]′ term is directly proportional to the [OH]′ term Now at ordinary temperatures 10% caustic soda solution is roughly 50% ionized, while 0 1% solution is 95% ionized

It therefore follows that, as the dilute solution contains almost twice as many hydroxyl ions without much affecting the molal concentration of the water, for a given equilibrium concentration of mercaptan in the oil layer, a unit weight of caustic soda should remove twice as much mercaptan in 1% solution as in 10% Meyer was able to demonstrate the soundness of this reasoning and the following table gives the overall distribution coefficients which he obtained

Mercaptan	*Soda solution g NaOH/100 ml*	*Overall distribution coefficient*
n-Propyl	10 0	17 8
	5 0	13 5
	1 0	3 5
n-Butyl	10 0	4 1
	5 0	3 2
	1 0	0 47
*iso*Amyl	10 0	1 1
	1 0	0 25

These results are relative to the molecular volume of the naphtha employed and to the temperature at which the experiments were carried out, approx 100° F

It will be noted that the overall distribution coefficients for 1% soda are about one-fifth those for 10% soda Since, however, for a given weight of soda, 10 vol of the weaker are available for every volume of the stronger, it follows that twice as much mercaptan can be removed by the weaker soda

The observation of Borgstrom [24, 1930] that the removal of mercaptans by a given amount of caustic soda increases with concentration up to molal and then falls away, appears to be at variance with Meyer's findings

The question of mercaptan removal has also been examined by Happell and Robertson [64, 1935] These authors make the following generalizations (*a*) For a given normal mercaptan the distribution coefficient is roughly four times as great as that of the next normal mercaptan with one additional carbon atom (*b*) Secondary mercaptans are less easily removed than the normal isomers (*c*) By assuming activity coefficients—to allow for incomplete ionization—of 0 95, 0 70, and 0 50 for solutions containing 0 0834, 0 417, and 0 834 lb caustic soda per U S gal an accurate correlation of the distribution coefficients at different concentrations is obtained For more dilute solutions an activity coefficient of 1 is employed (*d*) The characters of the hydrocarbon solvent has little if any effect, and (*e*) the data obtained indicates that a drop of 20° F in temperature will increase the distribution coefficient by about 50%—a factor hitherto inadequately considered

Meyer (loc cit) points out that although batch washing effects only a partial removal of mercaptans, and consequently would only be complete if an infinite number of washes was given, complete removal is theoretically possible by counter-current treatment In practice, in a system of mixing pumps and settling tanks, assuming equilibrium in each pump and supplying just sufficient soda to remove all of a given compound by countercurrent extraction theoretically, the efficiency of removal is actually $n(n+1)$ where n is the number of pump stages. As this efficiency is only increased from 80% for a four-stage plant to 83.3% for a five-stage unit, a point must be reached when it is cheaper to use more chemical to secure greater removal. It must also be remembered that gasoline and naphtha contain not one but a whole range of mercaptans, each of which possesses a different distribution coefficient. Thus, while the lower mercaptans may be completely removed and the middle mercaptans partially so, the high-boiling members will remain almost completely unaffected. The effect at which the refiner aims is as complete an overall mercaptan removal as is possible with the minimum consumption of soda.

The use of lime-water for mercaptan removal does not appear to have received the consideration it merits, which is surprising when the low price of lime compared with that of caustic soda is considered. It has been shown above that caustic soda is most effectively employed in concentrations sufficiently low for complete ionization. Even when saturated, lime-water is almost entirely ionized, it is consequently just as effective in removing mercaptans as a caustic soda solution of equal normality. Expressed another way, caustic soda and calcium hydroxide are equivalent, weight for weight, when employed in sufficiently dilute solutions. It naturally follows that a considerable saving can, therefore, be effected by the use of lime.

In order to overcome hydrolysis of the mercaptides, Vesselovsky and Kalichevsky [147, 1931] suggest the use of either caustic soda or potash dissolved in absolute alcohol as a treating reagent. Experimentally they showed that with the use of this solution mercaptans are extracted quantitatively from naphtha. Mercaptides and water are formed, but as the former is hydrolysed only to a very slight extent the reaction is practically irreversible and therefore complete. For similar reasons solid caustic alkalis can be used, sodium hydroxide reacting more rapidly than the potassium compound.

Recovery of Spent Soda.

From the ease with which mercaptides are hydrolysed in aqueous solution to liberate mercaptans, the recovery of 'spent soda' appears to be a perfectly straightforward operation. Possibly this may be so when the soda has been used solely for mercaptan removal, but as a general rule other compounds besides mercaptans are removed at the same time, particularly hydrogen sulphide and phenols. While the obvious method of steam-blowing is extremely effective in driving off the mercaptans it is without effect on the sulphides. As a consequence, unless steps have been taken by installing, for example, a preliminary alkali wash solely for hydrogen sulphide removal, after several cycles of use and recovery a considerable part of the soda is converted into useless sodium sulphide. Side-reactions also occur which complicate recovery. Mercaptans are extremely easily oxidized to high-boiling disulphides which, being insoluble in water but completely miscible with oil, will, unless completely removed from the recovered soda, find their way into the next batch of oil treated. This oxidation, which can be represented thus,

$$2RSH \rightarrow R_2S_2+2H,$$

can result from atmospheric oxidation or oxidation by sulphur or polysulphides present in the soda. Attention was first drawn to the atmospheric oxidation of mercaptans by Birch and Norris [13, 1925], but Lachman [192, 1931] studied the reaction more fully. He showed that in certain instances mercaptans could be completely oxidized at 20–25° C. merely by agitation in dilute alkali solution in the presence of air. The oxidation appears to take place through the mercaptan ion and is greatly influenced by the presence of certain solids. No doubt oxidation occurs when aerial agitation is employed during the preliminary alkali wash. Birch and Norris also observed the oxidation of mercaptans by sodium polysulphides, a reaction which occurs with considerable ease, particularly on warming. It takes place very definitely during the steam-blowing of spent soda, although most of the products are carried off with the steam. The formation of the polysulphides results from the solution of sulphur either in the aqueous sodium sulphide,

$$Na_2S+nS = Na_2S_{n+1},$$

or hydroxide, when the thiosulphate is also formed,

$$6NaOH+nS = 2Na_2S_{\frac{1}{2}(n-2)}+Na_2S_2O_3+3H_2O$$

The composition of the polysulphides themselves is uncertain. Both Bottger [23, 1884] and Gauthier [60, 1884] suggested that the sulphur is present only in simple solution, but the existence of chemical compounds now appears to be definitely established. Doubt, however, still exists concerning their actual constitution, and it is probable that, while no uniform compounds are present, various compounds are present in a condition of complex equilibrium with one another (cf. Bottger [23, 1884], Holmberg [67, 1908]). The constitution as determined by analysis varies between $Na_2S_{3.5}$ and Na_2S_5.

The alkali polysulphides are deep yellow to red in colour and it is to their presence that spent soda usually owes its yellow colour. The solution of sulphur in sodium sulphide forms the basis for a process for the removal of elementary sulphur from the lighter distillates, gasolines in particular. The treatment is carried out by continued agitation of the distillate with sodium sulphide solution or more usually a spent alkali wash containing it, removal is slow and several hours agitation are required to effect any measure of desulphurization. The reaction between the mercaptides and the alkali polysulphides is favoured by heat. So readily does the oxidation occur that spent soda containing polysulphides may after standing for some time be entirely free from mercaptans, only disulphides being present.

At elevated temperatures Billheimer and Reid [10, 1930] found that mercaptans and aqueous soda are capable of reacting. At 260° C. three reactions occur simultaneously, giving as products the corresponding alcohol, thio-ether, and olefine respectively. These reactions may be expressed as follows:

(1) $RSH+2NaOH = ROH+Na_2S+H_2O$

(2) $2RSH+2NaOH = R_2S+Na_2S+2H_2O$

(3) $R.CH_2.CH_2.SH+2NaOH = R.CH{=}CH_2+Na_2S+H_2O$

While there is no evidence that these reactions occur during the steam-blowing of spent soda, it is extremely probable that they do as the reactions appear to take place with great readiness. Secondary mercaptans react to a greater extent than the primary members: thus heated at 260° C. for 2 hrs. with 3 N caustic soda (i.e. 12%) 52.2% of *n*-propyl mercaptan was decomposed, while under identical conditions 65.4% of *iso*propyl mercaptan reacted. Presumably the tertiary mercaptans would react even more readily. Temperature was found to have a very considerable effect, a rise of 20° from 250° to 270° C. more than doubling the amount of mercaptan destroyed; increasing the period of heating at any definite temperature also favoured the reaction One curious fact observed by Billheimer and Reid was that increase in alkali concentration tended to decrease the relative proportions of thioethers in the products The importance of the reaction in soda recovery—particularly in the form of recovery which merely consists in boiling down the spent soda without the application of steam—is that although the organic products are all volatile and carried away part of the soda is lost as unrecoverable sulphide

In connexion with Billheimer and Reid's observations, the treatment of light distillates by countercurrent extraction with hot alkali solutions as suggested by Kimball [80, 1931] is of interest In this process the solution is kept at a sufficiently elevated temperature to maintain the distillate in the vapour phase From the hydrolytic standpoint these conditions would be the worst possible for mercaptan removal and it must be assumed that any desulphurization and sweetening occurring is due to reaction between the alkali and mercaptans

The complexity of these side reactions, and the formation of sodium sulphide, renders soda recovery very unsatisfactory and generally an uneconomical process In the past the use of high concentrations of soda, most of which left the plant unaltered, was a rather different undertaking Modern methods with efficient use of weak soda give a spent wash so dilute that it is cheaper to dispose of it than to attempt to recover it Possibly the development of uses for mercaptans or disulphides may eventually change this

The Estimation of Mercaptans.

The estimation of mercaptan sulphur is frequently required either for purposes of research or for checking the efficiency of mercaptan-removing processes While this is relatively simple when dealing with straight distillates or the carefully purified naphtha solutions generally employed for investigations on pure sulphur compounds, with cracked products the presence of unsaturated hydrocarbons renders special methods necessary

Since with most methods hydrogen sulphide and sulphur interfere with the determination, they must be first removed, this being conveniently accomplished by means of aqueous cadmium chloride and mercury respectively

The earliest method for the estimation of mercaptans was described by Klason and Carlson [85, 1906], it was based upon the iodine oxidation reaction which they claimed proceeds under certain conditions to completion It was observed that the addition of sodium hydrogen carbonate to neutralize hydrogen iodide formed was not only unnecessary but actually detrimental The reaction was later investigated by Kimball, Kramer, and Reid [81, 1921], who improved Klason and Carlson's procedure and showed that the method could be used satisfactorily to estimate both aliphatic and aromatic mercaptans Its application to mercaptans in hydrocarbon solution was first described by Sampey and Reid [134, 1932], who not only titrated the excess of iodine with thiosulphate but determined the hydrogen iodide liberated with sodium hydroxide The latter method did not prove as accurate as the former but was developed in the expectation that it would prove useful when applied to cracked distillates. It was found, however, that in the presence of unsaturated hydrocarbons neither method was applicable For many purposes the iodine method is convenient, rapid, and sufficiently accurate; it is employed in some refineries as a routine test for straight products A second acidometric method based upon the hydrogen chloride liberated when a mercaptan reacts with mercuric chloride,

$$RSH+HgCl_2 = RSHgCl+HCl,$$

was described by Sampey and Reid (loc cit) This, too, was shown to give good results if olefines were absent, but failed when they were present owing, as Hoffmann and Sand [66, 1900] had shown, to reaction between olefines and mercuric chloride forming hydrogen chloride

Several methods based upon the plumbite reaction have been suggested, but it is doubtful whether such methods can give reliable results owing to the complexity of the reaction and the readiness with which oxidation occurs Thus Youtz and Perkin [161, 1927] proposed to estimate mercaptan sulphur by the difference in total sulphur content before and after treatment with alcoholic plumbite solution containing some solid lead sulphide (cf Lachman [92, 1931]) No results were, however, given At practically the same time, Faragher, Morrell, and Monroe [53, 1927] published details of two methods based upon the use of plumbite In one, relying upon the solubility of alkyl mercaptides in benzene, the benzene solution of the gasoline was treated with basic lead acetate solution and, after removal of the excess of reagent, the lead remaining in the hydrocarbon layer estimated The second method resembled that suggested by Youtz and Perkin and was based upon differences in sulphur content before and after treatment with plumbite

The use of silver nitrate for the removal of mercaptans from petroleum distillates was first employed by Birch and Norris [15, 1926], but Borgstrom and Reid [25, 1929] showed that the reaction was quantitative Mercaptan sulphur could therefore be determined by difference in sulphur content before and after treatment with aqueous silver nitrate, but the preferred method consisted in titrating the excess of silver with thiocyanate in the usual way Since the occlusion of silver in the precipitated mercaptide gives high results, it is essential to ensure that the precipitate is thoroughly disintegrated, preferably by shaking with excess of thiocyanate in a shaking machine To obviate this, Malesoff and Marks [101, 1931] recommend adding methyl alcohol, claiming thereby to overcome the erratic results given by the original procedure Later Malesoff and Anding, Jr [100, 1935], published a detailed account of their modified procedure By adopting certain precautions to avoid oxidation of the mercaptan sample, employing more dilute solutions, adding methyl alcohol, and standardizing the indicator, much higher accuracy was obtained Tests on naphtha solutions showed a break-down of sensitivity at 0 001% mercaptan sulphur and a variation of 0 004% with a concentration of 0 035% mercaptan sulphur Recently Tamele and Ryland [138, 1936] have adapted the method to potentiometric titration, thus enabling it to be used on coloured samples Occluded silver nitrate is avoided by titration in alcoholic solution with alcoholic silver nitrate, which eliminates the separation into phases Titration is carried out with standard silver nitrate dissolved in isopropyl alcohol and in the presence of sufficient alcoholic sodium acetate solution to dissolve the hydrocarbons A silver electrode is employed which obviates an excess of silver nitrate and eliminates the simultaneous precipitation of impurities Since hydrogen sulphide and sulphur interfere they must first be removed, although, as the authors point out, since silver sulphide is less soluble than the mercaptide, it should be possible to estimate both sulphur and mercaptan by precipitating the sulphide first

The calculated error with a mercaptan (molecular weight 100) concentration of 0·01% is given as ±2 0%

Possibly the most convenient method so far devised for the estimation of mercaptan sulphur is due to Bond [22, 1933], who employs a kerosine solution of cupric oleate and titrates directly The estimation is based upon the reaction

$$4RSH+2Cu\overline{Ol}_2 - 2CuSR+R_2S_2+4H\overline{Ol}$$

in which the cuprous mercaptide is precipitated The kerosine solution is added from a burette to the sample until a pale green colour persists Although Bond recommends the use of the oleate (oleic acid prepared from elaine oil is stated to give a better colour than ordinary oleic acid), any kerosine soluble copper salt may be used e g the naphthenate An accuracy comparable with Borgstrom and Reid's silver nitrate method is claimed, coupled with much greater convenience The method gives satisfactory results with cracked products, for which it is particularly suited so long as peroxides are absent The latter, together with hydrogen sulphide, interfere, but phenols and naphthenic acids are without effect

Since disulphides on reduction (preferably with such reagents as zinc dust and acetic acid) give mercaptans,

$$R_2S_2+H_2 - 2RSH,$$

which can be estimated by one of the methods described above, this furnishes a useful method for their determination

IV. SWEETENING PROCESSES

The processes so far considered are associated with the removal from light distillates of substances possessing acid properties such as hydrogen sulphide and chloride, mercaptans and phenols Efficiency and extent of removal achieved are determined by such factors as plant conditions, involving intimacy of contact, &c, and the relative acidity of the substances involved Whereas hydrogen chloride and sulphide are entirely removed, providing of course sufficient alkali is used, complete removal of the whole of the weakly acidic mercaptans present, even in comparatively light distillates, is not possible Although alkali washing does very definitely improve the odour of the raw distillates, at the same time materially reducing the sulphur content, there is still left sufficient mercaptan sulphur to render the product unsaleable on account of bad odour and corrosive properties Mercaptans also act as catalysts in gum-formation Further treatment is, therefore, necessary to convert the undesirable mercaptans remaining after the preliminary alkali wash—for as such it should be regarded—into less noxious compounds, possessing a comparatively sweet odour or to remove them entirely

Of the two processes the former, which is termed 'sweetening'—untreated distillates containing mercaptans or hydrogen sulphide being referred to as 'sour'—is by far the most widely used, desulphurization only being employed when the sulphur content of the sweetened material exceeds specification value, or when special naphthas, e g painter's naphtha (white spirit), are being produced Obviously any treatment giving complete desulphurization must yield a sweet product

The process of sweetening is based upon the oxidation of mercaptans to the corresponding disulphides, a reaction which can be made to take place under comparatively mild conditions It can be seen from the equation representing the reaction,

$$2RSH = R_2S_2+2H,$$

that it merely involves the removal of two hydrogen atoms from two molecules of mercaptans with the linking up of the mercaptan residues Theoretically, therefore, no alteration should occur in the total sulphur content, although in actual practice, for reasons to be discussed later, this is rarely so Sweetening in certain processes, viz hypochlorite treatment, is accompanied by a certain amount of desulphurization, while in others, viz the plumbite process, a slight increase may and frequently does occur

Conversion of mercaptans into the corresponding disulphides results in a considerable change in boiling-point This difference is shown in the following table for several mercaptans boiling within the gasoline range

Boiling-points of Mercaptans and Corresponding Disulphides

Radical	Boiling-point, ° C	
	Mercaptan	Disulphide
Methyl	5 8	116-18
Ethyl	37	153
n-Propyl	67–8	192 5
*iso*Propyl	59	175
n-Butyl	98	90/4 mm
*iso*Butyl	88	215
*iso*Amyl	116–18	250
n-Heptyl	174–5	164/6 mm

The change in boiling-point is very marked, and if the mercaptan content is sufficiently high a noticeable effect will be observed in the final boiling-point of the product That this is possible seems unlikely with the comparatively low figures quoted for sulphur contents, but it should be realized that the *mercaptan* content is much larger than the *sulphur* content, a fact which is clearly demonstrated in the following table

Mercaptan	Sulphur content %	Mercaptan content equivalent to 0 1% sulphur
Methyl	66 6	0 15
Propyl	42 2	0 24
Amyl	31 4	0 32
Heptyl	24 2	0 42

It follows that redistillation following a sweetening treatment may result in a very definite reduction in sulphur content, the high-boiling disulphides remaining in the residue On this is based a process for the partial desulphurization of distillates rich in mercaptans

The Plumbite Process.

The plumbite process, which was first employed about 1910, is to-day one of the most widely used in the petroleum industry Originally discovered by what may be described as 'rule-of-thumb' methods, it was not until 1924 that the theoretical principles involved and the mechanism underlying the process were explained by Wendt and Diggs [150, 1924] Comparatively little change has been made in the method of operation and the treatment is still carried out very much as it was in 1910.

During the sweetening of a sour distillate a stage is reached when the mercaptan content is too low to be detected by the nose and some form of qualitative test becomes necessary The test employed is the so-called 'doctor' test, which consists in shaking the suspected sample with a solution of litharge in caustic soda solution, adding, if necessary, a small amount of sulphur. Any discoloration of the solution or of the sulphur particles at the interface indicates the presence of mercaptans or hydrogen sulphide, and the sample under test is said to be doctor positive. The coloration produced in borderline cases is frequently difficult to detect, so that the interpretation is apt to vary to a slight extent with the operator. While Borgstrom and Reid [25, 1929] give the sensitivity of the test as 0.00023 molar, Lachman [92, 1931] found that a positive test could still be obtained with a mercaptan solution at 0.00006 molar concentration. Assuming that the average gasoline is approximately 0.01 molar with respect to mercaptans, this requires removal equivalent to 98% for the higher figure or 99.5% for the lower figure to give a doctor negative product.

The curious observation has been made that a doctor negative distillate may give a positive reaction if alcohol is added during the test. Whether this is due to better contact of the reagent with hydrocarbon layer or to the decomposition of some comparatively unstable compound to regenerate traces of mercaptans is not known. It should be noted that besides mercaptans, peroxides also give a positive reaction and cracked distillates likely to contain them should be examined specially for their presence. The brown colour formed is due to lead peroxide (Brooks [28, 1924]).

Plumbite treatment closely follows the doctor test. The sour distillate, preferably after a preliminary alkali wash, is agitated with sodium plumbite solution and sulphur added until precipitation is complete. This operation is generally referred to as 'breaking', the precipitate formed being called the 'blackstrap'. After thorough settling to ensure that precipitation is complete, the product is finished and requires no further treatment.

Sodium plumbite solution, the so-called 'doctor' solution, is prepared by dissolving litharge in caustic soda, the formation of the plumbite being expressed by the equation

$$2NaOH + PbO = Na_2PbO_2 + H_2O$$

The solubility of litharge in solutions of sodium hydroxide is relatively high, the actual amount dissolved being of course determined by the concentration of the latter, and the temperature as shown by the following figures based upon those given by Berl and Austerweil [7, 1907].

Solubility of Litharge in Sodium Hydroxide Solution

Sodium hydroxide, %	4	7.9	19.9
Litharge, g per litre, 18° C	12.5	22.5	51.7
" " , 74° C	18.0	31.9	—

Solution is effected by the steam agitation of litharge suspended in strong caustic soda, the concentrated solution so obtained being diluted with water or soda to give one generally containing about 3½% litharge in 18° Bé caustic soda (13%).

While the actual concentration of plumbite is largely immaterial, a large excess of soda is always employed and this serves several useful purposes. Not only does it help to keep the lead in solution but it is extremely effective in bringing the mercaptans and the reagent into contact. Furthermore, it plays a very important part in plumbite regeneration by redissolving the oxidation products of the blackstrap, when all the plumbite is spent it can be used as an effective preliminary alkali wash. These points will be considered later.

It should be mentioned here that plumbite solution required in the laboratory for the doctor test is best prepared by the addition of an aqueous solution of lead acetate to a concentrated solution of sodium hydroxide, the precipitate at first formed redissolving. Not only does this method of preparation enable a more standard product to be obtained but it eliminates the possibility of plumbite formation. The latter is apt to interfere with the test in borderline cases by acting as an oxidizing agent, so giving samples actually slightly positive as doctor negative.

As mentioned above, the reaction between the plumbite and the mercaptans and hydrogen sulphide takes place in the aqueous layer. The distribution of mercaptans normally occurring between the aqueous soda and the hydrocarbon layer is upset by the formation of lead mercaptides or basic mercaptides which results in the mercaptan tending to pass completely out of the hydrocarbon layer,

$$RSH_{oil} \rightarrow RSNa_{aq} \rightarrow Pb(SR)_2$$

The lead mercaptides are either precipitated and so removed from the reaction zone or dissolve to a slight extent in the hydrocarbon layer, particularly if this is highly aromatic in nature. Similarly, hydrogen sulphide is converted into lead sulphide, which, being insoluble, separates as a black precipitate,

$$2RSH + Na_2PbO_2 = 2NaOH + Pb(SR)_2$$
$$H_2S + Na_2PbO_2 = 2NaOH + PbS$$

Both normal $Pb(SR)_2$ and basic $PbSR(OH)$ lead mercaptides are formed, an excess of plumbite favouring the formation of the latter. As a rule secondary mercaptans tend to form basic compounds and primary mercaptans normal derivatives (Ott and Reid [127, 1930]). Both normal and basic lead mercaptides form pale canary yellow amorphous compounds which, while unaffected by alkaline solutions, are readily decomposed by weak acids such as acetic acid, to regenerate the mercaptan and the corresponding lead salt. It is for this reason that it is impossible to precipitate a mercaptan completely with a lead salt when the acid from which the latter is derived is stronger than the mercaptan. Furthermore, owing to the low solubility of the mercaptan in water compared with hydrocarbons, contact is extremely bad. Even if lead salts were effective, sodium plumbite would still be preferable on account of its low cost, ease of formation, and the fact that unlike many lead salts it does not form insoluble basic salts.

While the normal mercaptides are insoluble in water and aqueous solutions, they are somewhat soluble in benzene and aromatic hydrocarbons, the solubility varying with the mercaptide. Thus the lead salts of the secondary mercaptans are more soluble than those of the corresponding primary mercaptans, increasing in solubility with increasing molecular weight, the reverse is true of the primary mercaptides. The basic mercaptides are also soluble in benzene, but whereas in the primary series the basic compounds are more soluble than the normal, in the secondary series the reverse holds true.

As all lead mercaptides are practically insoluble in paraffinic and naphthenic hydrocarbons, it follows that the yellow colour acquired by gasolines or naphthas containing mercaptans, when agitated with plumbite solutions, is due to the solvent action of the aromatic hydrocarbons present or to suspended mercaptides. Frequently on standing the yellow colour disappears and a pale yellow precipitate forms, whether this is due to settling of finely divided mercaptides or further reaction is uncertain.

Lead mercaptides are relatively unstable and tend to darken in colour, finally becoming converted into lead sulphide thus

$$\mathrm{Pb(SR)_2 = R_2S + PbS}$$

Both neutral and basic mercaptides undergo this decomposition, particularly when moist or in solution Heat, light, and the presence of free mercaptan all tend to favour the decomposition

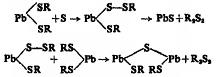
The reaction between the plumbite and the mercaptans, since it does not depend upon a state of equilibrium being reached, is rapid and is complete as soon as the reactants have been brought into contact with each other While efficient mechanical agitation effects this more rapidly, it actually offers little advantage, and air-blowing is generally employed for the purpose The fact that the air takes part in the reaction and can be made to play a very important role was, however, not discovered until comparatively recently The action of the air will be discussed later

At this point the distillate should actually be sweet, that is to say, it should contain no free mercaptan or, of course, hydrogen sulphide The next stage is the precipitation of the lead mercaptides, either dissolved or suspended in the hydrocarbon layer, by adding free sulphur which converts them largely into sulphides As an excess of sulphur will remain in the product and render it highly corrosive, it is desirable to estimate carefully the actual amount required This can conveniently be done by titrating a sample in an evaporating basin with a standard solution of sulphur in benzene, when the exact amount required to bring about the break is easily found From the equation

$$\mathrm{Pb(SR)_2 + S = PbS + R_2S_2}$$

the amount required corresponds with exactly half that originally present as mercaptan sulphur, in practice it is invariably less There are several reasons for this The lead mercaptides present in the precipitate tend to become coated superficially with lead sulphide which protects them from further action, and both aerial oxidation and complex side reactions occur

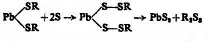
The equation given above can only be regarded as giving the main trend of the reaction Ott and Reid [127, 1930], who investigated the reaction for many pure mercaptans, showed that the addition of sulphur to a solution of normal lead mercaptides usually results in the formation of a precipitate containing both sulphide and mercapto-sulphides, thus



$$\mathrm{Pb}{<}^{\mathrm{SR}}_{\mathrm{SR}} + \mathrm{S} \rightarrow \mathrm{Pb}{<}^{\mathrm{S-SR}}_{\mathrm{SR}} \rightarrow \mathrm{PbS + R_2S_2}$$

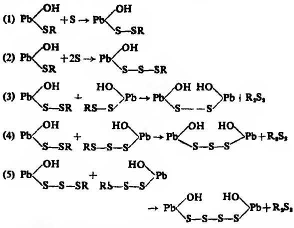
$$\mathrm{Pb}{<}^{\mathrm{S-SR}}_{\mathrm{SR}} + {}^{\mathrm{RS}}_{\mathrm{RS}}{>}\mathrm{Pb} \rightarrow \mathrm{Pb}{<}^{\mathrm{S}}_{\mathrm{SR}}\ {}^{}_{\mathrm{RS}}{>}\mathrm{Pb} + \mathrm{R_2S_2}$$

Lead disulphide was also detected



$$\mathrm{Pb}{<}^{\mathrm{SR}}_{\mathrm{SR}} + 2\mathrm{S} \rightarrow \mathrm{Pb}{<}^{\mathrm{S-SR}}_{\mathrm{S-SR}} \rightarrow \mathrm{PbS_2 + R_2S_2}$$

The action of sulphur on solutions of basic lead mercaptides appears to be even more complex Duncan and Ott [47, 1932] analysed some of the precipitates formed and showed them to be mixtures of lead sulphide and hydroxide From the basic mercaptide of *sec*-butyl mercaptan compounds of the type $\mathrm{Pb_2(OH)_2S_n}$ were formed, n being 3, 4, or even 5 Excess of sulphur again led to the formation of lead disulphide The suggested explanation for the formation of these compounds is as follows (Ott and Reid [127, 1930])



$$(1)\ \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{SR}} + \mathrm{S} \rightarrow \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-SR}}$$

$$(2)\ \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{SR}} + 2\mathrm{S} \rightarrow \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-S-SR}}$$

$$(3)\ \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-SR}} + {}^{\mathrm{HO}}_{\mathrm{RS-S}}{>}\mathrm{Pb} \rightarrow \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-}}\ {}^{\mathrm{HO}}_{\mathrm{-S}}{>}\mathrm{Pb} + \mathrm{R_2S_2}$$

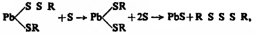
$$(4)\ \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-SR}} + {}^{\mathrm{HO}}_{\mathrm{RS-S-S}}{>}\mathrm{Pb} \rightarrow \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-S-S}}{}^{\mathrm{HO}}{>}\mathrm{Pb} + \mathrm{R_2S_2}$$

$$(5)\ \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-S-SR}} + {}^{\mathrm{HO}}_{\mathrm{RS-S-S}}{>}\mathrm{Pb} \rightarrow \mathrm{Pb}{<}^{\mathrm{OH}}_{\mathrm{S-S-S-S}}{}^{\mathrm{HO}}{>}\mathrm{Pb} + \mathrm{R_2S_2}$$

Since these reactions are accompanied by very considerable colour changes, the appearance of the oil and plumbite layer varies as the reaction proceeds Normally with a sour distillate, from which hydrogen sulphide and sulphur are absent, the addition of the plumbite leads to the formation of a yellow precipitate and a yellow coloration of the oil Should, however, elemental sulphur be present, as it generally is, both the precipitate and the hydrocarbon layer tend to be darker in colour, the actual colour, which may vary from orange to brick-red, brown or black, and shade depending upon the amount of sulphur present The same colour effects are usually observed when insufficient sulphur is present for complete reaction, i e when it is added slowly in solution or when the solid is added, and an appreciable time elapses before solution is complete These colour changes are due to the formation of mercapto-sulphides which, being in a very fine state of division, only settle after prolonged standing and then incompletely On further reaction with sulphur, the colour changes to black or very dark brown owing to the formation of lead sulphide, this being followed by flocculation which results in a rapid and complete precipitation of the lead compounds in solution and suspension The point at which the break occurs is very definite, and the exact amount of sulphur required is somewhat critical In view of the corrosive nature of free sulphur, it is essential to avoid any excess remaining, as an excess at this stage can only be removed by redistillation or blending back with untreated material containing mercaptans followed by further plumbite treatment

When the required plumbite and sulphur are added together to the sour distillate, an immediate blackening occurs and no colour changes are observed This is so because the mercaptide reacts with the excess sulphur to form PbS as quickly as it is formed from the mercaptan

The suggested mechanisms given above for the formation of complex lead compounds assume that the purely organic side of the reaction is simple and merely involves the conversion of the mercaptan into the corresponding disulphide The latter being miscible with hydrocarbons and insoluble in the aqueous layer pass back into the material being treated. Birch and Norris [16, 1929], however, found on examination that although the disulphides formed the main bulk of the product, higher polysulphides are formed as well. This was later confirmed by Duncan and Ott [46, 1931] Whether these polysulphides are formed through a complex lead derivative similar to those suggested by Duncan and Ott,



$$Pb\langle^{SSR}_{SR} + S \rightarrow Pb\langle^{SR}_{SR} + 2S \rightarrow PbS + RSSSR,$$

or by the direct addition of sulphur to the disulphide is not known,

$$R_2S_2 + S = R_2S_3$$

As Holmberg [67, 1908] showed that the second reaction only occurs very slowly, the first mechanism is more likely to be correct. Recent work by the author [20, 1936] has shown that treatment of ethyl mercaptan with a large excess of sulphur in the presence of plumbite, besides the disulphide, gives considerable quantities of the trisulphide, while indications were obtained that still higher polysulphides were formed as well.

Air, as mentioned above, can play a very important part in the treatment, to a large extent replacing the sulphur as oxidizing agent,

$$2RSH + O = R_2S_2 + H_2O$$

The extent to which this occurs, however, is determined by plant conditions. Under ordinary conditions involving aerial agitation, the effect due to the air is probably not very great, but by ensuring intimate contact between the hydrocarbon, the reagent, and air, it is possible to replace the sulphur almost entirely (cf. Rowsey and Whitehurst [132, 1927]).

The part played by the lead sulphide in promoting aerial oxidation is very important. Wendt and Diggs [150, 1924] showed that by acting as an adsorbent, lead sulphide effects desulphurization in a small measure. The sulphur compounds removed include not only those involved in the plumbite process but any other sulphur compounds as well. Lachman [92, 1931], who investigated the aerial oxidation of mercaptans in sodium hydroxide solutions, found that the reaction was governed by the speed of diffusion of the air into the alkaline layer. Any means which increased this rate of diffusion, as, for example, increase in air pressure, area of the alkaline film through agitation, or surface of contact by the addition of finely divided solids, thereby increased the rate of oxidation. Lead sulphide, by acting as a finely divided solid, catalytically aids the oxidation by providing a large contact area. Finely divided sulphur behaves in the same way when added in the solid form. Owing to the particles becoming coated with a protective film of lead sulphide, a considerable amount of the sulphur added remains undissolved and is withdrawn with the sludge.

Theoretically, the treatment of a sour distillate with air in the presence of a suspension of lead sulphide in caustic soda solution should require no additional sulphur. In practice, even when air is largely employed for the oxidation, as in the Rowsey and Whitehurst process, the addition of some sulphur is essential. This is necessitated by the oxidation of the lead sulphide to sulphate, which is converted by the caustic soda present into plumbite

$$PbS + 2O_2 + 4NaOH = Na_2PbO_2 + Na_2SO_4 + 2H_2O$$

$$2PbS + 2O_2 + 6NaOH = 2Na_2PbO_2 + Na_2S_2O_3 + 3H_2O$$

This then reacts in the normal manner with the mercaptans present to form lead mercaptides which are not completely oxidized by the air, and it is necessary to use sulphur.

The use of lead sulphide suspended in caustic soda solution has been suggested as a method for handling distillates so high in mercaptan content that ordinary plumbite sweetening methods are inapplicable on account of cost. The distillate is thoroughly agitated with sulphur in the presence of caustic soda solution and a relatively small amount of lead sulphide. The use of air is optional. When sweet the oil is removed and distilled to leave a residue containing most of the sulphur originally present as mercaptans in the form of di- and higher polysulphides. During the distillation the temperature should be maintained below 160° C., to prevent the decomposition of the polysulphides formed (Standard Oil Development Co. [137, 1926, 1931]). Other heavy metallic sulphides can replace the lead sulphide, but the presence of sodium sulphide is stated to be detrimental.

Effect of Plumbite Treatment upon the Knock-rating of Gasolines

It has been observed that plumbite treatment generally involves a small but definite fall in knock-rating, and G. M. Woods [158, 1935] advocates following the treatment by redistillation. Hebl, Rendel, and Garton [65, 1933] also observed that certain West Texas distillates after plumbite treatment had a much lower lead response than before treatment. After redistillation the response improves again and corresponds with that of the original untreated distillates.

While so far no explanation has been put forward to account for an effect of the order of magnitude of that observed by Hebl, Rendel, and Garton, it has been shown that all sulphur compounds reduce the lead response to a greater or lesser extent. Disulphides, mercaptans, and trisulphides proved to be particularly effective, the last possessing definite pro-knock tendencies as well. As these substances were tested in comparatively high concentrations, it appears probable that the small amount of higher polysulphides must have extremely pro-knock characteristics, and be capable not only of lowering the knock-rating of the gasoline itself but of considerably reducing the lead response at the same time [20, 1936].

Polysulphides and Corrosive Properties.

Although the excessive addition of sulphur gives a corrosive product, gasolines and naphthas in particular which have been carefully treated may prove corrosive under certain conditions. Thus Birch and Norris [16, 1929] showed that the corrosive action of certain acid-washed naphthas (white spirit or painter's naphtha) upon copper between 150 and 180° C. was due to the formation of traces of polysulphide during this treatment.

Further investigation showed that these compounds were also formed during the plumbite treatment of gasoline and that on heating they tend to decompose. The corrosive action is due to elementary sulphur formed in the decomposition.

The prevention of the formation of polysulphides in traces does not seem possible, although by limiting the sulphur as far as possible there is less tendency for them to be formed.

Plumbite Treatment of Cracked Distillates.

Plumbite itself possesses no polymerizing action and should therefore only be applied to cracked gasolines after a preliminary acid or other polymerizing treatment, e.g. fuller's earth or zinc chloride. The use of plumbite as a neutralizing agent after acid treatment and before redistillation is not to be recommended owing to the decomposition of disulphides, &c., during distillation, which renders necessary a still further sweetening treatment on the distillate Plumbite is most effectively applied as a finishing treatment, that is to say after acid, neutralization, and redistillation

The Recovery of Spent Plumbite

Litharge, which is by far the most costly chemical employed in the plumbite process, is eventually found in the sludge or blackstrap chiefly as lead sulphide suspended in an emulsion of oil and caustic soda For many years it was the practice to dispose of this material by the most convenient method available, which usually consisted in depositing it on waste land When later it became necessary to reduce treatment costs as much as possible, plumbite recovery proved an effective means of doing so with the added advantage that it solved the disposal problem, always a bugbear to the refiner In small refineries, however, with limited litharge consumption, recovery is still uneconomical and is not attempted

Early attempts at recovering the lead consisted in allowing the solid material to settle as completely as possible and then filtering or centrifuging, the dried cake was roasted in air to convert the lead sulphide into sulphate The latter was reconverted into plumbite by solution in caustic soda,

$$4NaOH + PbSO_4 = Na_2PbO_2 + Na_2SO_4 + 2H_2O$$

Wet methods which do not involve roasting are, however, preferable, and at the present time several of these are in use

Air-Blowing Process.

This process was originally employed by the Atlantic Refining Company of Philadelphia and is based upon the oxidation reaction already described The spent plumbite, still containing a little lead present in solution as plumbite (about 0 6%) and the remainder in suspension as lead sulphide, &c (4%), is allowed to settle in large storage tanks Three layers are formed, (*a*) a supernatant oil layer which is sent to storage, (*b*) a middle layer consisting of emulsified caustic soda solution with suspended lead compounds—this is sent to the 'break' tank—and (*c*) a bottom layer of caustic soda solution containing the unused plumbite, which is withdrawn and temporarily stored The middle layer in the 'break' tank is gradually heated to 150° F, causing it to separate into a further three layers Of these, the top layer of oil is withdrawn, while the bottom containing the lead sulphide is placed in tanks fitted with steam coils, thoroughly agitated with air, and heated to 175–200° F until all the sulphide is redissolved The generally accepted equation for this reaction is

$$2PbS + 2O_2 + 6NaOH = 2Na_2PbO_2 + Na_2S_2O_3 + 3H_2O$$

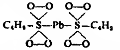
although probably the reaction

$$PbS + 2O_2 + 4NaOH = Na_2PbO_2 + Na_2SO_4 + 2H_2O,$$

also occurs to a considerable extent Should insufficient soda be present for complete solution more is added as required

The regenerated plumbite is finally washed with oil to remove colouring matter and sulphur compounds originally adsorbed on the lead sulphide For successful oxidation the presence of some hydrocarbon oil is essential, experiments carried out in the laboratory on pure lead sulphide suspended in caustic soda solution proving abortive in the absence of oil.

We have seen that the solids present in the spent plumbite contain besides lead sulphide varying amounts of disulphide, mercaptides, basic sulphides, and free sulphur All of these substances are involved in the oxidation, with the result that the process is extremely complex Little is known of the behaviour of lead mercaptides and the complex mercapto-sulphides when oxidized with air in caustic soda solution While Morrell showed that lead mercaptides gave only a low yield of alkyl disulphides under these conditions, Ott and Reid [127, 1930] found that solutions of lead mercaptides exposed to air at room temperature absorbed oxygen and formed comparatively stable peroxides of high though varying oxygen content There were indications that the oxygen was attached to the sulphur and not to the lead, the probable formula for the *sec*butyl compound being



$$C_4H_9-\overset{\text{O—O}}{\underset{\text{O—O}}{S}}-Pb-\overset{\text{O—O}}{\underset{\text{O—O}}{S}}-C_4H_9$$

Whether such compounds are formed even as intermediates at the elevated temperatures used in air-blowing is, however, open to question Undoubtedly decomposition of the lead mercaptides to form lead sulphide and the corresponding dialkyl sulphide takes place,

$$Pb(SR)_2 = PbS + R_2S$$

This reaction is known to be favoured by heat and moisture There is also the possibility of double decomposition occurring between the lead mercaptides and the caustic soda present, with the subsequent elimination of the mercaptan by hydrolysis thus

$$\begin{gathered} Pb(SR)_2 + 2NaOH = 2NaSR + Pb(OH)_2 \\ Pb(SR)OH + NaOH = NaSR + Pb(OH)_2 \\ NaSR + H_2O \rightleftharpoons NaOH + RSH \\ Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O \end{gathered}$$

Oxidation of the protecting layer of lead sulphide leaves particles of elementary sulphur These, apart from oxidizing any mercaptides remaining, react with the hot caustic soda solution to form thiosulphate and polysulphides—which of course at once react with the plumbite present This action can be summed up by the equation

$$6NaOH + nS = 2Na_2S_{\frac{1}{2}(n-2)} + Na_2S_2O_3 + 3H_2O,$$

although this by no means expresses all the intermediate reactions which no doubt occur Oxidation of the thiosulphate does not proceed further, but if the solution is sufficiently concentrated decomposition may occur with the formation of sulphite,

$$3Na_2S_2O_3 + 6NaOH = 2Na_2S + 4Na_2SO_3 + 3H_2O$$

As a result of these and similar reactions the recovered plumbite contains considerable quantities of various sodium salts which tend to build up during the recycling of the recovered soda To avoid this, some 10–20% of the recovered soda is replaced each cycle with fresh. Any lead present in the withdrawn liquor is recovered as sulphide by using it as a preliminary alkali waste or by direct precipitation with spent alkali

With effective plumbite recovery the lead loss is very small, the only chemicals consumed being sulphur and caustic soda A method for the recovery of sodium salts of definite market value from the spent plumbite has been described by Valentine and Maclean [146, 1935]. These authors give the composition of what they consider to be a typical spent doctor solution discarded at the end of ten cycles, allowing for a 5% liquid loss restored to the original volume and 18° Bé by caustic soda, as

Total volume, 10,500 gal (Am)	lb
Sodium plumbite (as PbO)	440
„ hydroxide	5,050
„ thiosulphate	8,510
Phenolates*	8,020
Sodium chloride	130
„ carbonate	240
„ sulphite and sulphate	1,600

* The raw material appears to have been abnormally rich in phenols

The lead is first removed This is done hot by precipitation with sodium sulphide or hydrogen sulphide, and is best carried out before separation of the blackstrap, as slightly soluble lead phenolates, which do not respond readily to oxidation on air-blowing, are then decomposed

After removal of the lead sulphide by settling the solution must be neutralized This can be done by either carbon dioxide, preferably from flue gas, or sulphur dioxide obtained either as a by-product in refinery operation or from a sulphur burner

Neutralization with carbon dioxide is preferably carried out at 120° F and should proceed until well on the bicarbonate side The composition of the solution obtained is

Total volume, 10 500 gal (Am)	lb
Sodium carbonate—bicarbonate	11 000
„ thiosulphate	8 510
Free phenols	8,020
Sodium chloride	130
, sulphate and sulphite	1,600

The free phenolic compounds are separated and, it is suggested, may be usefully employed as solvents for the refining of lubricating oil or in the manufacture of plastics The solution on evaporation to about 2,000–2,500 gal and cooling to 110° F deposits about 80% of the sodium carbonate as a cake contaminated with other salts This, causticized with lime, furnishes about 6,800 lb caustic soda On further concentration of the mother liquor sodium thiosulphate (about 9,500 lb) is recovered When sulphur dioxide is used, neutralization should be carried out at 180° F and proceed until all the alkali is converted into sulphate Rosolic acid is the ideal indicator to determine the correct end-point The composition of the solution prepared from the above spent plumbite is then

Total volume, 10,500 gal (Am)	lb
Sodium sulphite	13,700
„ thiosulphate	8,510
„ chloride	130
„ sulphate	1,000
Phenols	8,020

The phenols separate and are removed Sulphur is then added to convert all the sulphite present to thiosulphate, the reaction being carried out at the boiling point Concentration by evaporation gives sodium thiosulphate—about 35,000 lb It is pointed out that the operations involved are so inexpensive that it is possible actually to show a profit on what was almost waste material

The Kinsel Recovery Process.

This process (Kinsel [83, 1925]) serves two useful purposes. Not only does it recover lead from the blackstrap but it helps in the disposal of acid sludge

After settling, the spent plumbite is heated in a break tank as in the air-blowing process. The bottom layer, containing most of the lead, is then filtered to give as dry a cake as possible, i e about 30% of water This is placed in a tank containing the correct amount of dilute acid to convert the sulphide into sulphate,

$$PbS + H_2SO_4 = PbSO_4 + H_2S$$

The acid is obtained by diluting sludge acid to a gravity of 1 32–1 38 and settling the tar When the conversion is complete, the sulphate is washed by decantation to a low acid content and redissolved in fresh caustic soda solution

The F.C. Process.

This process (Fielschmidt and Cantrell [55, 1930]) involves the use of chlorine as an oxidizing agent, and is therefore more costly to operate than either of those previously described It has proved very convenient in refineries having comparatively small quantities of lead to recover

The spent plumbite is settled and the lead sulphide freed as much as possible from caustic soda by water washing, after which it is placed in the treating vessel This consists of a vertical cylindrical tank fitted with a paddle, a gauge glass, and draw-off cocks at different levels The sulphide, mixed with water and hydrochloric acid (obtained from a previous run) to act as accelerator, is thoroughly agitated, while a stream of chlorine is passed in Approximately 0 3 lb chlorine is required for every pound of sulphide treated When the reaction, which may take as long as three hours, is complete, the agitation is stopped and the products allowed to settle Three layers form the top consists of a flocculent suspension of sulphur, the middle is dilute hydrochloric acid with a little lead chloride in solution, and the bottom consists of a mixture of finely divided solid material, principally litharge with some sulphur and traces of lead chloride The three layers are separated by means of the draw-off cocks and the crude sulphur and litharge washed with water to free them from acid The litharge is redissolved in caustic soda in the usual way The sulphur present offers no disadvantage, generally sufficing for the treatment of the next batch of distillate

The chemical reactions involved are simple and merely consist in the oxidation of the sulphide thus

$$H_2O + Cl_2 = HCl + HOCl$$

$$PbS + HOCl = PbO + S + HCl$$

$$PbO + 2NaOH = Na_2PbO_2 + H_2O$$

Modified Doctor Processes.

Several modifications of the doctor process have been devised, but these do not appear to have been at all widely adopted

The use of either sodium or dialkyl polysulphides has been advocated to overcome the risk involved in adding too much sulphur and so producing a corrosive product The sodium polysulphide solution is prepared by dissolving sulphur in a mixture of caustic soda and spent soda which has been saturated with hydrogen sulphide, for example, by use as a preliminary caustic wash for gasoline The reactions involved are expressed by the following equations

$$Na_2S + nS = Na_2S_{n+1}$$

and

$$n(RS)_2Pb + Na_2S_{n+1} = nR_2S_2 + nPbS + Na_2S$$

This treatment must obviously be carried out in two stages, the first involving the plumbite and the second oxidation with the polysulphide solution

The use of low-molecular weight alkyl disulphides, for example the methyl or propyl derivatives, has been suggested for the same purpose by Hunn [69, 1930] On standing after treatment, lead sulphide is precipitated and a sweet product remains Analysis of the precipitate after the addition of methyl disulphide indicated it to be lead methyl mercaptide presumably formed by replacement

$$(RS)_2Pb+(CH_3)_2S_2 = (CH_3S)_2Pb+R_2S_2$$

In place of sodium plumbite solution, a solid reagent consisting of calcium hydroxide (slaked lime), litharge and sulphur can be used (Cannon and Gary [35, 1931]) The lime and litharge form the hypothetical calcium plumbite which is incapable of existence in solution Sour distillates agitated with this reagent are sweetened and only require filtering for finishing The reaction proceeds normally with the formation of alkyl disulphide and lead sulphide, this reacting with the lime to form calcium sulphide and litharge

$$2RSH+(PbO\ CaO) = (RS)_2Pb+Ca(OH)_2$$

$$(RS)_2Pb+S = R_2S_2+PbS$$

$$PbS+2Ca(OH)_2 = [PbO\ CaO]+CaS+2H_2O$$

Fresh sulphur is added to the reagent, when it is again ready for use

Probably a more convenient method of operating this process is given by Cannon [34, 1931] The necessary sulphur is dissolved in the sour distillate, which is then treated with a solid reagent consisting of a mixture of sodium and calcium hydroxides, litharge, diatomaceous earth (to increase the effective surface) and enough water to make a coherent mass

More recently a process involving the use of magnesium hydroxide in a modified doctor process in place of sodium plumbite has been described by Gardner and Higgins [59, 1932]

The treatment consists in passing the sour distillate, in which the requisite amount of sulphur has been dissolved, through a tower packed with magnesium hydroxide granules, when the following reaction occurs

$$Mg(OH)_2+RSH = Mg(SR)OH+H_2O$$

$$2Mg(SR)OH+S = MgS+Mg(OH)_2+R_2S_2$$

The coating of the surface of the granules with magnesium sulphide eventually slows up the process and regeneration becomes necessary This can be effected by steam or boiling water, although a dilute solution of sodium hydroxide (2%) is preferred

The use of lead can also be avoided if an alcoholic solution of sodium or potassium hydroxide is employed Under these conditions, the hydrolysis of the alkali metal mercaptides in the alcohol layer is suppressed and oxidation can then be readily accomplished by means of sulphur

$$RSH+NaOH = RSNa+H_2O$$

$$2RSNa+S = R_2S_2+Na_2S$$

Air is neither required nor is it desirable, as the rate of oxidation with air compared with that with sulphur is so slow that there is loss of gasoline by evaporation (Stagner [136, 1935]) The process can also be employed to sweeten high-boiling distillates such as kerosine. A description is given by Stagner of the treatment of a gasoline containing 0·023% mercaptan sulphur with methyl alcoholic—sodium hydroxide (0 31% by volume containing 15% NaOH) and elemental sulphur (0·029 g per litre gasoline treated). After agitation for 30 min followed by 10 min settling, the gasoline was sweet and non-corrosive The inorganic products of the reaction were found in the lower alcoholic layer, which on withdrawal followed by exposure to air was found to contain unchanged caustic soda, sodium sulphide, together with traces of the polysulphide and the thiosulphate Stagner states that, of the sodium hydroxide originally used, 25% is recovered as thiosulphate and 50% as sulphide Both of these substances have a definite market value Owing to the solubility of anhydrous methyl alcohol in gasoline—about 3–10%, the solubility being greater in the lower hydrocarbons—it is necessary to recover the alcohol from the sweetened distillate by water washing Recovery of the alcohol is effected by distillation of the water Methyl alcohol is preferable to ordinary alcohol because it does not form a constant-boiling mixture with water and can therefore be recovered in a substantially anhydrous condition, ready for use again By using the same water for washing, complete recovery is not necessary in each passage through the still, the overall loss of alcohol is stated to be negligible, i e 0 1–0 2%

V. THE HYPOCHLORITE PROCESS [11, 1929]

This process differs in many respects from the sweetening processes so far described The latter involved reactions almost entirely confined to the oxidation of the mercaptans into oil-soluble disulphides which pass back into the hydrocarbon layer and leave the total sulphur content unchanged Sulphur compounds other than mercaptans and hydrogen sulphide remain unaffected chemically although physically they are adsorbed to a slight extent upon the solids formed or originally present Aqueous hypochlorite solutions possessing much more powerful oxidizing properties not only carry the oxidation of the mercaptans beyond the disulphide stage but attack the sulphides and disulphides as well As the products from these oxidations are mostly water-soluble, desulphurization occurs to a greater or lesser extent depending upon the conditions and the nature of the sulphur compounds present in the distillate under treatment

Early attempts to use hypochlorite solutions in the refining of light distillates failed owing to the instability of the reagent used Not only did this tend to decompose spontaneously before and during use but the products acquired a peculiar sharp odour due to the presence of chlorine compounds, rapidly went off colour, and proved highly corrosive in use The successful application of the process was due to Dunstan and Thole, upon whose novel idea of using alkaline solutions to prevent chlorination the present process is based

The hypochlorite process is used principally for the sweetening or desulphurization of straight or cracked distillates Owing to the convenience with which it can be operated in a closed system, it has proved particularly suitable for treating natural gasoline and in the States it is most generally employed for this purpose A particular advantage of the process is that the spent wash is entirely valueless and contains no objectionable products, no recovery is therefore necessary and the effluent can be disposed of without difficulty

The process consists essentially in agitating the sour distillate, which has previously been alkali washed to remove any hydrogen sulphide, with an aqueous solution of sodium or calcium hypochlorite under controlled conditions. Traces of hypochlorous acid together with any objectionable organic compounds formed in the reaction are removed by a final thorough alkali wash It is essential that the hypochlorite solution employed should contain sufficient free alkali to stabilize it, that is to say, to suppress spontaneous decomposition while at the same time reducing any tendency towards chlorination of the distillate to a minimum If desulphurization is desired, the amount of free alkali is rather critical, too much retarding the oxidizing action of the hypochlorite very considerably The reason for this will follow later

Unlike the plumbite process which, as the addition of free sulphur forms an integral part of the procedure, can handle distillates containing free sulphur, hypochlorite treatment can only be successfully employed when free sulphur or hydrogen sulphide is absent Once formed, elemental sulphur can only be removed by distillation The necessity for avoiding the presence of either of these substances—hydrogen sulphide is readily oxidized by hypochlorites to sulphur—therefore becomes of paramount importance, and care must be taken to ensure that hydrogen sulphide is removed at as early a stage as possible by efficient alkali washing The most convenient point for this treatment is in the condensing system before aerial oxidation can possibly take place Actually this wash serves a dual purpose, for besides removing hydrogen sulphide it removes some of the lighter mercaptans and so materially reduces hypochlorite consumption It is because of the definite advantages offered by thorough alkali washing before the hypochlorite wash is applied, that the hypochlorite process lends itself so well to counter-current operation, the spent hypochlorite still contains a small amount of free alkali and this can effectively be used in countercurrent operation to reduce the mercaptan content of the raw material

As mentioned above, the hypochlorite process is most admirably suited to the treatment of natural gasoline The solution is usually placed in a series of vertical cylindrical vessels preferably packed with coke or some similar packing and the natural gasoline (previously alkali washed if hydrogen sulphide is present or the mercaptan content high) passed through them By by-passing each treater when it becomes spent and, after recharging it with fresh solution, making it the final stage, the operation can be carried out more or less countercurrently No complications are necessary as in plumbite treatment, for there is no sulphur to introduce and no sludge to withdraw The spent wash is run to waste

Treatment of the gasoline fractions can be conveniently carried out in ordinary treaters, although the Holley-Mott type of plant is the most suitable on account of the advantages offered by the multiplicity of stages

Preparation of Hypochlorite Solutions.

Both sodium and calcium hypochlorite solutions are easily prepared The sodium salt used in the original process was prepared by the electrolysis of brine, the current density and other conditions being adjusted to give the equivalent amounts of chlorine and caustic soda required for the reaction

$$Cl_2+2NaOH = NaOCl+NaCl+H_2O$$

By careful control of the temperature and the final alkalinity, chlorate formation was avoided and stable hypochlorite solutions between 0 2 and 0 3 N , with regard to available chlorine content and containing 0 5 to 1 g. caustic soda per litre, obtained The presence of the sodium chloride cannot be avoided, but it is not in any way detrimental Later, when liquid chlorine became available at a sufficiently low price, it proved more convenient to prepare sodium hypochlorite by passing either the gaseous or liquid chlorine into well-cooled and agitated caustic soda solution (10%), diluting the concentrated solution so obtained before use

A convenient source of calcium hypochlorite is bleaching powder which is prepared by passing chlorine over slaked lime, the moisture content together with the temperature of absorption determining the chlorine absorbed There is some doubt concerning the exact form in which the chlorine is combined, the analysis of a typical good sample containing 45% of available chlorine giving the following results (Lunge [96, 1911])

Ultimate analysis		*Cal*	*Proximate analysis*
Lime CaO	38 89	$2CaOCl_2H_2O$	82 65
Available chlorine	43 13	$CaCO_3$	0 95
Chlorine as chloride	0 29	$CaCl_2$	0 44
Water	17 00	$Ca(OH)_2$	6 80
Carbon dioxide	0 42	H_2O	9 16

It is generally assumed that calcium chlorohypochlorite is the active compound present

A solution of bleaching-powder in water reacts strongly alkaline and contains, besides calcium hypochlorite, the chloride, oxychloride, and hydroxide, the relative proportions (with the exception of the hydroxide, which is limited by its solubility) depending upon the freshness of the material According to Lunge the analysis of a solution prepared from a good fresh sample of bleaching-powder is as follows

	g per litre
Calcium hypochlorite	129 09
,, chloride	10 54
,, chlorate	0 38
,, hydroxide	4 21

Solutions, however, prepared from bleaching-powder which have been kept for some time have a higher proportion of chloride and chlorate

Bleaching-powder as a source of calcium hypochlorite has several disadvantages It does not keep well on storage, particularly in warm climates, decomposition taking place slowly with the evolution of oxygen

$$2Ca(OCl)Cl = 2CaCl_2 + O_2$$

(For this reason it must not be stored in sealed metal containers as these are liable to burst) As a result the available chlorine content, i e the amount of chlorine equivalent to the active oxygen present, which usually varies between 37 and 39%, falls rapidly and the material becomes useless Even when fresh, solution in water is far from complete and a considerable insoluble residue remains, consisting of lime together with some calcium carbonate To avoid loss of active material it is therefore essential to wash this residue once or twice thoroughly, the washings being employed either to dilute the more concentrated extract or in making the next batch As will be shown later, calcium hypochlorite solutions should only be diluted with saturated lime-water which is conveniently provided by the washings Even thorough washing still leaves a small amount of unknown active compound in the residue These drawbacks, together with its relatively high cost, preclude the general use of bleaching-powder excepting in refineries in which the consumption is small or where other sources of calcium hypochlorite are not available To some extent these disadvantages have been overcome in the last 10 years in the specially high active chlorine content bleaches which have become available Essentially these consist of solid calcium hypochlorites prepared by the action of sodium hydroxide on concentrated calcium hypochlorite solutions In this way the calcium chloride present is precipitated as lime while the low solubility of sodium chloride compared with that of the calcium salt causes a considerable amount of salt to precipitate also Concentration of the resulting solution enables a solid to be obtained consisting mainly of calcium hypochlorite contaminated with sodium chloride which is practically completely soluble in water and contains between 60 and 70% of available chlorine Much greater stability on storage is claimed for these preparations, a claim certainly quite justified for the Mathieson Alkali Works Inc product 'H T H' Even after 6 years in the laboratory, it was found that the available chlorine content of a sample had only dropped from 66 to 45–50% On account of their comparative high cost they are little used in the petroleum industry, but in the laboratory they form an extremely convenient source of calcium or sodium hypochlorite (the latter being formed by double decomposition with sodium carbonate)

On the large scale, calcium hypochlorite is most conveniently prepared by passing chlorine in the liquid or gaseous state into a well agitated cooled slurry of lime preferably prepared by slaking quick-lime The calcium hydroxide rapidly passes into solution, the end of the reaction usually being detected by the development of a pink colour which has been attributed to manganese—as permanganate—or calcium ferrate While it is desirable to keep the temperature as low as possible during the absorption, temperatures as high as 140° F have been observed without undue decomposition taking place When, however, the reaction does get out of control, the temperature rises rapidly, considerable quantities of chlorine and oxygen are liberated, and the hypochlorite is converted into a mixture of chloride and chlorate

$$Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2$$

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$$

In practice the lime slurry is prepared equivalent to gravity of 1 1 diluted to 1 05 and chlorinated to 1 1 again The concentrated solution so prepared has an available chlorine content equivalent to approximately 2 N and is diluted to 0 34 N with the leachings obtained by washing the insoluble residue, consisting chiefly of lime and calcium carbonate, the latter separates out on settling Further dilution to 0·07 N —the working concentration usually employed—is done at the plant, saturated lime-water, i e approximately 0 04 N, being used for the purpose to ensure that the solution is stable In continuous operation it is convenient to meter the lime-water and 0 34 N hypochlorite solution separately into a small mixing tank attached to the plant

Treatment is carried out by the agitation of the sour alkali-washed distillate with a comparatively large volume of the dilute hypochlorite solution It is usual to determine by preliminary tests in the laboratory the exact amount of available chlorine necessary to effect sweetening or desulphurization and adjust the treatment accordingly The sweetening action is very rapid, efficiency of contact alone determining the time required, desulphurization is slower and may need a much longer time, depending upon the sulphur compounds present, the alkali content of the hypochlorite wash, and the temperature The operation should be carefully controlled by analysis, the available chlorine being estimated by means of potassium iodide solution and acetic acid, and the free alkali by titration with standard acid using phenolphthalein as indicator after destroying the hypochlorite by boiling with ammonia When the operation is carried out effectively, the spent wash contains no hypochlorite but is still sufficiently alkaline to be usefully employed as a preliminary alkali wash Care should, however, be taken to avoid the use of the spent solution for this purpose on distillates likely to contain hydrogen sulphide unless entirely free from traces of hypochlorite Hypochlorite solutions are definitely mildly corrosive to steel equipment and it is necessary to take steps to overcome this as much as possible Cement or cast iron which is not corroded (excepting near the point of introduction of the chlorine) can be conveniently used for the vessels for preparing the solution, the former being preferable because cooling can be more effectively carried out Cement is used for settling or storage vats Treaters are best covered internally by spraying with a thin layer of cement which must be renewed after any cleaning operation Calcium carbonate is normally deposited from calcium hypochlorite solution and serves to protect the equipment, but even so it is better to ensure protection by a cement layer

The Action of Hypochlorite Solutions upon Sulphur Compounds

The effect of sodium hypochlorite solution upon various sulphur compounds dissolved in a sulphur-free naphtha of Iranian origin was investigated by Birch and Norris [14, 1925] Their results are summarized in the following table

These sulphur compounds represent typical substances which might be expected in the lighter distillates and many of them have actually been isolated from Iranian straight distillates (cf Birch and Norris [13, 1925], Thierry [140, 1925]) The others are, or could be, formed as a result of the action of the hypochlorite, viz *iso*amyl sulphoxide, ethyl sulphone, and sulphur

The conclusions reached as a result of these experiments are as follows

(1) Whereas hydrogen sulphide, mercaptans, and disulphides all react to give at least some acid products, no acid products are formed from sulphides (or, of course, sulphones)

(2) Thiophen, sulphones, and sulphur do not react under the conditions employed

(3) Increase in molecular weight of the sulphur compound (*a*) decreases the rate of oxidation—di-*iso*amyl disulphide hardly reacts at all—and (*b*) decreases the solubility of the oxidation products in the aqueous layer, at the same time increasing their solubility in the oil

(4) Increase in the free alkali content of the hypochlorite decreases the rate of reaction (excepting the oxidation of hydrogen sulphide and the first stage in the oxidation of mercaptans) and conversely.

(5) Dilution of the hypochlorite increases the rate of reaction

The first of these conclusions is of the greatest importance because the acid products neutralize the free alkali *of the reagent as they are formed, and thus progressively render the hypochlorite more reactive Consequently, if* insufficient alkali is originally present to neutralize the acid products, the aqueous layer may actually become acid, when there will be a tendency for 'chlorination' to occur As it was confirmed that the addition of free alkali stabilizes the hypochlorite, the explanation of the narrow limits for alkali content necessary in large-scale operation becomes clear The retarding influence of free alkali, and the accelerating effect of dilution, are convincingly explained on the assumption that the active oxidizing agent is not the hypochlorite itself but free hypochlorous acid produced by reversible hydrolysis

$$\mathrm{MOCl\quad H_2O \underset{MOH}{\overset{H_2O}{\rightleftharpoons}} MOH + HOCl}$$

On this assumption, added free alkali will displace the equilibrium to the left, dilution will move it to the right, and, in accordance with observed facts, the solution will be stabilized or activated respectively Other proposals for increasing the reactivity of hypochlorite solution, such as the addition of heavy metal salts and the use of flue gases or sodium bicarbonate, all act in the same direction, that is to say, reduce the free alkali content

Kauffmann [79, 1924] showed that the velocity of decomposition of aqueous sodium hypochlorite is inversely proportional to the concentration of hydroxyl ions and that the fraction of the total hypochlorite ions destroyed in unit time is independent of the actual hypochlorite concentration Thus, so long as the concentration of free alkali remains the same, i e the hydroxyl ion concentration remains unaltered, the stability of a hypochlorite solution is independent of concentration This is important when dealing with calcium hypochlorite solutions, for the amount of free alkali present is then limited by the solubility of calcium hydroxide in water In order to avoid instability, therefore, saturated lime-water is always used as diluent and the hydroxyl ion concentration maintained the same.

Hypochlorous acid itself is very unstable and decomposes to give a variety of substances including water, oxygen, hydrogen chloride, chloric acid, chlorine, and chlorine monoxide, the odour of which in hypochlorite solutions, particularly if nearly neutral, is very noticeable

$$2HOCl = 2HCl + O_2$$

$$HOCl + HCl = H_2O + Cl_2$$

$$2HOCl = H_2O + Cl_2O$$

$$3HOCl \quad HClO_3 + 2HCl$$

The decomposition is accelerated by light, heat, and certain mineral salts, in particular those of nickel and cobalt To avoid loss of reagent through spontaneous decomposition it is therefore of utmost importance to ensure that the reagent is always alkaline and never actually acid

In the treatment of cracked distillates the presence of ample free alkali to reduce hydrolysis or the possible formation of chlorine or chlorine monoxide is of even greater importance as all tend to form addition compounds with olefines with the greatest of ease

$$\mathrm{Cl_2 + R\ CH\quad CHR' = RCHCl - CHR'Cl}$$

$$\mathrm{HOCl + R\ CH{-}CHR' = RCH(OH){-}R'CHCl}$$

$$\mathrm{Cl_2O + 2RCH{=}CHR = (RCHCl{-}CHR')_2O}$$

The Action of Sodium Hypochlorite Solution upon various Sulphur Compounds (Birch and Norris [14, 1925])

	Reaction products		
Sulphur compounds	*Oil soluble*	*Water soluble*	*Insoluble*
Sulphur	No action	No action	
Hydrogen sulphide	(Sulphur)	Sulphuric acid	Sulphur
Ethyl mercaptan	Ethyl disulphide	Sulphuric acid (trace) Ethane sulphonic acid	
*iso*Propyl mercaptan	*iso*Propyl disulphide	Sulphuric acid (trace) *iso*Propane sulphonic acid	
*iso*Butyl mercaptan	*iso*Butyl disulphide	Sulphuric acid (trace) *iso*Butane sulphonic acid	
Ethyl sulphide		Ethyl sulphone	
n-Propyl sulphide	(*n*-Propyl sulphone)	*n*-Propyl sulphone	
*iso*Butyl sulphide	*iso*Butyl sulphone	*iso*Butyl sulphone	
*iso*Amyl sulphide	*iso*Amyl sulphone	(*iso*Amyl sulphone)	
Pentamethylene sulphide	Sulphone	Sulphone	
Diethyl disulphide		Ethane sulphonic acid Sulphuric acid	
*iso*Amyl sulphoxide	*iso*Amyl sulphone	(*iso*Amyl sulphone)	
Ethyl sulphone	No action	No action	
Thiophen	No action	No action	

The substances in brackets are fairly soluble in the stages under which they appear

Sulphides.

In considering the oxidation of individual types of sulphur compounds by hypochlorites, it is convenient to commence with the action of sodium hypochlorite on sulphides or thio-ethers These (provided the hypochlorite is sufficiently active when a higher member of the series is being treated) are quantitatively oxidized to sulphones. No traces of any intermediate compounds appear to be formed and hypochlorite is without further action on the resulting sulphones Four atoms of available chlorine are absorbed for each sulphur atom oxidized

$$R_2S + 2NaOCl = R_2SO_2 + 2NaCl$$

As no acid products are formed, the alkalinity of the hypochlorite does not change appreciably during the action The lower sulphones being more soluble in water than in light petroleum hydrocarbons are found chiefly in the spent aqueous reagent from which they can be extracted by suitable means With increase in molecular weight the sulphones tend to become less soluble in water and more so in oil so that they remain in the hydrocarbon layer. Thus, although diethyl sulphone is practically insoluble in petroleum and readily soluble in water, the reverse is true of di-*iso*amyl sulphone. The sulphur content of gasolines containing high-boiling sulphides may therefore remain unaltered, although as sulphones of intermediate molecular weight, e g dipropyl and di-*iso*butyl sulphones, are soluble both in oil and water, partition occurs when some desulphurization can be effected by thorough water washing As sulphones are very high-boiling they are left as residues on distillation of the gasoline containing them

The rate of oxidation of sulphides, particularly the lower members, is only slightly affected by the alkalinity of the hypochlorite The effect is so small that large quantities of free alkali are required to prevent the oxidation occurring within a comparatively few minutes

Sulphoxides R_2SO, which are intermediate between sulphides and sulphones, behave very similarly to sulphides excepting that only two atoms of available chlorine per atom of sulphur are absorbed No product other than the corresponding sulphone appears to be formed

Disulphides.

The primary oxidation products from a disulphide, unlike those from a sulphide, are acidic, i e the sulphonic acid together with a smaller quantity of sulphuric acid, these appear in the aqueous layer as their sodium salts The formation of the sulphuric acid is surprising, since sulphonic acids are not further attacked, and consequently it must be formed directly from the disulphide The gradual neutralization of the free alkali by the acidic products makes it necessary, in describing the effect of alkalinity on the reaction, to distinguish between two somewhat different cases (1) The free alkali present is more than equivalent to the total possible acid products, the reagent will then always remain alkaline (2) The free alkali is less than equivalent to the total possible acid products, if the reaction is continued long enough the reagent will become acid The reaction under the first condition may be described as normal and corresponds with refinery practice Plotting atoms of available chlorine absorbed per atom of sulphur originally present as disulphide against time, curves are obtained of which (i) for a strongly alkaline and (ii) for a weakly alkaline solution, are typical The influence of the excess of alkali is very marked If, however, the alkalinity of the reagent is so chosen that it falls into the second category, the additional complications cause the absorption-time curve to assume quite a different form (iii)

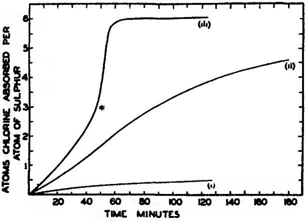


Fig 1

The initial part of the reaction takes the normal course until the acids formed have completely neutralized the free alkali present; at that point (*) there occurs a very rapid absorption of available chlorine which continues until the sulphur compound is entirely removed from the petroleum solution, the reaction then tails off and, finally, a slow spontaneous decomposition of the residual dilute hypochlorite tends to take place A considerable evolution of heat occurs at and immediately after the point in the reaction marked (*), the oxidation at this stage is so rapid that it is impossible to isolate any intermediate compounds (*vide infra*) Although the reaction is considerably slowed up by the addition of even a little alkali, it is interesting to note that even 20% of sodium hydroxide does not completely inhibit the oxidation

As shown by the figure the chlorine consumption is almost exactly six atoms for each atom of sulphur completely oxidized This is more than the amount required theoretically for the formation of the sulphonic acid

$$R_2S_2 + H_2O + 5O = 2RSO_3H$$

Mercaptans

The apparent course of the reaction between sodium hypochlorite and a mercaptan depends greatly upon the alkalinity of the solution The first action leads simultaneously to the formation of the corresponding disulphide and sulphonic acid together with some sulphuric acid, the first named, if the reagent is sufficiently reactive, is destroyed as it is formed, and the acids, as their sodium salts, are the sole products But with a more stable solution of hypochlorite a much slower oxidation of the disulphide occurs and this substance then appears as the chief product, accompanied by smaller quantities of the acids, which have been formed, for the most part, by direct oxidation of the mercaptan The first stage of the reaction, in which the mercaptan takes part, does not appear to be much affected by the alkalinity of the reagent and is very rapid, the factors which influence the destruction of the resulting disulphide are those which govern the normal interaction of this type of compound with sodium hypochlorite The oxidation may be represented diagrammatically thus

$$\begin{tikzcd}
 & H_2SO_4 & \\
RSH \arrow[ur] \arrow[rr] \arrow[dr] & & R_2S \arrow[ul] \arrow[dl] \\
 & RSO_3H &
\end{tikzcd}$$

Thiophen, Hydrogen Sulphide, Carbon Disulphide, and Sulphur

Sulphur and traces of sulphuric acid are produced by the action of hypochlorites upon hydrogen sulphide Part of the sulphur becomes dissolved in the oil, which emphasizes the necessity for a preliminary alkali-wash on any distillate likely to contain hydrogen sulphide that is to be hypochlorite treated Since sulphur is not attacked by hypochlorite the sulphuric acid must be formed directly from the hydrogen sulphide

Carbon disulphide does not appear to be a normal constituent of light distillates although it may be present in benzole or pyrolysis products. It is completely oxidized by sodium hypochlorite and is to be found in the products of the reaction in the form of carbonate and sulphate (Wood, Lowy, and Faragher [156, 1924]) The effect of alkalinity upon the action is not known

While hypochlorites in alkaline solution appear to be without action upon thiophens, Ardagh and Bowman [1, 1935] have found that in acid solution reaction occurs Acid hypochlorites are unlikely to find much application in the petroleum industry but the authors point out their possible value in removing thiophen from benzene The mechanism of the action has not yet been explained, 15–17% of the sulphur appears to be converted into sulphuric acid, the rest remaining combined as a high-boiling thiophen derivative which still gives the usual isatin reaction To free benzene completely from thiophen it is therefore only necessary to treat with an aqueous solution of calcium hypochlorite to which acetic or boric acid has been added, wash with caustic soda, and distil The distillate is thiophen-free For successful removal, the acidity of the hypochlorite solution must coincide with *pH* 3 9–4, the original solution prepared from Mathieson's 'H T H' had *pH* 11 8–12 and was ineffective

Desulphurization with Hypochlorites

The possibility of controlling the oxidizing action by the addition of alkali is of considerable importance and forms the basis for the present method of operating the process (cf Birch, Norris, and Thole [17, 1926]) Thus by varying the alkalinity of the hypochlorite solution over a comparatively narrow range, it is possible to limit the reaction very largely to one of sweetening or to effect, with certain distillates, almost complete desulphurization Naturally the extent to which desulphurization is possible is dependent upon the actual sulphur compounds present and the relative proportions in which they occur, the type of compounds predominating depending upon the crude oil from which the distillate originates Thus distillates from paraffin-base crude oils contain less thiophens than those of naphthenic origin and as a result are more likely to yield to desulphurization with hypochlorite Natural gasolines are generally easy to desulphurize because only low-molecular weight sulphur compounds are present, while distillates in which the sulphur compounds are concentrated in the heavier fractions will probably remain unchanged in sulphur content The fact that high-boiling mercaptans and sulphides become converted into disulphides and sulphones respectively, both of which boil well outside the range of the original distillate, must not be overlooked as these may interfere considerably with an evaporation test

Obviously a very much higher chlorine consumption is required for desulphurization To convert a mercaptan into a disulphide should theoretically require one chlorine atom per atom of sulphur, while two and a half are required to convert it into a sulphonic acid Actually the chlorine consumption is in both instances higher owing to the simultaneous oxidation to sulphuric acid Efficient preliminary alkali washing by reducing the mercaptan content results in a considerable saving in chlorine particularly when desulphurization is desired When it is intended to limit the action as far as possible to sweetening, the amount of alkaline hypochlorite applied should be reduced to the barest minimum

The octane rating of gasolines or the lead susceptibility are entirely unaffected by hypochlorite treatment

Acidity.

It has been stated above that no intermediate products have been isolated from the oxidation of mercaptans (other than disulphides) or disulphides by hypochlorites This is, however, not entirely correct, for, although the intermediate compounds have not been isolated, they can be identified in the distillates after treatment, and it is necessary to take steps to remove them if a satisfactory product is to be obtained

Light straight distillates which have been hypochlorite treated acquire a rather sharp unpleasant odour, go off colour in light, and are corrosive The more reactive the hypochlorite solution employed, the more marked is the odour and the corrosive nature of the product Attempts to remove the cause of the trouble—at first thought to be free hypochlorous acid—by an ordinary alkali wash failed, little or no improvement being effected Investigation showed that, even after the alkali wash, the product contained chlorine, although only in very small amount

Experiments with various sulphur compounds in sulphur-free naphtha showed that only mercaptans, disulphides, and, to a very much smaller extent, hydrogen sulphide, gave similar results Furthermore, although the substances responsible for the objectionable properties were formed to a greater extent from neutral or faintly acid hypochlorite solutions, even with considerable quantities of alkali present, traces were still formed Continued investigation showed that mercaptans produced the highest quantity—which even under the most favourable conditions for formation, a large excess of faintly acid hypochlorite, was very small—and that the greater the molecular weight of the mercaptans, the more stable the corrosive bodies became

On distillation it was found that the compound or compounds tended to remain in the residue but that the quantities present were too small for isolation While very prolonged and thorough agitation with caustic soda solution or lime-water eventually destroyed them, as indicated by the disappearance of the sharp odour and corrosive action, in the presence of alcohol very dilute caustic alkali was extremely effective Other means for removing them consisted in filtration through absorptive materials, e g bauxite, or steam distillation As a result of the latter, hydrogen chloride was formed and could be detected in the aqueous distillates Left in contact with an organic base such as aniline, the hydrochloride separated after a few hours as a white crystalline solid

These and other considerations indicated that sulphonyl chlorides RSO_2Cl or similar compounds were responsible, and experiments carried out with ethane sulphonyl chloride in naphtha solution gave almost identical results While aryl sulphonyl chlorides are comparatively stable, the alkyl compounds, such as ethane sulphonyl chloride, fume in moist air and are readily decomposed by water Yet in dilute solution, in a solvent in which water is for most practical purposes insoluble, hydrolysis is extremely slow The addition of a mutual solvent such as alcohol at once brings about rapid hydrolysis particularly if alkali is present, and it is upon this that the method for determining the relative amounts of these bodies in a hypochlorited distillate is based A definite volume of the gasoline under test (100 c c) is shaken with N/20 sodium hydroxide (20 c c) and alcohol (20 c c) for 3 min The results are usually expressed in terms of N/10 NaOH per 100 c c gasoline The amount consumed when the excess is determined by titration with standard acid is the so-called acidity The reaction involved is

$$RSO_2Cl + 2NaOH = RSO_3Na + NaCl + H_2O$$

The small amount of acid chlorides formed can best be gauged from the fact that figures of 8–10 c c N/10 caustic soda per 100 c c of gasoline are exceptional, 1–3 c c being more general Reckoned as ethane sulphonyl chloride 1 c c N/10 caustic soda per 100 c c gasoline corresponds with 0 064 g chloride per litre It follows from the equation given above that the hydrolysis products should consist of equimolecular proportions of sodium chloride and sulphonate While both of these substances have been identified in the aqueous layer, the proportions are never exactly equimolecular and the chloride is always in excess of that theoretically required The actual ratio appears to depend upon the conditions of formation for it is possible by treating *iso*amyl mercaptan in dilute carbon tetrachloride solution with chlorine in the same solvent to produce 'acidity' in which the chlorine/sulphur ratio almost corresponds with $RSCl_5$ Ratios covering the range from $RSCl_5$ to RSO_2Cl can be obtained by using excess of highly reactive hypochlorite solution, and it appears probable that at least a part of the mercaptans is converted into the sulphonic acids through such compounds Naturally the higher chlorides are much more readily hydrolysed than those containing less chlorine and are normally hydrolysed shortly after formation Similar bodies are formed from disulphides

The compound formed under similar conditions in very small amounts from hydrogen sulphide closely resembles the sulphonyl chlorides obtained from the mercaptans and disulphides, although much more easily hydrolysed Identification was not possible but from its behaviour it appeared to be sulphuryl chloride, SO_2Cl_2, which may account for the small amount of sulphuric acid formed in the reaction

Final Alkali Wash.

The presence of sulphonyl chlorides or bodies having similar properties in gasoline or special naphtha cuts such as painter's naphtha is obviously undesirable Not only do they impart a sharp odour but they hydrolyse slowly on storage or more rapidly in light to form hydrogen chloride The latter is not only corrosive but causes colour instability and catalyses gum-formation when blended with cracked distillates

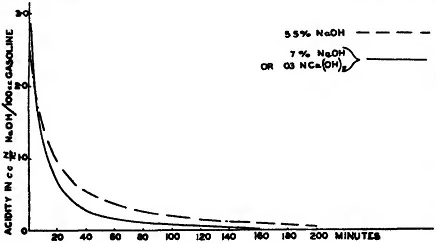


Fig 2

The removal of these substances is therefore of paramount importance in obtaining a satisfactory product and most of the failures to get successful results from the hypochlorite process can be traced to incomplete acidity removal While undoubtedly a small treatment with alcoholic caustic soda solution would be the most rapid and effective method, the use of alcohol in the treatment of gasoline and special naphtha cuts is undesirable Loss of alcohol in the hydrocarbon layer increases the cost considerably Treatment with adsorptive earths, which too is very effective, is to be avoided owing to the inconvenience that the handling of solid reagents in the refinery entails Investigation, however, has shown that with really adequate contacting, such as that possible in a Holley-Mott treater, caustic soda or lime can be successfully employed In the process as operated by the Anglo-Iranian Oil Co, Ltd [11, 1929] strong caustic soda solutions were at first employed but so much trouble was experienced with emulsification, particularly when calcium hypochlorite was used for the first stage of the treatment, that it was abandoned in favour of dilute soda and, later, lime-water, when the extremely efficient mixing that the Holley-Mott type of plant offers became available The relationship between acidity removal and time of contact is shown in figure 2 which was obtained from a Holley-Mott plant operating on hypochlorite-treated straight Iranian gasoline

It is usual to work to a final acidity equivalent to 0 2 c c N/10 soda per 100 c c of gasoline, this figure having been found in practice to give a satisfactory saleable product Acidity removal can, of course, be successfully carried out in other types of treating equipment but, as the contacting is invariably less efficient, longer treatment times are necessary

It is obvious from the small amount of material to be neutralized that the alkali consumption is almost negligible and the same wash can be satisfactorily used for a considerable period of time Some refiners still prefer to use a strong caustic wash (20%), and, when approximately half the soda has been used, transfer it for use in some other part of the refinery In this way the tendency to emulsify, which is considerably increased by the presence of the sulphonates, is to some extent overcome

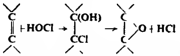
The acid chlorides formed from the mercaptans present in natural gasoline are much more easily hydrolysed and consequently the final alkali wash can frequently be omitted

Hypochlorite Treatment of Cracked Distillates.

The hypochlorite treatment of cracked distillates has not met with general favour, although it has yielded excellent results with both liquid- and vapour-phase cracked products of Iranian origin Much of the trouble experienced in hypochlorite treating cracked distillates can be traced to incomplete acidity removal which results in colour and gum instability on storage Blending cracked distillates sweetened by other methods with straight-run material, which after hypochlorite treatment has been incompletely alkali-washed, may give the same trouble

Hypochlorite should never be applied to cracked distillates unless they have received a preliminary polymerization treatment with acid, clay, or metallic chloride, e g aluminium or zinc chloride followed, after neutralization, by redistillation Hypochlorites do not possess polymerizing properties and it is essential that the reactive hydrocarbon should be removed first Provided this is done, alkaline hypochlorite should give results comparable with those given by plumbite The process is only applicable to sweetening, the conditions favourable for desulphurization, i e low free alkali content, being equally favourable to the so-called 'chlorination' which is actually chlorohydrin formation

The fact that hypochlorous acid is capable of addition to unsaturated compounds is well known The products, chlorohydrins, readily lose hydrogen chloride and form oxides, thus



The undesirability of having readily decomposable compounds of this type has already been emphasized As both olefines and diolefines form chlorohydrins when brought into contact with dilute solutions of hypochlorous acid, it is obvious that the use of solutions of low alkali content will favour their formation Alkaline hypochlorite treatment, on the other hand, not only tends to prevent chlorohydrin formation but also to convert any formed into olefine oxides by removing hydrogen chloride The presence of olefine oxides in gasoline does not seem to be objectionable in any way

The treatment should be restricted as far as possible to the minimum amount of alkaline hypochlorite necessary for sweetening It has been found that the use of very dilute solutions, e g calcium hypochlorite 0 07 N (available chlorine) in saturated lime-water, coupled with an efficient free alkali wash appears to overcome the formation of undesirable compounds and gives, with Iranian cracked distillates, results equal to, if not better than, those obtained with plumbite

VI. THE ACTION OF SULPHURIC ACID AS A REFINING AGENT FOR LIGHT DISTILLATES

Sulphuric acid has been in use in the petroleum industry since the earliest times, being adopted from the coal-tar and shale industries, in which it was in general use To-day it is undoubtedly the most important and most widely used refining agent, finding application not only for the treatment of the lighter distillates but throughout the whole range of petroleum products The fact that it can be used for a multiplicity of purposes renders it an extremely convenient reagent, particularly in view of its cheapness and general availability Its chief disadvantage lies in the refining losses which its use entails, especially in the treatment of cracked distillates when they are not merely confined to loss in volume but frequently in quality also The disposal of the waste acid sludge is nearly always a very real problem and many refiners are driven to operating a recovery process for the purpose In small refineries, however, these are not economical and the sludge is frequently allowed to collect on waste land

In the treatment of the lighter distillates, acid-washing is employed (*a*) to reduce sulphur content, (*b*) to remove basic and oxygenated compounds, and (*c*) to polymerize, remove, or destroy the extremely active gum-forming hydrocarbons present in unrefined cracked and certain straight distillates Although in practice it is not possible to limit the scope of the acid to any one operation, and two or more invariably take place simultaneously, the chemistry of each is distinct and will be considered separately Thus in the treatment of cracked distillates the acid reacts not only by virtue of its polymerizing properties, but also in its capacity as a desulphurizing agent, if nitrogen bases and oxygen compounds are present, these too are removed

Acid treatment alone is far from a complete process It must be followed either by neutralization with caustic soda or soda ash, or by treatment with an adsorbent earth, for example, bauxite, floridin, &c, to remove the traces of acid and acidic bodies left in the oil Furthermore, as a considerable change may occur in the boiling-range due to the formation of polymers or high-boiling sulphur compounds, it is desirable to complete the treatment with redistillation In the case of such products as kerosine this, however, can be advantageously avoided by the use of adsorbent materials which effectively remove the small amounts of high-boiling products formed

Action of Sulphuric Acid on various Sulphur Compounds

The action of sulphuric acid in reducing the sulphur content of light distillates is mainly physical and due to the preferential solubility of the sulphur compounds in the acid Oxidation and sulphonation, however, also occur but, unless sufficient acid is present to extract the products formed, these tend to remain in the hydrocarbon layer so that the sulphur content remains unchanged The extent to which chemical and physical action occur is determined by the sulphur compounds present, the concentration of the acid, and the temperature at which the operation is carried out Until comparatively recently it was common practice to use either concentrated (96%) acid or fuming acid (containing 20% SO_3) for both straight and cracked products but, in view of the extensive polymerization which occurs when cracked distillates are treated with strong acids, these acids are now only used on such straight products as gasoline, naphthas, and kerosine In these distillates the hydrocarbons are comparatively inert and, unless either the concentrated or fuming acid is used, little desulphurization takes place The tendency is therefore to treat cracked products with acid of such concentration that only the most reactive hydrocarbons are affected Since the more dilute the acid becomes the lower are its solvent and chemical action, it follows that less desulphurizing and sweetening occur when cracked distillates are treated with weaker acid than when straight products are treated with concentrated or fuming acids The effect of the concentration of the acid is clearly shown in the following table (Wood, Sheeley, and Trusty [157, 1926]), giving the effect of concentration of the acid upon the removal of certain sulphur compounds from naphtha solution under standard conditions

Sulphur compound	*Sulphur content*	*Acid concentration*					
		Fuming		*66° Bé*		*53° Bé **	
		4 c c	*16 c c*	*4 c c*	*16 c c*	*4 c c*	*16 c c*
Elemental sulphur	0 26	0 26	0 258	0 26	0 26	0 26	0 26
*iso*Amyl mercaptan	0 29			0 22	0 02	0 28	0 27
Hydrogen sulphide	0 034	0 03	0 03	0 03	0 03	Unchanged	
Dimethyl sulphate	0 04					0·01	0·008
Methyl *p*-toluene sulphonate	0 15			0 035		0 15	0 15
Carbon disulphide	0 08	0 08	0 08	0·08	0 08	0·08	0·08
n-Butyl sulphide	0 30			0 02	0 01	0·29	0·28
n-Propyl disulphide	0 38			0 016	0 02	0 35	0 34
Thiophen	0 09			0 01		0 08	0·08
Diphenyl sulphone	0·05			0 005	0 005	0 01	0·006
n Butyl sulphone	0 08					0 01	0 008

Time of contact, 1 hour
Volume of stock solution taken, 50 c c
* 66 5%

The influence of acid concentration upon desulphurization is most marked Weak acid (53° Bé) produces very little effect even when the treatment is extremely heavy, while the fuming acid brings about complete desulphurization excepting when elemental sulphur or carbon disulphide is present In practice dilution of acid takes place during use but this is largely due to the physical solution of sulphur compounds or hydrocarbon This form of dilution does not reduce the oxidizing action of the acid to nearly the same extent as aqueous dilution The latter also occurs owing to the reduction of the acid in the oxidation of both sulphur compounds and hydrocarbons Desulphurization due to the solvent action of the acid leads to a condition of equilibrium being set up between the sulphur compound in the acid and the hydrocarbon layers, to which the ordinary rules of distribution apply so that treatment is best carried out in counter-current operation

The action of sulphuric acid in removing sulphur compounds may be summarized as follows

Sulphur compound	*Product in oil layer*	*Product in acid layer*
Mercaptan	R_2S_2, traces of unstable compounds	(RSO_3H ?)
Carbon disulphide	Unchanged CS_2	
Hydrogen sulphide	Sulphur	
Sulphur	Sulphur	
Thioethers		R_2S
Disulphides		R_2S
Thiophen		$C_4H_3SO_3H$
Sulphoxides		R_2SO
Sulphones		R_2SO_2
Alkyl sulphates		$RHSO_4$

Sulphur, Hydrogen Sulphide, and Carbon Disulphide

Sulphuric acid is without action upon either elemental sulphur or carbon disulphide and, as both are practically insoluble in it, they remain unchanged in the hydrocarbon layer Hydrogen sulphide, however, is readily oxidized by both the concentrated and fuming acid with the formation of elemental sulphur and water, the acid being reduced at the same time to sulphur dioxide, thus

$$H_2S + H_2SO_4 = S + 2H_2O + SO_2$$

Since there is no further action between the acid and the sulphur formed, the latter dissolves in the hydrocarbon layer, the sulphur content of which consequently remains unaltered The formation of sulphur in this way during acid treatment is not as serious a disadvantage as in processes such as hypochlorite treatment because acid treatment is usually followed by redistillation The dilution of the acid by the water formed is a far greater disadvantage but the amount of hydrogen sulphide present is rarely or even sufficiently large to make a preliminary treatment for its removal economical

The oxidizing action of sulphuric acid upon hydrogen sulphide decreases with decreasing acid concentration Thus Wood, Sheeley, and Trusty [157, 1926] found that 53° Bé acid was without effect upon hydrogen sulphide dissolved in naphtha It must be emphasized, however, that sulphuric acid diluted with such non-aqueous solvents as phosphoric acid, sulphonic acids, thioethers, &c , retains its oxidizing properties to a greater extent than when diluted with water

Disulphides.

It is convenient to consider the disulphides next, for not only do they occur in light distillates *per se*, but they form the main products of the action of sulphuric acid upon mercaptans (q v) Wood, Lowy, and Faragher [156, 1924] who examined the action of acid upon various sulphur compounds found that with disulphide it was mainly solvent although some slight oxidation also occurs Dilution of the acid with water formed by this oxidation is so slight that it scarcely affects the solvent power The following table shows the effect of varying acid treatment upon the removal of ethyl disulphide from a naphtha solution during one hour

Acid used c c*	*Total sulphur, %*
0	0 61
2	0 37
4	0 10
6	0 02
8	0 0094

* 66° Bé acid 1 c c equivalent to 5 % treatment by weight

Oxidation, as indicated by sulphur dioxide formation, occurred only to an extent equivalent to 2 76% of the sulphur present in the naphtha per hr The solvent power of the acid, which is very marked in the fuming acid, falls away rapidly with decreasing concentration 53° Bé acid being without effect (Wood, Sheeley, and Trusty [157, 1926])

In view of the fact that the action of the acid is so largely confined to one of solution, it is perhaps surprising that neither Mabery and his collaborators [97, 1891, 1894, 1906], nor Thierry [140, 1925], both of whom investigated acid sludge, found any indications of disulphides The reason for this is possibly to be found in the following table based upon Birch and Norris's work in which it can be seen that under identical conditions of treatment the solvent action of the acid decreases with increasing molecular weight of the disulphide

Disulphide	*% removed from naphtha solution*	
	Concentrated acid	*Fuming acid*
Ethyl	61 9	71 4
n-Propyl	54 3	74 3
*iso*Butyl	26 4	45 3
*iso*Amyl	19 4	35 5

The result obtained for the fuming acid on the *n*-propyl derivative is anomalous but the remainder definitely shows the decrease in the solvent power of the acid with increasing molecular weight of the sulphur compound A similar observation was made by Youtz and Perkin [161, 1927]

No investigation appears to have been made into the products formed in the reaction, but it is probable that the corresponding sulphonic acids constitute the major part

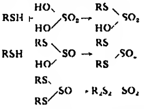
Mercaptans.

Although Erlenmeyer and Lisenko [51, 1861] found 75 years ago that the action of sulphuric acid upon ethyl mercaptan leads to the formation of the disulphide, it is only comparatively recently that the reaction has been examined at all closely Wood, Lowy, and Faragher [156, 1924], who were the first to investigate the action of acid upon mercaptans in naphtha solution, found that, providing sufficient acid was present and the time of contact long enough, sweetening occurred accompanied by a decrease in the sulphur content of the naphtha Less acid required a longer time to effect sweetening and there was then actually a tendency for the sulphur content to increase slightly Reaction was accompanied in the early stages by considerable sulphur dioxide evolution but this rapidly decreased as the action proceeded The effect of varying acid treatment upon the sulphur content of a naphtha containing ethyl mercaptan is shown in the following table (Wood, Lowy, and Faragher [156, 1924])

Acid treatment ml	*Sulphur content %*	
0	0 71	
2	0 93	Sour after 1 hr Sweet after 2 hr
4	0 85	
6	0 74	
8	0 64	
12	0 42	

Time of contact 1 hr 1 c c acid equivalent to a 5% treatment by weight

The only product of the reaction identified was the disulphide The action of the acid was therefore two-fold the mercaptan was first oxidized to disulphide and the latter then removed from the hydrocarbon by solvent action The oxidation mechanism suggested by Wood, Lowy, and Faragher was as follows

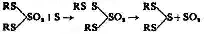


$$\mathrm{RSH} + \begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\!>\mathrm{SO_2} \rightarrow \begin{matrix}\mathrm{RS}\\ \mathrm{HO}\end{matrix}\!>\mathrm{SO_2}$$

$$\mathrm{RSH} \quad \begin{matrix}\mathrm{RS}\\ \mathrm{HO}\end{matrix}\!>\mathrm{SO} \rightarrow \begin{matrix}\mathrm{RS}\\ \mathrm{RS}\end{matrix}\!>\mathrm{SO}$$

$$\begin{matrix}\mathrm{RS}\\ \mathrm{RS}\end{matrix}\!>\mathrm{SO} \rightarrow \mathrm{R_2S_2} \quad \mathrm{SO_2}$$

Traces of the intermediate compounds remaining in the oil would account for the initial rise in sulphur content Wood, Sheeley, and Trusty [157, 1926] later extended this work but, apart from noting the greater solvent and oxidizing action of fuming acid and observing that 53° Be acid is without action, did not elicit any new facts of importance The isolation of *n*-butyl *n*-butylthiosulphonate by Bennett and Story [6, 1927] from the acid layer formed in the action of concentrated sulphuric acid upon *n*-butyl mercaptan, supports Wood, Lowy, and Faragher's hypothesis for the mechanism of the reaction, but Birch and Norris [16, 1929] were not able to repeat Bennett and Story's experiment They did, however, find that besides the disulphide traces of compounds were present in the hydrocarbon layer after the action, which possessed definite corrosive properties towards copper over the temperature range 130–190° C While both sulphoxides and disulphoxides (the latter is structurally identical with Bennett and Story's compound, $C_4H_9OS\ SO\ C_4H_9$) proved to be corrosive to copper under such conditions, it was found that these compounds were completely removed from naphtha by acid leaving a non-corrosive hydrocarbon layer Careful investigation showed that, besides the disulphide, traces of higher polysulphides were present in the naphtha and these were responsible for the corrosive behaviour The mechanism for the formation of the polysulphides is not obvious and may possibly be explained as follows the gaseous products from the action of acid upon mercaptans have been shown to contain hydrogen sulphide, sulphur dioxide, and the product of their interaction, sulphur Since, in tests carried out with sulphur and mercaptans in naphtha solutions, polysulphides have been identified in the products, it is possible that those formed as a result of the action of the acid were produced in the same way While this offers a reasonable explanation for the formation of such compounds, the possibility of their being formed as a result of the degradation of the intermediates postulated by Wood, Lowy, and Faragher cannot be entirely dismissed



$$\begin{matrix}\mathrm{RS}\\ \mathrm{RS}\end{matrix}\!>\mathrm{SO_2} + \mathrm{S} \rightarrow \begin{matrix}\mathrm{RS\ S}\\ \mathrm{RS}\end{matrix}\!>\mathrm{SO_2} \rightarrow \begin{matrix}\mathrm{RS}\\ \mathrm{RS}\end{matrix}\!>\mathrm{S} + \mathrm{SO_2}$$

The indications obtained pointed to the trisulphide, but the quantity formed was too small for identification This was to some extent confirmed by observing the action of ethyl trisulphide in boiling naphtha solution upon copper, which closely resembled that of the acid-treated material.

Sulphides, Sulphoxides, and Sulphones.

Sulphuric acid exerts a purely solvent action on sulphides, whether open chain or cyclic ('thiophanes') although according to Wood, Lowy, and Faragher [156, 1924], oxidation occurs to a slight extent The solvent action is very pronounced, quite a small volume of the concentrated acid being sufficient to effect complete extraction of comparatively large amounts of the lower sulphides Youtz and Perkin, however, found that, although this was true for the lower members, the higher sulphides, e g diphenyl and dibenzyl sulphides, are much less easily removed They also observed that secondary sulphides are more soluble in acid than the corresponding normal isomers The relative ease with which various types of sulphides are removed from naphtha solution by 95% acid is shown in the following table (Youtz and Perkin [161, 1927])

	Sulphur content	
Sulphide	*Before treatment* %	*After treatment** %
Ethyl	0 477	0 041
*iso*Amyl	0 586	0 185
n-Heptyl	0 418	0 131
sec-Heptyl	0 438	0 089
Allyl	0 624	0 051
Phenyl	0 507	0 416
Benzyl	0 400	0 210

* 3 3% of 95% acid

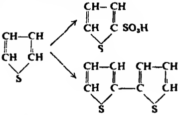
Owing to the comparatively low sulphur content in the higher sulphides, the quantity of the actual sulphide removed is much larger than it appears from the sulphur content Thus a decrease of 0 349% when treating a naphtha solution of *sec*-heptyl sulphide actually indicates the removal of 2 5 g per 100 c c, or roughly 3 c c, which is almost equal to the volume of the acid used Solvent action is even more marked with the fuming acid but falls away rapidly on dilution of the acid below 75%

Dilution by the addition of water to acid containing sulphides in solution merely results in their separating out unchanged (excepting possibly when they contain aromatic groups) This method has been employed by several investigators when studying the composition of the sulphur compounds present in light distillates

Sulphoxides and sulphones are similarly removed from solution and appear to be unaffected by the action of the acid While the lower members are extremely soluble in acid, nothing is known of those of higher molecular weight, it is probable that they resemble the sulphides, to which they are closely related

Thiophen.

Thiophen dissolves in concentrated acid with the formation of the sulphonic acid, the acid at the same time acquiring a reddish-brown hue According to Victor Meyer [113, 1883], however, long stirring in the cold leads to more deep-seated changes and both sulphur dioxide and hydrogen sulphide are formed Tohl [142, 1894] also investigated the reaction and found that at 0° C the addition of thiophen to the concentrated acid gave not only the sulphonic acid but also αα'-dithienyl



The action of the acid under conditions similar to those existing in the refining of light distillates was first examined by Wood, Lowy, and Faragher [156, 1924] Oxidation as evidenced by the formation of sulphur dioxide was equivalent to 0 21 % of the thiophen present per hour but quite a heavy treatment was necessary to effect desulphurization as the following figures for the removal of thiophen from a naphtha solution indicate

Acid treatment c c	*Sulphur content* %
0	1 08
2	0 63
4	0 33
6	0 02

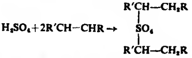
1 c c is equivalent to a 5% treatment by weight Time of contact, 1 hr

As is to be expected, dilution of the acid reduces its effectiveness (cf Wood, Sheeley, and Trusty [157, 1926])

Youtz and Perkin showed that sulphonation alone is not responsible for thiophen removal They found that trimethylthiophen and tetramethylthiophen are both removed by acid As the latter is incapable of sulphonation, it must be removed by solvent action alone

Dialkyl Sulphates.

Dialkyl sulphates cannot be regarded as normal constituents of light distillates, although they are generally to be found in acid-treated cracked material, formed as a result of reaction between the acid and the olefines present, thus



$$H_2SO_4 + 2R'CH{=}CHR \rightarrow \begin{array}{c} R'CH{-}CH_2R \\ | \\ SO_4 \\ | \\ R'CH{-}CH_2R \end{array}$$

where R and R' can be alkyl groups or hydrogen atoms

It is unlikely that dialkyl sulphates lower than the dibutyl derivative occur in ordinary cracked distillates as the olefines necessary for their formation are not generally present The higher members, although unstable in a pure condition, appear to be relatively stable in petroleum solution They decompose slowly, however, on standing or more rapidly at higher temperatures and are responsible for most of the corrosion which occurs during the rerunning of acid-treated pressure distillates Dialkyl sulphates react with sulphuric acid to form the corresponding alkyl sulphuric acids

$$R_2SO_4 + H_2SO_4 = 2RHSO_4$$

which being insoluble in the hydrocarbon layers are rapidly removed in the acid A condition of equilibrium appears to exist between the dialkyl sulphate and sulphuric acid on the one hand and the alkyl sulphuric acid on the other, which no doubt explains the traces of the dialkyl sulphate generally present in the petroleum layer Normally this is removed by alkali washing and not by the acid

The Action of Sulphuric Acid upon Saturated Hydrocarbons

Apart from its action as a sweetening and desulphurizing agent, sulphuric acid is capable of reaction with the hydrocarbons themselves, particularly those possessing unsaturated linkages It is usual to regard the saturated hydrocarbons, that is to say, the paraffins, naphthenes, and aromatic hydrocarbons, as unaffected by acid, but this is not entirely true, especially when the action of the fuming acid is being considered Under the conditions generally employed in the treatment of light distillates, however, the effect of the acid upon naphthenes and paraffins is so slight as to be practically undetectable, it must be taken into account, however, when acid is used for the estimation by absorption of either aromatic or unsaturated hydrocarbons

As a result of the action of the acid sulphonation, sulphation, oxidation, condensation, and polymerization all occur depending upon the type of hydrocarbon reacting Because of the diversity of these reactions, it is convenient to consider the effect upon each type of hydrocarbon separately

Paraffins.

In the cold practically no action occurs between paraffins and concentrated sulphuric acid even up to 100% concentration On the other hand with the fuming acid, reaction definitely takes place Thus Orndorff and Young [126, 1893] found that propane allowed to stand in contact with oleum was absorbed to an extent of about 50% over a period of 15 days, while Worstall [160, 1899] observed that the fuming acid absorbed methane less readily than ethane Investigations by other workers showed that the reaction was by no means limited to the three simplest paraffins and the relative rates of absorption of methane, ethane, propane, butane, *iso*butane, pentane, *iso*pentane, hexane, heptane, 2-methylheptane, and octane have been determined ([50, 1913], Tropsch and Dietrich [145, 1925], *et al*) Mabery working with petroleum fractions instead of pure individual hydrocarbons found that various fractions of Pennsylvanian origin were attacked by the fuming acid [99, 1902], and later McKee [106, 1912] claimed that the hydrocarbons present in Pennsylvanian kerosine boiling in the 200° C range could be sulphonated to disulphonic acids with concentrated acid provided that vigorous stirring was employed Brooks and Humphrey [30, 1918] were unable to verify McKee's statement in fact they found that neither *n*-heptane nor di-*iso*propyl could be made to react with 95% acid even after 48 hr at 25° C Sentke [50, 1913], however, states that *n*-octane is attacked at normal temperatures

A more detailed investigation of the action of the fuming acid upon *n*-hexane, *n*-heptane, and *n*-octane has been made by Worstall [159, 1898] who found that, while little if any action took place in the cold, the addition of the acid to the hot hydrocarbon resulted in a vigorous action in which the monosulphonic acid, together with traces of the disulphonic acid, was formed *n*-Hexane gave a yield amounting to 30–40% of *n*-hexanesulphonic acid, a light brown liquid very soluble in alcohol and water, but completely insoluble in ether Considerable oxidation occurred during the reaction The disulphonic acids were only obtained in quantity by passing sulphur trioxide into the boiling hydrocarbon Besides these, which proved to be dark syrupy liquids, brown brittle solids insoluble in water and organic solvents were also obtained which Worstall considered to be oxysulphones Whether these were in any way related structurally to the octane-sultone isolated many years later by Baldeschwieler and Cassar [4, 1929] from the action of sulphuric acid upon certain olefines is unknown

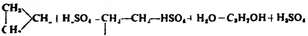
A further examination of the action of fuming acid upon *n*-hexane, *cyclo*hexane, and methyl*cyclo*hexane was later carried out by Burkhardt [31, 1930], who found that at 0–10° C sulphuric acid containing 30–65% sulphur trioxide readily attacked *n*-hexane All the sulphur trioxide was consumed and for each molecule of hydrocarbon attacked one molecule of sulphur dioxide resulted The products of the action were found to be partly unsaturated and to contain sulphuric ester groups, probably as sulphato-sulphonic acids in turn formed by the action of the fuming acid on the unsaturated hydrocarbons produced in the initial oxidation On hydrolysis, disulphonic and monosulphonic acids were formed in the ratio of 2 1, in which some 5% of the hexane chains were unsaturated and 30% contained hydroxyl groups Burkhardt considered that oxidation to the unsaturated hydrocarbon first occurred followed by the addition of the acid to the unsaturated linkage formed, hydrolysis then led to the formation of sulphonic acids containing either hydroxyl groups or double bonds

It appears, therefore, that the fuming acid is capable of both oxidation and sulphonation although, as Brooks and Humphrey [30, 1918] showed, the extent to which this occurs is dependent upon the configuration of the hydrocarbon While the normal members apparently require somewhat drastic conditions, such paraffins as tetramethylethane are readily attacked The aliphatic sulphonic acids are extremely stable strongly acid compounds, the lower members are colourless, very hygroscopic viscous liquids, while the higher homologues are comparatively low-melting solids which form mono-hydrates Unlike the alkyl sulphuric acids they are extremely resistant to hydrolysis, prolonged heating at 310–375° C with aqueous caustic soda being necessary As acid hydrolysis does not appear to occur to any measurable extent, it is unlikely that any breakdown of this kind takes place during the normal process of acid recovery

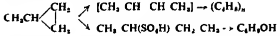
Naphthenes.

While naphthenes are rather more susceptible to sulphuric acid than paraffins, under normal refining conditions the action is probably only slight Excepting for the lower members and their substitution derivatives (the presence of which in petroleum products is somewhat doubtful), concentrated acid has little or no effect in the cold The fuming acid is, however, much more reactive and both oxidation and sulphonation readily occur This reaction was first observed by Markovnikov, who found that certain naphthenes reacted at ordinary temperatures or more readily at 40° C to give aromatic sulphonic acids, resins, and compounds volatile in steam

The simplest naphthene, *cyclo*propane, is easily the most susceptible to the action of the acid Even quite moderately concentrated acid ruptures the ring with the formation of either straight chain alkyl sulphates or polymerized olefines Rogenski and Rathman [131, 1933] investigated this reaction carefully and found that over a range of acid concentrations varying in gravity from 1 59 to 1 83 and at temperatures from 0 to 25° C, *cyclo*propane was always more readily absorbed than propylene Berthelot [9, 1893] states that concentrated acid absorbs 480 c c per g at 18° C On hydrolysis of the acid solution Gustavson obtained *n*-propyl alcohol [61, 1887]



Reactivity towards sulphuric acid is not confined to the parent hydrocarbon, for substituted *cyclo*propanes appear to be equally reactive Thus Demyanov [43, 1895] found that methyl*cyclo*propane is readily absorbed in concentrated acid with the formation of high-boiling hydrocarbon polymers and *sec*-butylsulphuric acid, the latter on hydrolysis gave *sec*-butyl alcohol



The *gem*-dimethyl derivative, 1,1-dimethyl*cyclo*propane, too, is stated by Gustavson and Popper [62, 1898] to dissolve in acid as weak as 75%

No references occur in the literature to the action of sulphuric acid upon *cyclo*butane or its derivatives, but from its chemical resemblance to *cyclo*propane it is probable that it reacts fairly readily *Cyclo*pentane is stated to be unaffected by the concentrated acid, but there is no reference to the effect of the fuming acid Zelinski [162, 1923], however, states that 1,4-dimethyl-2-ethyl-*cyclo*pentane dissolves in fuming acid containing 10% sulphur trioxide with darkening but that no heat or sulphur dioxide is liberated

While concentrated acid appears to be without effect upon *cyclo*hexane and its derivatives, the fuming acid both oxidizes and sulphonates them Burkhardt [31, 1930] examined the products of the reaction of *cyclo*hexane with acid containing a high percentage of sulphur trioxide (35–65%) at 0–10° C and found that the action was very similar to that which took place with *n*-hexane Each hydrocarbon molecule attacked resulted in the formation of one of sulphur dioxide and sulphato-sulphonic acids were formed, the latter on hydrolysis yielded both mono- and di-sulphonic acids, which were partly unsaturated or contained hydroxyl groups Benzene-sulphonic acid was also isolated from the products Menschutkin and Wolf [111, 1927, 1930] obtained similar results, although they isolated a much higher proportion of aromatic sulphonic acids from the products Methyl*cyclo*hexane, however, according to Markovnikov, yields little or no aromatic sulphonic acids when oxidized by the fuming acid [104, 1903, 1905] and this was confirmed by Burkhardt, who investigated this reaction also The latter investigator found that oxidation took place with less readiness than with *cyclo*hexane and the proportion of sulphur dioxide formed per molecule of hydrocarbon attacked was only half that obtained with *n*-hexane The polymethyl*cyclo*hexanes appear to be much more susceptible to oxidation and give moderately high yields of the corresponding aromatic sulphonic acids Thus Markovnikov obtained xylene from octanaphthene [105, 1887] and Konovalov [90, 1890] ψ-cumene from 1,2,4-trimethyl*cyclo*hexane

The Action of Sulphuric Acid upon Aromatic Hydrocarbons

Of the so-called saturated hydrocarbons, the aromatic hydrocarbons are the most susceptible to the action of acid Sulphonation occurs very readily compared with the paraffins or naphthenes, even 85% acid having been shown by Faragher, Morrell, and Levine [52, 1930] to have an appreciable effect upon benzene and toluene, Carpenter also showed [36, 1926] that the effect of 80% acid upon a xylene-toluene mixture is quite detectable Towne [143, 1931] has examined a whole series of aromatic hydrocarbons and studied the effect of time, constitution, and acid concentration The results are summarized in the following table

	% soluble in		
	93% acid		*98% acid*
Hydrocarbon	*1 min*	*10 min*	*10 min*
Benzene	6	27	100
Toluene	11	100	100
Xylenes (mixed)	14	98	100
Ethylbenzene	10	78	100
Diethylbenzene	6	44	100
Mesitylene	23	100	100
*iso*Propylbenzene	2	37	100
sec-Butylbenzene	1	19	100
tert-Butylbenzene	0	23	100
tert-Amylbenzene	0	18	100
p-Cymene	0	73	100

It can be seen that the effect of the 93% acid is considerable even after the comparatively short period of contact, while the ease of sulphonation is noticeably increased by the introduction of methyl groups into the benzene nucleus Mesitylene is particularly readily sulphonated, but the introduction of a fourth methyl group results in steric hindrance (Telicheyev and Dumski [139, 1927]) Besides the tetra-substituted derivatives, benzene itself and derivatives containing *para* substituents have also been shown to be less readily attacked by 91-2% acid than most aromatic hydrocarbons Sulphonation of aromatic hydrocarbons is accompanied by considerable evolution of heat which, as the reaction is accelerated by increase of temperature, very definitely affects the extent to which sulphonation takes place The action is also very susceptible to the action of certain catalysts such as silver and vanadium compounds, while surface effects also play their part in aiding sulphonation Wendt claims that the sulphonation of benzene is materially assisted by the presence of kieselguhr Under normal conditions the action of the acid is almost entirely limited to the formation of the mono-sulphonic acid, fuming acid or a large excess of the concentrated acid at elevated temperatures being required to form the disulphonic acid Small amounts of the disulphonic acid, together with traces of diphenylsulphones, have, however, been isolated from the action of concentrated acid upon benzene at ordinary temperatures The sulphonic acids themselves are deliquescent colourless solids which, unlike the paraffin and naphthene sulphonic acids, are readily hydrolysed by steam or acids to give the original components This reaction is of considerable interest not only because it provides a means for separating aromatic hydrocarbons from accompanying naphthenes or paraffins of the same boiling-range, but also because the difference in ease of hydrolysis of the sulphonic acids formed can sometimes be used to separate isomeric aromatic hydrocarbons themselves (cf separation of mesitylene and ψ-cumene by Jacobsen's method [77, 1877])

Normally the acid treatment of the light distillates has little effect upon the aromatic content unless a particularly heavy treatment with fuming acid is employed for the reduction of sulphur content Only under such conditions is there any detectable effect upon the octane number (such an effect might be somewhat mitigated by the removal of pro-knock sulphur compounds, cf Birch and Stansfield [20, 1936])

That aromatic hydrocarbons are, however, removed by the acid has been demonstrated by several workers Birch and Norris [15, 1926] found that acid sludge from the refining of Iranian kerosine contained, besides sulphur compounds, aromatic sulphonic acids and the free hydrocarbons themselves The presence of the latter was at first inexplicable but it was later found that the aromatic sulphonic acids (and sulphur bodies) in the acid sludge were capable of a selective extraction of the aromatic hydrocarbons On dilution of the sludge with water, these were immediately thrown out of solution with the sulphur bodies, while the aromatic sulphonic acids remained dissolved Manning and Shepherd [102, 1930] also found that aromatic sulphonic acids exerted a definite solvent action upon saturated hydrocarbons, although this may have been caused to a certain extent by the aromatic hydrocarbons already in solution

For the complete removal of the aromatic hydrocarbons from cuts intended for special purposes, e g as solvents, it is desirable to start with a material as free from aromatic hydrocarbons as possible This is usually accomplished by sulphur dioxide extraction, which, although only substantially complete at temperatures in the neighbourhood of −80° C reduces the aromatic content very considerably The remaining aromatic hydrocarbons can then be removed by means of 98-9% acid or, if loss of part of the naphthene content is immaterial, fuming acid A very heavy treatment, i e 200-300%, is necessary for complete removal and should be applied in two or three washes Although some slight oxidation of aromatic hydrocarbons occurs with concentrated acid and is more marked with the fuming acid, no information on the subject appears to be available

Mention must be made of the condensation of olefines with aromatic hydrocarbons under the influence of sulphuric acid, a reaction which has been known for many years Brochet [26, 1893] found that benzene and hexene react to yield a hexylbenzene and other products, but less success attended his efforts with pentene in place of hexene Kraemer and Spilker [91, 1890, 1891] showed that styrylxylenes were formed from a mixture of xylene and styrene in the presence of sulphuric acid The olefine itself is not essential, for Barbier [5, 1932] obtained *tert*-butyl-*p*-cymene from *tert*-butyl alcohol and *p*-cymene at 0° C Egloff [49, 1935] claims that alkylated derivatives are produced from the lower olefines and aromatic hydrocarbons using sulphuric acid as catalyst Thus benzene and propylene gave *iso*propylbenzene

$$C_6H_6 + C_3H_6 = C_6H_5C_3H_7$$

A recent examination of the condensation of olefines with aromatic hydrocarbons in the presence of sulphuric acid has been made by Ipatieff, Corson, and Pines [73, 1936] These authors have shown that three reactions are involved

(1) condensation of the olefine with the aromatic hydrocarbon,

(2) polymerization of the olefine, and
(3) ester formation,

the predominating reaction being determined by the acid concentration and olefine. Thus, with propylene and sulphuric acid (96%) the first reaction predominates, little ester and no polymer formation taking place. When 80% acid is used, however, ester formation becomes marked, although alkylation still occurs. With isobutene at 4–20° C and 96% acid, alkylation predominates and there is little ester formation, while with 80% acid reaction is almost entirely confined to polymerization. At a still lower acid concentration (70%) ester formation only occurs. Brochet's failure to obtain amylbenzene from his reaction with pentene, benzene, and sulphuric acid was due to the presence of amyl sulphates in his product which on distillation decomposed to form tars. Ipatieff, Corson, and Pines examined the condensation of olefines varying from propylene to dodecene with benzene, toluene, and naphthalene and found that the reaction was general. The products were not limited to the mono-alkyl derivatives, the di-, tri-, and tetra-*iso*propylbenzenes being obtained from propylene and benzene.

Still more recently, Ipatieff and Pines [75, 1936] have shown that when certain polymerized olefines are condensed with aromatic hydrocarbons in the presence of sulphuric acid (96%), depolymerization occurs and aromatic condensation products are formed corresponding to the monomeric olefines. Thus di-*iso*butene and benzene in the presence of 96% acid give a mixture of mono-, di-, and tri-*tert*-butylbenzenes.

Egloff [49, 1935] claims that the higher alkylated compounds are themselves capable of alkylating unchanged or fresh material, thus

$$C_6H_4(C_3H_7)_2 + C_6H_6 \rightarrow 2C_6H_5C_3H_7$$

If this reaction proceeds as easily as Egloff claims, it should prove a valuable source of mono-alkylated benzenes.

The Action of Sulphuric Acid upon Unsaturated Hydrocarbons

While the action of sulphuric acid upon paraffins, naphthenes, and even aromatics can for most practical purposes be disregarded by the refiner, the effect of the acid upon the unsaturated hydrocarbons, the olefines and diolefines, is of the utmost importance. In the cracking operation enormous quantities of light distillates are produced annually, which consist to a greater or lesser extent, depending upon the type of cracking employed, of olefines and diolefines. It was early discovered that, unlike straight distillates, cracked gasolines on storage went off colour, acquired a rancid odour, and deposited gum, all of which objectionable properties were found to be due to the unsaturated hydrocarbons present. To a very considerable extent these undesirable characteristics could be eliminated by acid treatment, followed by neutralization and redistillation, but the refining losses incurred were extremely heavy. Brooks and Humphrey [30, 1918] actually give figures ranging from 8.2 to 28% for losses which they obtained when acid-treating certain cracked distillates in the laboratory. Furthermore, in spite of the fact that the raw distillate was carefully cut at 150° C before treatment, as much as 15 to 30% of the treated material boiled above this temperature, while the dry point was not reached at 260° C. Such drastic treatment must have affected a very high proportion of the unsaturated hydrocarbons initially present and given a refined product largely composed of paraffins, naphthenes, and aromatic hydrocarbons. In practice less drastic acid treatment was employed but even so the refining losses generally amounted to 5 to 10%, and at times even more. When later a demand arose for high anti-knock fuels, it was realized that not only did the acid treatment reduce the yield very considerably, but it also had a very adverse effect upon the anti-knock value. Investigation in fact showed that the very hydrocarbons which were being destroyed by the acid were largely those responsible for the anti-knock properties. It was also discovered that many of the olefines either destroyed or polymerized to compounds boiling outside the gasoline range, were in themselves relatively stable. The result of these discoveries has been the tendency in recent years to so modify acid treatment that only the most reactive hydrocarbons responsible for instability, gum-formation, &c., are removed or destroyed, while at the same time leaving the relatively stable olefines unaffected. So successfully has this been accomplished that to-day, by the use of light treatments employing comparatively weak acid, refining losses have been reduced to very low figures with little or no loss in anti-knock value. The use of inhibitors has allowed treatment to be reduced even further, for with their aid it is possible to render stable products which otherwise, owing to the extremely light treatment given, would be definitely unmarketable.

The reaction between sulphuric acid and olefines is generally very complex. Addition to form sulphuric esters, i.e. alkyl sulphuric acids or dialkyl sulphates, polymerization, depolymerization, isomerization, and condensation either with dissimilar olefines or with aromatic hydrocarbons, all occur together with other reactions of a less indefinite nature such as hydrogenation, dehydrogenation, and cyclization. Alcohol formation, which occurs under certain circumstances, since it must take place through the intermediate esters (although these may not be isolable), is included with ester formation or 'sulphation', as it is frequently termed. With the higher acid concentrations these reactions are generally so closely interconnected that it is not possible for one to take place without being accompanied by at least one of the others. Certain reactions as a rule predominate, however, the nature of which is determined by the olefine involved and conditions employed. Only with the lowest olefine, ethylene, is the reaction simple and confined almost entirely to ester formation, which takes place in two stages:

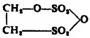
$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5\ HSO_4,$$
$$C_2H_5\ HSO_4 + C_2H_4 \rightarrow (C_2H_5)_2SO_4$$

When sufficient ethylene has been absorbed, both ethyl sulphuric acid and diethyl sulphate are formed, it is not, however, necessary that all the sulphuric acid be converted into the alkyl sulphuric ester before the formation of the dialkyl sulphate commences. All three substances can exist together and Damiens [40, 1922, 1923] considers that a state of equilibrium is reached

$$(C_2H_5)_2SO_4 + H_2SO_4 \rightleftharpoons 2C_2H_5HSO_4$$

As evidence he points out that at lower temperatures a higher proportion of the dialkyl sulphate is formed.

When fuming sulphuric acid is used, besides the above products, carbyl sulphate

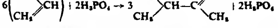


is also formed in considerable quantities, but in neither case does any appreciable amount of polymerization occur

In fact, only under very exceptional conditions, e g in the presence of a catalyst consisting of a solution of cuprous oxide in sulphuric acid and mercury, does polymerization take place (Damiens [40, 1923]) Under normal conditions, apart from slight oxidation and consequent sulphur dioxide formation, the reaction is limited almost entirely to addition

While many of the remarks concerning the formation of sulphuric esters apply equally well to propylene (and indeed to all olefines capable of forming them), the reaction of sulphuric acid with propylene is rather more complex than with ethylene Under identical conditions absorption is more rapid and the products contain, besides sulphuric esters, appreciable quantities of polymers Thus Sidgwick and Plant [135, 1921] found that 97% acid at 25° C gave a considerable amount of a colourless oil boiling from 55 to 150° C Ormandy and Craven [124, 1927-9] later investigated the reaction more closely and showed that, apart from sulphuric esters, alcohols, and polymers, considerable quantities of saturated hydrocarbons were also formed The passage of propylene into 98% sulphuric acid resulted in an immediate separation of a colourless oil which, from its physical properties, appeared to be a mixture of paraffins Dilution of the acid furnished another oil, highly unsaturated in character, which darkened in air and possessed a high refractive index, this, Ormandy and Craven considered, contained triolefines With less concentrated acid, however, the tendency to form polymers was considerably reduced and a higher proportion of esters formed

Whereas diethyl sulphate is a stable product which distils at 208° C with decomposition, the propyl derivative, obtained by saturating 98% acid with propylene at as low a temperature as the melting-point of the mixture permits, is much less stable It is a colourless liquid which when freed from all traces of acid can be distilled *in vacuo* without appreciable decomposition (Medvedev and Alekseeva [108, 1932]) In the presence of acid, however, it is very unstable and when warmed decomposes rapidly to form tarry products Whether the decomposition of unstable compounds of this type is responsible for polymer formation is a debatable point The observations of Ipatieff and his co-workers [71, 1935] on the decomposition of alkyl phosphoric acids to give polymers similar to those produced in catalytic polymerization certainly support this theory originally put forward by Kondakov [88, 1893, 89, 1896] to explain the formation of *iso*butene polymers The polymerization of propylene by phosphoric acid is represented by Ipatieff as follows



$$6\left(CH_3{-}CH{=}CH_2\right) + 2H_3PO_4 \rightarrow 3\,(CH_3)_2CH{-}C({=}CH_2){-}CH_3 + 2H_3PO_4$$

The product is not, however, limited to the dimeride, for the latter, being an olefine, is itself capable not only of combining with a further propylene molecule to give a trimeride but also with similar molecules to give yet another series of polymers The reaction is considerably complicated by accompanying reactions, for the product contains aromatic hydrocarbons besides olefines, paraffins, and naphthenes When allowance is made for the difference in reactivity of the two acids, the similarity in products (all but the aromatic hydrocarbons have been reported formed in the sulphuric acid-olefine reaction) suggests that polymerization occurs with both through the same mechanism, i e the formation and decomposition of intermediate esters Unfortunately, sulphuric acid is so drastic in its action that it is not possible to study the products formed by the decomposition of dialkyl sulphates with heat owing to the formation of tars In this connexion Ipatieff's observation [72, 1936] that dialkyl sulphates are decomposed by phosphoric acid is of interest Nielsen [121, 1934] takes advantage of the lower reactivity of phosphoric acid by employing it as a diluent for sulphuric acid in the refining of cracked distillates, it is claimed that besides reducing refining losses, the treatment is easier to control and, as less oxidation occurs, the sludge remains light in colour and easier to recover The advantages claimed by Nielsen may, however, be due to the action of the phosphoric acid in decomposing dialkyl sulphates

The olefines so far considered are not normal constituents of gasolines, but the next homologue, butene, is present to an extent depending upon the degree of stabilization Unlike ethylene and propylene, which are capable of existing in one structural modification only, the butenes exist in three (or four, if both the *cis* and *trans* forms of butene-1 are included), namely, butene-1, butene-2, and *iso*butene All three forms react far more readily with acid than either ethylene or propylene and, as is to be expected, the reaction products are complex Only when dilute acid is employed can the reaction be limited to ester or alcohol formation, the higher concentrations causing immediate polymerization to an extent dependent upon the structure the acid concentration, and the temperature Brooks and Humphrey, who first made a general study of the effect of sulphuric acid upon olefines [30, 1918] observed that the tendency for olefines to form sulphuric esters under the conditions of minimum polymer formation, increases with molecular weight until it reaches a maximum with the pentenes, after which it decreases The final falling off can no doubt be explained by the fact that conditions favourable for ester formation from the higher olefines are equally favourable for their decomposition and subsequent polymer formation

All three butenes are highly active towards sulphuric acid, the relative absorption rates as calculated by Davis [41, 1928] being as follows

*iso*Butene	280–390
Butene–2	2
Butene–1	1

The last has approximately the same absorption rate as propylene for any acid concentration

Although by selecting sufficiently weak acid and working at a low enough temperature, both butene-1 and butene-2 can be converted into *sec*-butyl sulphuric acid, no evidence has so far been obtained to indicate the formation from *iso*butene of the corresponding compound, *tert*-butyl sulphuric acid Hydrolysis appears to take place immediately on absorption and *tert*-butyl alcohol is formed No acid is consumed in the reaction, only the amount of water required for the alcohol formation being abstracted from the system

$$C_4H_8+H_2O \rightarrow C_4H_{10}O$$

When the alcohol-acid solution formed in this way is sufficiently dilute, decomposition occurs on warming and *iso*butene is formed With increasing acid concentration, however, the tendency to form *iso*butene becomes less and polymer formation occurs to an extent determined by acid concentration and temperature Thus at the lower concentration limits at which polymerization commences i e about 45%, the only polymer formed is the dimeride With increasing acid concentration the tendency is towards formation of higher molecular weight polymers at the expense of the lower It can be seen from the following table giving the boiling-points and gravities of the various *iso*butene polymers that a mixture containing them can cover a very wide boiling-range

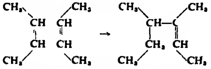
Polymeride	*B p C*	D_4^{20}
Di*iso*butene	101 2° 762 mm	0 7195
Tri*iso*butene	178 5–179 5°/760 mm	0 7600
Tetra*iso*butene	106°/7 mm	0 7944
Penta*iso*butene	148 /7 mm	0 8176
Hexa*iso*butene	158–61 /2 5 mm	0 8340
Hepta*iso*butene	183–6° 2 mm	0 8455

(Lebedev and Koblianski [95, 1930])

With concentrated sulphuric acid, *iso*butene reacts extremely vigorously to give a mixture of polymers [120, 1901], considerable heat being evolved in the reaction The latter eventually slows down, largely owing to reduction of the acid and dilution by the water formed The formation of high-boiling polymers of high gravity is one of the chief characteristics of the action of acid upon olefines, and is responsible, as we shall see, for the change in gravity and boiling-range of cracked distillates upon acid treatment

The effect of temperature upon the polymerization of *iso*butene is of interest Acid-alcohol mixtures which at elevated temperatures give largely di-*iso*butene, on long standing at room temperatures give almost exclusively the trimeride It therefore appears that slow polymerization favours the formation of the higher polymers, while rapid reaction, possibly because the hydrocarbon is more quickly disengaged from the solution, favours the monomeride and lower polymerides

Butene-2, as mentioned above, more closely resembles propylene in its behaviour towards acid It is only polymerized to a slight extent by acid of lower concentration than 78% although recently Drake and Veitch, Jr [45, 1935], have shown that *sec*-butyl alcohol heated with 75% acid under pressure gives a polymerization product consisting of 3,4-dimethylhexene-2 This is the compound which normally would be expected from the condensation of two butene-2 molecules thus



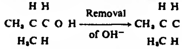
3,4-dimethylhexene-2

It will be observed that combination occurs in a manner similar to that postulated by Ipatieff for the phosphoric acid polymerization of propylene

At moderate temperatures below 78% concentration, the action of the acid is normal and limited to ester and alcohol formation No evidence has so far been obtained for the formation of the corresponding dialkyl sulphate which is probably extremely unstable King [82, 1919] attributed the absorption of an excess of nearly 21% of butene over that theoretically required for *sec*-butyl sulphuric acid to direct hydration to the alcohol

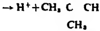
That direct hydration does occur under such circumstances has been definitely shown by Brooks and Humphrey [30, 1918] who found that when C_5, C_6, and C_7 olefines were carefully treated with 85% sulphuric acid and the reaction product poured into water, alcohols were formed These authors point out that as 30 to 40% of the original hydrocarbon remains in solution as the alkylsulphuric acid and does not hydrolyse on further standing, hydration must occur during the initial absorption As supporting evidence they showed that when 100% acid or benzenesulphonic acid was used in place of 85% acid, no alcohols could be detected The fact that 94% acid gave less alcohol than 85% acid was further proof that the water present is the determining factor in alcohol formation Direct hydration in this way explains the presence of the alcohols which have been reported from time to time in acid sludge from cracked distillates

When branched chain olefines are concerned both hydration and dehydration are much complicated unless the unsaturated linkage is situated in a position sufficiently remote from the branching Such hydrocarbons then resemble normal olefines in their behaviour Bulterov [32, 1877] in his classic studies on the action of sulphuric acid on *iso*butene, first observed besides the normal hydration product, *tert*-butyl alcohol, the formation of a second product which he identified as *iso*butyl alcohol This, presumably, could only have been formed by a rearrangement of the type which has been investigated in recent years by F C Whitmore and his colleagues The fact that many alcohols, particularly those containing tertiary groupings, do not give the expected product on dehydration or give it only in poor yield, has puzzled many investigators The changes involved resemble the well-known pinacol-pinacoline change as well as the corresponding retrograde reaction From a study of the fundamental changes occurring when a strongly electro-negative group is removed from an organic molecule during a reaction, Whitmore [151, 1932] has evolved a theory explaining the formation of products other than those of simple metathetical or eliminating reactions The mechanism is simple and fits all rearrangements which involve the transfer of an atom or group from one atom to an adjacent one The dehydration of *iso*butyl alcohol to give normal butenes as well as *iso*butene furnishes an excellent example of such a reaction.



$$CH_3\,\underset{H_3C}{\overset{H}{C}}\,\underset{H}{\overset{H}{C}}\,O\,H \xrightarrow[\text{of } OH^-]{\text{Removal}} CH_3\,\underset{H_3C}{\overset{H}{C}}\,\underset{H}{\overset{H}{C}}$$

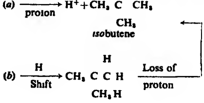
The fragment can now be stabilized by the loss of a proton from the carbon atom bearing the two methyl groups thus



$$\rightarrow H^+ + CH_3\,\underset{CH_3}{C}\,CH_2$$

*iso*butene

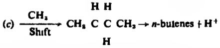
Rearrangement may also occur depending upon which carbon atom has the greater electron attraction or which can more readily dispense with a pair Whitmore postulates that any shift in the electron pair includes the atom or group which it holds An exchange of methyl group for hydrogen thus still leaves a carbon atom with an open sextet Depending on the other groups attached to the carbon atom, the resulting hydrocarbon formed by the loss of proton or stabilization may or may not be identical with that obtained by stabilization of the original fragment



$$(a)\ \xrightarrow[\text{proton}]{\text{Loss of}} H^+ + CH_3\,\underset{CH_3}{C}\,CH_2$$

*iso*butene

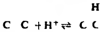
$$(b)\ \xrightarrow[\text{Shift}]{H} CH_3\,\underset{CH_3}{C}\,\underset{H}{\overset{H}{C}}\,H \xrightarrow[\text{proton}]{\text{Loss of}}$$



$$(c)\ \xrightarrow[\text{Shift}]{CH_3} CH_3\ \overset{H}{C}\ \underset{H}{\overset{H}{C}}\ CH_3 \rightarrow n\text{-butenes} + H^+$$

Similarly, the dehydration of *normal* butyl alcohol gives *iso*butene and all three *n*-butenes instead of the expected butene-1, while *sec*-butyl carbinol gives trimethylethylene together with small amounts of pentene-2 and *unsym*-methylethylethylene

Whitmore's theory thus explains many of the unexpected results obtained in dehydrating alcohols with acid Furthermore, since in the reaction of olefines with acid catalysts the first step [151, 1932, 1934] consists in the addition of a hydrogen ion (proton) to the extra electron pair in the double bond



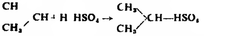
$$C\ C + H^+ \rightleftharpoons \overset{H}{C}\ C$$

the theory can also be applied to hydration, ester formation, and polymerization, and the positive fragment formed can undergo rearrangement similar to that described above before further reaction This can occur in three ways (1) loss of proton to yield possibly a new olefine, (2) combination with sulphate or hydroxyl ion to yield sulphuric ester or alcohol, and (3) addition to an olefine molecule to form another larger fragment in a manner similar to that in which the original reaction between proton and olefine occurred Upon the last reaction is based Whitmore's theory of polymerization, for obviously stabilization by loss of a proton from the newly formed fragment yields a more complex olefine, a polymer Since the addition of positive fragments to olefines can occur presumably indefinitely under suitable circumstances, the formation of a whole range of polymers can be envisaged

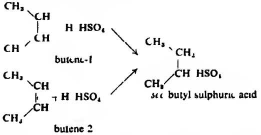
Little mention is made in the literature of the behaviour of butene-1 although it is well known that it forms an important constituent of the C_4 fraction of cracking gases It appears to be slightly less reactive than butene-2, but otherwise to be very similar in its properties

Five isomeric pentenes exist, pentene-1, pentene-2, *iso*propylethylene, trimethylethylene, and *unsym*-methylethylethylene, all of which have been identified in the C_5 fractions of cracked distillates Like the butenes, they all show a marked affinity for sulphuric acid, the relative reactivity and products formed being determined by the structural configuration and conditions of treatment Norris and Joubert, who made a detailed study of the reactivity of the pentenes towards sulphuric acid [122, 1927] placed them in the following order of activity (1) trimethylethylene, (2) *unsym*-methylethylethylene, (3) pentene-2, (4) pentene-1, and (5) *iso*propylethylene Compared with the butenes, Davis and Schuler [42, 1930] found that the pentenes were far more reactive Thus the vapour of trimethylethylene was absorbed three or four times as rapidly by 80% sulphuric acid as *iso*butene under similar conditions, while *iso*propylethylethylene, the least reactive, was slowly absorbed by 70% acid at a rate commensurate with that of propylene and butene-2

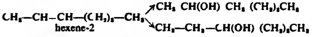
The similarity between trimethylethylene, *unsym*-methylethylethylene and *iso*butene is very marked All are readily absorbed by comparatively weak acid—below 60% at room temperature—with little or no polymerization, giving tertiary alcohols from which the monomeric hydrocarbon or its polymerides can be obtained by suitable adjustment of acid concentration From none has evidence for the formation of a tertiary alkyl-sulphuric ester been obtained although it is almost certainly intermediate in the formation of the alcohol The addition of sulphuric acid to olefines—whether the product finally obtained is a sulphuric ester, alcohol, or polymer—follows Markovnikov's rule, that is to say, the hydrogen goes to the unsaturated carbon atom richest in hydrogen Thus in the addition of acid to propylene, the acid radical attaches itself to the middle carbon atom, thereby completing a second methyl group so that an *iso*propyl derivative results



Similarly both butene-1 and butene-2 give the same product *sec*-butyl sulphuric acid

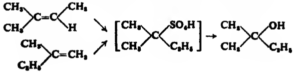


A study of all the known examples of acid addition reveals the fact that the acid radical never attaches itself to the terminal carbon atom This point was very carefully investigated by Brooks [29, 1934] in the case of propylene and pentene-1 but in neither instance was he able to detect the slightest trace of the primary alcohol In olefines in which the ethylene linkage occupies the 2-position both possible compounds are formed, although the position closer to the end of the chain, the 2-position, is preferred That both the 2- and 3-derivatives were formed was first observed by Michael and Hartman [115, 1906] who found that when hexene-2 reacted with sulphuric acid, the hydrolysis products contained the two possible hexyl alcohols in the proportion of 77% methylbutyl carbinol and 23% ethylpropyl carbinol



Brooks also found that with pentene-2 the acid favours the 2-position for, while 23% of diethyl carbinol is present in the products of hydrolysis, there is 77% of methylpropyl carbinol

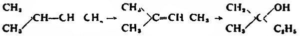
When the ethylenic linkage is even further removed from the end of the chain as, for example, in heptene-3, the evidence indicates that while both possible compounds are formed (Brooks and Humphrey [30, 1918]) that in which the acid radical is nearer the terminal carbon atom again predominates With olefines, such as *iso*butene and trimethylethylene, which do not form stable alkyl sulphuric acids, the hydration product is mainly that which would be expected from the addition of the acid radical to the tertiary carbon atom



It can be seen that both trimethylethylene and *unsym*-methylethylethylene give the same alcohol Bultenov [32, 1877] found that a state of equilibrium exists between trimethylethylene, dimethylethyl carbinol, and water in the presence of sulphuric acid

$$C_5H_{10} + H_2O \rightleftharpoons C_5H_{12}O$$

As *unsym*-methylethylethylene is also converted by dilute acid into the same alcohol under similar conditions, double bond isomerization must take place and part of the *unsym*-methylethylethylene become converted into trimethylethylene Furthermore, since Norris and Joubert [122, 1927] found that trimethylethylene prepared by dehydrating dimethylethyl carbinol invariably contains some *unsym*-methylethylethylene, it follows that the isomerization must be reversible Although isomerization of this type involving the shift in position of a double bond under the influence of sulphuric acid is probably very common amongst aliphatic hydrocarbons, little mention of it is to be found in the literature Brooks [27] states that *iso*propylethylene is isomerized to trimethylethylene but gives no reference That it does occur in the presence of certain catalysts such as silica or alumina at temperatures in the neighbourhood of 500° C was shown by Ipatieff [70, 1903], who obtained as much as 80% conversion, Norris and Reuter [123, 1927] later found that at slightly lower temperatures such acid catalysts as phosphoric acid and aluminium sulphate were also effective Attempts, however, by the last two authors to bring about isomerization in the liquid phase were less successful, although they were able to demonstrate that, using 69% acid, a small but definite amount of dimethylethyl carbinol was formed from *iso*propylethylene This can only have been formed from trimethylethylene, itself derived from the *iso*propylethylene by isomerization



$$\overset{CH_3}{\underset{CH_3}{>}}CH{-}CH\,CH_2 \rightarrow \overset{CH_3}{\underset{CH_3}{>}}C{=}CH\,CH_3 \rightarrow \overset{CH_2}{\underset{CH_3}{>}}C\overset{OH}{\underset{C_2H_5}{<}}$$

The reactions between trimethylethylene and *unsym*-methylethylethylene and sulphuric acid are very susceptible to change in acid concentration, with both, polymerization commences at comparatively low concentrations Thus while trimethylethylene is scarcely polymerized at all by 57% acid, polymerization is stated to be complete in two days in the cold with 70% acid, *unsym*-methylethylethylene behaves similarly

Pentene-1 and pentene-2 resemble butene-2 and propylene in their behaviour towards acid Both resist polymerization by acid concentrations below 84%, but are converted by concentrated acid into polymers higher than the dimerides (cf Norris and Joubert [122, 1927]) With acids of lower concentrations, i e 75–84%, they are slowly absorbed to form pentane-2-sulphuric acid and methylpropyl carbinol These observations have been recently confirmed by Campbell and Cramer [33, 1937]

The fifth pentene, *iso*propylethylene, is unique in its behaviour in being only affected by acid of polymerizing strength when polymerization but little or no alcohol formation occurs With comparatively weak acid, 75%, polymerization is slow and requires 6 days for completion, when the dimeride is the main product More concentrated acid gives only higher polymers (Norris and Joubert) Campbell and Cramer, however, found *iso*propylethylene to be somewhat more reactive, dissolving in 81% acid at room temperature and, after 2 days, being about 75% polymerized The polymer was found to contain 57% of the dimeride.

Relatively small amounts of acid only are required to bring about polymerization of considerable quantities of *iso*propylethylene, this also being true of the polymerization of such hydrocarbons as *iso*butene, trimethylethylene, and *unsym*-methylethylethylene

The polymerization of trimethylethylene and *unsym*-methylethylethylene was found by Norris and Joubert to proceed smoothly with relatively weak acid to give a product consisting largely of the dimeride Increase in acid concentration not only results in higher polymers being formed but the rate of polymerization is so accelerated that the action becomes almost explosive The dimerides from these hydrocarbons are colourless liquids boiling from 155 to 160° C and possessing a pleasant odour, the trimeride appears to be much more complex and boils over a wider range, 225–250° C Whether the dimerides from trimethylethylene and *unsym*-methylethylethylene consist of the same mixture of hydrocarbons is unknown, although they closely resemble each other (*vide infra*)

Recently Cramer and Campbell [33, 1937] have prepared a number of diamylenes by polymerization of the pentenes with acid and by direct dehydration of the corresponding alcohols (which would be expected to yield the pentenes) Their results are shown in the following table

Properties of the Diamylenes

Source	*Sulphuric acid, wt %*	*Yield %*	*B p C*	n_D^{25}	d_4^{23}
Diethyl carbinol (pentene-2)	81	29	155–173	1 4303	0 760
Methyl *iso*propyl carbinol, synthetic	75	70	145–170	1 4346	0 766
Dimethylethyl carbinol (trimethylethylene)					
Synthetic	70	90	152–158	1 4357	0 771
Technical	60–75	72	145–165	1 4358	0 770
A (*a*)	75	57	150–163	1 4349	0 767
B (*b*)	75	80	149–157	1 4356	0 769
unsym-Methylethyl ethylene	75	43	150–158	1 4367	0 772
Trimethylethylene	75	85	151–158	1 4353	0 769
*iso*Propylethylene	81	26	143–162	1 4303	0 754

(*a*) Diamylene from total mixed pentenes ex-technical dimethylethyl carbinol and activated alumina at 375° C

(*b*) Diamylenes from total mixed pentenes prepared by selective dehydration of technical dimethylethyl carbinol

The logical expectation that, regardless of their exact structure, the dimerides derived from trimethylethylene and *unsym*-methylethylethylene would yield the more highly branched and centralized molecules was confirmed by the critical compression ratios of the decanes derived from the diamylenes by hydrogenation

Comparatively little is known of the composition of the polymers of even the simplest hydrocarbons Until recently it was assumed that they were complex mixtures containing a large number of isomeric olefines, but the work of Ormandy and Craven, Nametkin, and others has shown that hydrocarbons other than olefines are formed when the higher acid concentrations are used Mention has already been made of Ormandy and Craven's [124, 1927, 1928] identification of paraffins in the product from the reaction of 98% acid upon propylene Later these authors observed that when pentenes reacted with a large excess of 96% acid the high-boiling fraction of the insoluble layer contained only paraffins, while olefines were present in the lower-boiling fraction These findings were at the time by no means generally accepted, although, as shown by later workers, saturated products are definitely produced in reactions of this type Thus Nametkin and Abakumovskaya [118, 1932, 1933] first confirmed Ormandy and Craven's results when examining the polymerization products of *cyclo*hexene, and again later [119, 1936] when working with aliphatic olefines Both Ormandy and Craven and Nametkin and Abakumovskaya observed the formation of highly unsaturated compounds which separated from the acid on dilution The reaction has been recently investigated by Ipatieff and Pines [76, 1936] whose observations, although somewhat at variance with those of Ormandy and Craven, confirm the formation of paraffins and of highly unsaturated hydrocarbons, which they identified as cyclic olefines corresponding to the formula C_nH_{2n-4} Their conclusions are summarized as follows

(1) Olefinic hydrocarbons treated with large amounts of 96% sulphuric acid at 0° C yield a mixture of paraffins, olefines, and cyclic olefines The two latter are present in the fractions boiling above 250° C, while the fractions boiling below this temperature consist entirely of saturated hydrocarbons

(2) The treatment of olefinic hydrocarbons with small ratios of 96% acid at 0° C yields products having a higher boiling range than those treated with large quantities of acid The product obtained consists of a mixture of hydrocarbons, olefines are present in the fractions boiling below 250° C

(3) The yield of paraffin hydrocarbons increases with increase in the ratio of concentrated sulphuric acid to olefine treated

(4) The treatment of olefines at −35 C with large or small amounts of 96% acid yields liquid hydrocarbons having a higher boiling range than the product resulting from similar treatment at 0° C

(5) Di- and tri-*iso*butene when treated with concentrated acid yield liquid hydrocarbons of identical boiling range

(6) The treatment of olefinic hydrocarbons like di- and tri-*iso*butene with concentrated acid causes the cleavage of the chains followed by hydrogenation Tri-*iso*butene yields a fraction corresponding with octane, and di-*iso*butene one corresponding with dodecane

(7) Cyclic olefines of the formula C_nH_{2n-4} occur in the decomposition products from the acid layer

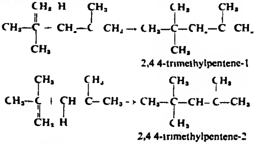
(8) Acid concentrations of 87, 77, and 67% do not cause the formation of paraffinic or cyclic hydrocarbons

(9) Dilute acid at higher temperatures causes depolymerization

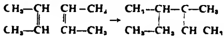
Sulphuric acid thus appears to be capable not only of polymerization and depolymerization but hydrogenation coupled with dehydrogenation and cyclization as well No attempt has been made so far to identify the paraffins produced, and the mechanism of the reaction is exceedingly obscure

As a general rule the main hydrocarbon products from the action of sulphuric acid upon olefines are olefinic in nature True polymerides derived from mono-olefines possess only one double bond in the molecule and are still, therefore, mono-olefines Brooks and Humphrey [29, 1918] pointed out that, while they are invariably more stable towards polymerizing conditions, they can be induced to polymerize further This is well illustrated by di-*iso*butene which, although formed by polymerization of *iso*butene, is still further polymerized with considerable evolution of heat by more concentrated acid

Only in recent years has the development of laboratory distillation technique made it possible to separate polymerization products into individual compounds As a result it has been found that complex mixtures of isomeric olefines are not always formed but that in certain instances the number of individuals present is small Thus it has been shown that the dimerides of *iso*butene, butene-2, and *unsym*-methylethylethylene can be separated by careful fractionation In this way Whitmore and Wrenn [154, 1931] succeeded in separating di-*iso*butene into two isomers, 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 Of these the former was present in the greater proportion Graphically the formation of these compounds can be expressed as follows

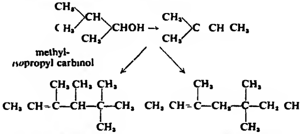


The polymer derived from secondary butyl alcohol by the action of 75% acid under pressure at 80° C has been shown by Drake and Veitch Jr [45, 1935] to consist largely of 3,4-dimethylhexene-2 formed by a similar condensation of two butene-2 molecules thus



3 4-dimethylhexene 2

Kline and Drake found that the dimeride of *unsym*-methylethylethylene formed by the action of 75% sulphuric acid upon methyl*iso*propyl carbinol at 80° C consisted of two isomers, 3,4,5,5-tetramethylhexene-2 and 3,5,5 trimethylheptene-2 [86, 1934]



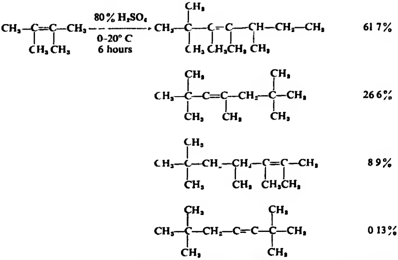
3,4,5,5-trimethylhexene-2 3,5,5-trimethylheptene-2

Several theories have been put forward to explain the formation of these isomerides, but so far none completely covers all the facts Kline and Drake deduce from the theory, which they have suggested to explain the formation of dimerides from methyl*iso*propyl carbinol that, although 2,281 isomers corresponding with tri-*iso*butene can theoretically exist, only four of these are probable

Other than Drake and Veitch Jr 's work upon the dimeride of butene-2, little is known of the constitution of the polymers derived from the straight-chain olefines If polymerization with phosphoric acid can be regarded as strictly analogous to the action of sulphuric acid—a not unreasonable assumption—Ipatiev's work (*vide infra*) indicates that polymers must consist entirely of branched-chain olefines Whether the addition of one olefine to another follows the same general rule as alcohol formation, that is to say coupling occurs at the β-carbon atom or its equivalent, is not known The work of Ormandy and Craven on propylene (q v) appears to indicate that the polymerization products of the normal olefines are far more complex than the more readily formed and comparatively simple dimerides of *iso*butene and butene-2, probably because more concentrated acid is necessary to effect reaction

When more than one olefine is present the problem of polymerization is complicated by the possibility of dissimilar olefines combining to form condensation products which in their general properties and behaviour closely resemble true polymerides Recently Birch, Pim, and Tait [18, 1936] have shown that by the action of sulphuric acid upon mixtures of two easily dehydrated alcohols, besides the expected polymerides, hydrocarbons are formed derived from both Thus a mixture of tertiary butyl alcohol and tertiary amyl alcohol yields besides the normal polymerization products, di-*iso*butene and diamylene, '*iso*-nonene' corresponding with the combination of one molecule of *iso*butene with one of trimethylethylene Similarly, tertiary and secondary butyl alcohols heated with acid in equimolecular proportions yield, as well as the normal polymers, *iso*-octene derived from *iso*butene and butene-2 Such products resemble normal 'polymers' in consisting of mixtures of individual olefines and boiling over a wide range A careful examination of the product from the action of sulphuric acid on a mixture of secondary and tertiary alcohol has been shown by Whitmore, Laughlin, Matuszeski, Crooks, Jr , and Fleming [152, 1936] to contain butenes, di-*sec*-butyl ether, and di- and tri-meric butenes with higher polymers The chief dimeric butenes were the two di-*iso*butenes (2 2,4-trimethylpentenes-1 and -2) with 2,2,3-trimethylpentene-3 and 2,3,4-trimethylpentene-2 in the approximate ratio 50 35 15 The last compound is due to a new type of arrangement involving as a final a 1 3 shift of a methyl group

Of the sixteen possible hexenes only four appear to have been investigated Brooks and Humphrey found that hexene-1 reacts with 85% acid at 0° C to give *sec*-hexylsulphuric acid without any polymer formation at all Under similar conditions tetramethylethylene polymerizes chiefly to the dimeride boiling-point 180 to 200° C, but the barium salt of the alkyl sulphuric acid and a small quantity of the alcohol were also isolated The isolation of the barium salt is of interest, for the free acid must be the tertiary derivative which in the case of the C_4 and C_5 hydrocarbons are too unstable to exist It is therefore hardly surprising that the barium salt proved to be less stable than similar salts derived from secondary alcohols The observations of Bacon [2, 1929] are of interest in this connexion, for while investigating the composition of acid-sludge from light oils he found indications of the presence of tertiary alkyl sulphuric acids He also observed that the higher alkyl sulphuric acids were surprisingly resistant to hydrolysis More recently Whitmore and Meunier [153, 1936] have examined the polymerization of tetramethylethylene with 80% acid at 0-20° C for 6 hours The polymer on fractionation gave a yield of mixed dimers boiling between 151 and 178 5° C. at 741 mm equivalent to 45% The dimers identified (by ozonolysis) with the percentage of each in the total dimer were as follows



$$CH_3{-}C(CH_3){=}C(CH_3){-}CH_3 \xrightarrow[0\text{-}20°\ C,\ 6\ \text{hours}]{80\%\ H_2SO_4} CH_3{-}C(CH_3)_2{-}C(CH_3){=}C(CH_3){-}CH(CH_3){-}CH_2{-}CH_3 \quad 61\ 7\%$$

$$CH_3{-}C(CH_3)_2{-}C{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3 \quad 26\ 6\%$$

$$CH_3{-}C(CH_3)_2{-}CH_2{-}CH(CH_3){-}C(CH_3){=}C(CH_3){-}CH_3 \quad 8\ 9\%$$

$$CH_3{-}C(CH_3)_2{-}CH_2{-}C{=}C{-}C(CH_3)_2{-}CH_3 \quad 0\ 13\%$$

Another hexene, 2-methylpentene-1, on treatment with 85% acid at 10° C gave a tertiary alcohol, presumably dimethyl-*n*-propyl carbinol The remaining hexene was that derived from mannitol, hexene-2, which Michael and Hartman [115, 1906] observed gave both possible alkyl sulphuric acids, no mention is made of polymerization products, from which it appears that the behaviour of hexene-1 and hexene-2 is very similar

Very few of the higher olefines have been examined, and such information as is available is largely due to the work of Brooks and Humphrey Their results are summarized in the following table

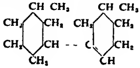
Olefine	*Acid concentration %*	*Temp ° C*	*Products*
Heptene-3	85	15	Alcohol only
3-Ethylpentene-2	95	0	Mainly alcohol, 10% dimer
5-Methylhexene-1	85		Considerable proportion of dimer
Octene-2	85	20	Mainly polymer
5-Methylheptene-1	85	15	Mainly polymer, 50% dimer
2-Methylundecene-2	85	20	Almost entirely dimer

The tendency towards polymerization with increasing molecular weight is very apparent, the higher olefines giving almost entirely polymers Michael and Brunel [114, 1909], observed that the resistance to acid also increases with molecular weight, the straight-chain hydrocarbons being more resistant than those having a highly branched configuration

A recent patent (U S Pat 2,027,896, 4 Nov 1929) claims that the formation of dialkyl sulphates from the higher molecular weight olefines can be readily accomplished at 0° C with the use of mild sulphating agents. This would tend to indicate that the higher alkyl sulphates are more stable than is generally supposed

Cyclic Olefines.

Comparatively little is known of the effect of acid upon cyclic olefines The reaction appears to be complicated by the formation of saturated or less unsaturated hydrocarbons than those expected, possibly formed in a reaction similar to that observed by Ormandy and Craven with propylene The effect of acid upon the simplest cyclic olefine, *cyclo*hexene, was investigated by Nametkin and Abakumovskaja [118, 1932, 1933] who treated it with 96% acid at 2 to 5° C and obtained an oil equivalent to a 37% yield On fractionation three hydrocarbons $C_{12}H_{22}$, $C_{18}H_{32}$, and $C_{24}H_{20}$ were obtained, of these the first was fully saturated, while the others contained one ethylene linkage Kishner [84, 1908] also observed this tendency to form saturated compounds in 1-methyl-Δ^1-*cyclo*hexene which gave, amongst other products, methyl*cyclo*hexane Brooks and Humphrey also examined the effect of acid on 1-methyl-Δ^1-*cyclo*hexene but as they employed much weaker acid, namely 85%, at 0° C they obtained only the dimeride with some of the corresponding tertiary alcohol, 1-methyl-1-*cyclo*hexanol Mark [103, 1904] showed that the isomeric methyl-Δ^3-*cyclo*hexene behaved similarly with 50% acid, giving the dimeride I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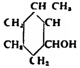

II

and the alcohol II

No mention is to be found in the literature of the behaviour with acid of other naphthenes containing ethylene linkages in the ring or in the side chain Whether or not *cyclo*pentene derivatives are to be found in cracked distillates is a moot point, for although *cyclo*pentane itself can be dehydrogenated, under the influence of heat the ring is ruptured and straight olefines formed

Aromatic Olefines.

The only hydrocarbons falling under this heading which have been examined are styrene and indene, both of which have been identified in the pyrolysis products from natural gas (Birch and Hague [12, 1934]) Brooks and Humphrey found that styrene reacts energetically with 85% acid at 0° C to form hard resins (loc cit) With concentrated acid the reaction is explosive Indene is stated to form paraindene with dilute sulphuric acid

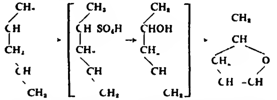
Aliphatic Diolefines.

Since the conjugated diolefines are now known to be largely responsible for gum-formation, it at first appears somewhat surprising that so little is known of the chemistry of the process which is largely directed towards their destruction The very reactivity to which is due their gum-forming properties renders it possible to attack them under such conditions that most other hydrocarbons remain unattacked

Practically nothing is known of the reactions which take place between conjugated diolefines and sulphuric acid, although several investigators are to-day engaged upon the problem The action with concentrated acid is extremely vigorous, tars are formed and considerable reduction of the acid takes place With less concentrated acid the products are very complex and appear to be determined to some extent by the acid concentration The simplest conjugated diolefine, butadiene, is unexpectedly resistant, Dobryanski [44, 1925] stating that it is absorbed by 83% acid about as rapidly as propylene or by 61% acid as rapidly as the normal butenes So far the products have not been determined Some light on the reaction between conjugated diolefines and acid has been furnished by Wagner-Jauregg [149, 1932], who showed that *iso*prene and acetic acid react in the presence of sulphuric acid to form geranyl acetate and a dicyclic hydrocarbon of the caryophellene type The formation of geranyl acetate indicates that under the influence of the acid two or more *iso*prene molecules are capable of linking together to give an open chain from which cyclic hydrocarbons are formed by ring closure Farmer and Bacon (private communication [54]) have found that under similar conditions 2,3-dimethylbutadiene gives a mixture of cyclic polymers from which the di- and tri-merides have been isolated and indications of the presence of a tetrameride obtained

The structure of the cyclic polymerides formed in these reactions is by no means easy to elucidate It is interesting to note that although the formation of a six-membered ring structure appears certain, Bergman [8, 1935] has shown that the dimeride formed by the action of heat on α-phenylbutadiene contains a five-membered ring

The only non-conjugated diolefine examined is diallyl, hexadiene-1,5 Pogorzhelsky [128, 1898] found that on treatment with 70% acid, this hydrocarbon was converted into the anhydride of hexane-2,5-diol The mechanism of the reaction is presumably



The strong tendency for the formation of the 5-membered ring which is so prevalent throughout organic chemistry is responsible for the ring closure

Cyclic Diolefines.

The only cyclic diolefines which appear to have been examined are *cyclo*pentadiene and $\Delta^{1\ 3}$-*cyclo*hexadiene Of these the first is invariably present in the products obtained by the pyrogenic decomposition of hydrocarbons, particularly in vapour-phase cracked distillates, pyrolysis benzole and the forerunnings from coal-tar benzole, the presence of $\Delta^{1\ 3}$-*cyclo*hexadiene in these products is only suspected and has not been proved

Both hydrocarbons are extremely reactive They are particularly prone to autoxidation and peroxide formation and are consequently very effective polymerization catalysts Not only does the peroxide formed catalyse the polymerization of the parent hydrocarbons and other diolefines, but of otherwise relatively stable hydrocarbons as well Both *cyclo*pentadiene and *cyclo*hexadiene react explosively with concentrated sulphuric acid forming tars, much sulphur dioxide and water More dilute acids give high molecular weight resins

Summarizing, the action of sulphuric acid upon unsaturated hydrocarbons is as follows

(1) All the lower molecular weight olefines so far examined react with sulphuric acid

(2) The effect is influenced not only by the structure of the hydrocarbons but by such conditions as acid concentration, temperature, and time of contact

(3) The reactivity of the aliphatic olefines increases with

molecular weight, reaching a maximum with the pentenes and hexenes

(4) The reaction is complex sulphation, hydration, condensation, polymerization, depolymerization, hydrogenation, dehydrogenation, and cyclization all occur depending upon the olefine and the conditions

(5) Higher acid concentrations tend to bring about polymerization, the higher the concentration the more complex being the products Lower concentrations give sulphation products or alcohols, *iso*propylethylene being exceptional in this respect

(6) Hydrocarbons in which two radicals are attached to an unsaturated carbon atom are generally more reactive than isomeric olefines not containing this grouping The lower olefines of this type do not form stable alkyl sulphuric acids

(7) No general rules concerning polymerization have been formulated completely fitting the facts

(8) The properties of the polymerization products vary with the parent hydrocarbon As a general rule they are olefinic in nature--saturated by-products when present are probably due to side-reactions—and are more resistant to the action of acid and other reagents than the original hydrocarbon

(9) All the simple olefines dissolve (or polymerize) in acid without the formation of tars The latter are formed from conjugated diolefines or unsaturated aromatic hydrocarbons

(10) Practically nothing is known of the chemical reactions involved in the action of acid upon conjugated diolefines

The Acid Treatment of Cracked Distillates

From the foregoing review of the action of sulphuric acid upon hydrocarbons, it is clear that the reactions involved in the acid treatment of cracked distillates are many and varied and are rendered even more so by the presence of non-hydrocarbon constituents The final effect of the treatment must therefore consist of the combined results of all these reactions To what extent these reactions interfere with each other is obviously unknown, all that can be safely stated is that the diluents resulting from the various chemical and physical processes have a very important bearing upon the action, for by diluting the acid they render its action less drastic and so help to confine it to the desired limits It is in fact largely owing to the modifying effect of the diluents that the acid treatment of many cracked products, particularly the more highly unsaturated ones, is possible The diluents are to a considerable extent responsible for the excellent contact normally obtained

The function of the acid is to produce a product free from gum and reasonably free from gum-forming constituents At the same time reduction in sulphur or nitrogen content and improvement in colour and odour may be desired, although to-day the two latter qualities are regarded less seriously Normally cracked distillates contain besides non-volatile bodies which on evaporation are left as resins, certain volatile substances capable of conversion into resins under the conditions of the gum test Unlike the existent gum these substances are not left behind on distillation, but are to be found in the distillate, where they eventually become converted into resins On treatment with sulphuric acid these bodies are converted into non-volatile gummy substances which remain behind on distillation This, then, is the main function of the acid It should be noted, however, that the acid is capable of converting olefines which normally do not give gum also into non-volatile gum-like substances Thus Cassar [37, 1931] treated solutions of various pure olefines in straight gasoline with concentrated acid under more or less normal treating conditions and examined the products His results are tabulated below

Olefine Solution 20%	*Gum formation mg per 100 c c*	
	After acid	*After acid and redist*
Pentene-2	773	148
Trimethylethylene	181	2
Diamylene	20	
Di-*iso*butene	26	
*cyclo*Hexene	1,039	5
Styrene	14,786	2

While the result obtained from pentene-2 appears abnormal, it can be seen that even comparatively stable olefines form bodies capable of gum-formation on acid treatment There seems little doubt that these substances are actually high-boiling or, in the case of styrene, non-volatile polymers The results emphasize the necessity for the subsequent redistillation In the course of this work Cassar showed that olefines in contact with sulphur dioxide formed gum, which he assumed to be due to its oxidation to sulphur trioxide by traces of peroxides present, since when the latter were removed no gum was formed

The complexity of cracked distillates renders impossible the control of the numerous reactions involved on any but the broadest lines While theoretically it is desirable to limit the action of the acid completely to the reactive unstable constituents, this is obviously impossible on account of the wide range of reactivity possessed by the various hydrocarbons present Fortunately the most unstable hydrocarbons are extremely reactive towards such reagents as acid, so that it is possible by choosing conditions to achieve a reasonably successful removal of the undesirable constituents Treatment conditions which may be varied include amount of acid and the concentration, time of contact, temperature, and the unsaturated hydrocarbon content of the product itself The last can sometimes be conveniently reduced by blending with straight or cracked material produced by some less drastic cracking process, and this occasionally proves a useful way of overcoming excessive losses, for example in the treatment of such products as polymer gasolines

In practice the most important factors in treating a cracked distillate are the acid concentration and amount employed, these are necessarily closely related, for the effective treating concentration is largely determined by the dilution due to the reaction products For this reason the concentration is to a large measure outside the chemists' control, for shortly—if not immediately depending upon the thoroughness of the agitation—after the fresh acid enters the treater, it becomes diluted with sulphur bodies, traces of water—cracked distillates are rarely dry unless specially dried—phenols, sulphuric esters, alcohols, polymers, and tar, while nitrogen bases when present reduce the concentration by direct neutralization In continuous operation, it is the sludge already formed which acts as the diluent In any case, reaction products rapidly dilute the acid until a more or less definite concentration is reached when further change occurs only slowly As the most reactive hydrocarbons are the first to be affected it follows that in batch operation the hydrocarbons remaining unaffected become increasingly resistant to the action of the acid, at the same time owing to the increasing dilution, the acid itself becomes less effective, eventually becoming incapable of further reaction with the hydrocarbons present It must not, however, be thought that at this stage the acid is quite incapable of further reaction, for place it in contact with more reactive hydrocarbons and it will again react In counter-current continuous treatment advantage is taken of this to bring the raw distillate containing the most reactive hydrocarbons into contact with the least reactive acid, and then gradually to increase the strength of the acid until the necessary degree of refining has been effected In this way heat evolution is less rapid and is spread over a longer period of time, with the result that the reaction can be more carefully controlled

Although at one time the use of oleum for cracked distillate was not uncommon, the use of the concentrated acid for these products is to-day becoming increasingly rare So vigorous is the action when concentrated acid is added to highly unsaturated, particularly vapour-phase cracked distillates, that the reaction is almost explosive and polymerization excessive Considerable oxidation, as evidenced by sulphur dioxide formation, also takes place That uncontrolled heat evolution is responsible is proved by the ease with which the same operation can be successfully carried out at 20° F, when the reaction proceeds smoothly and losses from tar formation, polymerization, and loss of volatile material are largely avoided Indeed, concentrated acid can only be safely employed—if loss in yield and octane rating are to be avoided—under such conditions that dilution with acid sludge rapidly occurs or too rapid reaction and evolution of heat, e g by operating at relatively low temperatures or employing only brief times of contact are precluded

To-day the tendency is definitely away from the higher acid concentrations, and it is customary to employ the lowest concentration capable of ensuring a reasonably stable product—with the use of inhibitors if necessary Although acid concentrations as low as 80% have been advocated, usually concentrations nearer 90% are employed As diluent, water is invariably used, but some others such as phosphoric acid, benzene-sulphonic acid and so on are mentioned in the patent literature Phosphoric acid in particular is claimed as a particularly valuable diluent, treatment, it is stated, proceeds smoothly, and the sludge is light in colour and easy to recover While such diluents possibly possess the advantage over water that the solvent action of the acid is less impaired (this probably applying equally well to its sweetening action), it is doubtful whether in view of the increased cost they are ever likely to replace water excepting for special products

Acid treatment is most effectively applied as a continuous counter-current process Apart from the advantages already mentioned, that is to say, more gradually regulated reaction and consequently heat evolution, this form of treatment enables the most economical use to be obtained from the acid Even in batch operation considerable economies can be effected if the acid instead of being applied as one large wash, is given in two or three smaller ones The use of 'spent' sludge from a previous batch for the preliminary treatment of the raw distillate is particularly advantageous as it not only dehydrates but at the same time definitely effects a measure of refining In other words, batch treatment is most effectively applied in the form of a rudimentary counter-current process So effective is continuous counter-current treatment that it enables extremely reactive distillates which otherwise are only refined with difficulty, to be processed with comparative ease While the form of equipment used does not concern us here, mention must be made of the Holley-Mott type of treating plant owing to its special features The plant consists of a number of pairs of treaters or 'pots', one, the agitator, being equipped with an efficient paddle stirrer, while the other acts as separator To ensure good mixing, approximately equal volumes of acid and distillate are employed in the plant, but the acid moves forward extremely slowly compared with hydrocarbon As the first acid, equivalent to 0 2 to 0 5% of the distillate, entering the final agitator is at once diluted by the large volume of sludge present, it is possible to add concentrated acid even when treating highly unsaturated products Treatment is in fact carried out by acid sludge and only sufficient fresh acid is added to maintain the free acid concentration sufficiently high to give a satisfactory product in the time it takes to pass through the plant In other forms of continuous counter-current plants, the principle is the same but, as less sludge is present, dilution is less rapid, and the addition of acid of a lower concentration is consequently desirable

The composition of acid sludge is very indefinite It consists of a complex mixture of acid, water, sulphur dioxide—depending upon the extent to which oxidation has occurred—alcohols, phenols, nitrogen bases (as salts), sulphation, and sulphonation products together with hydrocarbons, sulphur compounds, and tarry bodies present in physical solution (cf Birch and Norris [15, 1926]) No very exact analysis is possible, but by dilution with chloroform or some similar solvent, it is possible to get an approximate estimate of the free and partly combined acid Using such a method, W H Thomas (private communication [141]) examined acid sludge from the various stages of an experimental continuous counter-current plant of the Holley-Mott type refining a vapour-phase cracked material and found that the free acid content remained surprisingly constant at 30–32% in each stage The acid/water ratio also tended to remain constant at approximately 83–6% It would appear probable from Thomas's results that some form of equilibrium similar to that suggested by Damiens [40, 1922, 1923] for the ethylene-sulphuric acid system also exists in acid sludge between the acid, dialkyl sulphates, and alkyl sulphuric acids

Acid sludge is in fact an excellent diluent Consisting as it does largely of non-hydroxylic substances, it reduces the free acid concentration without materially changing its action It is not essential that the sludge should be derived from the product being treated, for 'spent' sludge obtained in the treatment of other light distillates is frequently equally effective Thus sludge from the treatment (usually with fuming acid) of kerosine or special naphtha cuts can be satisfactorily employed, although as such sludges will contain both sulphur compounds and hydrocarbons in solution these will tend to pass into the cracked distillate, so affecting its sulphur content, octane rating and dry-point The last, and to a large extent the former, can be rectified in the redistillation which follows Whether it is necessary or not to add any fresh acid to such spent sludges depends upon its free acid content Usually this is high enough without fresh addition The substances, e g sulphur bodies and hydrocarbons held in physical solution in acid tar should be in equilibrium with those present in the hydrocarbon layer itself provided that contact has been maintained sufficiently long

The actual quantity of acid employed varies very considerably with the cracking-stock and the degree of refining required The extremely heavy treatments used in the early days of cracking to-day seem impossible, and it is not surprising that losses were so high, indeed it is surprising that any unsaturated material remained In spite of the large amounts of sludge present in continuous counter-current plants, particularly in the Holley-Mott type, the actual acid consumption is very low, amounting to 0 2 to 0 5% of 96% acid

Desulphurization of cracked distillates cannot be so effectively accomplished as with straight material, and the employment of the relatively low concentrations of acid favoured to-day has a definitely adverse effect upon the selective solvent tendencies for these compounds Certainly attempts by the author to desulphurize cracked distillates to a low sulphur figure proved unsuccessful

The remaining factors influencing acid treatment do not appear to have received very much consideration Certainly little attention has been paid to temperature, although Halloran [63, 1933] has described the treatment of cracked distillates at comparatively low temperatures He points out that under normal treating conditions, temperature rises as high as 154 to 166° F occur which cause heavy losses through excessive reaction By operating at 20° F Halloran claims (*a*) an increased yield (about 39%) of finished product with lower treating losses, (*b*) lower acid consumption—about 50%, (*c*) decreased caustic soda consumption in subsequent neutralizing wash, (*d*) the sludge is more easily recovered, being cleaner, and (*e*) the chemical consumption for sweetening is less At the temperature employed the operation proceeds so smoothly that Halloran recommends the use of 98% acid In spite of the advantages claimed for it, the process does not appear to have found general favour probably owing to the special plant required

Reduction in the time of contact has also been advocated in order to reduce unnecessary polymerization while at the same time giving a satisfactory product The operation is carried out by feeding the distillate and acid continuously into some form of mixer such as a centrifugal pump and then immediately separating the acid in a centrifuge In this way the time of contact is reduced to a few seconds, and it is stated to give very satisfactory results After a clay treatment, a finished product is obtained, which it is claimed satisfies the necessary requirements for stability, and so on This method of operation does not appear to have received much consideration Instead of reducing contact time to such extremes, it is frequently quite considerably prolonged—as in the Holley-Mott treating plant—but under such conditions that reaction only takes place extremely slowly

The Effect of Acid Treatment upon the Distillate.

In the early days of acid treatment, the increase in gravity and change in boiling-range, which invariably occurred, was assumed to be due to loss of volatile matter Later, Brooks and Humphrey showed that such losses were not of sufficient magnitude to account for these changes, which were actually due to polymerization

While a small amount of the polymerization products remain in the acid layer, by far the greater part passes back into the hydrocarbon layer An examination of the physical properties of the hydrocarbons and the derived polymers given in the following table will show the large change which takes place in these properties on polymerization It is very obvious that changes of this nature occurring in a cracked distillate are bound to make themselves noticed in the final product

The shift in boiling-range which must take place when olefines, themselves boiling over a range as wide as that embraced by a normal cracked distillate, are polymerized results in a considerable part of the treated material falling well outside the range of the original material In practice the necessary correction is obtained by redistillation, although the cutting of the raw distillate at a temperature sufficiently low to bring the final product within the desired boiling-range after treatment has been tried As, however, during rerunning objectionable compounds, i e dialkyl sulphates, gum, &c , are also removed, it is usual, if distillation is omitted, to employ an adsorptive earth for a finishing treatment It is doubtful whether this method of operation is very successful as acid followed by rerunning probably gives a somewhat higher yield of finished product

From the table on p 1754 of boiling-points quoted by Egloff [48, 1934] it can be seen that although dimerides resulting from the polymerization of olefines containing more than 5 or 6 carbon atoms (or trimerides from those containing more than 4) will tend to fall outside the range

Properties of Hydrocarbons and Derived Polymers

Hydrocarbon	*Physical Properties*		
	Monomeride	*Dimeride*	*Trimeride*
*iso*Butene[*]	6 8	101–4 d_4^{20}0 720	178 5–179 5 d_4^{20} 0 760
*iso*Propylethylene[†]	20 d_4^{15} 0 6320	153–8	
Trimethylethylene[‡]	38 4 d_4^{15} 0 6671	154–6 d_4^{20} 0 7715	245–8 d^0 0 8139
2-Methylpentene-2[§]	65–7 d^{19} 0 687	193–7 d^{19} 0 786	
2-Methylpentene-3[¶]	69 5–71 d^{19} 698	196–9 d^{19} 0 798	
*iso*Heptene-1[¶]	85–86 d_{15}^{15} 0 716	220–4 d_{15}^{15} 0 7933	
2-Ethylpentene-2[¶]	97–8	210–20 sp gr 0 793	
Tetramethylethylene[¶]	73–4 d_{20}^{20} 0 7075	175–80 d_{20}^{20} 0 7750	
Octene-1[¶]	122–4 sp gr 0 724	195–230	
*iso*Octene-1[¶]	111–12 d_4^{20} 0 7125	112–14/16 mm sp gr 0 798	
2-Methylundecene-2[¶]	210-211 5/752 mm d_4^{20} 0 759	230–4/28 mm sp gr 0 814	
1-Methyl-Δ^1-*cylo*hexene[¶]	105-6 d_{20}^{20} 0 820	255–60 d_4^{20} 0 906	
Petroleum hexene mixture[¶]	55–63 sp gr 0 7045	190–200 sp gr 0 784	Higher Over 200 sp gr 0 836

[*] Lebedev and Koblianski [95, 1930]

[†] Norris and Joubert [122, 1927]

[‡] Norris and Reuter [123, 1927]

[§] Jawien [78, 1879]

[¶] Brooks and Humphrey [30, 1918]

of the finished gasoline, a considerable number of polymers will still be included (This is of course a very approximate generalization for the more branched olefines give polymerides boiling over a range considerably lower than those derived from the normal isomers, e g *iso*butene gives a dimeride boiling-point 101 to 104° C and a trimeride boiling-point 175 to 180° C) Cutting the acid-treated material to the original final boiling-point will therefore give a product not only higher in gravity but with a slightly different distillation curve indicating a gain in higher boiling constituents at the expense of the lower The magnitude of these changes will naturally be determined by the extent to which polymerization has proceeded, so that, if this could be entirely confined to the conjugated diolefines usually present only in small amounts, it would probably be hardly noticeable Such changes in gravity and volatility are, however, readily remedied when desired by slight modification of distillation conditions or the addition of butane A very much more important point is the change in octane rating which the polymerization involves, for to-day gasolines are sold, other things being equal, on their anti-detonating qualities

		b-p °*C*
Hexene	Dimer of propylene	68 3
Octene	Dimer of butene	123 9
Decene	Dimer of pentene	161 7
Dodecene	Dimer of hexene	213 9

The knock-rating of a cracked distillate can be affected in several ways by the acid treatment (*a*) The aromatic hydrocarbon content may be reduced by sulphonation or physical solution in the acid sludge (*b*) Conjugated diolefines, both aliphatic and cyclic, are converted into tars (*c*) Olefines are polymerized They may also be isomerized, form condensation products with aromatic hydrocarbons, or become sulphated Conjugated diolefines normally possess high octane ratings

The extent to which these reactions occur will naturally be determined by the conditions of treatment, but *in* every case the tendency will be to bring about a fall in the octane rating, this is, however, under normal conditions when the polymerization of olefines is reduced to a minimum, largely recovered on redistillation

Ordinarily the removal of aromatic hydrocarbons is so slight that any resulting drop in octane rating is negligible The destruction of the conjugated olefines with their high octane blending values would at first appear a serious loss, but apart from the fact that their removal is very much an essential part of the treatment, the amounts in which they are present, even in a vapour-phase cracked distillate, appear to be so small that it is doubtful whether their removal causes more than a slight fall

The main cause of the drop in octane rating is undoubtedly due to polymerization of olefines, this may act in several ways to reduce the anti-detonating quality of the product For example, the polymerides generally possess a lower octane rating than the parent hydrocarbon from which they are derived Should they possess relatively high octane numbers they may still be left in the residue on account of their high boiling-points, as the saturated hydrocarbons are for most practical purposes unaffected by the acid under the conditions employed this will result in an increase in the saturated at the expense of the unsaturated hydrocarbon content

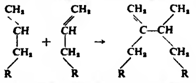
To what extent the more reactive olefines are associated with the diolefines in being responsible for gum-formation is uncertain (cf Cassar [37, 1931]) It is of course well known that such olefines as styrene readily polymerize and would therefore be removed on acid treatment with the conjugated diolefines, but whether many such abnormally reactive olefines are present in normal cracked distillates is doubtful Judging from the relatively small loss claimed for the Lachman process using zinc chloride in producing a stable gasoline, it would appear that the proportion of gum-forming hydrocarbons present is small However, in ordinary acid treatment it is not possible to limit the action of the acid solely to the undesirable constituents and some of the more valuable hydrocarbons must become polymerized We have seen that as a general rule the higher olefines are more resistant to acid polymerization than the lower members As these, excepting the more highly branched heavier olefines, possess the higher octane ratings, it follows that the very olefines it is desirable to conserve are those most susceptible to polymerization

As mentioned above, comparatively little is known of the polymerization products of even the simplest olefines In general, they appear to be extremely complex mixtures containing saturated as well as unsaturated components, the latter, if Ormandy and Craven's conclusions are correct, not being limited to mono-olefines, but containing also more highly unsaturated bodies The anti-knock value of such a mixture is generally very much below that of the parent olefine, particularly when paraffins occur in the products Polymerization products of this type appear to be formed from the lower normal olefines which only yield polymers under rather drastic conditions, i e high acid concentrations, *cyclo*hexene and its derivatives behave similarly and also give a mixture of saturated and unsaturated products Under the less drastic conditions required by the more easily polymerized olefines, deep-seated reactions probably do not take place—at least not to any appreciable extent—and the polymers consist entirely of mono-olefines

What is likely to be the result on the octane rating of the conversion of low-boiling *iso*-olefines into comparatively high boiling polymers? Obviously this is entirely determined by the structure of the latter

While it is not in the purview of the present article to discuss the relationship between anti-detonating properties and the constitution of hydrocarbons, it may be stated as a general rule that the octane rating is determined by the length of the longest saturated chain The larger the chain the lower the rating and vice versa Anything therefore which affects the chain, such as rearrangement, alteration in position of the double bond, or ring formation must influence the anti-knock value

Although at present there seems no reason why all possible combinations should not take place during polymerization, actually certain definite laws appear to exist So far, however, no rules have been formulated to fit all the facts at present available While heat and drastic acid polymerization conditions lead to deep-seated changes involving ring and paraffin formation, mild acid polymerization normally results in branched-chain formation, for example,



(cf Drake and Collaborators [86, 1934, 45, 1935], also

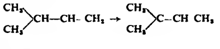
Ipatiev and others [71, 1935, 74, 1935] on catalytic polymerization with phosphoric acid.) Whether the new hydrocarbon has a high or low octane number will be determined by the length of its carbon chain and the groups attached to it. Hydrocarbons of this type derived from the lower olefines, i.e. propylene and butylene, have comparatively high octane ratings falling off rapidly with increasing length of the chain in the group R.

The polymerides of *iso*butene furnish good examples of compact hydrocarbons which in consequence have excellent anti-knock values. It is particularly interesting to note that in spite of being a mixture of dodecenes, tri-*iso*butene has practically the same octane rating as di-*iso*butene, a mixture of octenes. So valuable in fact, are 'di-*iso*butene' and 'tri-*iso*butene' on account of these qualities that they are now being produced technically from cracking gases rich in *iso*butene by acid polymerization for use alone or after hydrogenation in aviation gasoline blends. Diamylene, the dimeride of trimethylethylene or *unsym*-methylethylethylene is also valuable, for although it possesses a comparatively low octane rating when neat, it has a high-blending value. The octane ratings of these polymerides are given below, trimethylethylene (the mixture of this hydrocarbon and *unsym*-methylethylethylene obtained when dimethylethyl carbinol is dehydrated) being included for comparison with diamylene.

Hydrocarbon	Octane Rating C.F.R. Motor method O.N.
Di-*iso*butene	88.0
Tri-*iso*butene	86.6
Trimethylethylene	84.1
Diamylene, b.-p. 155–60° C	75.5

While the conversion of trimethylethylene into diamylene results in a considerable fall in the octane rating for the neat polymer, in blends this drop is much less marked. In fact it has been observed that di-*cyclo*pentadiene has a higher blending value than the parent hydrocarbon *cyclo*pentadiene, in view of the extreme vigour, however, with which the latter reacts with acid to form tars and resins, the formation of di-*cyclo*pentadiene by acid polymerization does not appear likely.

The extent to which isomerization and condensation occur during acid treatment is unknown. Isomerization of olefines may be expected to have a beneficial effect upon the octane rating because of the tendency to produce a more stable form which is generally one having a shorter saturated carbon chain. Thus the isomerization of *iso*-propylethylene to trimethylethylene observed by Norris and Joubert [106, 1927] would result in an improvement in anti-knock value.



$$(CH_3)_2>CH—CH-CH_2 \rightarrow (CH_3)_2>C-CH\,CH_3$$

Sulphuric Esters.

After acid treatment it is usual to allow the suspended sludge to settle before further treatment. Since the amount which normally separates is quite considerable, it is desirable to allow sufficient time for this operation, otherwise, during the next stage of the treatment, which consists in water-washing, an appreciable quantity of undesirable material is thrown out of the acid by dilution and passes back into the hydrocarbon layer. The function of the water wash is to remove any free acid together with other water-soluble compounds, thereby reducing the soda consumption in the subsequent soda wash. The latter serves not only to remove free acid left behind by the water but sulphur dioxide and alkyl sulphates as well. The last, while normally readily hydrolysed, are very resistant to hydrolysis when in petroleum solution owing to the almost negligible mutual solubilities of the aqueous and hydrocarbon layers. Contact is thus poor and hydrolysis takes place extremely slowly. A similar difficulty is experienced in the removal of the acid bodies formed in hypochlorite treatment (*vide supra*), for the same reason. Although the actual concentration of dialkyl sulphates in the acid-treated material is low, owing to the distribution between acid sludge and petroleum being almost entirely on the side of the former, a sufficient amount, probably of the higher compounds, to prove troublesome does remain. This, during the rerunning, either decomposes *per se*, or is hydrolysed (when steam is present), the products including sulphur dioxide and sulphuric acid, both of which are extremely corrosive under the conditions normally obtaining in a redistillation unit. To overcome this corrosion, it is the practice of many refiners to feed caustic soda solution into the plant in sufficient amount to ensure that there is no free acid present while in at least one refinery a solution of soap and soda ash was added as reflux to the column. The inorganic salts formed remain suspended after the evaporation of the water and were withdrawn with the bottoms, from which they could readily be removed by settling.

The dialkyl sulphate content of acid-treated distillates is influenced to a considerable extent by the conditions obtaining during the acid treatment. Thus Halloran [63, 1933] claims that as a result of cold treatment a considerable economy is effected in soda consumption during the following alkali wash as well as in the chemicals required for the final sweetening. A study of the factors influencing sulphur dioxide formation during rerunning has shown that it is desirable to acid-treat at as low a temperature as possible and with the lowest concentration of acid necessary to give a satisfactory product. To reduce decomposition as much as possible, distillation should be carried out under low temperature conditions. Below 275° F sulphur dioxide formation was found to be slight but between 320 and 370° F it rises to a peak while decomposition is virtually complete at 450° F.

The use of clay or other adsorbent earths to remove gumming products, dialkyl sulphates and other acid bodies in place of rerunning has been recommended, but to what extent it is in use is not known. The finished product is claimed to be entirely satisfactory.

Ipatiev recommends treatment with phosphoric acid to destroy dialkyl sulphates. After rerunning, the distillate invariably requires a final treatment. For gasolines derived from practically sulphur-free crudes this may merely be confined to a small alkali wash or even omitted, but most distillates, even if doctor sweet before rerunning, require a slight sweetening treatment to finish. The use of plumbite after acid and before redistillation has been advocated, but as sulphur bodies, particularly disulphides, tend to decompose under the influence of heat to give traces of hydrogen sulphide and mercaptans, it is necessary to repeat the sweetening treatment after the distillation. While plumbite is generally used for the final treatment, hypochlorite has been shown to give equally satisfactory results provided it is properly applied and controlled. Hypochlorite treatment must of course be completed with a thorough alkali wash.

VII. THE ZINC CHLORIDE (LACHMAN) PROCESS

The refining action of certain metallic halides, in particular those of aluminium and zinc, upon cracked distillates has been known for a considerable time but the disadvantages attached to their employment on a large scale has, in the past, outweighed the advantages. Sulphuric acid is so easy to handle, cheap and effective, that it is a formidable rival for any other refining agent which must possess very definite advantages to displace it. When, however, several years ago interest in high temperature cracking was revived, it was at first thought that sulphuric acid was too drastic for the comparatively highly unsaturated products obtained and search was made for other less drastic materials. Among other compounds zinc chloride was tried and gave excellent results, the final product being colour and gum stable. Treatment, which was carried out in the vapour phase, consisted in passing the vaporized distillate over zinc chloride supported on a carrier at approximately 200° C. Under these conditions the highly reactive hydrocarbons present polymerized and left the bottom of the treater as a thick viscous brown liquid which readily oxidized in air to a varnish-like substance. Sweetening and some desulphurization occurred in the early part of life of the catalyst, but this ceased some considerable time before the effective polymerizing action of the zinc chloride ended. Investigation showed that the formation of a liquid film on the surface of the catalyst was essential, and attempts to remove the polymer as formed resulted in failure to refine. Little of the chemistry of the process was understood, but it was found that some zinc chloride, oxychloride, and sulphide were present in the polymer. The octane rating of the product was practically identical with that of the raw material. This zinc chloride process never, however, reached full-scale operation, it was abandoned in favour of acid which, during the development of the zinc chloride process, had been shown to give satisfactory results when the conditions of treatment were modified. One factor which weighed heavily in favour of acid was the necessity of handling a solid reagent in the zinc chloride process which is always avoided in the Refinery as much as possible.

Lachman described his process in 1931. It possesses the advantage over the earlier process in that the zinc chloride is handled in solution, thus avoiding the serious drawback of conveying a solid reagent.

Lachman states [93, 1931, 94, 1935] that any metallic salts in solution such as the halides, sulphates or nitrates of copper, cadmium, mercury, iron, zinc, and so on can be employed. The treatment is carried out in the vapour phase by passing the vapour of the crude distillate under pressure through the solution at 130 to 210° C. The product is water-white, colour and gum stable, and practically unchanged in octane rating.

According to Lachman, the optimum treating conditions vary with the feed stock. Normally treatment is carried out at 170 to 175° C., a solution containing 70 to 85% zinc chloride by weight being employed. As it is desirable to keep the concentration as nearly constant as possible, it is necessary to provide for the water vapour carried away with the hydrocarbons. This can be done by injecting steam or very conveniently by feeding zinc chloride into the plant at a slightly lower concentration than that required for optimum operating conditions and allowing concentration to take place *in situ*. For effective treatment intimate mixing is required and this can be effected by packing the treater or using baffles. The time of contact necessary is stated to be 2 to 12 sec.

Very little is known of the chemistry involved. The action of the zinc chloride appears to be mainly catalytic, although it definitely reacts with sulphur compounds and pyridine bases when present. As the octane rating is little affected it must be assumed that most of the hydrocarbons emerge unaffected, only the highly reactive gum-forming constituents being polymerized to high-boiling products. It is stated that the amount of polymerization which takes place is small, the polymers are removed with the bottoms in the fractionation which follows.

Reduction in the sulphur content varies with the nature of the sulphur compounds present. The average reduction is from 30 to 40% under normal operating conditions, the treated material is still sour, but the mercaptan content is considerably diminished. The reduction in mercaptan content appears, other things being equal, to be a function of time, for by considerably increasing the time of contact it is possible to obtain sweet distillates. The reaction involved appears to be

$$2RSH + ZnCl_2 \rightarrow R_2S + ZnS + 2HCl$$

although there are indications that other reactions take place in which the sulphur bodies are converted into high-boiling derivatives (disulphides?). Desulphurization then results from these being left as a residue in the succeeding fractionation. Hydrogen sulphide, when present, reacts with the zinc chloride to form the sulphide, the reaction being reversible

$$ZnCl_2 + H_2S \rightleftharpoons ZnS + 2HCl$$

The formation of zinc sulphide results in a loss of zinc chloride, another factor contributing being hydrolysis to the oxychloride

$$ZnCl_2 + H_2O \rightleftharpoons Zn(OH)Cl + HCl$$

This reaction is also reversible. Overall losses are, however, stated to be small (0.3 to 1.5 lb $ZnCl_2$ per bbl treated) and the zinc can be recovered as sulphide or oxychloride which readily dissolve in dilute hydrochloric acid to regenerate the chloride.

When pyridine bases are present, some part but not all reacts to form double compounds. It is to be supposed that under the conditions employed the latter would tend to break down and regenerate the original components which would eventually result in a state of equilibrium being reached. As, however, the zinc chloride solution is drawn off continuously some removal of these bases occurs.

Lachman considers that the 'impurities' responsible for gum formation and colour instability cannot exceed 1% and that they are in all likelihood aldehydes or other oxygen-containing substances on which zinc chloride is well known to have a condensing action. He considers that this theory is supported by the fact that the higher fractions from the treated material contain small amounts of highly coloured, fluorescent substances. Whether he is correct or whether these substances are highly condensed hydrocarbons—which are also known to be fluorescent—must remain for the present a matter of conjecture.

As mentioned above, the zinc chloride sludge is continuously withdrawn from the bottom of the treater, after being diluted to give a 50 to 60% solution, it is settled and the small amount of heavy oil which collects on the surface skimmed off. The residue is passed through a filter-press to remove the oxychloride and sulphide present in suspension and the filtrate returned to process by way of the make-up tank It is questionable whether the recovery of the oxychloride and sulphide in the cake is profitable excepting in very large plants, the bulk of the cake is composed of solid and semi-solid organic matter and is of doubtful value

Corrosion of the plant is overcome by lining with suitable material such as brick To remove traces of hydrogen chloride, the vapours leaving the plant pass into a tower packed with limestone, the hydrogen chloride forms calcium chloride which is drawn from the bottom of the tower continuously From this tower the vapours pass into a column where the heavy ends and polymers are removed as bottoms Ammonia is injected during the final condensation to safeguard against traces of hydrogen chloride which may have escaped the limestone

So far as is known the zinc chloride process operates successfully on all types of gasoline The treated material leaving the plant is entirely free from chlorine but requires sweetening Unlike many gasolines, the zinc chloride treated material does not change colour or develop gum during plumbite treatment but remains water-white

Lachman claims that the process can also be successfully applied to kerosines and that after treatment they give a good burning test and possess a good odour

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THE CHEMISTRY OF REFINING PROCESSES (LUBRICATING OIL)

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THE available knowledge concerning the chemical constitution of crude petroleums cannot be claimed to be extensive, and though the chemistry of the lighter low-boiling constituents of straight-run and cracked gasolines is now fairly well understood, the chemistry of the higher boiling hydrocarbons and compounds present in the fractions of crude oil used for lubricating oil manufacture is almost completely unknown This side of the subject is, however, becoming increasingly prominent in present-day research, as witness, for example, the work of the American Petroleum Institute [24, 1935]

The properties which characterize a good lubricating oil have been summarized many times, the most obvious characteristic being, of course, viscosity In addition are included lubricating value or oiliness which enables the lubricating oil film to withstand high bearing loads at low rates of shear, good stability against oxidation and sludging in general use, minimum variation of viscosity with temperature change, ability to flow freely at low-operating temperatures, and non-corrosiveness to bearing metals

While the development of the internal-combustion engine has increased the demand for lubricating oils, it has also been the chief factor in raising the general standard of quality in petroleum lubricants The continual striving after greater mechanical efficiency on the part of the automobile manufacturer has resulted in increased running speeds and greater bearing pressures, and these factors, combined with the extreme temperature conditions under which modern engines, such as aircraft machines, may be compelled to operate, are gradually forcing the lubricating oil industry to produce oils which will retain their original properties under increasingly drastic conditions of service

Viscosity considerations alone limit the use of materials for lubricating oil manufacture to those fractions of crude oil boiling above about 350° C at atmospheric pressure, and for the production of the more viscous lubricants high-vacuum distillation is necessary to avoid decomposition and destruction of the oil

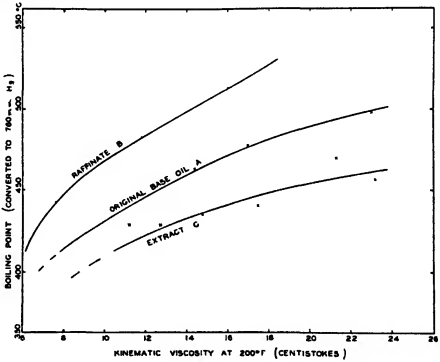

FIG 1

As a general rule, the boiling-point of a petroleum fraction increases with the viscosity of the fraction, but the boiling-point-viscosity relationship also depends on the type of crude being distilled For example, a fraction from a Pennsylvanian crude will boil at a higher temperature than the fraction of the same viscosity from a Californian crude under similar conditions of distillation This variation of boiling-point with chemical nature is clearly illustrated in Fig 1, which gives the approximate boiling-point-viscosity curves for a lubricating base oil (*A*), and for the corresponding refined oil (*B*), and reject oil (*C*) obtained therefrom by solvent extraction

Constituents of the Crude Lubricating Oil Base

While none of the individual chemical compounds present in the crude lubricating oil base has been isolated, the principal compounds present can be classified in fairly well-defined groups such as the following

1 Crystalline wax
2 Paraffinic, naphthenic, aromatic, and unsaturated hydrocarbons
3 Asphalts and resins
4 Sulphur compounds
5 Oxygen compounds

Any system of classification must, in the nature of things, be approximate, since no hard-and-fast distinctions can be made between many of the groups, and certain compounds may be classified with equal justification in more than one category Nevertheless, such a system has advantages in clarifying discussion, as the following comments illustrate

1. Crystalline Wax.

Crystalline wax is probably the most stable constituent of lubricating oils, and owing to the ease with which the higher melting-point waxes can be separated and purified, its constitution is fairly well known The petroleum waxes are saturated hydrocarbons of the paraffin series C_nH_{2n+2}, where the values of *n* probably lie between 21 and 57

Clark and Smith [7, 1931], using a series of carefully prepared and purified waxes, examined their crystal structure by the X-ray diffraction method and concluded that even the most carefully prepared samples were impure, but that paraffin wax itself is composed of normal and *iso*-paraffins to the extent of about 65 and 25% respectively, with the bulk of the crystalline waxes consisting of the five hydrocarbons of 29, 31, 34, 38, and 42 carbon atoms respectively

Crystalline wax must be regarded as an objectionable constituent of lubricating oils when present in more than small amounts because of its obstruction to free flow of the oil at low temperatures In automobile and high-speed Diesel lubrication, the presence of crystalline wax, if not causing obstruction in the oil-feed lines themselves, would quickly lead to clogging of the oil-feed pump-filters, with consequent failure of the lubrication system and irreparable damage to the machine On the other hand, the presence of small amounts of wax in solution is definitely beneficial, and the object of the refining processes should be to retain the maximum amount of wax consistent with pour-point and set-point specifications

Davis and Blackwood [9, 1931] have studied the effect of dissolved wax on the quality of finished lubricating oils, and conclude that in order to obtain the advantages of low pour-point oils by dewaxing, i e pumpability and quick distribution of the oil throughout the lubrication system when starting at low temperatures, it is necessary to degrade the oil to some extent in most of its other characteristics The effect of small quantities of dissolved wax in lubricating oils is in some respects greater than would be expected from the law of mixtures, despite the fact that wax itself possesses exceptional values for most of the tests usually applied to lubricating oils, and the removal of the dissolved wax is shown to affect the oil adversely in that it will

(1) Decrease the viscosity index of the oil, with resultant increased viscosity and difficulty in starting at low temperatures
(2) Increase the carbon-forming tendencies of the oil
(3) Decrease the oxidation stability, with consequent increased sludging tendencies of the oil under service conditions
(4) Decrease the lubricating characteristics of the oil as indicated by the lessened load-carrying ability and 'oiliness' values

When the quantity of wax present in an oil exceeds the limit of solubility for the wax at any given temperature, the wax will crystallize out of solution, and the temperature at which this crystallization commences is known as the 'cloud-point' The temperature at which the oil ceases to flow when subjected to slight shearing force is called the 'setting-point' The 'pour-point' of the oil is usually some few degrees below the cloud-point, but above the setting-point, and in the case of oils containing dissolved wax, represents the temperature at which the wax crystals have grown to a sufficient size to form an interlacing network throughout the oil, which, partly on account of its greater viscosity at low temperatures, is retained within the network in much the same way as water is held by a sponge

In the lubricating oil fractions as taken from the crude, the wax is associated with more or less asphaltic and resinous matter which prevents the formation of large crystals and hinders the formation of this interlacing network Under the normal conditions of refining, however, these inhibiting bodies are largely eliminated, owing to the ease with which they are attacked by sulphuric acid, or selectively adsorbed by active earths, or dissolved by solvents The wax, on the other hand, is unaffected under such conditions, and the general result of refining waxy oils is to increase the pour-point due to the formation of larger wax crystals, although the point of incipient wax crystallization (i e cloud-point) is not appreciably affected If, however, the oil contains no wax originally, or has been thoroughly dewaxed before treatment with acid, &c , the effect of the refining treatment is to reduce the pour-point since in this case the pour-point is a viscosity effect only, and the refining has resulted in a general lowering of viscosity by the preferential removal of the more viscous asphaltic and resinous constituents

2 Paraffinic, Naphthenic, Aromatic, and Unsaturated Hydrocarbons.

Apart from the crystalline waxes which have been definitely established as normal and *iso*-paraffin hydrocarbons, the constitution of the other constituents of the lubricating oil distillates is a matter of uncertainty In the case of the lighter petroleum hydrocarbons, the presence of each type of the above compounds has been definitely established, but it is probable that the hydrocarbon constituents of the lubricating fractions are not in the main pure representatives of any of these types, but consist of complex molecules partly paraffinic and partly naphthenic or aromatic in structure

Paraffinic hydrocarbons may be defined as straight- or branched-chain saturated hydrocarbons of the general formula C_nH_{2n+2}, ring structure being absent The paraffin waxes are members of this type of hydrocarbon

Naphthenic hydrocarbons are essentially ring structures of the general formula C_nH_{2n-2a}, where a represents the number of closed rings in the molecule The structure is saturated in that it contains no double bonds and the term is usually taken to include molecules containing paraffinic chains attached to naphthene rings

Aromatic Hydrocarbons These are molecular structures having one or more benzene, naphthalene, anthracene, or similar nuclei in the molecule, attached perhaps to paraffinic side chains or naphthene rings, or both

Numerous empirical analyses of lubricating oil fractions have been made, in particular by Mabery [19, 1902, 1906], who found that the high-boiling fractions of Pennsylvanian, Californian, and Canadian lubricating oils had empirical formulae ranging from C_nH_{2n} to about C_nH_{2n-8}, with the carbon-hydrogen ratio increasing with rise in boiling-point

In a further study, Mabery [20, 1923, 1926] has examined the fractions obtained by solvent fractionation of the heavier constituents of crude oil residues, and concludes that the pure naphthene series C_nH_{2n}, claimed to be the major constituent of Russian lubricants, is not present in the heavier fractions of American crudes, but that the first series of lubricating viscosity is C_nH_{2n-2}, which forms a large proportion of the lighter lubricants The series C_nH_{2n-4} is most frequently present in light and medium lubricating oils of good quality, though the general lubricants, especially of the heavier grades, are composed mainly of the series C_nH_{2n-8}

The series C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}, and C_nH_{2n-18} also possess some lubricating properties but in diminishing order as they approach the asphaltic hydrocarbons which include the series C_nH_{2n-20} and others less rich in hydrogen

Smith [26, 1930] has made an extensive examination of the lubricating oil fractions of West Virginian crude, and has found empirical formulae ranging from C_nH_{2n-2} to C_nH_{2n-8}, with molecular weights of 300 to 900

The presence of unsaturated olefinic hydrocarbons in the heavier ends of natural petroleum crude oil is open to question Unsaturation is definitely established in the lubricating oil fractions, but must be largely attributed to aromatic ring structures, though with the slight cracking which occurs in practically all commercial types of distillation equipment producing high-boiling viscous lubricating oil cuts, the presence of olefinic material is probable

Vlugter, Waterman, and Van Westen [27, 1935] have advanced the knowledge of the constitution of lubricating oils considerably by correlating the change in physical properties with complete hydrogenation of the oil By applying their method of analysis, the percentage of aromatic rings, naphthenic rings, and paraffinic chains or side chains can be determined directly from the physical characteristics of the oil, and these authors find, for example, in the case of a Pennsylvanian oil of molecular weight 512

Aromatic rings	8%
Naphthenic rings	15%
Paraffinic side chains	77%

as contrasted with a sample of naphthenic base oil of molecular weight 349

Aromatic rings	32%
Naphthenic rings	29%
Paraffinic side chains	39%

This evidence, combined with the fact illustrated by Rossini [25, 1935], that even aromatic nuclei attached to paraffinic chains may possess high viscosity indices (c 100 V I) illustrates the complexity of the problems facing the study of lubricating oils and the looseness of such terms as 'paraffinic', applied to Pennsylvanian stocks, and 'naphthenic', applied to Californian stocks and extracts from solvent refining processes

3. Asphalts and Resins.

Asphalts and resins have been represented as oxidation products of heavier hydrocarbons, and it is a fact that the precipitable material present in petroleum hydrocarbon fractions is increased by oxidation, though it is doubtful if all the compounds designated as asphaltic and resinous contain oxygen

In a well-prepared distillate lubricating oil base the amount of asphalt is extremely small and decreases as the cut is more thoroughly fractionated from the pitch or heavy residue The resin content, on the other hand, may be quite large and, owing to the ease with which resinous and asphaltic bodies further oxidize under service conditions to form sludge and petroleum acids, both these constituents must be removed as completely as possible during the refining process

It is doubtful if asphaltic substances are volatile under any condition without decomposition, and certainly the presence of hard asphalt in the lubricating base oils produced in actual practice can be easily explained by entrainment during the vaporization process, or by cracking and subsequent oxidation of complex aromatic bodies in the fractionating column The fact that petroleum resins are volatile and also partition fairly readily between petroleum hydrocarbons and solvents generally, suggests that they are much nearer the true hydrocarbon stage than the asphaltic

Asphalt is precipitated almost quantitatively by concentrated sulphuric acid and is readily removed during the refining process, but the presence of resins can be detected in most lubricating oils even after fairly heavy acid treatments The petroleum resins are preferentially absorbed by the active earths and clays used in lubricating oil refining, and the absorption follows the usual Freundlich isotherm [14] However, as the general practice is to apply the clay in one addition (occasionally in two), or to percolate the oil through a stationary bed of clay, it is obvious that the resins cannot be completely removed by such methods

4. Sulphur Compounds

Sulphur compounds form a very high percentage of some lubricating oils, and while a high sulphur content is generally regarded with suspicion, there appears to be little need for apprehension in this respect if the oils are judged on their merits and not merely on the result of a quantitative estimation of sulphur without consideration of the chemical state in which this sulphur exists

There would appear to be several forms in which sulphur may be present in a lubricating oil, and of these free sulphur is probably the least desirable constituent of oils required to exhibit stability under fairly drastic conditions of temperature and oxidation, though its use in the cold as an extreme pressure lubricant dope for such requirements as cutting oil cannot be questioned

Birch and Norris [4, 1929] have demonstrated the existence of active sulphur compounds containing more than 1 sulphur atom to the molecule in light kerosene, and discuss the possibility of chain sulphur compounds, but it is doubtful if such bodies are present in highly refined lubricating oils produced from sulphurous stocks in view of their stability to copper, and it would seem probable that the more stable sulphur compounds contain only 1 atom per molecule, probably within a ring structure It follows from this assumption, however, that in the case of an oil with a mean molecular weight of 500 and with a sulphur content of 1%, the content of sulphur compounds must approximate to 15% by weight

5 Oxygen Bodies

Naphthenic acids constitute the greatest proportion of the oxygen-containing bodies present in the lubricating oil fractions of petroleum, and while they may be largely removed by the conventional acid and clay refining processes [13], recent refining practice shows an increasing tendency to remove these compounds during the distillation or redistillation stages, by injecting caustic soda into the oil-feed to the still, and removing the non-volatile soda soaps in a short, heavy residue or still bottoms

Lubricating oils should be freed as thoroughly as possible from naphthenic acids, which attack the metal of the bearing surfaces lubricated by the oil to form oil-soluble metallic soaps [6, 1918] Oil-soluble soda or lime soaps may be formed during the refining processes, and may cause the oil to become cloudy and to deposit a flocculent precipitate of soaps on exposure to moist or atmospheric conditions In general, the naphthenic acid soaps are stated to accelerate oxidation and sludging of the oils in service [18, 1933], and all precautions should be taken to avoid their formation

Chemistry of the Refining Processes

The refining processes employed for the manufacture of lubricating oils from a given crude oil depend firstly on the type of crude oil to be handled, and secondly on the market specifications to be met. Frequently numerous grades of lubricating oil of various viscosities are prepared from the same stock, and with the refining processes available to-day, nearly all grades from the lowest to the highest can be prepared from any type of crude oil.

The preparation of a range of lubricating oils from any crude may be considered under the following headings:

1. Selection and preparation of the crude fraction (or fractions) to form the lubricating oil base stock.
2. Dewaxing of the base stock.
3. Finishing treatments.

The third heading is capable of further subdivision according to refinery programmes, as, for example:

(*a*) Solvent refining.
(*b*) Redistillation.
(*c*) Acid and/or clay treatments.

1. Selection and Preparation of the Base Stocks

The lubricating oil base stock is usually a fairly wide-range, high-boiling fraction of crude including, as its lightest constituents, varying quantities of gas oil. The end-point of the fraction is limited in most cases by the amount of asphaltic material in the crude and the length of pitch residue required for bitumen markets, while the decision to handle the lubricating oil base stock in one or more fractions depends on the subsequent treatment and the quantity of wax present.

The older processes of pressing and cold settling or centrifuging for the removal of wax required the production of lubricating oil base stock in two cuts, but for the modern, more efficient dewaxing processes there appear to be definite advantages in dewaxing a single long cut. It may be necessary, however, owing to limitations imposed by distillation and/or dewaxing equipment, to reject a high viscosity slop cut contaminated with asphalt lying after the lubricating oil base-stock fraction and before the pitch residue, although this slop cut contains considerable quantities of useful high-viscosity lubricating oil.

In the case of paraffinic base crudes such as certain of the Pennsylvanian crudes which are practically asphalt-free, the lubricating oil base stock is itself a crude residue and includes all material boiling above about 320° C. at atmospheric pressure, and, of course, fractions of considerably higher boiling range than distillate base stocks can contain. This is usually reflected in high carbon residue values of Pennsylvanian residue Bright Stocks.

Until the application of the pipe-still and fractionating column to vacuum distillation, lubricating oil manufacture was limited to shell-still equipment operated under reduced pressure. Fractionation was practically non-existent, and the significance of rigid control of skin temperatures was not generally appreciated, with the result that flash-points and viscosities were low, owing to incomplete separation of light ends and also to cracking and destruction of the more viscous fractions. The loss of viscosity units due to inadvertent viscosity cracking by excessive skin temperatures in shell-still equipment may easily amount to over half the available yield of Bright Stock on the crude, and the difference in yields of high-viscosity lubricants may be very much greater between inefficient and efficient shell-still operation than between efficient shell stills and modern vacuum pipe still and column. The amount of cracking which takes place in the modern pipe-still and vacuum fractionation equipment is still appreciable and depends on the volume of material maintained at high temperatures (above about 350° C.) in the pitch well and lower trays and stripping sections of the tower.

In contrast to the production of crude lubricating oil base stocks by vacuum distillation, and neglecting considerations of costs, it is possible to handle asphaltic and mixed base crudes in a similar manner to Pennsylvanian crudes by first applying a de-asphalting process such as liquid propane to the reduced crude oils after topping off the spirits and white oil fractions. This has the advantage of giving the maximum yield of high-viscosity lubricants on crude, and the quality of the lubricating base oil so obtained will be higher than can be obtained by vacuum distillation in practice. This is due partly to the elimination of cracking, but mainly to the selective action of the propane, which removes, in addition to asphalt, hydrocarbons of medium and high viscosity but of low hydrogen-carbon ratio, and retains the very high-boiling paraffinic hydrocarbons normally lost in the pitch bottoms.

The relative yields and quality of the heavy lubricants obtained by the distillation and the de-asphalting processes are exemplified by a series of results for a mixed base crude oil given in Table I. It will be noted that the bitumen yield by the propane de-asphalting process was 9%, while the Bright Stock yield by the same process was about equal to that produced by the vacuum distillation to a 4% pitch residue. The quality of the propane-produced Bright Stock, however, is considerably better than the Bright Stocks produced by vacuum distillation and refined with the same amount of acid and clay.

TABLE I

Distillation versus Propane Treatment of a Mixed Base Residue Oil

	Vacuum flash distillation (*3 mm. Hg press. abs.*)		*Propane de-asphaltizing* (*700% liquid propane by vol. at 60° F.*)
Vol. % asphalt or bitumen residue on crude	10.5	4.3	9.0
Analyses of waxy lub. base			
Sp. gr. at 60° F.	0.895	0.908	0.899
Viscosity at 100° F. (centistokes)	43.3	65.1	66.7
Viscosity index	89	74	99
Coke number (Ramsbottom)	0.72	1.70	1.34
Pour-point (A.S.T.M.), ° F.	80	70	70
Analyses of refined bright stocks (Identical dewaxing and finishing treatments in each case.)			
Vol. % yield on crude	6.2	11.4	11.3
Viscosity at 200° F. (centistokes)	36.9	36.7	35.2
Viscosity index	48	49	67
Coke number (Ramsbottom)	1.90	2.43	2.05
Pour-point (A.S.T.M.), ° F.	10	15	10

2. Dewaxing of the Lubricating Base Stock.

The dewaxing of lubricating stock by the older process depends for its success on the removal of crystalline wax from the less viscous fractions by chilling and cold filtering ('Pressing') [3, 1923], while the viscous 'amorphous' fractions of the crude are dewaxed by dilution with naphtha of low specific gravity and either centrifuged as in the original Sharples [8, 1922] process, or cold settled, when the crystalline wax is allowed to settle by gravity from the chilled naphtha solution of the stock [3, 1923]

The newer processes all depend upon the use of solvents in which the wax is relatively insoluble at low temperatures typical processes depend on such solvents as the following

(*a*) Acetone-benzole [12, 1933]
(*b*) Liquid propane [2, 1933, 1, 1936, 28, 1934]
(*c*) The chlor-ethylenes and similar compounds [23, 1933, 25, 1935]

Each of these types of process has special advantages and disadvantages depending on the nature of the stock to be dewaxed, which render them particularly adapted to certain circumstances The acetone-benzole process, for example, gives efficient wax removal with small temperature differential between filtration temperature and pour-point of the dewaxed oil, but practically all the asphaltic and resinous impurities in the stock remain in solution and result in relatively high losses during the subsequent acid or solvent refining

The propane process, on the other hand, gives efficient dewaxing, but requires a large differential in temperature (about 30 F) between filtration temperature and pour-point of the filtrate owing to the greater solubility of the wax in liquid propane However, owing to its selective solvent action, all the asphaltic matter, and more or less of the resinous constituents depending on conditions, are precipitated and may be eliminated before chilling so that in addition to yielding very clean dewaxed oils of high quality (giving reduced losses on subsequent refining), it is possible to obtain a relatively clean wax by this process

The chlor-ethylene compounds permit efficient wax removal, and are associated with centrifugal as opposed to filtration processes The advantage of this type of solvent is a mechanical one in that the crystalline wax obtained on chilling is less dense than the oil-solvent mixture Thus the difficulties encountered in centrifugal processes operating with low-gravity naphtha as solvent, in which the wax is discharged from the periphery of the bowl of the centrifuge, are eliminated The chlor-ethylene compounds also have an added advantage in reduced fire risks

While the newer dewaxing processes may be applied to cuts of various length, there are definite advantages in dewaxing a single long cut if a range of wax-free lubricants of low pour-point is required to meet market specifications, since more efficient removal of wax is possible in the medium viscosity range of lubricants than can be achieved by the separate dewaxing of pressing and centrifuging cuts by the older processes In all cases where a solvent is used to reduce the viscosity of the liquid phase and to facilitate crystallization of wax on chilling, some soft wax is dissolved with the oil and passes into the filtrate Moreover, of the total wax present, the softest or lowest boiling waxes in the waxy distillate appear to be preferentially dissolved, with the result that on evaporating the solvent from the 'dewaxed oil' after removal of the crystalline wax by filtration or centrifuging, the lower boiling fractions of the oil show the highest wax-content as exhibited by pour-point Thus when dewaxing is carried out in two stages, the lightest fractions of the dewaxed heavy 'amorphous' fraction show a concentration of soft wax in the front ends, or medium viscosity range, which becomes especially marked after solvent refining

Mention should be made of the use of 'dopes' such as Paraflow [9, 1931], and material such as Voltolised oil [21, 1934] and Electrion oil [22, 1934] for lowering the pour-point of waxy oils The addition of these materials to the oil does not in any way prevent the formation of crystalline wax, nor modify the temperature at which crystallization of the wax commences The effect of these substances is attributed to preferential adsorption on the surface of the wax which prevents the growth of large crystals and the consequent formation of the interlacing crystal structure associated with waxy oils at their pour-point [29, 1933]

3. Finishing Treatments.

(*a*) **Solvent Refining** The increasing application of solvent refining to the production of lubricating oils can be attributed to the market demands for lubricants of increased stability in service, with improved viscosity index, and on the part of the manufacturer to the natural desire to produce such oils with greatest economy, i e maximum yield with minimum treatment cost and smallest production of useless by-products

Ferris, Birkhimer, and Hendersen [11, 1931] have made an extended study of solvents generally with a view to determining their relative selectivity, and numerous processes have been described in the literature which claim to fulfil all the manufacturers' requirements, but it is a difficult matter to assess the relative claims of the different processes which have seldom been tested under comparable conditions Moreover, it is obviously desirable that the process selected shall be fundamentally efficient, and not owe an apparent advantage to more efficient plant design It must be remembered that any process may, in a matter of a few years, be greatly surpassed by further development in plant or operating technique of competing processes at present handicapped by poorly designed equipment or unsatisfactory operating conditions

The application of triangular graphs to solvent refining problems has received considerable attention within the last few years [10, 1934, 16, 1933, 17, 1935], and allows an accurate and complete comparison of solvent efficiency to be made The effect of a selective solvent on a given stock may be completely represented by an equilibrium curve expressed in triangular co-ordinates, and by obtaining a series of such curves for the same oil stock, but using different solvents it is possible to determine in each case all the necessary design data for the construction of large-scale plant (with the exception of mixer efficiency and separation rates), together with amount of solvent and number of theoretically perfect stages and yield for any quality raffinate A series of such curves is given in Figs 2 and 3, from which the following general conclusions regarding solvent treatment may be easily deduced

(1) For any given solvent, the most naphthenic extracts are obtained by operating at the lowest practicable temperatures
(2) For any given solvent, the production of high-quality raffinates is favoured by operating at higher temperatures
(3) For any efficient solvent process, the theoretical yield of raffinate (of any definite quality) is determined solely by the quality of the extract produced, and hence the maximum yield of raffinate obtainable from a given starting stock will be given by that process which yields the most naphthenic extract
(4) The advantages of maintaining a temperature gradient throughout a counter-current system are

(*a*) reduction of the amount of solvent required, and/or

(*b*) reduction in the number of counter-current stages required to achieve a given separation into extract and raffinate

The effect of solvent refining is, as with acid refining, a loss of viscosity units which, as the series of curves, Fig 4, illustrates, increases progressively with increasing solvent treatment To counteract the reduced yield of viscosity units when producing improved lubricants, it is essential that an efficient solvent process be employed which will give high raffinate yields In addition, this loss of viscosity may be further offset by using a base stock made by distilling more deeply into the crude, though, as already explained, this will result in increased carbon residue figures

In general, the selectivity of solvents is greatest in the highest boiling fractions of the oil, but that the effect is fairly evenly distributed throughout the boiling range and is not preferentially confined to the fractions of lowest quality is illustrated by the set of curves, Fig 5, for a lubricating oil base from a South American crude in which the abnormal shape of the viscosity—viscosity index—curve persists even after heavy solvent extraction

(*b*) **Redistillation.** What has already been said concerning the loss of viscosity units by cracking during the primary distillation for production of the lubricating oil base cuts applies equally to the subsequent redistillation operations for finished grades

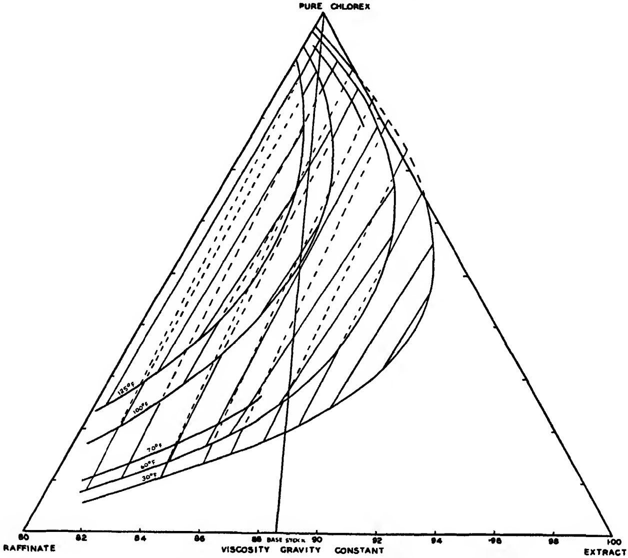

FIG 2 Equilibrium curves for chlorex and medium viscosity lubricating oil of mixed base origin

In many cases no additional treatment is required after the solvent process, and, generally speaking, the lighter lubricating fractions can be finished by high-temperature clay treatments alone, leaving only the heaviest fractions which require acid treatment The injection of soda to the still-feed gives distillates of reduced acidity and improved colour stability, and the present tendency is to re-run solvent-treated lubricating oils to very small residues with soda injection into the still-feed so that even the heavier lubricants are produced as distillates This has the advantage of enabling all the grades of lubricating oil to be refined to good colour stability and low carbon residue by clay alone

(*c*) **Finishing Treatments, Acid and/or Clay.** In discussing the acid and clay finishing treatment of lubricating oils, distinction is usually made between distillate oils and residues such as those obtained from paraffinic base crudes and used for the manufacture of cylinder stocks. The distinction does not, however, represent any marked change in characteristics in the oil, but is due rather to the greater percentage of impurities (resins, asphalt, &c.) present in the residual fractions. The lubricating oils requiring acid treatment are usually produced from asphaltic and mixed base crudes, though occasionally the residual oils left from the distillation of paraffinic crudes require acid treatment to remove small amounts of asphaltic material originating from the crude itself or from the effects of cracking during the distillation processes.

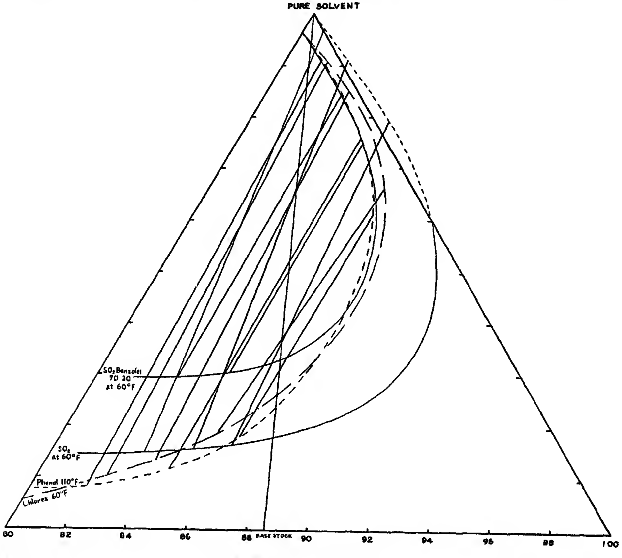

FIG. 3. Equilibrium curves for medium viscosity lubricating oil (mixed base origin) with various solvents

The amount of finishing treatment required to produce a finished lubricant will depend on the quality of the oil, and especially on the amount of aromatic and unsaturated material present. If the amount of undesirable constituents present is high, then the acid treatment necessary will be correspondingly heavy, and the oil losses as acid tar will be considerable. On the other hand, if the oil has been adequately solvent treated, the amount of aromatics will be small, and the finishing treatment will correspond to that required for paraffinic stocks of similar viscosity, the distillate fractions may consequently be refined by a light clay treatment only. It is worthy of note that the residue fractions of high viscosity (cylinder stocks) obtained by solvent treatment of long cuts from naphthenic or mixed base crudes are much more difficult to refine than the distillate fractions from the same solvent-treated long cut. The solvent-treated long cut may, in fact, be regarded as a synthetic base oil from a paraffinic crude. This is due to the imperfect fractionation obtainable, in the first place, between the heaviest fractions of the long cut and the asphaltic residue, which results in entrainment of appreciable amounts of asphaltic material in the original long cut or lubricating base oil.

While sulphuric acid will remove the unsaturated and aromatic constituents from lubricating oil cuts it does not compare favourably with the solvent processes for effecting large improvements in quality, and the present tendency is to confine its use to decolorizing and milder refining operations such as the production of medium-grade oils Sulphuric acid will remove asphaltic constituents completely, by solution (in the case of soft asphalt), and by coagulation or flocculation (in the case of hard asphalt) Gurwitsch [15] states two theories for the removal of asphalt by the acid, one, polymerization, and the other, adsorption of the asphalt by the acid, and quotes evidence of an adsorption equation of the exponential type obtained by Schulz It is probable that both these theories are true in part but, owing to the confusion which exists in referring to asphalt, and the indefiniteness of the present methods for analysis and isolation of these substances, no single explanation can be expected to cover all cases.

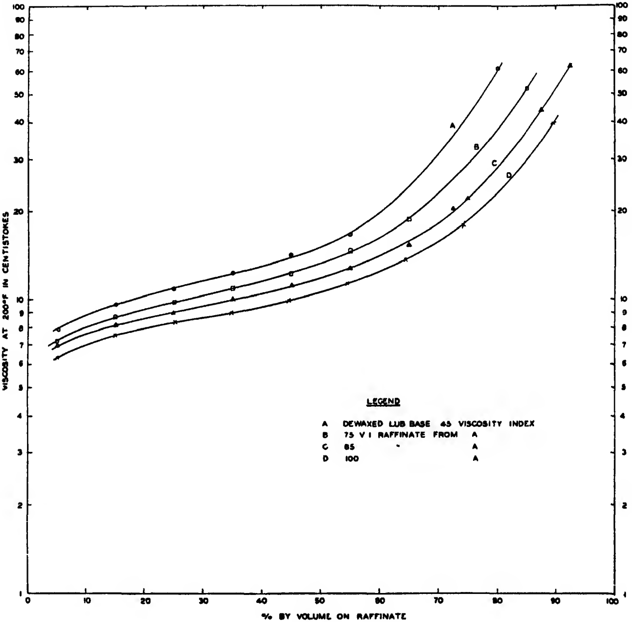

Fig 4

Naphthenic acids are present in most crudes in various proportions and are partially removed by the acid treatment, traces being found in most refined lubricating oils Resinous material also is only partially removed by acid treatment, and can be detected in appreciable amounts even after heavy solvent and acid treatment of certain stocks It is probable that the petroleum resins are much more nearly related to the paraffinic state than to the asphaltic, and that in their case an adsorption isotherm of the type discussed by Schulz applies

In the removal of the undesirable constituents by sulphuric acid a certain amount of unavoidable side reaction occurs, depending on the temperature of treatment and the concentration and amount of acid used, which results in acid or 'sour' oils containing, in addition to dissolved sulphur dioxide, appreciable amounts of oil-soluble sulphonic acids

Moreover, if during the acid treatment the oil is heated excessively or subjected to high skin temperature, exceedingly stable oil-soluble colouring bodies may be formed which are very difficult to remove

The conditions found most suitable for oil-refining by sulphuric acid are generally suggestive of physical solution rather than chemical reaction i e minimum operating temperatures and counter-current or subdivided treatment Where, from mechanical considerations or because of the high viscosity of the oil at normal temperatures, higher treatment temperatures are employed, the results are generally less satisfactory The subject has, however, been fully discussed by several authors, and the reader is referred to the works of Gurwitsch [13] and Kalichevsky and Stagner [18, 1933]

Neutralization of the acid-treated oils is effected in certain cases with caustic soda solution, especially on the less viscous grades, but the results are generally inferior in colour to the corresponding finished products obtained using clay and lime, and owing to presence of dissolved soda soaps the oils are more prone to emulsify and occasionally develop turbidity on exposure to moisture

While it is probable that none of the constituents of petroleum is completely inert to the adsorption effects of decolorizing clays, for practical purposes only the most active constituents need be considered Gurwitsch [15] gives a comprehensive discussion of the effect of adsorbents on petroleum products, and states the two principal rules which govern the phenomenon

(1) When an adsorbent acts on equally concentrated

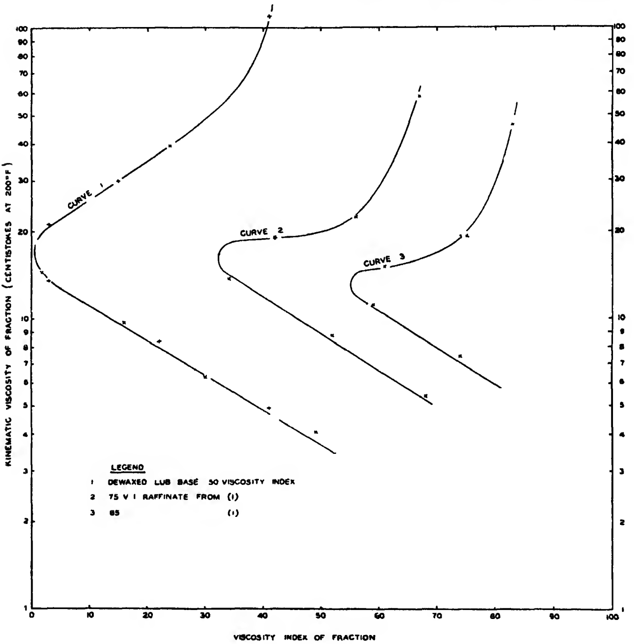

Fig 5

solutions of various substances in the same solvent, the substance most strongly attracted by the adsorbent is removed to the greatest degree

(2) For equally concentrated solutions of any particular substance in different solvents, the substance will be most completely adsorbed from the solvent which has least attractive power for the adsorbent

There is thus an equilibrium state in every case between the amount adsorbed and the amount remaining in the solvent The effect is expressed mathematically by the Freundlich Adsorption Isotherm

$$X = KC^{\frac{1}{n}}$$

where C is the concentration of the adsorbed substance (e g resinous material) in the adsorbent, e g g resin per g of adsorbent (clay), X the concentration of the substance (resin) remaining in the oil when equilibrium has been reached between the oil and the clay, and K and n are constants K is proportional to the active surface per unit of weight of the adsorbent, and n is characteristic of the adsorbed substance and is greater the greater the activity of the substance for the adsorbent It follows, therefore, that complete removal by adsorption is not theoretically possible, but actually, for large values of n, the amount remaining in solution after treatment with adsorbent may be negligible for practical purposes In cases where the activity coefficient n is low, the amount of clay required to reduce the concentration in the oil to the required limit will be excessive, and it is in such cases that recourse is made to more selective and drastic refining methods, as, for example, the refining of residual oils as above mentioned, with acid and clay

Certain of the heavy resinous and asphaltic substances present in lubricating oil cuts are strongly reactive to adsorbents and, since it is these constituents of the oils which are mainly responsible for the dark colour of unrefined oils, the decolorizing effect of clay treatment is explained Not all of the resinous bodies possess the same activity, however, as is evidenced by the fact that appreciable amounts of resins are present in the finished lubricating oils from certain stocks Naphthenic acids boiling in the lubricating oil range are partially removed by clay treatment, but the amount of clay required for practically complete removal is, as in the case of the resins, uneconomical It will be appreciated that the active surface of the clay must be saturated during its use and, if sufficient active material is not present, then greater proportions of inactive material will be adsorbed up to this amount In practice it is generally estimated that the minimum amount of oily material which is lost by adsorption and absorption in the clay after use approximates to one-half the weight of the clay

The distillates from paraffinic stocks, either natural or from solvent refined naphthenic or mixed base crudes, are readily decolorized and stabilized by a light clay treatment In the case of stocks containing appreciable amounts of naphthenic acids (which are difficult to remove completely by acid, clay, or solvent-refining generally), the oils are redistilled over soda, as explained above, in preparing the distillate cuts, and in some cases even the heaviest grades are produced as distillates from soda-treated oils

The amount of clay required depends on the quality of the oil and on the temperature of treatment In the newer processes temperatures up to 600 F are employed with short time of heating, the advantages of such processes are claimed to be reduction in clay requirements and improved appearance of the treated oils

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SULPHURIC ACID TREATMENT

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THE use of sulphuric acid as a refining agent for mineral oils dates from the very early days of the industry, being adapted from the coal-tar and shale industries in which it was in general use. To-day, although many changes have taken place in petroleum products and the manner in which they are produced, it is still probably the commonest and most universally employed refining agent. The advantages it offers are many. It is, for example, generally applicable to the whole range of petroleum products, being at the same time cheap, readily available, and easy to apply and handle in the refinery. On the other hand, sulphuric acid refining is regarded by some as wasteful, uneconomic, and troublesome. Admittedly, sulphuric acid is corrosive, may cause a drop in octane rating when treating gasolines, and give rise to heavy losses, particularly when applied to unsaturated products, furthermore, considerable quantities of sludge are formed which are not disposed of readily. However, in the light of more recent knowledge, these difficulties can to a very great extent be overcome. The last, the disposal of the sludge, is a very real problem in small refineries where acid-recovery plants cannot be justified economically. As a result, large accumulations of sludge are to be seen on waste land adjoining such refineries, particularly in arid zones, although this is not now so frequent as formerly. The tendency to-day is either to burn the sludge directly or to dilute it and, after removal of separated oil, neutralize with spent alkaline reagents. Any hydrogen sulphide eliminated in the process may be burnt and the aqueous product disposed of with comparatively little trouble.

As in most branches of the petroleum industry, considerable advances have been made in acid refining since the early days when treatments were developed by rule-of-thumb methods and a considerable amount of guess-work was employed in the application. The last ten years have seen very big strides made in the use of acid, particularly for the treatment of cracked distillates, largely as a result of better understanding of the reactions underlying the process. Yet even to-day, although certain rules based upon the chemical reactions concerned may be observed, a satisfactory treatment for a new product is invariably developed by methods involving trial and error. Possibly it is for these reasons that the acid-refining process has frequently been referred to as a 'barbarous art'.

The chemical reactions involved in the treatment of petroleum products are extremely complex. A certain amount of information is available which can be applied to the lighter distillates, but practically nothing is known of the reactions in which the heavier products are concerned. In any case it must be realized that the effect produced during the refining process is the result of numerous reactions of widely differing type, some of which may improve the product while others may not. Since it is obviously not possible to control a complex process of this type so as to limit or prevent any particular reaction or reactions taking place without affecting others, it is invariably necessary to compromise and select conditions which most nearly produce the desired result. To accomplish this, changes may be made in any of the following variables:

(1) Amount of acid used
(2) Method of addition
(3) Strength of acid
(4) Temperature
(5) Time of contact
(6) Method of agitation
(7) Final treatment

These will be considered separately.

Amount of Acid.

The quantity of acid necessary to refine a petroleum product is largely determined by the nature of the product and the degree of refining desired. It is affected by the concentration of the acid used and the manner of its application as well as the time of contact and temperature at which treatment is carried out.

With the possible exception of natural gasoline, sulphuric acid is used as refining agent for the whole series of petroleum products. The object of the treatment, however, varies, for while acid is used on gasolines and kerosines for the purpose of desulphurization it is employed on lubricating oils to destroy constituents which render them unstable to heat and oxidation. The lower fractions (as a general rule) require a much lighter treatment than those of higher boiling range, although this is not without exception, as for example when treating gasolines of exceptionally high sulphur content.

While acid treatments are generally given as volume percentages in Europe, in American refineries it is usual to express them in terms of pounds per U.S. barrel (lb/bbl.). Obviously in converting from one to the other, it is necessary to take into account the gravity and in Table I the equivalent quantities are given for 93.2% acid (66° Bé.) *d* 1.835.

TABLE I

% *by volume*	*Pounds per U.S. barrel of 42 U.S. gal. = 35 Imp. gal.*
0.1	0.642
0.2	1.285
0.3	1.927
0.4	2.569
0.5	3.211
0.6	3.854
0.7	4.496
0.8	5.138
0.9	5.780
1.0	6.42
1.5	9.63
2.0	12.85
2.5	16.06
3.0	19.27
3.5	22.48

Usually straight gasolines can be effectively treated with 0.1 to 1% of acid (66° Bé.) by volume, the exact amount being determined by the quantity required to bring the sulphur content within the limits set by specification which, in the United States, is 0.1%. The correct quantity of acid required to bring about any degree of desulphurization is difficult to predict, depending as it does upon the nature of the sulphur bodies to be removed A distillate in which most of the sulphur present is combined as organic sulphides is much easier to desulphurize than one in which mercaptans and disulphides are present, since the latter are much less soluble in acid than the sulphides Mercaptans, since they are oxidized by the acid to disulphides with the formation of water, tend to reduce the effectiveness of the acid by dilution Similarly Nitrogen bases when present reduce its refining action by neutralization Straight gasolines containing comparatively low sulphur contents which are not readily amenable to acid treatment are exceptional and the operation is usually simple and easy to carry out

Kerosines require a somewhat heavier treatment than gasolines, depending upon the purpose for which they are intended and their previous treatment Considerable quantities of kerosine are burnt in lamps for illumination and, unless satisfactorily refined, fouling of the lamp glass and charring of the wick result Both of these can frequently be traced to a high sulphur content, and this is therefore usually limited by specification to 0 1 %, and considerably lower for special grades Acid treatment, as with gasolines, is thus largely directed at desulphurization although gum-forming and coloured constituents may be removed and to some extent those responsible for smokiness as well The satisfactory removal of the latter cannot always be effected by acid unless extremely heavy treatments are given, and it is in such instances more economical to employ a preliminary extraction with liquid sulphur dioxide followed by a relatively small acid wash

Provided that it is sufficient to effect the required degree of refining, the amount of acid employed for the treatment of the lighter straight distillates is not critical A heavier treatment, apart from increasing acid consumption and thereby treating costs, does not have a very serious effect since the losses involved are small and the fall in octane rating negligible unless, of course, very excessive treatments are applied On the other hand, extreme care must be exercised when acid treating cracked distillates, particularly with regard to the quantity of acid employed and its concentration The function of the acid is no longer confined to desulphurization as with straight distillates, but includes the removal or conversion of the highly reactive gum-forming constituents into harmless products by polymerization Since the latter process not only involves loss in material but also a fall in octane rating, it is desirable to confine the action of the acid as far as possible to the objectionable constituents This is by no means easy, as there is no hard-and-fast line separating the desirable from the undesirable hydrocarbons and it is difficult to destroy the latter without affecting the former This is particularly true of cracked products formed as a result of more drastic cracking conditions in which the proportion of highly reactive bodies is higher than in those produced under milder conditions Since both polymerization and desulphurization are determined by the amount of acid employed, it follows that to desulphurize a highly sulphurous cracked distillate and yet avoid loss in octane value and yield is not possible

The heavy acid treatments required for desulphurizing highly sulphurous cracked distillates give finished gasolines of good stability because the unstable and gum-forming compounds are removed during the desulphurization The satisfactory treatment of a low-sulphur distillate is a much more difficult matter because the amount of acid required is governed by the required stability of the finished product and not by the sulphur content Much more room for improvement consequently exists in the treatment technique of low-sulphur distillates than in treating those of high sulphur content

The degree of refining as indicated by the normal properties of the finished product is not proportional to the amount of acid employed This is shown by the effect produced upon sulphur, colour, potential gum, and octane rating given in Tables II–IV

TABLE II

Conventional treatment of Cracked Gasoline (Kalichevsky and Stagner [8, 1933])

93 % acid lb per bbl	*Refined product sulphur %*	*Loss of stock based on gasoline treated %*
0	0 88	0 0
8	0 61	2 9
20	0 32	7 9
30	0 24	14 4
40	0 19	19 1

TABLE III

Effect of Quantity of Acid upon Colour of Finished Gasoline (Nash and Howes [12, 1934])

Acid, lb per bbl	*Finished product colour (Saybolt)*	*Finished product potential gum (mg per 100 ml)*
0	8	274
1	16	268
2	17	243
3	21	196
5	25	143
6	27	92
9	22	46
10	21	22
15	20	12
20	20	3
40	20	0

TABLE IV

Effect of Acid Treatment on Dubbs Cracked Distillate on the Properties of Finished Gasoline (Potthoff [14, 1931])

Acid lb per bbl	*Sludge loss, %*	*Polymer loss, %*	*Total loss, %*	*Octane rating octane no*
0	0	0	0	73
2	1 0	0 6	1 6	72
5	1 8	1 0	2 8	70
10	3 5	1 8	5 3	69
20	8 0	3 3	11 3	64
50	15 3	6 3	21 6	51

It will be observed that so far as colour is concerned there is an optimum treatment above or below which the colour of the finished product is unsatisfactory The effect produced by varying the quantity of acid employed upon the boiling range of the material treated is well illustrated in Table V in which A S T M distillations are given corresponding with the acid treatments in Table III

Storage has a marked effect upon the ease with which the lighter distillates yield to treatment, some becoming more and others less easy to treat This can usually be traced to changes due to aerial oxidation and spontaneous polymerization

The quantity of acid which may be applied to lubricating oil without injury is not critical providing certain precautions are taken with regard to temperature Excessive application of acid in one batch may cause overheating with considerable evolution of sulphur dioxide, and result in a permanent darkening of the oil, presumably due to oxidation

TABLE V

Effect of Acid Treatment upon Dubbs Cracked Distillate as shown by A S T M Distillation, Colour, and Gum

Treatment lb per bbl	*0*	*2*	*5*	*10*	*20*	*50*
Sp gr at 60° F	0.749	0.749	0.749	0.751	0.752	0.754
I B P, F	98	100	101	106	105	104
10% distillate, °F	148	148	152	158	163	166
20% ,, ,,	180	182	185	187	195	198
30% ,, ,,	209	210	212	214	223	230
40% ,, ,,	235	236	239	239	250	256
50% ,, ,,	259	260	263	264	273	281
60% ,, ,,	282	284	286	284	294	301
70% ,, ,,	300	306	309	307	312	327
80% ,, ,,	334	336	335	338	340	346
90% ,, ,,	362	362	361	361	368	372
End-point, °F	399	397	405	410	405	404
Colour	16	20	25	25	25	24
Gum (copper dish), mg per 100 ml	370	219	140	24	63	59

It is, of course, not possible to give more than a very rough approximation of the quantity of acid required to refine petroleum products, but a useful indication based upon Kalichevsky and Stagner [8 1933] is as follows

Natural gasoline	Usually none occasionally 2-5 lb per bbl
Straight-run gasoline	0-3 lb per bbl
Cracked gasoline	2-10 lb per bbl To effect desulphurization of highly sulphurous distillate prohibitive treatments are required
Kerosine	1-75 lb per bbl depending upon degree of refining required
Lubricating oils	0-60 lb per bbl depending upon preliminary treatment Residual oils require more than distillates
Transformer oils	0-100 lb per bbl (fuming acid)
'Water-soluble' and spray oils	0-200 lb per bbl (fuming acid)
Medicinal oils	200 lb per bbl or more (fuming acid)
Wax	Up to 300 lb per bbl, usually considerably less

Method of Application—Fractional Addition.

In batch operation it is usual to apply the acid treatment in two or more stages, settling and drawing off the sludge formed before the next addition This method of treating is definitely advantageous Not only is the refining action better than when the acid is added altogether, but a considerable economy in acid may be effected It also prevents excessive temperature rises and enables a better control to be maintained on the process Schulz [17, 1909] maintains that the effect of acid treatment follows the laws of physical adsorption, an observation not generally accepted There is little doubt actually that better results can always be obtained in the treatment of cracked distillates when the acid is added in fractions or 'dumps'

Since distillates are rarely free from water even when settling has been properly carried out, particularly those with high contents of aromatic and olefine hydrocarbons, it follows that appreciable dilution of the acid is liable to occur This is further increased by any oxidation of mercaptans to disulphides with the formation of water One of the benefits to be obtained by a relatively small preliminary acid wash is consequently the dehydration of the oil under treatment and oxidation of the mercaptans, thus allowing full advantage to be taken of the better refining action of the more concentrated acid applied subsequently The action of the preliminary acid is not limited solely to dehydration, for phenols, nitrogen bases, the more soluble sulphur bodies and, when treating cracked distillates, the most highly reactive hydrocarbons, are also removed It has furthermore been observed that the addition of a small amount of acid to certain distillates produces a feebly acid sludge containing only a little acid and mostly soluble in benzene

On the addition of further acid, reaction occurs between the sludge and the fresh acid as a result of which the former entirely loses its solubility in benzene Since the same insoluble sludge is a normal product in the treatment of light distillates, it follows that unless the benzene-soluble sludge is removed by a preliminary acid treatment, at least a part of the acid added later is utilized in converting it into the insoluble form

It is particularly important to settle and remove the spent sludge completely at each stage The part played by a preliminary acid wash of this nature in the batch treatment of cracked distillates is particularly valuable After being rapidly diluted when first added by water, &c, the acid proceeds to react in its diluted form as a mild polymerizing agent attacking only the most reactive hydrocarbons The fractional addition of acid to cracked products thus provides a graded treatment which is particularly advantageous

As a general rule, acid sludge formed in a previous batch is employed for the preliminary treatment, thus enabling a considerable economy in acid consumption to be effected This mode of application is best to be seen in countercurrent treating where the raw distillate is first contacted with the spent acid leaving the plant, and then passes on to meet acid of steadily increasing concentration until it finally reaches the fresh acid entering the plant Countercurrent treatment is thus particularly economical, since the acid is used to the greatest advantage, under certain circumstances leaving the plant entirely spent

An interesting application of fractional acid treatment has been suggested when using oleum on certain products It is claimed that treatment with concentrated acid both before and after the application of the fuming acid is beneficial since the preliminary treatment removes water and easily resinified materials while the subsequent one takes out undesirable compounds formed by the action of the oleum

Strength of Acid

The concentration of acid most suitable for treating a product depends upon the nature of that product and the purpose of the refining process Thus, for the treatment of cracked distillates, a relatively weak acid is desirable, while for the preparation of such products as petroleum jelly and white oils drastic treatment with large volumes of oleum is essential As a general rule it may be stated that the stronger the acid employed as a refining agent the greater the degree of refining attained and the greater the resulting losses The refining action, particularly that involving sweetening, falls off very rapidly with increasing dilution, the rate of decrease being largely determined by the nature of the diluent Water, for example, appears to influence the refining action of acid to a much greater extent than dilution by the products normally formed during the refining process itself

Since the higher the concentration employed the greater are the losses (cf Table VI) and the tendency for undesirable changes to take place in the product, the lowest acid concentration capable of giving the required degree of refining should be employed. While this needs no very serious consideration when dealing with straight run distillates, as these are relatively insensitive to acid, it is particularly true for cracked distillates and lubricating oils. Some idea of the relationship between acid concentration and loss as sludge can be obtained from Table VI, which gives the results obtained when treating a lubricating oil distillate, diluted with half its volume of gasoline, with acid of varying concentration and equal in volume to one-half that of the heavy oil (Gurwitsch [6, 1932]).

TABLE VI

Sludge Formation from Acid and Unrefined Lubricating Oil Distillate

Acid concentration, %	100	97	95	92	87	82	75	71	65
Increase in volume of acid layer, %	25	23	20	15.5	10	7	5	0	0

The most reactive form in which acid is employed in the refinery is as oleum containing 15–20% sulphur trioxide. Although in the past this was used in small amounts for straight-run gasoline in place of the 66° Be acid, its use to-day is mainly confined to kerosine and special products such as naphtha cuts, transformer oils, and medicinal products. It is particularly effective for desulphurizing kerosines derived from asphaltic crude oils to produce high-grade products. These kerosines are not only rich in aromatic hydrocarbons but high in sulphur content, and unless previously extracted with liquid sulphur dioxide require a heavy acid treatment with oleum to give a satisfactory product. The extent to which desulphurization takes place is approximately proportional to the acid concentration (reckoned as H_2SO_4). Thus 66° Be acid (93%) is only about 50–60% as efficient as oleum (104% acid) for desulphurizing kerosine. An interesting observation in this connexion is that certain kerosine acid sludges on standing separate up to 20% of their volume of highly sulphurous oil in the course of a day or so. This explains why, when acid treating plant has been shut down for several days with acid and kerosine in contact, the sulphur content of the latter is high and an increased quantity of acid is necessary to reduce it to the required extent.

Oleum is also employed in the production of painters' naphtha where a particularly low sulphur content is required in the finished product.

For the production of medicinal and transformer oils, fuming acid must be employed, as otherwise it is impossible to obtain the complete removal of the undesirable constituents. Even then extremely heavy treatments are essential to obtain satisfactory products, although these may be reduced by preliminary extraction with selective solvents.

Oleum has the disadvantage of being a strong oxidizing as well as sulphonating agent, and considerable quantities of sulphur dioxide are evolved during treatment even at ordinary temperatures. The products from these oxidation reactions are soluble in the oil and frequently impart to it a bad colour. A final treatment with 66° Bé acid to remove the compounds responsible for the colour has been recommended (V. Bibra [2, 1922]).

The addition of oleum to partly spent acid tar to bring up the strength is often a convenient method of effecting a considerable economy in acid.

Concentrated sulphuric acid, 93–6%, although at one time in general use for cracked distillates, straight-run gasolines, and lubricating oils, is to-day largely limited in use to the last two. As mentioned above, it is only roughly 50–60% as efficient as oleum in removing combined sulphur from the lighter straight distillates. While it has the disadvantage that approximately double the quantity is required to produce a doctor negative product, the latter is less corrosive and gives a better copper-dish test.

Although under suitable conditions, for example at low temperatures or in certain forms of treating equipment, the concentrated acid gives good results with cracked distillates, as a general rule it is better to employ the weakest acid which will give a satisfactory product. Thus the treatment necessary is considerably influenced by the possible use or otherwise of inhibitors in the finished gasoline and the relative importance of colour. The high temperature-cracked distillates, having a much higher unsaturated content than those produced with less drastic cracking conditions, are much more sensitive to acid. Too high a concentration of acid may produce almost explosive results through heat evolution, while the octane rating of the treated material is much reduced.

It is obvious from a study of the hydrocarbons likely to be present in cracked distillates that their reactivity towards acid must vary over very wide limits. Thus, while diolefines, particularly certain cyclic diolefines such as *cyclo* pentadiene, are extremely reactive, many of the higher normal olefines are unaffected by even relatively strong acid. Between these limits there are hydrocarbons varying in reactivity from one extreme to the other. Very few of those present in cracked distillates have so far been identified, but it is known that they cover the whole range of reactivity. The relative proportion in which the various hydrocarbons are present is, however, largely determined by cracking conditions, drastic conditions such as those employed in high-temperature operations not only resulting in a higher olefine content but at the same time favouring the formation of the more reactive hydrocarbons. High-temperature cracked distillates of this type are consequently much more sensitive to polymerizing agents than those produced under less drastic conditions and, since it is largely owing to the presence of the reactive hydrocarbons that they owe their high octane rating, much more care is necessary in acid-treating them. Unless such care is exercised much of the advantage gained in producing materials of this type is lost and a gasoline of comparatively low value obtained.

In consequence much attention has been directed during the past decade to improving the technique of the acid treatment of cracked distillates. The realization that the drastic treatment necessary to produce a stable finished gasoline water-white in colour and of pleasant odour at the same time materially reduces the octane rating has led to a changed outlook. The consumer has become better informed and now knows that colour and odour are less important than the octane rating and gum-content, actual and potential. Even the much-debated question of sulphur content is not so seriously regarded as formerly, particularly in Europe where the introduction of coal-tar benzene rendered a low sulphur content impossible.

The use of dyes served a useful purpose in bridging the gap between the time when the consumer, generally correctly so, considered colour an indication of incomplete refining and the present time when colour is relatively unimportant. The greatest advance has been due to the introduction of inhibitors which have enabled cracked distillates of high octane value to be converted into reasonably stable finished gasolines with little or no loss in octane rating.

While it is possible to eliminate refining almost entirely by lowering the end-point and adding an inhibitor after a small alkali wash or doctor treatment, as a rule it is better to employ a small acid treatment either with comparatively weak acid or sludge and then, after neutralization, re-run and inhibit As an alternative, it is possible to inhibit the lightest fractions containing the hydrocarbons of high octane rating and acid treat the heavier fraction, a procedure which has been adopted in certain refineries An important consideration in deciding upon the most favourable process is the period between refining and consumption since, of course, the effective life of inhibitors is limited

While acid concentrations as low as 40% have been stated to have a slight polymerizing effect on hydrocarbon, it is not until concentrations in the neighbourhood of 70% have been reached that the refining action, in particular colour removal, is sufficiently marked to be useful The most satisfactory concentrations for refining cracked distillates have been found to range from 70 to 83%, while those ranging from 83 to 93% may be used for both straight run and cracked materials

Probably the most satisfactory method of refining cracked distillates, particularly those produced under drastic cracking conditions, is to employ a series of treatments with steadily increasing acid concentrations until the desired degree of refining has been effected Such a procedure by removing the most reactive unsaturated bodies with weak acid enables a much better control to be kept over the process by avoiding undue evolution of heat Thus Retailliau [15, 1932] advocates treating vapour-phase cracked distillates first with 30% acid to remove the most active hydrocarbons followed by a subsequent treatment with 75% acid

Graded treatment of this kind is a natural consequence of counter-current treatments, for the acid first meeting the raw distillate has become diluted at an earlier stage and the more concentrated acid only comes into contact with the partially refined oil In counter-current treating plants, the relatively large volume of acid normally present acts as an excellent diluent and a very much higher concentration may be fed into the plant than would be desirable for batch operation This applies particularly to the Holley-Mott type of plant [1, 1931] in which the volume of acid present varies from 10 to 20% of the volume of the oil Fresh acid entering the plant is so rapidly diluted that even concentrated acid may be added without ill effects Since the sludge leaving the plant is completely spent and is practically devoid of refining action, this method of operation is extremely efficient and economical Thus the acid consumption for a high temperature cracked distillate in a plant of this type is often below 1 6 lb per bbl

The chief advantages of counter-current contacting for the treatment of cracked distillates is given by Walton [18, 1936] as follows

1. The most active of the unstable molecules are removed by the weakest acid, allowing strong undiluted acid to be added at the last contacting point to remove the most inert of the undesirable constituents
2. Residual acid in the sludge is utilized which is too weak to be used in securing a finished product and which would too greatly dilute fresh acid if the two acids were mixed
3. Easily oxidized molecules tend to be mildly treated and extracted into the acid layer rather than vigorously oxidized with the evolution of sulphur dioxide and formation of oil-soluble esters

It has already been mentioned that acid sludge forms an excellent preliminary treating agent Under certain circumstances, it may be employed entirely in place of fresh acid as, for example, when acid sludge from the treatment of kerosine is utilized in refining cracked distillates As a general rule the use of sludge in this way increases the sulphur content of the material treated, although since redistillation forms an integral part of the process this is not important A more serious consideration is the possible reduction in octane rating

As a means of avoiding excessive polymerization, highly unsaturated products are frequently mixed with straight-run distillates or those relatively low in olefine content This expedient is particularly useful when treating such products as polymerization gasolines which consist almost entirely of unsaturated hydrocarbons and which are consequently extremely difficult to treat alone owing to the violence of the reaction

Temperature

The reactions between hydrocarbons and sulphuric acid are very sensitive to temperature changes, a fact of considerable importance, and very evident when acid-treating certain petroleum products as a very small rise in temperature produces a most marked increase in the speed of reaction Careful control of the heat evolution, which invariably takes place during acid treatment, is therefore essential since otherwise the reaction tends to go too far and gives inferior products

The optimum temperature for treatment is determined largely by the material and the object of the refining process In general, higher treating temperatures are employed for heavier products for the removal of aromatic and unsaturated hydrocarbons, bituminous compounds, and asphalts The treatment of the lighter distillates for the removal of combined sulphur and colour is carried out at low temperatures The treatment of cracked gasolines at temperatures as low as 18° is particularly recommended by Halloran [7, 1927–8] and Klemgard [10, 1927], who claim that polymerization losses and treatment costs are much reduced

As a general rule it may be said that the lower the temperature of treatment the better the appearance of the product Treatments at higher temperatures can usually be carried out with a lower acid consumption, or alternatively with weaker acid, the higher temperature compensating for the decreased activity of the reagent

Polymerization losses can be very largely reduced by avoiding rise of temperature when treating cracked distillates and climatic temperature changes are for this reason often reflected in the refined product Pierce [13, 1930], from an investigation of the conditions affecting the acid treatment of cracked gasoline concludes that, while a rise in temperature favours desulphurization, it results in a poorer colour in the finished product and increased corrosive acid formation on re-running This is well illustrated in the figure based on Trusty and Pierce's results (Nash and Howes [12, 1934])

In the refining of straight-run gasolines, the quantity of the acid is largely determined by the temperature at which treatment is applied Usually this is conveniently carried out between 70 and 90° F, but when heavy treatments are necessary for any special reason it is better to operate at a much lower temperature For average gasolines, however, cooling is costly and uneconomical High treating temperatures tend to cause discoloration of the finished product

For the production of kerosines, particularly those derived from naphthenic base crude oils, a preliminary extraction with a selective solvent is to-day employed in the larger modern refineries to remove the hydrocarbons responsible for poor burning qualities In the older processes this is effected by a heavy acid treatment using fuming acid at a comparatively high temperature, conditions favouring the sulphonation of the undesirable constituents Even so, too high a temperature is undesirable since the colour is badly affected and redistillation becomes necessary In practice the limiting temperature is usually in the region of 100° F

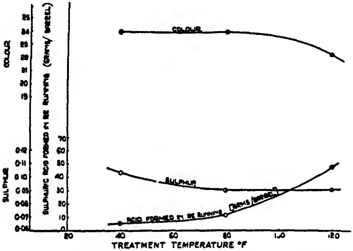

FIG 1 Curves showing the effect of temperature in the acid refining of cracked distillates (Trusty and Pierce)

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While a higher treating temperature generally results in a much greater rate of settling in the case of viscous oils owing to the decrease in viscosity, the opposite appears to hold true for certain kerosines Thus, according to Gurwitsch [6, 1932], the sludge from Californian and Galician kerosines settles more rapidly and completely at lower temperatures, this is not true, however, for Russian kerosines

Lubricating oils are treated as a general rule at as low a temperature as possible, consistent with good settling A lower treating temperature has the advantage that the quantity of acid is not nearly so critical, a much larger treatment being possible without deleterious effects at a lower than at a higher temperature The usual treating temperatures for various lubricating oils are given in the following table (Kauffman [9, 1927])

Heavy residual stocks require much higher temperatures owing to their high viscosities, temperatures as high as 130–170° F and even higher being necessary

Too high a treating temperature for lubricating oils results in discolorized oils which cannot as a rule be improved by further acid treatment although subsequent treatment with adsorptive earth is sometimes effective On the other hand, too low a temperature may give a dark colour owing to incomplete settling The viscosity of heavy oils may be overcome by dilution with a low viscosity distillate, such as a naphtha, before treatment The disadvantage of this method of operation is the difficulty experienced in removing the solvent without undue heating of the oil although this can be readily effected under reduced pressure A recent modification of this method employs liquid propane as the solvent

The asphalt or resin content of the lubricating oil exerts a considerable effect upon the ease with which settling takes place It has been found that highly solvent-treated oils practically free from asphaltic and resinous bodies on acid treatment can only be settled with considerable difficulty and even centrifuging is not always successful in such cases

The treatment of such oils as transformer and medicinal oils where the removal of the sludge-forming components is essential, is carried out at comparatively low temperatures (60–95° F) using several batches of fuming acid These oils are, of course, low viscosity products and the sludge, which is not generally viscous, settles easily and rapidly

Time of Contact.

The time of contact between the acid and the oil is of considerable importance, the relative importance depending upon the nature of the oil While for the lighter straight distillates increased time of contact is advantageous rather than otherwise, for cracked products and lubricating oils an excessive contact time not only results in poor colour stability but frequently poor colour in the finished product as well This is especially true for temperatures above the optimum, although in carefully controlled counter-current systems very long times of contact may be maintained without ill effects

The actual period during which the oil and acid are in contact is determined by a number of considerations such as the degree of agitation, the time required to obtain the necessary intimacy of contact the speed of the reaction, the method of adding the acid and the rate of settling The ease with which efficient contact is obtained is, of course, dependent upon the product and the form of agitation employed Very rapid intimate mixing can be obtained by passage through a centrifugal pump and this may be sufficient for gasoline treatment A comparatively viscous product such as a lubricating oil agitated by air at a comparatively low temperature requires, however, a considerable time before contact is sufficiently thorough While intimate contact for a short period of time is sufficient for the treatment of certain products, this is not always so and it may be necessary to maintain the reactants in contact for a relatively long period depending upon the speed with which the reaction proceeds Thus, the removal of aromatic bodies by sulphonation requires a much longer time than the polymerization treatment of a cracked gasoline Any factors, therefore, which affect the speed of the

TABLE VII

Treating Temperatures for Lubricating Oils (Kauffman)

Viscosity of oil at 100° F sec Saybolt	*Temperature of oil on addition of acid, ° F*
50	70–80
75	80–90
100	85–95
150	90–100
200	95–105
300	100–110
500	105–115
1,000	110–120
1,500	110–120
2,000	115–125

reaction such as acid strength and temperature influence the time of contact necessary to produce any definite degree of refining

It is thus obvious that the time of contact is dependent upon a number of considerations, one of the most important of which is the form of treating equipment employed In general, prolonged agitation of oil and acid is regarded as harmful Accordingly for the treatment of cracked distillates arrangements are usually provided to ensure rapid intimate contact of acid and oil with quick removal of sludge Walton [18, 1936], however, points out that there is ample laboratory evidence to show that, provided the temperature is not allowed to exceed a certain limit, the longer the time of contact the better the quality of the treated oil and the less acid needed for the treat This observation is confirmed by the excellent results which are obtained with both liquid- and vapour-phase cracked distillates in the refineries of the Anglo-Iranian Oil Company, Ltd , using Holley-Mott type treating equipment in which the time of contact is in the region of one hour As a rule, however, as short a contact time as possible is preferred varying from minutes to seconds or even less, as, for example, when a centrifugal contactor is employed to provide agitation and is followed immediately by a centrifuge to withdraw the sludge Pierce [13, 1930] found that 3 5 minutes' contact gave the most satisfactory results for with a longer time, although the sulphur content was reduced, the colour was impaired and more corrosive acid formed on re-running

Walton [18, 1936], on the other hand, states that, when fresh 66° Be acid is injected directly into the distillate and the sludge withdrawn immediately, the minimum time of contact depending upon the intimacy of mixing will range from 30 sec to 1 min For modern recirculation treaters this is probably nearer 10–20 sec

The acid treatment of lubricating oils generally requires at least 30 min agitation although periods of 1–2 hr are usual in practice (v Bibra [2, 1922]) Prolonged agitation is usually harmful owing to the tendency for the hydrocarbons, &c , present in the sludge to polymerize, and with part of the sulphonic acids, to redissolve and discolour the oil Since these oil-soluble compounds are mainly sulphonic acids, their presence in oil tends to cause emulsification during alkali treatment

When acid and oil have been in contact for the desired period either agitation is stopped and settling allowed to take place *in situ* or the oil with the acid in suspension allowed to flow out and settle elsewhere During the settling period, although contact between acid and sludge may not be good, reaction may still proceed and the bad effects of prolonged agitation result It is consequently necessary to take the settling period into account and if necessary provide means to hasten it, for example by centrifuging

Apart from the desirability of separating the sludge as rapidly as possible to prevent further reaction or solution complete separation is usually necessary to facilitate further operations and reduce subsequent treatment costs This is well illustrated in Table VIII which shows the variation in alkali consumption for neutralization of a kerosine with settling time (Cupit [4, 1928])

Thus incomplete settling may result in a very material increase in alkali during neutralization with consequent resolution of undesirable compounds produced by hydrolysis of the sludge with the soda On the other hand, too prolonged settling in contact with sludge has on occasions also been observed to have an adverse effect For example, fresh kerosine-acid sludge on standing separates a considerable amount (up to 20% by volume) of highly sulphurous oil which passes back into the oil, thereby considerably affecting its sulphur content and colour

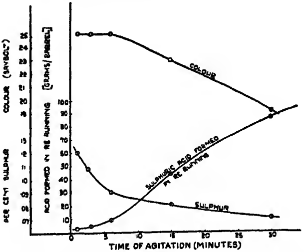

FIG 2 Curves showing the effect of time of contact in the acid refining of cracked distillates (Trusty and Pierce)

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Whether this is due to subsequent reaction between acid and sulphur bodies in the acid sludge or some form of adsorption phenomenon is not known Settling is, of course, dependent upon the viscosity of the oil and the nature of the sludge Although gasolines are generally satisfactorily settled in a short period, it is often observed that cracked distillates frequently continue to deposit an acid material for many hours

TABLE VIII

Settling time, hours	N NaOH *per 100 c c oil c c*
0 5	10
1 0	9
1 5	7
2 0	6 8

Lubricating oils, depending upon their viscosity and the settling temperatures, may require a very considerable period unless, of course, recourse is had to centrifuging or when a clay or other adsorbent earth treatment is given Although as efficient settling as possible is to be preferred, it is not essential

Method of Agitation.

The physico-chemical influences in an agitator or other plant in which chemical reaction takes place between reactants which are present in two immiscible liquids has not been thoroughly studied In most cases, and particularly when treating hydrocarbon oils with solutions of electrolytes, the reaction may be considered to take place in only one of the phases, usually that containing the electrolyte Thus, according to Docksey [5] in the case of treatment of oil containing a compound *A* which reacts with sulphuric acid to give a product soluble in the acid phase the controlling factors are

(1) The rate at which the compound A diffuses across the interface between the two phases
(2) The reaction velocity between A and the acid in the acid phase

The rate of diffusion depends on the area of interface between the two phases, the coefficients of diffusion in the two phases, the film coefficient, and the concentration of A in the two phases on either side of the film The rate of reaction depends on the reaction velocity constant and the concentrations in the acid phase of the reactants and products, following the Law of Mass Action

The two factors are not independent of each other since both depend on and affect the concentration of A in the acid side of the interfacial film It frequently occurs, however, that one factor controls the overall rate of reaction to the exclusion of the other Thus, if acid is used in excess and the rate of reaction in the acid phase is high, the rate of diffusion will be of major importance

Again, the various factors affecting the rate of diffusion are not all of equal importance The rate of diffusion of A in the bulk of the continuous phase is not of great importance since the general agitation tends to produce a uniform concentration throughout this phase The rate of diffusion of A or of the products of reaction from the interfacial surface to the interior of the particles of the continuous phase may have to be considered, since the amount of stirring inside a sphere of liquid may be small and decreases as the diameter of the sphere is reduced

A further factor which may have to be considered is the back diffusion of the product of reaction from the acid to the oil phase, should it be appreciably soluble in the latter

If there are two compounds A and B both capable of reacting the overall reaction rates in each case depend on the above factors, and it may be possible, for instance by adjusting the acid concentration, to vary the relative rates of the two reactions should it be found desirable to do so

Various devices have been employed for bringing the oil and acid into the necessary degree of contact Not all of these have, however, been universally adopted and comparatively few, cheap to install and operate, are in general use

While mechanically operated agitators have not been widely adopted they are being used to an increasing extent since the development of improved alloys and acid-resisting compounds for the acid treatment of the lighter distillates As a rule they consist of a turbine or propeller immersed in the liquid and rotated at a speed sufficient to give the desired mixing The Holley-Mott system employs, however, a carefully designed paddle, the efficiency of which is determined by its position in the treater and the speed of rotation, both of which are somewhat critical

The commonest form of mixer relies upon orifice mixers or mixing jets Several forms of mixing jets are in use which enable the acid to be dispersed in a very fine state Pressure drop in this arrangement is high but, since the pressure is borne by a pipe and not a large vessel, the high pressure is only objectionable from the point of view of pumping costs Mixing nozzles and orifices are also employed, through which oil and acid are forced at high velocity A very high degree of dispersion is attained by placing special devices in the path of the liquid It is stated by Walton [18, 1936] that such systems are objectionable in an acid treater on account of the difficulty of settling and separating Injectors which secure the necessary mixing by drawing the acid into the oil stream, are, however, free from these objections and give excellent results Such injectors are cheap to make and can be adjusted to give various acid/oil ratios

Another common form of mixing device relies largely upon the mixing obtained by the passage of the reactants through a centrifugal pump Incorporated in a recirculating system this form of agitation gives good results and has been widely adopted It is essential that the capacity of the pump be sufficiently large to ensure that the whole contents of the treater pass through it at frequent intervals for otherwise the treating time is much prolonged Thus, for a 1,000-bbl agitator a pump having a capacity of at least 1,000 gallons per minute is desirable By providing the necessary connexions (cf Morrell and Bergman [11, 1928]), two or more batch agitators fitted with centrifugal pumps may be used as a semi-continuous treating system

Too intimate mixing appears to be undesirable because when the acid is in a very fine state of dispersion the rate and efficiency of settling are low The extremely intimate mix produced also tends to bring about increased combination between the acid and the oil It has further been observed that the treated oil is much more difficult to free from acid 'pepper', especially is this true of high-temperature cracked distillates or other highly unsaturated products On neutralization the esters present are converted into sodium salts which remain in suspension and decompose during re-running to produce acid products, mainly sulphuric acid and sulphur dioxide These not only corrode the system but cause oxidation and sulphonation of the overhead leading to high gum contents and fuel colour stability, especially in the presence of sunlight

Forms of agitation which tend to give too high a degree of dispersion of the acid are, therefore, undesirable and those such as mixing jets or paddle agitators, which give the necessary contact and yet avoid high dispersion, are to be preferred

Towers either packed with inert material, e g rings, coke, &c , or provided with baffles operating on a continuous system have been stated to give good results when properly designed Throughput rates are, however, small compared with their size

A common form of agitation which has at times been employed for all products ranging from gasolines to heavy residual stocks is by means of compressed air This provides agitation which is thorough, rapid, easy to control, and cheap to operate It has the disadvantage when treating the lighter distillates that evaporation losses are high and there is a considerable fire hazard Furthermore, unless steps are taken to dry the air employed there is a tendency for dilution of the acid to occur Drying can be effected by contact with acid tar or some form of air conditioning plant, or the air may be replaced with inert flue gases It is, however, doubtful, whether agitation of this type is much in use to-day for the acid treatment of lighter distillates and its use is confined to the treatment of lubricating oils With certain of the latter it has actually been claimed that compressed air gives better results than mechanical agitation There is, at higher temperatures, a definite tendency towards oxidation and both temperature and time of contact should accordingly be reduced as far as possible

Final Treatment.

The freshly acid-treated product invariably contains, besides a certain amount of sludge in suspension in which there is free acid, appreciable quantities of sulphur dioxide together with sulphuric esters, both acid and neutral, and sulphonic acids in solution Some form of neutralizing treatment is therefore essential, combined in the case of the lighter distillates when insufficient acid has been employed to give a doctor negative product with some form of sweetening treatment Since with these products the end point is invariably raised by acid treatment owing to the formation of polymers, condensation or oxidation products boiling outside the desired distillation range, it is necessary to re-run or in some other way correct the boiling range Furthermore, re-running of gasoline fractions has the added advantage that the traces of polysulphides formed by the action of the acid on mercaptans which so adversely affect the lead response (Birch and Stansfield [3, 1936]) are also removed with the result that an appreciable improvement in octane rating is frequently obtained The extent to which higher molecular weight compounds are formed is dependent upon the product for, while cracked distillates may form very considerable amounts of high boiling materials, the end point of straight distillates may be raised only a few degrees

The removal of the sludge after acid treatment should be carried out as completely and generally as expeditiously as possible The desirability of efficient sludge removal is obvious, for not only are some of the objectionable compounds previously extracted from the oil and held dissolved in the acid thrown out of solution by the subsequent water or alkali wash, but the increased alkali consumption for neutralization substantially raises treatment costs

The ease with which settling takes place is largely dependent upon the viscosities of the oil and the acid at the settling temperature and the interfacial tensions between them The method of agitation also plays an important part, for as mentioned previously finely dispersed acid settles with difficulty, particularly from highly cracked products, while the presence of minute air or gas bubbles resulting from certain forms of agitation stabilizes the acid-oil suspension and hinders settling The lighter distillates are generally settled in tanks having a comparatively large area compared with their capacity Various methods for accelerating settling have also been employed particularly when prolonged contact through slow settling is harmful Centrifuging is generally effective in removing suspended sludge from both light and heavy products although it is not always the case Centrifuges have been used for some time with considerable success with lubricating oils, but until the recent developments in acid-resisting alloys they have not been adopted for the lighter distillates It is claimed that when employed on cracked distillates not only are alkali costs reduced but less sulphur dioxide is formed on re-running the re-run stills also require less frequent cleaning and the stability of the product is improved

The lighter products may be freed from sludge by passage through a system containing a series of baffles, or better by percolation through filters containing a bed of inert material such as sand The action appears to be purely mechanical and consists in the agglomeration of the finer sludge particles to form droplets sufficiently large to settle rapidly According to Walton [18, 1936], reduction in acidity of about 400% is attained by the use of these filters, the consequent saving in alkali being sufficient to pay for their installation and maintenance Renewal of the sand from time to time is necessary, the average life being about 550 bbl per cu ft Grading of the sand particle sizes is desirable to provide for pressure drop, coarse gravel or pebbles being used at the bottom Adsorbent earths such as fuller's earth have been tried and from the point of view of acid removal give good results The operating cycle is short, however, and the process consequently expensive

The separation of acid tar is facilitated by the addition of a small amount of water, the procedure usually being to spray the surface of the oil while settling The dilution of the acid generally, however, reduces the life of the treating equipment (unless lead-lined) by corrosion and the practice has been largely discontinued Weak acid does very definitely facilitate the removal of sludge and advantage is taken of this fact in the treatment of certain naphtha cuts in the continuous counter-current units operated by the Anglo-Iranian Oil Company Ltd The acid-treated oil leaving the last counter-current acid stage is allowed to flow into a lead-lined vessel where it meets the spent soda from the succeeding neutralization stages Conditions are so arranged that in this intermediate stage the soda is completely neutralized and the aqueous layer is actually 4N with respect to acid This arrangement has been found to give better results than an intermediate water wash alone

While a water wash prior to neutralization is generally employed, there would appear to be some doubt concerning its effectiveness Little if any improvement in the treatment of cracked distillates has been observed when a water wash is used although the reduction in the alkali consumption is marked The hydrolysis of easily hydrolysable acid esters, which with alkali are at once converted into water-soluble salts and removed as such, may result in the formation of oil-soluble compounds detrimental to stability Water washing does, however, materially improve the odour of certain kerosines provided that the water itself has not a 'stale' odour This, it has been observed may be imparted to the kerosine and contaminate it

For neutralization, caustic soda is most commonly employed, although for straight distillates, including gasoline, naphtha cuts, and kerosine, lime water has proved cheap and effective Attempts to utilize lime water on cracked distillates have not been so successful owing to the tendency to form emulsions The strength of the caustic soda used for neutralization is preferably 3–4% by weight There is usually no advantage to be gained from using a more concentrated solution although it has been found that in certain cases diakyl sulphuric esters are more easily removed by 23 6–28 5% solution

Neutralization is usually effected in a circulatory system using mixing devices, baffles, or injectors Centrifugal pumps and mechanical agitators are also employed The fine state of division which is so objectionable in acid treatment is here rather an advantage since, owing to the lack of mutual solubility, contact between the esters in the petroleum layer and the alkali in the aqueous layer is poor Settling is conveniently carried out in large storage tanks to which the distillate is pumped and allowed to stand as long as necessary Pierce [13, 1930] observed when treating certain cracked distillates the longer the storage time elapsing between neutralization and re-running the better the colour of the finished gasoline and the smaller the amount of acid formed during re-running Sand filters are very effective in agglomerating the finely dispersed alkali, a comparatively small filter being necessary for quite large throughputs. According to Walton, unless the oil is freed from alkali and sodium salts in suspension, decomposition takes place in the re-run unit with the liberation of sulphur dioxide, free sulphur, and even sulphuric acid Frequently, too, a heavy deposit of coke is formed even though the maximum temperature of the still does not exceed 400–450° F.

Decomposition of this type is not so noticeable in steam stills, but there is then a tendency for hydrolysis to take place and alcohols and other oxygenated compounds to find their way into the overhead

The lighter lubricating oil fractions and gas oils are conveniently treated with hot caustic soda which enables a much quicker separation to be obtained As a general rule it is customary to re-run the lighter distillate oils up to and including the gas oil, after acid treatment, for the reasons given previously, while the heavier fractions, including the lubricating oils, are finished with adsorbent earths Kerosines may be redistilled or treated with adsorbent earths depending upon which gives the more satisfactory results and is the more convenient Certain adsorbent earths, in particular bauxite, when correctly roasted possess sweetening properties also, owing to adsorbed oxygen and, besides removing traces of objectionable compounds from the kerosine by adsorption, oxidize and adsorb the high-boiling marcaptans together with other sulphur bodies They can, therefore, be employed for sweetening as well as desulphurization Heavily acid treated kerosines must be re-run owing to the relatively large amounts of high-boiling material formed including possibly diphenyl sulphones

With the object of avoiding re-running adsorbent earth treatment has been advocated by certain refiners for the gasoline fractions So far as straight-run gasoline is concerned there seems to be no objection other than the fire hazard and the difficulties invariably experienced in handling solid reagents and recovering a volatile product from the spent material With cracked gasolines, however, although successful results have been claimed, it is doubtful whether there is much to be gained over re-running Allowance must be made for the rise in end-point normally occurring on the acid treatment of an unsaturated material and the raw distillate has accordingly to be cut at a somewhat lower end-point

In the re-running of cracked products it is desirable to operate at as low a temperature as possible to avoid decomposition of the sulphuric esters which is accelerated by high temperatures

The factors determining sulphur dioxide formation have been carefully studied by Rigden [16, 1933], for an acid-treated Iranian pressure distillate It was found that while sulphur dioxide formation is negligible below an oil temperature of 275° F decomposition is most marked between 320° and 370° F Over this range during which 21% distilled overhead, 65% of the total sulphur dioxide liberated was evolved At 420° F sulphur dioxide formation was complete Other factors affecting sulphur dioxide formation were the concentration of the acid used in the treatment together with the time of contact and temperature at which it was carried out Acid concentration had the largest effect while increase in temperature also resulted in increased sulphur dioxide formation as shown by the following figures

TABLE IX

Acid concentration, %	*Temperature, ° F*	*Sulphur dioxide lb SO_2 per 1,000 gal*
96	60	0 25
80	60	0 029
96	120	0 44
80	120	0 094

The relationship between time of contact and sulphur dioxide formation was linear with the contact times investigated Rigden also observed that a thorough caustic wash did not always reduce sulphur dioxide formation

To overcome corrosion of the distillation equipment, caustic soda or soda ash is frequently fed in with the feed stock The addition of a soda ash-soap solution with the reflux at the top of the column has also been stated to give satisfactory results, owing to the presence of soap the alkali remains in a finely dispersed condition and is consequently used to the greatest advantage The sodium salts are run off with the bottoms and removed by settling

Since even under comparatively mild conditions there is a tendency for sulphur bodies to break down or any free sulphur present to react with the oil and produce a doctor positive product, it is usually necessary to complete the treatment of lighter products which have been re-run with either an alkali wash, if hydrogen sulphide only is present, or a sweetening treatment with doctor or hypochlorite Kerosines or special naphtha cuts may be improved by filtration through an adsorbent which by removing minute particles of water held in suspension 'brightens' and produces a clear product

With the possible exception of the lightest spindle oils which are sometimes finished with an alkali wash at 125° F, the transformer, lubricating, and special oil factions are finished after sludge removal with clay Neutralization is effected by adding hydrated lime together with the clay excepting when the alkalinity of the latter is sufficient for the purpose More recently high temperature clay treatment has been evolved which is particularly suited to solvent refined oils After a small acid treatment and removal of the sludge, the oil is mixed with special acid-treated clays and passed through a pipe-still In this way the temperature of the oil is rapidly raised to as high as possible without cracking taking place, usually about 600° F The pressure maintained on the still prevents the evolution of water-vapour from the clay and so avoids frothing The oil is rapidly cooled and passed into a steam-stripping section where the so-called 'stink oils' are removed Neutralization is effected at this stage by the addition of alkali (hydrated lime) after which the clay is removed by filtration

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EQUIPMENT FOR CHEMICAL AND SOLVENT TREATING OPERATIONS

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REFINING petroleum products by chemical or solvent treating usually involves one of the following operations:

1. Contacting an oil with a solution of a chemical reagent or a solvent completely or partially immiscible with the oil phase.
2. Contacting an oil with a suspension of a chemical reagent, the reagent suspension being completely or partially immiscible with the oil phase.
3. Contacting an oil with a solid chemical reagent.

By far the majority of chemical and solvent refining processes necessitate the contacting of two liquid phases, usually oil and an aqueous solution in chemical treating, and oil and an organic solvent in solvent refining.

An example of the first type of contacting is treatment of oil with acid, caustic, or plumbite solutions, or with nitrobenzene, phenol, or furfural for solvent refining. Sweetening operations employing suspensions of chloride of lime and suspensions of lead sulphide in sodium hydroxide solution are examples of the second type of contacting, while neutralizing with solid magnesium hydroxide, sweetening with a powdered mixture of litharge, hydrated lime, and caustic soda, and earth or clay treatments furnish examples of the last type of operation.

After the actual contacting process has been completed the separation of two liquid phases or of a liquid and a solid phase is often necessary.

Physical Factors in Contacting

The objective in contacting two immiscible liquid phases or a liquid and a solid phase in petroleum refining operations is

(*a*) to promote the rate of extraction of a substance from one phase by the other, or

(*b*) to promote a chemical reaction between the phases or between substances in each phase. In addition to hastening the reaction, by thorough contacting, undesirable side reactions are partially prevented by eliminating the danger of local excess of reagents or local overheating.

In a contacting process mass transfer and reaction rates are promoted by increasing the turbulence of the system and increasing the interfacial area by dispersion.

The overall chemical reaction involved in a liquid-liquid system, for example, is controlled by two processes: firstly, the diffusion of one of the reacting substances into the adjacent liquid phase and, secondly, the chemical reaction between this substance and the reagent already in solution in this adjacent phase. Either the first or second process may control the overall reaction rate.

The rate of extraction depends only upon the diffusion of a substance from one phase to the other. Extraction processes, and reaction processes controlled by diffusion, are hastened by the promotion of the mass transfer rate of a substance from one phase to the other. This rate of mass transfer can be increased by increasing turbulence and increasing interfacial contact area. Extraction processes, and chemical reaction processes controlled by diffusion, are speeded up, therefore, by efficient contacting which increases turbulence and interfacial contact area.

A chemical reaction process not controlled by diffusion is not hastened by efficient contacting. Nevertheless, efficient contacting is still beneficial in this case in reducing undesirable side reactions by eliminating local excess of reagents and overheating.

In a two-phase system the degree of turbulence may be altered by varying the relative velocity and relative density of the two phases, and also by varying the viscosity ratio of the two phases, if both are liquids, or by varying the dimensions of the contacting apparatus [34, 1937]. The interfacial contact area may be altered by varying the fineness of the dispersion of one phase within the other. As shown in Table I the available surface area increases rapidly with increasing subdivision.

TABLE I

Results of Progressive Subdivision of a Cube

Length of edge	*Number of cubes*	*Total surface area*
1 cm	1	6 sq. cm.
1 mm	1×10^{3}	60 sq. cm.
0.1 mm	1×10^{6}	600 sq. cm.
0.01 mm	1×10^{9}	6,000 sq. cm.
0.0001 mm (= 1 μ)	1×10^{12}	60,000 sq. cm.

In a dispersion the continuous phase is the external phase, while the discontinuous or disperse phase is the internal phase. The particle size of the disperse phase, if small, is measured in microns (1 micron = 1 μ = 0.0001 mm.). Dispersions may be classified roughly by the particle size of the disperse phase as in Table II.

TABLE II

Rough Classifications of Dispersions

Particle size of disperse phase	*Type of dispersion*
1 mm. upwards	Macroscopic or coarse suspension
1 μ to 1 mm	Microscopic suspension or emulsion
0.1 μ to 1 μ	Colloidal suspension or emulsion
0.001 μ to 0.1 μ	Colloidal solution

Too fine a dispersion, as in an emulsion, is not, however, always desirable owing to separation difficulties which may cancel any advantages gained by the increased contact efficiency.

The physical factors, apart from equipment dimensions and design, which play a part in contacting operations are:

(1) The viscosities of the liquid phases, and the apparent viscosity of any dispersion produced.
(2) The relative density of the two phases and the density of the continuous phase.
(3) Surface tension.
(4) The diffusion coefficients of substances taking part in the extraction or reaction processes.
(5) The relative proportion of the two phases.

Viscosity.

The viscosity of the liquid phases or of the dispersion produced determines the degree of turbulence which may be attained. The viscosity of a dispersion is not the same as the viscosity of a truly viscous liquid, but varies with different rates of flow. The viscosity, at any given temperature, of a truly viscous material never changes, but the so-called apparent viscosity of all other types of material varies widely with variation of stirring speed or rate of flow. When a dispersion is being produced the initial and final viscosities may vary widely and consequently the contactor provided must be efficient over the whole viscosity range. The apparent viscosity is one of the most important factors determining power requirements. The application of the Stormer viscometer, as used for determining apparent viscosities of suspensions, to contacting problems appears to be promising. Its use should aid in determining the type of contactor, speed and power requirements, to be employed for any particular contacting problem.

Density.

Density has a bearing on the power requirements. For systems of the same viscosity or apparent viscosity the power varies directly as the average density of the system at constant stirring speed in the same contactor. For large density differences between phases great effort must be required to overcome the tendency of the phases to separate.

Surface Tension.

This influences the particle size in dispersions and the permanence of dispersions.

Diffusion.

The ease of diffusion of reacting substances or substances to be extracted in liquid phases is important in determining contacting efficiencies.

Relative Proportion of the Phases

At equal agitating speeds contacting efficiency is a function of the relative proportion of the two phases. This is undoubtedly connected in some way with the apparent viscosity of dispersions. For example, water and kerosine, both of low viscosity, when agitated in the ratio of four parts of oil to one part of water result in a thick, fairly viscous emulsion. Four parts of oil agitated with one part of water result, on the other hand, in an emulsion only slightly more viscous than the kerosine itself. Wide viscosity and interfacial area differences exist in these two systems which result in wide differences in contacting efficiency at equal stirring speeds.

Contact Methods

Methods of contacting which can be applied equally well to either extraction, absorption, or chemical refining process fall into three classes

(1) Single contact processes
(2) Multiple contact processes
(3) Countercurrent contact processes

In the single contact process, contact or mixing is carried out in a single stage or operation. After contact the two phases, usually two liquid phases, are separated. The process may be carried out either by batch or continuous working. In the latter case the two liquids are mixed continuously in a mechanical contactor or pumped concurrently through an orifice column and finally separated by centrifuges or by continuous settling.

The multiple contact method of working a refining process is illustrated diagrammatically in Fig 1. Mixing and separation of the treated and treating liquids is followed by contact of the treated liquid with fresh reagent. This operation is repeated as often as required. The method may be carried out in batches, or semi-continuous working may be employed. In the latter case the two liquids entering each stage of a multi-stage process are mixed continuously in a suitable mixing device and finally separated either by centrifuges or continuous settling. The method finds its main application as a laboratory or small-scale method and is seldom used commercially. It is generally recognized that the multiple contact method is much less efficient than the countercurrent method of contacting. The latter method, however, is not always practicable, particularly on the laboratory scale, although it can be readily applied by using a tower in place of a series of mixers, such towers, however, are generally equivalent only to a relatively small number of ideal mixers and are not very satisfactory. The multiple contact method, therefore, finds its greatest application in the laboratory and, where drastic restriction in the volume of treating agent employed is seldom essential, can be used very effectively. It is often desirable, however, to reproduce countercurrent effects in the laboratory without an extensive outlay of time and equipment. Such an effect can be reproduced very simply with ordinary laboratory apparatus by an extension of the multiple contact method. The process, called 'pseudo-countercurrent contact', was first developed by Watanabe and Morikawa [39, 1933]

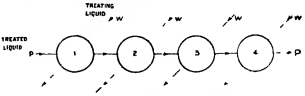


FIG 1 Multiple contact process

The method is illustrated diagrammatically in Fig 2. In this example a countercurrent process is simulated in which P volumes of treated liquid is contacted with W volumes of reagent in n stages. The first horizontal row in Fig 2 shows the multiple contacting of P volumes of treated liquid in n stages with W volumes of reagent at each stage. In every row, R_m, which lies below the first row, P volumes of

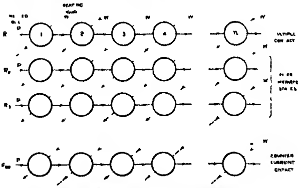


FIG 2 Pseudo-countercurrent contacting

treated liquid are contacted at each stage, *n*, with *W* volumes of exit reagent from stage $(n+1)$ of row R_{m-1} If such a series is infinitely repeated, it approaches more and more closely to the true countercurrent effect

The utility of the countercurrent method of operation is universally recognized, and it has been widely employed in many processes, notably in distillation, absorption, leaching, washing, extraction, and chemical operations

In this method the liquid to be treated is contacted with treating liquid which has been employed in a previous contact stage, except that in the final stage of the process the treated liquid is contacted with fresh reagent This effect is most readily produced by causing the two liquids to flow continuously and countercurrently through a suitable vertical tower The method may also be applied by contacting and separating in stages, the mixers and separators so employed being provided with suitable cross-connexions to ensure countercurrent flow of the two liquids

The above methods are most easily applied for contacting two liquid phases, but can also be used for contacting a liquid and a solid phase

Of the three contacting methods the countercurrent method is the most efficient, and by its use the same degree of refining can be obtained as in the other methods, but with the employment of smaller quantities of treating reagents

While computations for extraction processes employing any of these three contacting methods have been worked out, no attempt has yet been made to develop quantitative computation methods for forecasting the results from a chemical refining treatment Meyer [26, 1931], however, has indicated a method by means of which the problem might be attacked and has applied his method to the removal of weak organic acids from oils by treatment with caustic alkali Jantzen [22, 1932] has described very similar computation methods to those proposed by Meyer, while MacMullin and Weber [28, 1935] have discussed a theory of continuous reactors Reaction computations are nearly identical with extraction computations, a general discussion of which will be found in the article by Hunter on Principles of Solvent Extraction

Equipment for Contacting Two Liquid Phases

Contacting equipment does not yield itself readily to a rigid classification, but for the purposes of this article it can be conveniently divided into

1 Mechanical mixers
2 Jet contactors
3 Column contactors

The first class comprises apparatus in which intimate mixing of the two liquids is produced by some mechanically operated device, such as a stirrer or propeller In the second class, both liquids are passed concurrently through an orifice or jet and intimacy of contact is obtained between the two phases in consequence of the turbulence produced in the liquid after it has issued from the orifice

In the column contactor a series of restrictions is introduced into the fluid stream flowing up a vertical column, with the result that a series of turbulent regions is maintained in the apparatus which serve to produce the desired contact

Apparatus of the first class often aims at the production of fine dispersions, relying largely on an increase of interfacial area to bring about the desired contact With equipment included in the last two classes, maximum turbulence is produced without much dispersion of phases, so that the efficiency of the device depends more on increasing the rates of mass transfer and reaction by increasing the velocities of the liquid This can by no means be considered as a rigid generalization, however, since some types of jet and column contactors do give rise to dispersions and some types of apparatus in the first class rely mainly on liquid velocity effects

The degree of contact produced by a mechanical mixer depends on the physical contact between the ingredients of the mixture and the mixer itself, or on turbulent flow of the two liquid phases The latter effect is usually most pronounced in the vicinity of the agitating elements, for liquid velocities are highest in that region A substantial part of the total power input is expended in bringing about this dispersion or intimacy of mixing, whilst the remainder is utilized in producing and maintaining the necessary flow

The production of the necessary flow in order to mix the two liquid phases uniformly and thoroughly is important Stratification and settling will render the results of an otherwise efficient contacting apparatus quite worthless Unless both horizontal and vertical flows are sufficient, and unless all the material in the container is moved repeatedly into the zone of action, whatever mixing, break-up, or dispersion takes place there will be completely nullified

Contacting capacity cannot, with our present state of knowledge, be safely predicted on a theoretical basis It will depend on the type of contactor, its capacity and speed of operation Power consumption, which depends on similar factors can, however, be predicted approximately by the use of empirical equations

Mechanical contacting devices may be subdivided into four fundamental types The oldest and best known form is the simple paddle mixer All such mixers have flat or angled blades, which usually are driven at low speeds, with tip velocities ranging from 75 to 350 ft per minute

A second fundamental type includes all contactors which rely on a pump located outside the container This is usually a centrifugal pump drawing material from the conical bottom of a tank and returning it to a different point of the container

The third general type includes all kinds of propellers As propellers produce a high rate of shear when rapidly rotated, they are extremely useful for dispersing immiscible liquids Propellers may be mounted either singly or in multiple on a shaft They may produce either unidirectional or opposed flow, and are often set within a draught tube or mounted off-centre in the tank to prevent mass rotation Their peripheral speed usually ranges from 1,000 to 2,000 ft per minute

Turbine mixers form a fourth type, and are similar to centrifugal pumps, but without casings, being arranged to rotate horizontally within a tank on a single vertical shaft They may or may not be provided with deflecting blades round the impeller to prevent swirl and promote radial flow. A typical apparatus is a dish-bottom tank, with two or more impellers on one vertical shaft, driven at a peripheral speed of 600–900 ft per minute Because of the large rate of circulation, over 12,000 gal per minute in a 500-gal treater, and the high degree of dispersion and intimacy of contact produced, such turbine mixers are very efficient

Blade corrosion of paddles, propellers, and turbines in mechanical contactors can be reduced by the construction of such equipment out of bakelite or a suitable metal alloy Agitation by this type of equipment is satisfactory in batch systems, but suffers from the disadvantage of requiring a packing gland when used for continuous systems At the low pressures usually existing in a continuous treating system glands have, however, been employed which will give long service without trouble

The use of mixing jets to promote contact between two liquids is a development of rapidly increasing importance Their efficiency, combined with low cost and small back-pressures all favour their adoption for this purpose

The simplest type of jet consists of a small tubular constriction fixed inside a pipe of larger diameter, through which the two liquids to be contacted are pumped A typical jet is illustrated in Fig 3

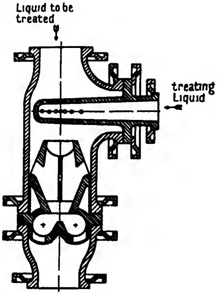


Fig 3

An important matter to be considered in the design and installation of mixing jets is the introduction of the treating agent into the stream of liquid being treated A very satisfactory method is to use an elbow jet installed in a tee just ahead of the first mixing nozzle as in Fig 4 This tee delivers the treating liquid into the centre of the second liquid stream Improved performance is obtained if the treating liquid enters the second stream through a perforated pipe situated immediately in front of the first mixing nozzle Flexibility is obtained by using two or more jets and varying the space between them and also by varying the rate of flow of the treating liquid, which is best accomplished by using proportioning pumps of the plunger type

Other types of jet mixers consist of a simple Venturi tube or a number of smaller tubes in parallel, whilst a jet and plate device may be used, in which a jet is discharged at high velocity through orifices to impinge against a flat plate It is doubtful if much turbulence is produced in the latter type of equipment, since a jet of liquid impinging on a solid surface tends to glide along the surface in a thin stream until it reaches the boundaries, where it leaves approximately tangential to the surface

Jets function well for acid treating in furnishing large ratios of acid to oil without producing a high dispersion A system of jets can be readily arranged to secure an acid/oil ratio of as high as four to one

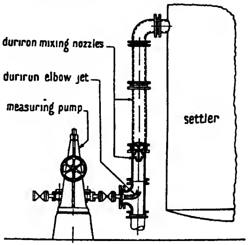


Fig 4

The principle of column contactors depends on the creation of successive zones of turbulence or dispersion in the liquids flowing through the column by means of bends, orifices, or obstructions introduced into the path of the fluid When the column is used purely as a mixing device, both liquids are passed through it concurrently, and issue from the discharge end in a state of dispersion dependent on the efficiency of the apparatus

One of the simplest types of column contactor is the baffle-plate column (Fig 5), which is not an efficient mixer, but may be used to maintain a dispersion by recirculation, and may also be used as an auxiliary mixing element It has the advantage, however, of causing only a small decrease in pressure A 6-in diameter column, for example, fitted with 20 baffle plates 1 ft apart registers a decrease in pressure of 10 lb per sq in with liquid flowing at 7,000 gal per hr

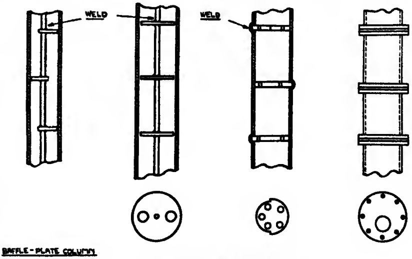


Fig 5 Baffle and orifice plate columns

An extension of the baffle-plate device is the use of column packing such as Raschig rings, crushed rock, screened gravel, or coke. Such packed columns are relatively cheap, and easily constructed, usually from a few lengths of pipe packed with some convenient filling. As a rule, they are more efficient than the baffle-plate column, and give good results with a comparatively low drop in pressure. Gravel, quartz, and coke packings plug rather easily, and ring fillings are on the whole more satisfactory.

A special packing which has the property of acid wetting in preference to the oil is sometimes employed for acid treating. No precise information on the design of packed columns or baffle-plate columns for bringing about contact or reaction in liquid-liquid systems is available. Design is usually based on pressure drop. Morrell and Bergman [27, 1928] discuss the pressure drops found by experience to be most suitable for different refining treatments, while White [40, 1935] and Chilton and Colburn [9, 1931] give data enabling pressure drops of fluids flowing through packed columns to be calculated.

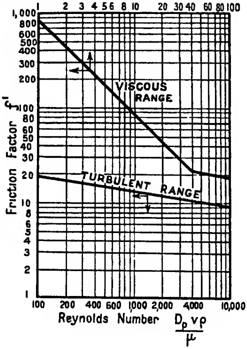


FIG. 6

The recommended equation of Chilton and Colburn is

$$\Delta p = \frac{0.00517 f' A_f \rho v^2 L}{D_p},$$

where Δp is pressure drop in lb. per sq. in., f' is a friction factor dependent upon $D_p v\rho/\mu$ and may be obtained from Fig. 6 where the relationship is plotted. A_f is a wall effect factor plotted in Fig. 7 as a function of

$$\frac{\text{packing element diameter}}{\text{column diameter}},$$

ρ is the average fluid density at column entrance and exit in lb. per cu. ft., v is average fluid velocity corresponding to density ρ over the total cross-section of the column, L is the length of the packed portion of the column in feet, and D_p is the average diameter of the packing elements in inches. In the case of hollow packing elements the friction factor obtained from Fig. 6 must be multiplied by a correction factor from Table III.

One of the best types of mixing columns is the orifice column, which has proved very satisfactory for making contact between two liquids. Intimate contact between the fluids is obtained by pumping them together in the proper proportion through a series of perforated plates in a length of pipe as in Fig. 5. The energy of the high-velocity jets issuing from the orifice is dissipated in the formation of eddies, giving the contact required. Relatively low liquid velocities are used in this type of column, a velocity of 0.6 ft. per sec. being quite usual. A high drop in pressure between each plate is necessary to obtain efficient dispersion, the orifice area being usually divided into several small holes rather than one large one. The normal drop in pressure per plate is about 2 lb. per sq. in., and since 15 to 20 plates are required in an efficient column, a total back-pressure of 30 to 40 lb. per sq. in. is set up, exclusive of the liquid head upon the column. This high back-pressure is a definite disadvantage of this type of equipment, and is certainly large when compared to the back-pressure prevailing in apparatus of the jet class.

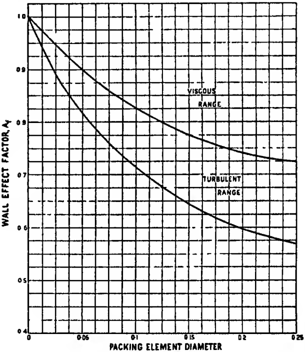


FIG. 7

TABLE III

Correction Factors for Hollow Packing Elements

Element	Dimension (in.)	D_p	Correction factor: Turbulent flow	Correction factor: Viscous flow
Raschig rings	1 × 1 × 0.014	1.0	0.28	0.5
Glass rings	0.49 × 0.45 × 0.03	0.47	0.44	0.6
Glass rings	0.39 × 0.38 × 0.03	0.39	0.44	0.6
Glass rings	0.23 × 0.22 × 0.03	0.23	0.84	0.9
Triangular rings	1.75 × 0.2 × 0.2	1.75	0.2	0.4

The conventional orifice formula $Q = CA\sqrt{(2GH)}$ may be used to design orifice type mixers, where

Q = liquid quantity in cu. ft. per sec.,
C = coefficient (0.61 for small-diameter orifices),
A = area of orifice, sq. ft.,
G = gravity acceleration = 32.2 ft. per sec.,
H = head of liquid in feed

An adaption of this formula in more convenient terms is $Q_b = 18\ 26\ D^2\sqrt{H}$, where

Q_b = flow in barrels per hour,
D = diameter of orifice in inches,
H = head of liquid in feet

Experience has shown that a total pressure drop through an orifice column of 30 lb per sq in is satisfactory for acid treating, while a total pressure drop of 15 lb per sq in is sufficient for plumbite or caustic treating

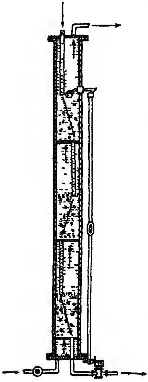


FIG. 8

A second and important type of column contacting equipment may be employed for obtaining contact between two liquid phases without the production of a dispersion of one phase within the other Here, the two liquids flow countercurrently through the apparatus, and turbulence in both phases together with the formation of new surfaces of contact is produced by the use of some special form of plate or tower filling

The simplest column consists of a plain tower in which a level of one liquid is maintained automatically, and through which the second liquid is sprayed downwards The efficiency is greatly improved by the introduction of tower packing, usually perforated plates or Raschig rings, the function of the filling being to promote turbulence and increase the interfacial area

An example of this type of contacting column is illustrated in Fig 8 The column shell is divided into several vertical sections by means of horizontal perforated plates A pipe extends downwards from each plate for a length far enough to permit the accumulation of a layer of the heavier liquid of sufficient depth to provide a differential head which will transfer it to the next section The lighter liquid passes upwards through the perforations in the plate and through each heavier liquid layer in fine drops, reuniting to form a liquid layer before passing through the next plate The level of heavier liquid is maintained constant by means of a float regulating device connected to a valve in the outlet line By reversing the vertical pipes, the heavier liquid can be made to pass down through the perforations and fall in fine drops through the lighter liquid layer

A very similar type of contacting column, widely used on the Continent, consists of a number of perforated plates, which do not, however, fill the whole of the column cross-section, but are placed one above the other in segments The number and size of the perforations are so adjusted that the liquid descending the column is dammed up above each plate until it reaches a certain height, when it flows through the perforations in a number of thin streams on to the next lower plate, where the process is repeated, and so on, until the last plate is reached The liquid ascending the column finds its way out around the plate The belief that this type of column is adaptable only to limited conditions and that with an inadequate flow of descending liquid the latter would fall through the column in a direct stream, or that at high velocities of the liquid it would flow around the plates, appears to be erroneous

The design of countercurrent columns for liquid-liquid extraction purposes has been investigated by Hunter and Nash [19, 1932], and Varteressian and Fenske [37, 1936], Meyer [26, 1931], Jantzen [22, 1932], and Happel and Robertson [12, 1935] have discussed the design of liquid-liquid countercurrent columns for carrying out chemical treating processes The work of Happel and Robertson is undoubtedly the most scientific and noteworthy attempt to devise a design method for chemical treating plant It will be discussed in detail later on in this article The rate of reaction involved in a chemical treating process may be controlled by either the diffusion of one of the reagents or by the chemical reaction involved In the first case the design becomes similar to that for a pure extraction process The second case has not yet been investigated, although an interesting theoretical discussion of this case is given by Davis and Crandall [10, 1930]

Mechanical and jet mixers and columns employing concurrent flow can readily be used for single contact processes When employed for the successive or countercurrent methods of contact, several such devices must be coupled together, with any convenient form of separator, by suitable cross-connexions to produce the required successive or countercurrent type flow

Efficiency of Liquid-Liquid Contacting Equipment

In order to select the most suitable contacting equipment the various types should be compared on a standard efficiency basis Unfortunately, however, practically no information of this character is available, and in consequence the comparison of equipment types made here, though employing all the published information obtainable, is unavoidably indirect in character

Practically no investigations have been carried out to determine the efficiency of mechanical mixing devices in producing contact between two immiscible liquids, although the efficiency of such apparatus when used for mixing two miscible liquids and for the dissolution of a solid in a liquid, has been investigated Wood, Whitemore, and Badger [46, 1922], and also Badger and McCabe [2, 1931], investigated the time for complete mixing of a saturated salt solution and water at different stirring speeds in a 600-gal tank, 5 ft high by 5 ft diameter, provided with both plain-paddle and propeller-type stirrers The results of these investigations are summarized graphically in Fig 9

Increasing the size of the plain paddle improved the mixing efficiency, whereas the addition of vertical baffles resulted in a marked decrease in performance Greater rapidity of mixing was attained with the plain paddle compared with the propeller A definite advantage was also gained by increasing the distance between the stirrer and the bottom of the vessel and also by lowering the water-level

The efficiency of a mechanically propelled paddle agitator for the production of a suspension of sand in water has been studied by White, Summerford, Bryant, and Lukens [45, 1932], who confirm the conclusion of Badger and his colleagues by finding that uniformity in the concentration of suspended solid is approached most closely when the paddle is near the liquid surface

A good deal of work on the efficiency of mechanically propelled agitators for contacting a solid and a liquid phase has been published which is applicable to the present case of liquid-liquid contact This, however, is fully discussed later in connexion with the efficiency of liquid-solid contacting equipment

The efficiency of a plain paddle stirrer for dispersing water and lubricating oils has been examined by Herschel [14, 1917], and experiments were made on lubricating oil and aniline by Hunter and Nash [21, 1936] In chemical treating processes the greater the efficiency of dispersion attained, the greater will be the contact area between the two liquids, and hence the greater will be the contacting efficiency The results of these two investigations are summarized in Fig 10 In this figure the degree of dispersion is measured by the average rate of settling of the dispersed mixture, and obviously the slowest rate of settling indicates the most intimate dispersion It will be seen from Fig 10 that efficiency increases with increasing paddle speed and with time of stirring up to a critical point of maximum efficiency, after which an increase in either of these variables results in a decrease of efficiency The efficiency also increases with increasing ratios of treating liquid to oil, and again passes through a critical point In Table IV the variation of the overall extraction efficiency with solvent-oil ratio for the solvent extraction of different lubricating oils with nitrobenzene at 10° C is given for air-agitated mixers [20, 1935] These results confirm the fact that contacting efficiency increases with decreasing treating liquid/oil ratio Othmer [29, 1934], in discussing the solvent extraction of acetic acid solutions, records that extraction efficiency as high as 100% for mechanically stirred contactors can be readily obtained

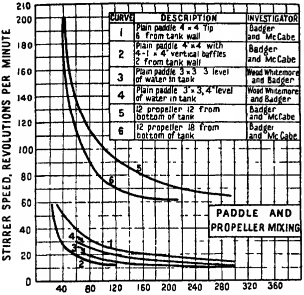


Fig 9

Table IV

Overall Stage Efficiency for Air-Agitated Stage

Lubricating oil stock used	Volumes solvent per 100 volumes of oil	V G C of solvent free raffinate oil produced	Number of ideal extraction stages required	Number of air-agitated stages required	Percentage overall stage efficiency
Stock No 2 0 853 V G C	100 0	0 811	2 42	3	80 6
	136 4	0 807	2 05	3	68 3
	185 0	0 804	1 80	3	60 0
	375 0	0 799	1 53	3	51 0
Stock A, 0 867 V G C	98 0	0 835	2 43	3	81 0
	188 0	0 831	1 53	3	51 0
Stock B, 0 864 V G C	75 0	0 828	2 70	3	90 0
	150 0	0 814	2 45	3	81 6
	225 0	0 811	1 90	3	63 3
Stock C 0 828 V G C	150 0	0 803	2 30	3	76 6

These high efficiencies were obtained on a mechanical agitator, where both phases were contacted and then allowed to settle out in contact with each other, and where no continuous flow of the two phases took place in the agitator For mechanical agitators where continuous counter-flow of the two liquids actually occurs in the agitator very high performances can be obtained In reality such contactors are mechanically agitated counter-current columns Jantzen [22, 1932] has investigated the performance of this type of equipment, and the results of his experiments are summarized in Table V

It will be seen from this table that quite small contactors of this type are equivalent to a very high number of ideal stages This affords an excellent illustration of a fact, not generally recognized by designers of liquid-liquid extraction equipment, that contactors of the mechanically agitated type should be constructed to allow, if possible, a continuous counter-flow of both liquids through the region of agitation

No work has yet been reported on the efficiency of a jet or nozzle either for mixing or for chemical contacting

The only similar information with regard to concurrent type columns is some work carried out on the mixing of adjacent miscible liquid layers in pipes [32, 1911] The mixing effect was measured by the percentage length of pipe over which admixture had extended, and was found to increase with the diameter in similar pipes at similar fluid

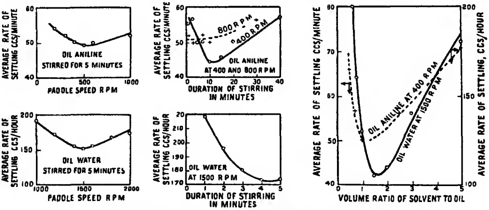


Fig 10 Effect of paddle-speed, duration of stirring, and solvent-oil ratio on paddle-stirred mechanical contactor

velocities, that is, the mixing increases with increasing turbulence.

Table V

Contacting Efficiency of Mechanical Agitators

Test	Contacting apparatus	Treated liquid	Treating liquid	Treating liquid/treated liquid ratio	Number of equivalent ideal stages
1	40 cm wide 50 cm long with double stirrer, mixer arms moving in opposite direction to outer arms and twice as fast	Ether solution of quinoline and *iso*-quinoline	Dilute solution of HCl	1	2
2	As in test 1, but 12 plates placed on inner stirring arms, and 12 rings on outer arms	Ether solution of quinoline and *iso*-quinoline	Dilute solution of HCl	1	3.5
3	As in test 2, but stirrers lengthened and provided with 3 longitudinal rods or baffles	Phenanthrene in petroleum ether	Methyl alcohol	2	4.4
4	As in test 3	Acetic acid in ether	Water	1.1	5.7
5	47 cm wide 51 cm high fitted with vertical rotating roller 36 cm diam and 51 cm high velocity of roller 150 r.p.m.	Phenanthrene in petroleum ether	Methyl alcohol	2	5.4
6	As in test 5 velocity of roller 1 000 r.p.m.	Acetic acid in ether	Water		over 10

In Fig. 11 the results from the removal of phenol from an oil with aqueous alkali for both a jet and a concurrent type contacting column are compared. It is apparent that for this particular case, at least, the jet contactor is much more efficient than the column contactor.

For the countercurrent type of contacting column, a little more information is available. Hoening [18, 1929] has investigated the relative merits of different kinds of countercurrent columns used to extract an aqueous solution of phenols with benzol, and the percentage of the total amount of phenols present in the aqueous liquor extracted by a given quantity of benzol under similar conditions was employed to measure the equipment efficiency. This investigator described a test on different types of column packing, using a column 6 metres in height with an effective height of 4 metres, and a diameter of 2 metres. Identical liquor rates, benzol rates, and temperatures prevailed during these tests. Liquor and benzol were first countercurrently contacted by forcing them in broken-up streams into the empty tower. Later, the tower was packed with pieces of coke (Grade II), then filled with different sizes of Raschig rings, and finally operated with perforated baffle plates.

The comparative extraction efficiency on the basis of the percentage of the total removal of inlet phenols is shown in Table VI.

Table VI

Column filling	Efficiency, %
Empty tower	55
Coke granules (Grade II)	60
60 mm Raschig rings	70
25 mm Raschig rings	73
Perforated baffle plates	73

Some further experiments on the removal of phenols from water by extraction with benzol were carried out by the Koppers Company [24, 1928] in a column of 0.90 metre diameter, both empty and filled with perforated plates. The results obtained agreed very well with those for the 2-metre diameter tower reported in Table VI. Using perforated plates as packing, the ideal stage equivalents of this tower for the removal of phenol and the three cresols from aqueous ammonia liquor are given in Table VII together with similar data obtained by a test run carried out by the author on a commercial plant operated in England.

It will be seen from the figures in Table VII that the efficiencies for both these towers are very poor, each of these tall towers being only equivalent to 1 or at the best 2 ideal contacting stages. Judging from these data the countercurrent contacting tower compares very unfavourably with the mechanically agitated type of contacting device where one actual stage was almost the equal of an ideal stage.

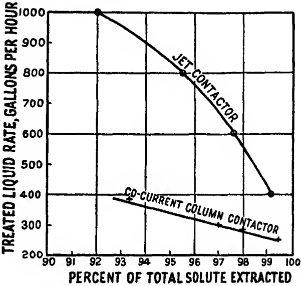


Fig. 11. Extraction performance comparison between jet and concurrent column contactors

Table VII

Ideal Stage Equivalents for the Removal of Phenols from Aqueous Ammonia Liquor using Perforated Plate Columns

Solute extracted	Ideal stage equivalents for I	Ideal stage equivalents for II	Ideal stage equivalents for III
Phenol	1.05	1.01	0.77
o-Cresol	1.32		0.88
m-Cresol	2.39	0.62	0.22
p-Cresol	2.39	0.64	1.95

I 0.9 metre diameter tower, packed height 4 metres
II 0.9 metre diameter tower, packed height 4 metres
III 1.52 metre diameter tower, packed height 14 metres

This performance compares even more unfavourably with that of the mechanically agitated contactor embodying internal countercurrent flow. On comparing Tables V and VII, it will be seen that an agitator of this type, 50 cm high, is from 5 to 10 times more efficient than a packed countercurrent tower 4 to 14 metres high. Jantzen [22, 1932], also obtained very poor performance from laboratory-size countercurrent columns He examined the action of two columns, one 4 cm diameter by 1 m long packed with 10 mm glass rings, the other 1 2 cm diameter by 15 m long laid in zigzag form Neither of these towers was equivalent to a single ideal stage The packed countercurrent type of column is not an efficient liquid-liquid contactor It is interesting to note also in this respect that the countercurrent column type of contactor used for the removal of phenol from aqueous liquors has now been replaced in Germany to a large extent by mechanically agitated contactors

Varteressian and Fenske [37, 1936] have investigated the performance of a packed column for liquid-liquid countercurrent contact Their experimental work was of such a nature as to give a general indication of the effect, on the performance of the column, of each of a number of common variables, rather than to study the effect of each of them in detail Of the variables studied, the packing material, the inversion of continuous and discontinuous liquid phases in the column, and the throughput rate were found to be without appreciable influence on the efficiency of the column The shape and size of the packing, however, materially affected the performance

In a 3-metre column, diameter 1 41 cm, packed with 4-mm metal rings, the equivalent number of ideal stages varied from 2 1 to 4 0 This is a much better performance than that obtained by Jantzen [22, 1932] and that recorded above in Table VII

Rushton [31, 1937] has examined the efficiency of a packed tower for contacting two liquids, in connexion with the solvent refining of oil by nitrobenzene He finds that there is a limit to the amount of oil that can be handled by a given size of packing Throughput is lower but contact efficiency is better with small size packing Graded packing (larger at the bottom and smaller at the top) gives better results than uniform packing For a given height of packing with increasing treating liquid/oil ratio the contacting efficiency decreases, while the efficiency increased if the oil rate was increased with a given height of packing Preferential wetting of the packing appeared to have no appreciable effect

A tower 6 ft high by 3 in diameter packed with either ring-rod or saddle packing varying in size from ½ to 1 in was found to be equivalent to 0 85 up to 3 1 ideal stages The data given by Rushton are unfortunately open to criticism Insufficient data are given in the paper to allow his experimental results to be checked for accuracy by means of weight balances From the meagre information given experimental errors appear to be high The method adopted by Rushton for calculating the efficiency of the contact equipment used appears to be at fault and to be a direct consequence from the apparently large experimental error

Rogers and Thiele [30, 1937] have studied the operation for liquid-liquid contact of a three-plate rectangular bubble column provided with a glass front so that its operation could be observed It was used both in the ordinary position and inverted Several different types of caps were tried In all cases the contact of the two liquids appeared to be poor This result was attributed to the low efflux velocity of liquid from beneath the bubble caps They concluded that this type of equipment was not well adapted for liquid-liquid contact, which conclusions are in agreement with the statements made above in connexion with the comparison of the data in Tables V and VII

Elgin and Browning [11, 1935, 1936] have carried out an excellent and helpful theoretical analysis on a spray liquid-liquid countercurrent column as a dispersion apparatus They show that the contact area in such a system is fixed by three interrelated variables, drop size, time of contact between the dispersed and the continuous phase, and the number of drops passing a given point in unit time Given size drops will rise or fall through a stationary continuous phase with a certain static velocity v_0 Bond [5, 1927], and Bond and Newton [6, 1928] have shown that the static drop velocity where the densities of the phases involved are of the same order of magnitude is given by

$$v_0 = \frac{1}{k}\left(\frac{2}{9}\,\frac{\Delta\rho\, g d^2}{\mu_c}\right),$$

where $\Delta\rho$ is the density difference, d drop diameter, μ_c viscosity of continuous phase, and g the gravitational constant k is a constant varying from 1 to 1 5 for very small drops and is a function of the viscosity ratio of the two liquids, mass and diameter of the drop, and the interfacial tension If the continuous phase has an appreciable countercurrent velocity, the actual drop velocity $\bar{v}$ is less than the static velocity If F'_C is the linear velocity of the continuous phase and F'_D the linear velocity of the dispersed phase through the column, and α equals F'_D/F'_C, the flow ratio, then

$$v = \tfrac{1}{2}\left\{v_0+\left(\frac{\alpha-1}{\alpha}\right)F'_D+\left(\left[v_0-\left(\frac{\alpha+1}{\alpha}\right)F'_D\right]^2-\frac{4(F'_D)^2}{\alpha}\right)^{\frac{1}{2}}\right\}$$

When d, the drop diameter, is defined as the diameter of each drop necessary to produce the total contact area, if the volume of the disperse phase in the column were divided into spherical drops of equal size, then the contact area per unit volume, or specific contact area A, is given by

$$A = \frac{6F'_D}{\bar{v}d}$$

Drop diameter is determined by operating conditions and by the densities and viscosities of the two liquid phases, their interfacial tension, diameter of entrance nozzle, and velocity through it The mechanism of drop formation is complicated, and a relation between drop diameter and the physical properties of the phases which also expresses drop diameter as a function of entrance conditions through the nozzle has been obtained

Experimental observations indicate that when v_0 is fixed the liquid velocities for which a column will continue to function as a countercurrent dispersion apparatus are definitely limited Increase in the flow of either phase, or both, eventually results in a volume of the dispersed phase in the column at any instant sufficient to fill it completely and prevent the passage of the other phase In this event the dispersed phase disappears, one phase will push the other ahead of it, and both will leave at the same end of the column This limiting condition has been termed the 'critical state' and the corresponding liquid flow rates the 'flooding velocities' The latter are independent At the critical point $\sqrt{v_0}$ must exceed $\sqrt{F'_D}+\sqrt{F'_C}$ for a spray column to operate The minimum value of $\bar{v}$ for a spray column to function as dispersion equipment is given by

$$v_{\min} = \frac{(\alpha+\sqrt{\alpha})v_0}{(1+\sqrt{\alpha})^2}$$

For fixed conditions at the entrance point of the dispersed phase and fixed rates of liquid flow a minimum column diameter is required The latter may be altered by varying the inlet conditions or by varying the flow ratio Conversely, for fixed flows and column diameter a critical

v_0 must be maintained by suitable control of entrance conditions.

Elgin and Browning determined the performance of a spray column 2 in. diameter by 4 ft. high for the extraction of acetic acid from an aqueous solution with isopropyl ether, and also for the extraction of the acid from the ether solution with water. They found this column to be equivalent to 0.37 up to 1.98 ideal stages under the conditions investigated. At a later date Appel and Elgin [1, 1937] determined the performance of a spray and a packed column for the countercurrent extraction of benzoic acid between toluene and water. The results are reported in terms of an extraction capacity coefficient, which in the spray column, 2 in. diameter by 5 ft. high, increased with both liquid flows. The capacity was increased markedly by decreasing drop size which was found to be the most important factor in its determination. For large drop size capacity proved to be a linear function of the rate of flow, while for small drop size capacity passed through a maximum and then decreased with flow. Under these conditions the column was found to operate with a greatly increased hold-up of the disperse phase, attributed to drop coalescence in the column. Flooding velocity with respect to one phase was found to decrease with increase in flow of the other phase and was markedly decreased by small drop size. In the packed column, water, preferentially, wet the packing, and if dispersed flowed down over it in a continuous film, whereas toluene, if dispersed, rose in distinct drops. The capacity coefficient was relatively independent of initial drop size and was of the same order of magnitude found for the intermediate drop diameter in the spray column. With toluene dispersed it increased with toluene flow and decreased with water flow except at very low toluene velocities. With water dispersed it increased with flow of either liquid. The flooding velocity with respect to either phase was lower the larger the flow of the other and practically independent of initial drop size. The packed column flooded at approximately half the velocity found for the intermediate drop size in the spray column. The capacity of the spray column was either much lower or much higher than that of the packed column, depending upon the drop size employed in the former.

A reasonable basis of comparison for a countercurrent contacting column is the column height equivalent to a theoretical contacting stage. A theoretical stage is considered to be a stage in which the two liquid phases reach equilibrium. The column height equivalent to an ideal or theoretical stage is usually referred to as the H.E.T.S. or sometimes as the H.E.T.P., the height equivalent to a theoretical plate, the terms theoretical stage and theoretical plate being synonymous. The efficiency of various countercurrent columns on this basis is compared in Table VIII.

From this table it will be seen that the H.E.T.S. of laboratory-size packed and spray countercurrent columns varies from 1.5 to 50 ft., while plant columns so far examined have an H.E.T.S. varying from 5.5 to 209 ft. Laboratory-size columns fitted with a mechanical stirrer show an H.E.T.S. of 0.16 to 0.82 ft. It would appear from this data that the packed or spray countercurrent column is not an efficient contacting device, but that a countercurrent column fitted with a mechanical stirrer can be made an efficient item of equipment.

A too intimate mixing effect is sometimes undesirable. In acid treating when the acid is in a very fine state of dispersion the rate of settling and the degree of freedom secured by a settler is low. With some highly unsaturated distillates a vigorous contacting with acids will result in an acid oil which cannot be clarified by settling, and even when filtered such an oil will retain much of its acidity until neutralized. Upon neutralization sodium salts of esters may form and remain in the oil layer. These salts are partially decomposed upon re-running, resulting in corrosion of re-running equipment and sulphonation and oxidation of the finished overhead product. Because of the undesirability of forming a highly dispersed acid in oil system the modern tendency is to use large ratios of acid to oil and eliminate a too vigorous contacting. The effectiveness of a large amount of acid gently agitated with an oil as compared to a smaller acid quantity intimately mixed can be illustrated on the mass action principle.

TABLE VIII

Efficiency of Countercurrent Contact Equipment on H.E.T.S. Basis

Size of column	*Packing*	*Duty*	*H.E.T.S. ft.*	*Authority*
9.84 ft. × 0.55 in. diam.	4 mm. metal rings	Extraction in alcohol-benzene water system	2.46–4.7	Varteressian and Fenske [37, 1936]
6 ft. × 3 in. diam.	½ to 1 in. ring rod, or saddle packing	Extraction in nitrobenzene lub. oil system	1.48–5.4	Rushton [31, 1937]
4 ft. 1 in. × 2 in. diam.	spray	Extraction in acetic acid water-isopropyl ether system	1.5–8.1	Elgin and Browning [11, 1936]
3.28 ft. × 1.57 in. diam.	10 mm. glass rings		3.28	Jantzen [22, 1932]
49.2 ft. × 0.47 in. diam.			49.2	Jantzen [22, 1932]
1.64 ft. × 15.7 in. diam.	stirred	Reaction in ether-quinoline hydrochloric acid system	0.47–0.82	Jantzen [22, 1932]
1.64 ft. × 15.7 in. diam.	stirred	Extraction in phenanthrene petroleum ether alcohol system	0.37	Jantzen [22, 1932]
1.64 ft. × 15.7 in. diam.	stirred	Extraction in acetic acid-ether water system	0.29	Jantzen [22, 1932]
1.64 ft. × 1.85 in. diam.	stirred	Extraction in phenanthrene-petroleum ether-alcohol system	0.30	Jantzen [22, 1932]
1.64 ft. × 1.85 in. diam.	stirred	Extraction in acetic acid-ether-water system	0.16	Jantzen [22, 1932]
13.1 × 2.95 ft. diam.	perforated plates	Extraction in phenol-water-benzol system	5.5–12.5	Hunter and Nash [21, 1936]
13.1 × 2.95 ft. diam.	perforated plates	Extraction in phenol water-benzol system	13.0–21.2	Hunter and Nash [21, 1936]
46 × 4.92 ft. diam.	perforated plates	Extraction in phenol-water-benzol system	23.6–209	Hunter and Nash [21, 1936]

Raw distillate + fresh acid = treated distillate + sludge acid.

$$\frac{(C_{\text{treated distillate}})\times(C_{\text{sludge acid}})}{(C_{\text{raw distillate}})\times(C_{\text{fresh acid}})}=1/K,$$

where K is the extent to which the reaction proceeds Now if the concentration of the acid be denoted by the amount of exposed surface, it can be seen that a large amount of acid in large droplets will cause the same extent of reaction as a smaller amount of acid in small particles

These advantages of mild agitation still hold for the smaller ratios of acid to oil, providing sufficient time is allowed to compensate for the lower exposed surface when mild agitation is used Provision of a long time element in any reacting system means, however, that for a given capacity equipment must be larger, which in turn means higher initial costs and more maintenance In order to surmount this obstacle, and, more important, to fully utilize acid content of sludge, recirculation systems are in operation

Happel and Robertson [12, 1935] have evolved a method of testing and designing countercurrent chemical treating systems They have applied it to the scrubbing of naphtha to remove mercaptans by means of caustic soda solution

The two-phase system of naphtha and aqueous caustic solution contains mercaptan in three forms, free (HSR) in the oil phase, and (NaSR) and (SR^-) ions in the caustic phase

The equilibrium equation for the system can be written

$$K = \frac{A_{(SR^-)}}{A_{(HSR)}\,A_{(OH^-)}},$$

where $A_{(SR^-)}$, $A_{(HSR)}$, and $A_{(OH^-)}$ represent activities of the mercaptide ion, mercaptan, and hydroxyl ion, respectively Since the solution is very dilute with respect to mercaptan content, $A_{(SR^-)}$ is assumed to be proportional to mercaptide concentration in the caustic phase, and $A_{(HSR)}$ to the mercapatan concentration in the oil phase Therefore, for a given hydroxyl ion concentration, the ratio of the ion concentrations of mercaptan in the oil and aqueous phases, that is the distribution coefficient, is a constant as demonstrated experimentally by Meyer [26, 1931]

Using the data of Meyer, of Birch and Norris [4, 1935], and of Borgstrom and Reid [7, 1929], Happel and Robertson have correlated the distribution coefficients obtained at different caustic concentrations

If, in a treating operation, a large excess of caustic is used so that the caustic concentration does not change, the distribution coefficient would be constant throughout the operation Calling x the concentration of any given mercaptan in the caustic and y the corresponding concentration in the naphtha, a plot of the equilibrium relationship is a straight line passing through the origin In fact, however, caustic concentration falls because of conversion to mercaptide Assuming a suitable percentage utilization, i e conversion of caustic in the operation as a whole, fixes once for all the value of the distribution coefficient in the final stage of contact If *OA* in Fig 12 represents the equilibrium of a given component for fresh caustic and *OB* the corresponding line for fresh caustic, the actual equilibrium line for each stage of contact, other than the final one, will be represented by some line through the origin with a slope intermediate between the two The exact position of each line must be determined by trial and error

The operating line for any given component is fixed and is a straight line with a slope equal to the ratio of the volume of caustic to the volume of naphtha passing through the treating system per unit time To locate its position a trial and error method is used The terminal conditions are thus fixed, and it is possible to proceed with a stepwise calculation of the number of countercurrent stages required to effect the desired caustic utilization A suitable efficiency, equal to the percentage approach to equilibrium of the mercaptan removal for any given stage, may be used to advantage

The following plant test illustrates the applicability of the method

Twelve thousand gallons of naphtha were washed with 5,300 gal of caustic containing 0 05 lb per gallon of sodium hydroxide at 40° F in a two-stage countercurrent system In the first stage raw naphtha was bubbled through partially spent caustic In the second stage the washed naphtha was intimately mixed in a centrifugal pump with fresh caustic and allowed to settle

It is desired to determine the efficiency of extraction of each of the stages

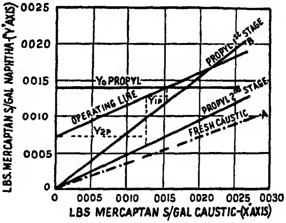


Fig 12 Extraction diagram for mercaptan removal

Naphtha analyses were as follows

Raw naphtha	*Mercaptan sulphur, lb per gal*
Methyl mercaptan	0 0077
Ethyl mercaptan	0 0027
Propyl mercaptans	0 0014
Butyl mercaptans	0 0005
Amyl mercaptans	0 0002
Hexyl+mercaptans	0 0003
Total	0 0128
Total after first stage	0 0073
Total after second stage	0 0032

It is possible to compute the free caustic concentration at the end of each stage Then, using the distribution coefficient correlations given in the paper, these coefficients may be calculated to be as follows

	Methyl	*Ethyl*	*Propyl*	*Butyl*	*Amyl*
Second stage	41 9	15 7	2 1	0 59	0 20
First stage	25 2	9 4	1 3	0 35	0 12

A separate calculation for the scrubbing of each mercaptan is then carried out as illustrated in detail below for the propyl mercaptan

In Fig 12 the equilibrium relationships for propyl mercaptan are plotted as two straight lines The analyses of the feeds (using subscript p to denote propyl mercaptan) are $Y_{0p} = 0\ 0014$ lb per gallon in the naphtha and $X_{3p} = 0\ 0$ lb per gallon in the caustic The slope of the operating line is

5,300/12,000 = 0 44 To locate it a trial and error method is employed and a position is assumed The intersection of the operating line and the horizontal line $Y = Y_{0_p}$ gives the concentration of mercaptan in the caustic leaving the system

A vertical line dropped from this intersection to the equilibrium line for the first stage would give the mercaptan content of the naphtha leaving the first stage, Y_{1_p}, if equilibrium were attained in this extraction An efficiency of 60% is assumed, and consequently the value of $Y_{1_p} = 0\ 0013$ will be given by a point 60% of the distance between the operating and equilibrium lines The intersection of the horizontal line $Y = Y_{1_p}$ with the operating line gives the mercaptan content of the caustic leaving the second stage The same procedure as above is followed in obtaining the mercaptan removal from the naphtha in the second stage, except that in this case an efficiency of 80% is assumed Since the horizontal line representing the concentration of mercaptan sulphur, $Y_{2_p} = 0\ 0007$ lb per gallon, intersects the assumed operating line at the Y axis, the assumed operating line is correctly placed when using fresh caustic solution containing no mercaptans

A similar calculation is made for each of the other mercaptans present in the system The mercaptan concentrations in pounds per gallon for all components leaving the first and second stages are calculated in this way to be as follows

Mercaptan	*First stage*	*Second stage*
Methyl	0 0036	0 0009
Ethyl	0 0014	0 0005
Propyl	0 0013	0 0007
Butyl	0 0006	0 0004
Amyl	0 0002	0 0002
Hexyl+	0 0003	0 0003
	0 0074	0 0030

Since the sums of the mercaptan concentrations are practically the same as the data obtained in the actual operation, the assumed efficiencies of 60 and 80% are correct

Liquid-Liquid Contactor Power Requirements

Data on power consumption of mechanical agitators of the paddle, propeller, and turbine agitator type have been reported Wood, Whitemore, and Badger [46, 1922], White, Brenner, Phillips, and Morrison [42, 1934] have determined data on power consumption for paddle agitators, while Hixson and Wilkens [17, 1933] have obtained similar data for a four-blade propeller, all of which has been correlated by White and Brenner [41, 1934]

The power consumption of a simple paddle agitator depends on the paddle length and width, tank diameter, liquid depth, agitator speed, the physical properties of the liquid stirred, and the equipment roughness Paddle thickness and position relative to the tank bottom have a negligible effect From a consideration of these values a dimensional equation may be derived, namely,

$$\frac{P}{\rho N^3 L^5} = K\left(\frac{\eta}{L^2 N\rho}\right)^a \left(\frac{W}{L}\right)^b \left(\frac{H}{L}\right)^c \left(\frac{D}{L}\right)^d,$$

where P = power consumption,
L = length of paddle,
N = paddle speed,
W = paddle width,
D = tank diameter,
H = liquid depth,
ρ = liquid density,
η = liquid viscosity

K, a, b, c, and d = constants to be determined experimentally In this equation $(L^2 N\rho/\eta)$ is a modified Reynolds number

White and Brenner found that the exponents in the above equation were not constant over the entire range investigated, and hence the form of the function is best expressed graphically A direct mathematical expression which does not fit the data quite so well is

$$\frac{P}{L\eta N^2 D^{1\ 1} W^{0\ 3} H^{0\ 6}} = 0\ 000129 \frac{(L^2 N\rho)^{0\ 86}}{\eta},$$

where N = revs per sec,
η = absolute viscosity in lb per sq ft,
ρ = lb per cu ft,
L, D, W, and H = feet

This equation expresses the experimental data satisfactorily for a Reynolds number of 10,000 or over, but diverges at lower values It can be used for determining power consumption in the region of turbulent flow

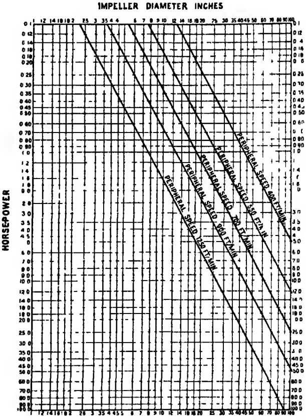


FIG 13

Buckingham [8, 1915] in a study of the windage of turbine wheels concludes that power can best be expressed by the equation

$$P = C\rho^{0\ 9} N^{2\ 8} L^{4\ 8} \eta^{0\ 1},$$

where L is the turbine wheel diameter, the other symbols having the same significance as in the previous equations

Fig 13 shows also the effect of turbine size and peripheral speed on power consumption for contacting liquids with a viscosity of 1 centipoise

Power consumption of rotating bodies in fluids has been shown to vary markedly with surface conditions. A more or less definite sharp increase of power takes place at speeds associated with the region of change from viscous to turbulent flow (see Unwin [36, 1880], Buckingham [8, 1915], and Kerr [23, 1913])

Very little need be said on the power requirement of jet and column contactors, as this is purely the power to pump the liquids through the system Since pressure drop through orifices and packed columns has already been dealt with in this article no further discussion is necessary here

Equipment for Contacting a Liquid and a Solid Phase

Contacting equipment for this purpose may be classified into

(1) Mechanical mixers
(2) Column contactors

The first class consists of apparatus in which contact between a finely divided solid and a liquid is produced by a mechanically operated device In the second class contact between a finely powdered, granular, pelleted, or agglomerated solid is produced by passage of the liquid phase through a column packed with the solid

Apparatus in the first class normally employed comprises paddle, propeller, or turbine mixers, ball mills and colloid mills Air agitation is very unsatisfactory and is seldom employed in modern plant Outside circulation has limited usefulness and is usually only used for maintaining a dispersion previously produced by other means

The specific gravity of the solid phase is most important in determining the type of mechanical contactor to be employed The specific gravity of the liquid phase is not so important, as for petroleum products it only varies over the range 0 7 to 1 0, whereas with solids it often varies from 0 9 to as much as 7 0

When correctly designed, paddles are satisfactory for low gravity solids except for very rapid dispersion They are economical because of their low first cost and because of their moderate power requirements at low speeds They are not satisfactory, however, for maintaining suspensions of high gravity solids in low viscosity liquids

Propellers are useful over a wide range of liquid and solid mixtures, being satisfactory for suspension and intimate contacting Their first cost is low and their power requirements moderate

Turbine mixers are very satisfactory for speedy and intimate contact Being true dispersers they are efficient for producing intimate dispersions for all size of batch or continuous operations Their first cost is somewhat higher than paddles or propellers, but their power consumption is often considerably lower than that for propellers

Ball and colloid mills usually produce very intimate dispersions, and, because of the increased cost of separating such dispersions, are seldom, if ever, employed for contacting in the petroleum industry

Column contactors are packed with the solid chemical reagent and the liquid hydrocarbon material to be refined is allowed to filter or percolate through the solid bed If the solid is in the form of a very fine powder, filtration is slow If the particle size of the solid is increased, contact surface and contacting efficiency is reduced but filtration speeded up Particle size of the solid packing depends, therefore, on the contacting time required It is advantageous to pack the tower as far as possible with solid particles of equal size, and the best results are obtained when the solid is granulated or pelleted

The most satisfactory methods for granulating fine powders are extrusion or agglomeration from nuclei A hard compact granule is obtained by using a pressure extrusion process This may be accomplished by passing the powder moistened with water between two rollers (Fig 14) rotating in opposite directions One roller is perforated with a number of holes By a continuous extrusion of the powder a series of cylinders is obtained, which on leaving the holes are broken up by the combined action of the roller and centrifugal force or by the use of suitable scrapers into short cylinders Another method is to extrude a paste of powder and water through a die press to form string-like rods of suitable diameter, which are broken into short lengths, dried or calcined in a rotary furnace, sieved and graded In the agglomeration process the powder, moistened with water, is rotated in a U-shaped vessel or drum by means of revolving paddles Wet particles of the powder given a rolling motion down the periphery of the drum accumulate upon their surface, in the manner of a snowball rolling down hill, other particles, and so become agglomerated into perfect spheres, whose size is directly proportional to the total time of rotation The resulting wet granules are soft and easily crushed, but possess sufficient strength to withstand screening before drying, if a slowly rotating or vibrating screen is used Drying of the granules, preferably in a rotary drier where a certain amount of glazing takes place, gives a hard product Both the cylindrical and spherical granules produced by these two methods are satisfactory for packing contacting towers If a really hard resistant particle of constant size is required, the most satisfactory method is to pellet the powder in a pelleting machine This machine compresses the powder into hard tablets or pellets all of equal size and shape A large number of such machines are on the market suitable for manufacturing pellets of all sizes and shapes In order to accomplish the compression of powder into tablets efficiently and economically, a preliminary granulation of the powder into spherical granules by the agglomeration method is advantageous By this means a smooth, easy flow of the material to the pelleting machine is assured, with the production of a harder and more compact pellet

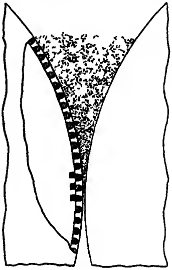
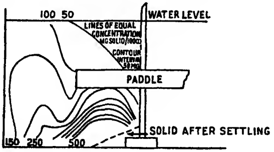


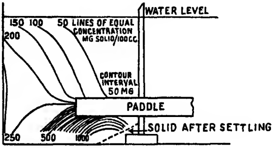
FIG 14

Efficiency of Liquid-Solid Contactors

The performance of a mechanical agitator of the paddle type has been investigated by White, Summerford, Bryant, and Lukens [45, 1932] for the production of a suspension of sand in water The equipment used for this work consisted of a 500-gal tank, 4 ft 4 in in diameter, with a 2-ft paddle 3½ in wide vertically mounted in the centre of the tank and agitated at a constant speed of 37 r p m The sand used was screened to give a product of approximately 65 mesh They found that maximum suspension of the solid is attained after a very short period of agitation Uniformity of concentration of the suspended solid was never obtained, but was approached more closely when the paddle was near the surface of the liquid than when it was close to the bottom of the tank



MIDDLE PADDLE



LOW PADDLE

Fig 15

Maximum suspension of the solid was obtained when the paddle was near the bottom of the tank, and in the design of agitators for this type of contacting the agitating device should be situated here When the paddle is situated at the bottom of the tank the liquid above the paddle is low in suspended matter and large depths of liquid above the paddle must be avoided The difference in solid suspensions when using a middle and low paddle are shown in Fig 15 White and Summerford [44, 1934] also found a hydraulic sizing of solid particles in the tank The large particles remained on the bottom near the centre of the tank, while the small ones were carried into suspension by the flow of liquid, so that careful screening of the solid can improve the contacting efficiency

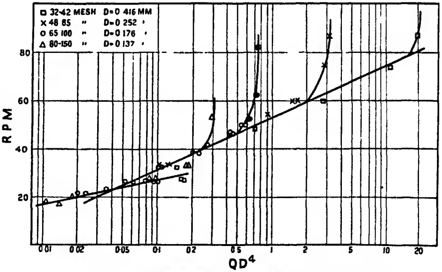


Fig 16 Relation between solid size, concentration, and agitator speed

Hixson and Crowell [15, 1931] have noted three types of agitation when a solid is stirred in a liquid At low agitator speeds a 'passive or non-flow' régime is maintained in which the solid particles remain on the bottom of the container with little or no motion This régime is one in which the vertical currents set up by the agitator are not sufficient to raise the solid particles from the bottom of the tank At somewhat higher agitator speeds the solid particles move inward towards the centre of the tank In this flow régime, characterized as curvilinear flow, the vertical currents are of sufficient magnitude to produce considerable suspension, the amount suspended being a function of agitator speed In the third type of agitation prevailing at high agitator speeds the solid particles were thrown outward from the centre and the regime described as turbulent flow was established In this third, or high speed, zone centrifugal forces eventually become sufficiently strong to combat effectively the forces tending to produce a more uniform sand concentration, and for any given position in the tank there exists an agitator speed beyond which an increase in speed accomplishes little or no increase in solid concentration This point is called the upper break, or saturation-point White and Summerford [43, 1933] found that curves of solid concentration against agitator speed showed these three distinct zones and they correlated empirically curves for various solid sizes by a plot of log Q/D^4 against R, where Q is solid concentration in mgm per 100 c c of liquid, D is logarithmic mean clear opening of screens forming the limits of the mesh fraction, and R is stirrer speed in r p m A plot of Q/D^4 against R is shown in Fig 16 for the suspension of sand in water using a paddle agitator with the dimensions given above The graph shows the three distinct flow zones and the saturation-point for different solid (sand in this case) sizes Since the saturation-point occurs at approximately the same agitator speed for different points in the tank if solid size and total amount of solid are constant, it is suggested that agitator speed at which saturation occurs should be used as a measure of intensity of agitation

Quantitative studies of agitation in a liquid-solid system have been made by Hixson and Crowell [15, 1931], and Hixson and Wilkens [17, 1933], in which emphasis has been placed on the effect of agitation on the phenomenon of dissolution The performance of agitators in these studies was interpreted on the basis of the kinetics of solution expressed as the velocity constant of the 'cube-root law' developed by Hixson and Crowell In the later study of Hixson and Wilkens experiments were conducted in a series of geometrically similar cylindrical vessels, ranging in volume from 0 73 to 353 gal, with corresponding stirrers of the propeller type In free rotational agitation the effects of stirrer speed, size of equipment, and fluid viscosity were found to be very great Baffles were found to slow down the fluid flow and were a hindrance to the agitating process More effective agitation was found in a shallow vessel than in a deep one at the same stirrer speed Agitation, as measured by rate of solution, was greater in the free rotational than in the baffled system at low stirrer speeds of 100 to 300 r p m The freely rotating turbine was found to be more effective than the propeller under the same conditions At higher stirring speeds of 300 to 500 r p m the most effective agitation was obtained from a turbine agitator operating in a fixed central deflecting ring

Hixson and Tenney [16, 1935] have studied the quantitative evaluation of agitation in a liquid-solid system on the basis of a 'mixing index' If a solid be dispersed in a liquid in such a manner that any small volume of the liquid shows the same ratio of solid to liquid as any other and the same ratio as total solid to total liquid, the system may be said to be perfectly mixed Obviously, the system so arranged is in dynamic equilibrium Suppose the total quantities of solid and liquid present in the system are in the ratio x/y If any small sample from this system in dynamic equilibrium analyses for solid and liquid in the ratio x/y, it is 100% mixed Intermediate degrees of mixing may be expressed linearly by the relations

$$P = \frac{S}{S_0}100 = \frac{100-L}{100-L_0}100$$

if the liquid is in excess, or

$$P = \frac{L}{L_0}100 = \frac{100-S}{100-S_0}100$$

if the solid is in excess S and S_0 here represent the weight per cent of solid in a sample and in the total mixture respectively, and L and L_0 the weight per cent of the liquid in a sample and in the total mixture, while P represents the per cent mixed An average of the percentages mixed of a sufficient number of samples taken from different arbitrary locations within the agitating vessel for a given set of conditions gives a quantitative measure of the degree of uniformity of agitation throughout the vessel and is referred to as the 'mixing index' for that set of conditions The variation of mixing index with different sets of conditions in a vessel 18 in diameter by 29½ in high agitated with a four-bladed propeller is shown in Figs 17 and 18 The figures show that mixing index increases slowly with increasing agitator speed at low speeds and low fluid viscosities, and that it increases sharply at higher speeds, finally flattening off at still higher speeds The lower flat portion of the curves in Fig 17 is probably associated with passive flow, while change from passive to curvilinear flow is indicated by the sharp increase of mixing index with speed With increasing speed in the curvilinear flow region mixing index increases rapidly up to the saturation-point where the curves flatten off at some definite speed for a given viscosity The chief factor influenced by viscosity is probably the settling rate of the solid particles Slower settling of solid particles produces better mixing, as is indicated by the higher values of mixing index at high liquid viscosities

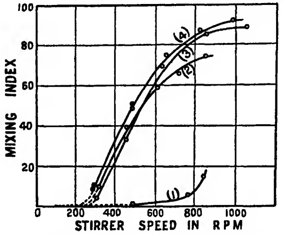


Fig 17 Degree of mixing v speed Curve (1), liquid viscosity 0 89 centipoises Curve (2), liquid viscosity 21 3 centipoises Curve (3), liquid viscosity 33 8 centipoises Curve (4), liquid viscosity 43 9 centipoises

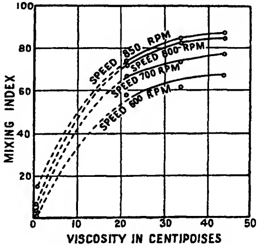


Fig 18 Degree of mixing v viscosity

The contacting of liquid and solid in a tower packed with solid particles has been examined by Scott [33, 1935], Mayo, Hunter, and Nash [25, 1935], and by Baker, Chilton, and Vernon [3, 1935] In long columns of small diameter, Mayo, Hunter, and Nash found that the liquid in its passage down the tower tends to flow away from the centre of the packing towards the tower walls, where it continues its passage by flowing down the wall The percentage of the total available packing surface wetted increased with increasing rate of liquid flow up to a flooding-point, when the total packing surface was suddenly wetted At the flooding- or loading-point the packing is completely wetted by virtue of the fact that the whole tower is full of liquid In contacting a liquid with solid packing in a tower it is essential to use liquor rates which will flood the tower, or, better, to run the contacting column full of liquid by some means of flow control or by running the liquid up the tower If running with full towers is for any reason undesirable, large diameter packed towers may be employed and good liquid distribution over the packing obtained Baker, Chilton, and Vernon have shown that in sufficiently large packed towers the tendency for the liquor flow to concentrate near the walls is absent, and that uniform distribution, once attained, persists down to any reasonable depth of packing Some device for uniform initial distribution of liquid is essential, however, since the flow from a single stream does not become uniform until four or five tower diameters have been traversed.

Phase Separation after Contacting

Three general methods are almost universally employed in the petroleum industry for separating two liquids or a liquid and a solid after a contacting operation. These are

(1) Filtration
(2) Settling
(3) Centrifuging

Filtration is usually employed for separating a liquid and a solid phase where a liquid and finely divided powder have been agitated together. Settling and centrifuging are employed chiefly for the separation of two liquid phases.

Filtration.

Enclosed pressure filters are generally used for separating oil from a finely divided solid. These filters have a number of filter leaves suspended inside a shell into which the material to be filtered is charged under pressure. The leaves may be parallel or perpendicular to the horizontal axis of the shell. Usually the leaves are stationary, but sometimes they can be rotated during the filtration cycle, or the filter medium may be installed as an inner lining of the shell and rotate with it. In principle a filtering medium is stretched over a frame provided with channels for the collection and drainage of solution, and the material to be filtered is forced under pressure into the space between filter medium and outer housing. Manual labour in operation may be reduced by opening and closing the shell by mechanical means. The high pressure employed results in a good, dry cake. The Sweetland filter consisting of a series of circular disks suspended inside a cylindrical cast-iron shell is often employed.

During filtering a solid particle by the force of its impact penetrates the filter medium pores and comes to rest, or if a deposit has already formed exerts a compressive action upon it. The impact is proportional to the weight of the particle and to the pressure. A high initial pressure rapidly decreases the rate of filtrate flow when the solid material is composed, as it usually is, of uneven sized particles. A low initial pressure reduces compacting of the cake and results in a higher average rate of flow of filtrate. In a liquid having a low concentration of suspended solids the solid particles are deposited with more force than if the solid content is high, owing to the greater rate of flow depositing the particles at higher velocity and producing a denser cake. For these reasons low initial pressures increasing steadily as the cake builds up are desirable in pressure filters, the increasing pressure maintaining the rate of filtrate flow with increasing cake thickness, and consequently centrifugal pumps are ideal for feeding pressure filters. Filter aids are useful when the solids to be removed are in a very finely divided state. A filter aid should be porous, chemically inert, and of low specific gravity so that when mixed with the liquid to be filtered it will remain in suspension. Comparatively small amounts of filter aid are required and their cost is more than balanced by increased filter efficiency. Kieselguhr or diatomaceous earth of high silica content and having a low gravity is the most widely used of all filter aids for handling petroleum products. A coating of filter aid may sometimes be applied to the filter medium to act as a clarifying agent and to prevent binding of the filter medium. Precoating with filter aid is often used with advantage in the filtration of lubricating oils.

Spent solid is sometimes separated from oil by filtering through sand or by a combination of continuous settling in a tank and filtering the overflow.

Settling.

Settling is the operation normally employed for the separation of the treated oil phase from the treating liquid phase. The separation depends on the difference in densities of the two phases. The dispersed phase moves through the continuous phase with a velocity influenced by gravitational force, viscosity of the dispersion medium, difference in specific gravity between the phases, and size of the particles of the dispersed phase.

Stokes' law for the constant velocity of a small sphere falling in a liquid is given by

$$V = \frac{2r^2(\rho_1-\rho_2)g}{9\mu},$$

where r is the radius of the sphere, and ρ_1 its density, ρ_2 the density and μ the viscosity of the continuous phase, and g is the gravitational constant. This equation applies when the dispersed phase is the denser of the two phases and hence is settling downwards through the continuous phase. Where the dispersed phase is the less dense of the two phases and is settling upwards through the continuous phase this formula has been modified by Bond [5, 1927]

$$V = \frac{1}{K}\left[\frac{2r^2(\rho_1-\rho_2)g}{9\mu}\right],$$

where $1/K$ is a constant equal to 1.43 as determined for air bubbles rising through water-glass and castor oil.

In a later paper Bond and Newton [6, 1928] show that values of K vary from 1 to 1.5 and that K is a function of the viscosity ratio of the two liquids, mass and diameter of the dispersed particles and of the interfacial tension where the densities of the phases involved are of the same order of magnitude.

From these equations it is obvious that although density difference is important the importance rapidly diminishes when the particle diameter is sufficiently reduced, since the velocity is proportional to the square of the radius. With very small particles and with little density differences suspensions of great stability are possible sometimes, even defying centrifugal treatment.

Settling is generally accomplished in tanks large enough to give the required time element for separation. Either vertical or horizontal tanks may be used. The rate of settling in horizontal tanks per unit volume is greater than with vertical tanks, although the depth of the clarified layer is approximately the same. Advantages are claimed for both types of settlers, but experimental comparisons of the practical advantages of one type over the other remains to be made. In some cases where vertical tanks are used the inlet to the tank is tangential, and sets up a swirling motion to the tank contents which is claimed to aid in the separation. Horizontal tanks are used with or without baffles, and also with special arrangements for the inlet flow.

The exact settling time that is required is best determined experimentally for each treating operation. In general, alkali solutions and water washes settle more rapidly than acid sludge. Fifteen to thirty minutes usually suffices for caustic or doctor settlers, but an hour may be required for acid sludge.

Settlers are usually about 40 ft high varying in diameter from 2 to 10 ft , and are often fitted with a water spray for water washing The water spray is made from pipe in the shape of a cross either welded or connected by fittings Two crosses, one above the other to cover the tank area, are used in large diameter tanks The perforations are arranged in one or two sets in the bottom of each pipe Spray holes are sometimes made on one side of each pipe only so that the water-flow through the holes will assist rotary motion set up by the tangential inlet to the tank and assist washing Unless very hard water is used $\frac{1}{8}$ or $\frac{3}{32}$ in holes are satisfactory, countersinking of the holes from the outside assists in preventing plugging The spray is best situated 5 to 10 ft below the overflow in order to settle out as much water as possible before the oil goes to the next tank

Settling tanks may be employed for both batch and continuous settling of liquid-liquid and liquid-solid dispersions In continuous settlers the fluid velocity should not exceed 3 ft per minute

In acid treating, especially acid treating of cracked gasoline, it is sometimes important for stability of colour to remove most of the acid sludge in 2 minutes or less after contacting acid and oil This is best done by centrifuging but is sometimes carried out in a desludger Water washing or alkali neutralization of distillates containing sludge causes hydrolysis of the sludge and the liberation of tarry products which dissolve in the treated distillate with deleterious effect upon the final product In order to ensure complete removal of acid sludge the distillate from the acid settler is sometimes put through a desludger A desludger consists of a suitable vessel packed with sand, gravel, or special packing and the sludge is removed from the treated oil by selective adsorption or selective wetting on the surfaces of the material in the desludger Arrangements of trays or shelves over which the oil is given an elongated contact time and length of travel path are also used The special packing material used in desludgers has the property of acid wetting in preference to the oil The desludging towers are so designed that as the finely divided sludge and oil move upward, the sludge accumulates on the packing to form droplets heavy enough to settle to the tower bottoms countercurrent to the oil stream Many packing materials are also suitable for removing moisture from oil after a caustic wash Sludge or caustic which may accumulate on the tower packing after a period of operation may be removed by the introduction of steam for 4 to 6 hours

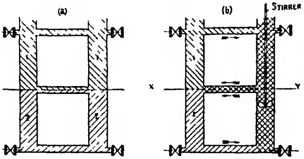


FIG 19

One of the most interesting settling systems is the Holley Mott System developed by the Anglo-Iranian Oil Company Ltd in which continuous contacting, settling, and reagent circulation are induced by the rotation of a single paddle stirrer The principle employed is illustrated in Fig 19 If the bottom half of the vessel in Fig 19 is filled with a heavy liquid of density 2 0 and the top half filled with a lighter liquid of density 1 0, three distinct exactly balanced U-tubes result If the contents of the right-hand vessel are converted into a dispersion, the resulting density of the dispersion will be 1 5 Under these conditions, in the upper half of the system, above the line *XY*, Fig 19, the liquid in the agitator will be heavier than the liquid in the separator, and a flow of dispersion from agitator to settler through the centre tube will result The upper connexion also allows liquid to flow from the settler to the agitator so that a circulation is produced A similar circulation results in the lower half of the vessel If a flow of fresh oil and reagent is introduced into the agitator, it is possible to remove from the separator separated light and heavy liquids and to take a flow of these two liquids wherever required In this way, in a single pair of vessels, a continuous contacting, settling, and circulation is induced by a single stirrer A single pair of vessels may be used as a stage unit in either batch, multiple contact or countercurrent contact treatment The design of the stirrer in the contacting vessel, as shown in Fig 20, consists of three plain diamond blades set at angles of 120° to each other along the length of a shaft mounted eccentrically in the contact vessel The settler is a plain vessel of a size and shape suitable to the work required Separating rates of 50 to 200 gal per hour per sq ft of interfacial area, depending on the oil and reagent used, are normally employed

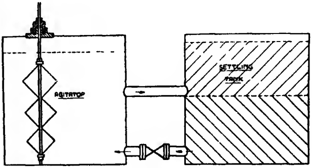


FIG 20

For separating liquid-solid dispersions cone settlers are now being used in the petroleum industry The cone settler consists of a conical tank, the angle at the apex of which is 45° to 60° The conical tank is mounted with its apex pointing directly downwards and is provided with a manually or automatically controlled sludge discharge valve at the bottom and a central loading-well and some suitable type of overflow at the top The feed enters through the central loading-well usually fitted with a baffle to prevent undue agitation Clarified oil overflows from the top of the cone and solids settle to the bottom Solids settling in the cone increase in density until the buoyant power of the settled solids raises an actuator which in turn operates a mechanism to unseat a valve from the orifice in the apex of the cone and allow the solids to be discharged Alternatively, the solids may be discharged by a plug valve or gooseneck siphon When using the siphon the greater the elevation of the siphon the greater the density of the discharge The solids separated by settling devices contain a good deal of liquid and the sludgy discharge has to be treated by some suitable means to recover this liquid Capacities of different size settling cones with an apex angle of 60° are given in Table IX

TABLE IX

Capacities of 60° Apex Angle Settling Cones

Outside diameter ft	*Depth, ft*	*Peripheral overflow capacity, gal per hr*
5	5	480
6	6	720
7	7	1 000
9	9	1 800

Settling cones can be used for continuous operation if equipped for continuous overflow and continuous discharge Trescott [35, *1934*] has described the use of cone settlers for continuously separating acid sludge

Centrifuging.

Two types of centrifuge may be employed for separating liquid-liquid dispersions, the hollow bowl type or a type using bowls with shallow settling spaces

The hollow bowl type was the first type developed for centrifuges This type has the advantage of simplicity and permits attainment of high values for maximum centrifugal force at the bowl wall, but material located at the centre portions of the bowl is subjected to only small centrifugal force Bowl type centrifuges are usually made with diameters up to 12 cm and bowl speeds of about 15,000 r p m The mixture to be separated is fed into the bowl revolving at high speed and the heavier liquid in the mixture is thrown by centrifugal force to the outside of the bowl, while the lighter remains in the centre As the operation continues the two vertical layers rise to the top of the bowl and by suspending a suitable ring diaphragm into the two layers the two liquids may be drawn off from separate exit spouts The centrifugal force applied is gravitational force enormously magnified so that the whole centrifuging operation is really an enhanced gravity settling

Bowls with shallow settling spaces are often employed In the majority of such separators the bowl is packed with cone-shaped disks, with thin spacer caulks giving shallow settling spaces, long liquid travel paths, and guided liquid flow The space thicknesses are two to three times as great as the diameter of the liquid globules to be separated The bowl is provided with two spouts through which the separated liquids are discharged Cone-packed disk-bowl separators have larger bowl diameters and lower rotational speeds than the hollow bowl type

The centrifuge finds its main application in quick contact acid treating processes for refining high sulphur content pressure distillate and lubricating oils High sulphur pressure distillate is treated with acid in a high-speed mechanical contactor, such as a Stratford contactor, in which the total contact time is of the order of 1 to 2 sec The dispersion produced is immediately transferred to centrifuges and separated The entire time of treatment, including contacting, transfer, and sludge separation, is about 4 sec The short total contact time avoids polymerization of valuable unsaturated hydrocarbons and allows acid desulphurizing of high sulphur content cracked distillates without excessive reduction of anti-knock properties In treating lubricating oil, heated oil and acid are contacted in a mechanical agitator for about 10 minutes Water is then added to the dispersion to prepare the sludge and the whole is centrifuged Acid is sometimes added in two portions, the first in the agitator, the second at the centrifuge itself which aids in producing a fluid sludge The De Laval acid sludge separator, a widely used centrifuge, is of the cone-packed bowl type The bowl speed is 6,000 r p m and oil capacity varies from 200 to 1,200 gal per hour with corresponding power requirements of 3 to 5 h p The advantages of employing centrifugal separation in acid treating are

(1) Separation of oil and sludge is very sharp and oil which is otherwise lost in the sludge is saved
(2) All 'pepper' sludge is removed, giving an oil of lower acidity and a reduced consumption of neutralizing agent
(3) The process may be run continuously
(4) Long contact time with acid is avoided with saving in oil losses

Walker [38, 1934] has given the following direct comparison data between conventional batch and continuous treatment with centrifugal acid sludge separation of lubricating oils

Characteristics of Stock Treated — Paraffin Distillate from East Texas Crude

Gravity ° API	29 5
Viscosity at 100° F , Saybolt seconds	75
Pour-point, ° F	75–80
*Colour, A S T M No	3

* Original colour at still, 2½ A S T M , darkened to 3 A S T M by heating during transfer

The batch-treating cycle was as follows

	Time (hr)
Charging agitator, 2,000 lb	4
Addition of first acid (1½ lb per 50 gal)	½
Blow period	½
Settling period	12
Drawing first sludge	1
Addition of second acid (4½ lb per 50 gal)	½
Blow period	½
Sousing water	½
Blow period	½
Settling period	3
Drawing sludge	1
Transfer period	4
Total cycle	28

The continuous treatment was carried out at a throughput rate of 600 gal per hour per machine, with the following results

	Batch	*Continuous*	
Quantity of acid, lb , 66° Bé per 50 gal	6	6	4
Tests on acid oil			
Gravity, ° API	29 9	29 9	29 9
Viscosity at 100° F , Saybolt sec	73	73	73
Colour, A S T M No	2¼	1½	2¼
Acidity, mg potassium hydroxide per gram	1 1	0 62	0 30
Appearance	heavy traces of sludge	microscopically free of sludge at 300 diameters	
Tests on sweetened oil (3° Bé lye solution used)			
Gravity, ° API	29 9	29 9	29 9
Viscosity at 100° F , Saybolt sec	73	73	73
Colour, A S T M No	2 dark	1½	2
Neutralization No , mg potassium hydroxide per gram	0 06	0 01	0 01
Colour stability (24 hr at 210° F)	poor	good	good

Sludge Characteristics

	Batch	*Continuous*	
Oil loss, % of charge	1 7	1 1	0 73
Sulphuric acid in sludge, %	23	25	25
Appearance	hard, viscous	soft, of readily pumpable viscosity	

Subsequent tests on the pressability of the acid-treated distillates shows no differences between the two methods of treating

To summarize, a large number of tests on oils of widely different characteristics have shown that continuous treatment with centrifugal sludge separation as compared with batch treatment will, in general, show the following advantages

1 A saving of 25 to 50% in acid requirements

2 A saving of 25 to 50% in earth or neutralizing agents

3 A reduction of treating loss amounting to 25 to 50% of that encountered in batch treatment

4 The sludge discharge from the centrifugal machine is less viscous, and more readily disposed of, than that drawn off by the agitators

5 Greater flexibility of operation

Centrifuging may also be employed for separating liquid-solid dispersions, but in this case continuous operation requires expensive special type centrifuges, while batch separation by centrifuging offers little or no advantage over filtration

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REFINING CRACKED NAPHTHA WITH SULPHURIC ACID AT LOW TEMPERATURES

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ONE of the chief problems of the petroleum refiner is the conversion of cracked naphtha into a refined gasoline suitable for use as motor fuel Such conversion involves removal of a variety of undesirable constituents such as sulphur compounds, gums, colour bodies, potential gum and colour-forming compounds, corrosive and acidic oxygen compounds, &c All refiners recognize the importance of eliminating such constituents, but the particular means of accomplishing this is dependent upon the crude oil source of the naphtha and the type of cracking process used, both factors contributing towards a wide variation in the quantities and properties of impurities present

Sulphuric acid has long been and continues to be the most important agent for refining cracked naphthas The present chapter is concerned with one of the more important developments in the use of this reagent, namely, low-temperature treatment

Chemistry of Cracked Naphtha Treatment

The ultimate object in any naphtha-treating process is the efficient removal of impurities with minimum loss of valuable constituents In this respect the action of sulphuric acid varies with temperature Since acid treatment is fundamentally a chemical process, involving various competing reactions, it is desirable to review briefly the chemistry of cracked naphtha treatment before proceeding to a detailed discussion of the temperature effect

Of the various types of hydrocarbons present in any cracked naphtha two of the most important, the paraffins and the naphthenes, are not affected by sulphuric acid under the conditions required for refinement This statement applies to the aromatic hydrocarbons also, except in those instances where a large quantity of strong sulphuric acid is required for treatment The fourth main class of hydrocarbons in cracked naphtha, the olefines, is subject to two types of reaction with sulphuric acid, polymerization and formation of acid or neutral sulphates Either reaction is undesirable since olefines are very satisfactory constituents of motor fuels Since as much as 60% by volume of a crude cracked naphtha [4, 1928] consists of olefines, one of the chief objects in sulphuric acid treatment is the development of conditions under which undesirable compounds are removed without seriously reducing the olefine content In addition to hydrocarbons containing one double bond, crude naphthas contain appreciable proportions of hydrocarbons containing two or more double bonds These compounds form resinous materials when the fuel is stored, especially in the presence of air The diolefines are, however, readily polymerized by sulphuric acid, and their removal presents no particularly difficult problem unless the naphtha has been severely cracked and abnormally high proportions of these compounds are present

Comparatively little exact information is available concerning the chemical composition and properties of the sulphur compounds present in cracked naphthas The types of compounds which have been definitely identified include the mercaptans, sulphides, thiophens and thiophanes Unquestionably, various unsaturated derivatives of these compounds are also present The hydrogen sulphide formed in cracking operations is normally separated from the crude naphtha before treatment and no further discussion of its removal is required here

The sulphur compounds mentioned above undergo five types of reaction when treated with sulphuric acid namely, oxidation, physical solution [1, 1926, 5, 1934, 8, 1926], sulphation, sulphonation, and polymerization The compounds most subject to oxidation are the mercaptans, the products being disulphides under mild conditions and sulphonic acids when the treatment is more severe The other types of sulphur compounds are probably not appreciably oxidized under the usual treating conditions Physical solution of sulphur compounds in strong sulphuric acid is known to be important in the case of sulphides and disulphides [8, 1926] In connexion with this action the formation of weak double compounds between the acid and organic sulphur compounds has been suggested [1, 1926] Sulphation of unsaturated sulphur compounds to yield acid or neutral esters similar to those derived from the olefine hydrocarbons is also probably of substantial importance All the sulphur compounds in cracked naphtha are subject to formation of sulphonic acid derivatives, but the relative rates and the importance of these reactions in practical treating operations are at present matters of conjecture Ample evidence is available showing that the unsaturated sulphur compounds in cracked naphtha are polymerized by acid treatment [5, 1934, 2, 1932] Presumably the sulphur atom has a considerable activating effect on the sensitivity of the molecule to polymerization

Little is known concerning the chemical constitution of the nitrogen and oxygen compounds present in cracked naphthas The former contribute to the colour of the distillate but their basic character permits ready removal by sulphuric acid Acidic oxygen compounds are removed by the alkaline wash which always follows acid treatment

Practical Fundamentals of Acid Treatment

One of the reasons for the extensive use of sulphuric acid in cracked naphtha treating is that its action may be readily modified to meet the needs of the particular problem at hand The most important factors capable of independent control are acid strength, temperature, ratio of acid to naphtha, time of contact, and method of application

Low-temperature treatment was developed for the treatment of cracked naphthas of high sulphur content, particularly of the California type, in which an abnormally high proportion of the sulphur is present in the form of inert thiophens and thiophanes When such material is treated for substantial sulphur reduction the product normally has a very satisfactory colour, gum content, colour stability, &c Consequently, in the section which follows, the degree of refinement will be indicated in terms of sulphur content only. It may be noted that in the case of low-temperature treatment of a naphtha prepared by severe cracking, the sulphur content control must be supplemented or even replaced by gum content and gum stability

In connexion with the determination of gasoline yield from crude naphtha it has become customary to refer to the treating loss and polymerization loss as separate items Treating loss represents the actual reduction in volume of naphtha caused by the removal of certain constituents in the acid sludge The polymerization loss is a figure indicating the loss in yield of fractions boiling within the gasoline range, but the exact figure is dependent upon the volatility specifications to be met For example, with end-point control a given naphtha might contain 80% by volume of fractions boiling below 400° F and 85% boiling below 420° F Assuming that after acid treatment the respective figures are reduced to 70 and 76%, the polymerization loss in the first case would be $\frac{80-70}{80} \times 100 = 12.5\%$ and $\frac{85-76}{85} \times 100 = 10.6\%$ in the latter In the following section the polymerization loss is expressed in terms of 400° F end-point material

Effect of Temperature

The reactions which take place when cracked naphtha is mixed with sulphuric acid are attended by the evolution of considerable heat and in the absence of any temperature control this effect is evidenced by a sharp rise in temperature of the mixture Fig 1 illustrates the temperature effects observed when a typical California cracked naphtha is mixed in a Dewar flask with varying proportions of 98% sulphuric acid In this particular series of experiments the initial temperature of the naphtha was 70° F However, it has been demonstrated that the temperature rise is practically independent of the initial temperature and the same curve would be applicable for initial temperatures varying from 30° F to 110° F

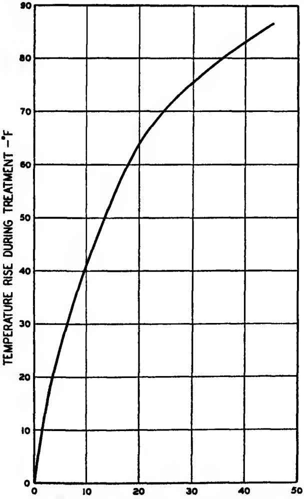

Fig 1

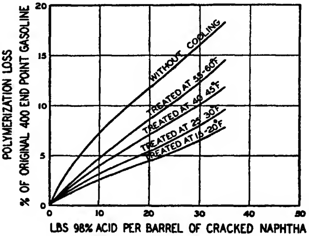

Fig 2

Specific data presented in this section in the form of charts and tables are limited to the treatment of California naphthas as obtained from liquid phase cracking processes In all cases acid requirements refer to pounds per barrel of 42 U S gallons (35 imperial gallons) of cracked naphtha In Fig 2 are plotted experimental results showing the effect of temperature on polymerization losses As noted above, the method of application of acid to naphtha and time of contact are important factors influencing the results obtained The isotherms of Fig 2 are reasonably comparable in these respects, since in all tests the acid was applied in several increments, the naphtha and acid layers were intimately mixed for 15 minutes after the last addition, and no sludge was withdrawn until after the final stirring operation

In the comparison of the curve labelled 'Without cooling' and the lower temperature curves one point requires further explanation The data are all based on laboratory experiments, and in obtaining the points for the four lower curves the procedure was as follows a 2-litre round-bottomed flask equipped with a mechanical stirrer was partially immersed in a cooling bath, 1 litre of naphtha was added, and with gradual acid addition the rate of cooling was so adjusted that the treatment was effected within the indicated temperature range In obtaining points for the 'Without cooling' temperature curve, the original temperature of the naphtha was 70° F and the acid was again added gradually but no attempt at temperature control was made Consequently, in the latter experiments the heat of reaction was partially dissipated and due to the relatively small apparatus the final temperature was appreciably lower than would be representative of large-scale operation Experience with commercial equipment has shown that, in the absence of any temperature control, actual polymerization losses are considerably higher than those obtained in such laboratory tests.

The experiments designed for comparison of polymerization losses at different temperatures also serve to illustrate the effect of temperature on treating losses. These data are plotted in Fig 3.

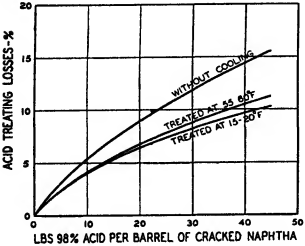

Fig 3

Fig 4 illustrates the effect of temperature on acid requirements to yield gasoline of various sulphur contents. The original naphtha used in obtaining these data contained 0.62% sulphur. However, the sulphur content of the untreated 400° F end-point stock contained in this naphtha was 0.53% and so the treating curves start from the latter point. A particularly interesting feature in Fig 4 is the reversal in temperature effect at about 15 lb. of acid per barrel of naphtha, smaller proportions of acid effecting greater sulphur reduction without cooling, while larger proportions are more effective at low temperature. No explanation of this phenomenon is forthcoming [6, 1933], but it may be noted that it represents a laboratory result only and it has not been observed in commercial treating operations. The curve for commercial three-stage treatment in Fig 4 and the discussion following under 'Commercial Application' substantiate this statement.

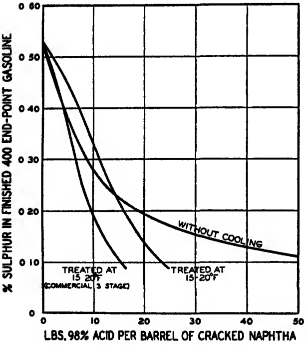

Fig 4 Sulphuric acid required for sulphur reduction

Data on polymerization loss, treating loss, and sulphur reduction are combined in Fig 5 to illustrate the effect of treating temperature on yields of gasoline for treatment to various sulphur contents. For treatment to given sulphur content the reduction in losses resulting from the use of low temperature is additive to the reduction caused by the use of less acid. Therefore, when a highly refined product is being prepared the excessive loss in yield accompanying treatment without cooling is particularly striking.

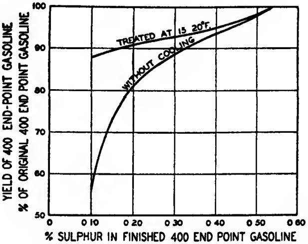

Fig 5 Gasoline yields after sulphuric acid treatment of a California cracked naphtha

Although the practical significance of the above temperature effects cannot be questioned, the theoretical explanation is far from adequate. At first sight it might appear that the decrease in polymerization and treating losses with decrease in temperature are merely examples of the well-known effect of temperature on reaction rate. However, the decrease in reaction rate is not the complete explanation, since the low-temperature contact between acid and naphtha-phases may be continued for several times the above-mentioned 15-minute period with no substantial decrease in gasoline yield. Another theory is that the selective removal of sulphur compounds at low temperatures, either by solution or reaction, so dilutes the acid phase that its polymerizing and sulphating activity is greatly diminished. Further factors to be considered are the relative rates of change of individual reactions with change in temperature, as well as the effect of temperature on purely physical solution. The whole problem is difficult and a comprehensive explanation must await further data.

It has been mentioned above that olefines, in general, are very satisfactory constituents of gasoline. A recent comprehensive investigation [7, 1934] of the knock ratings of pure hydrocarbons proved that the average knock rating of olefines is much higher than that of the corresponding paraffins. It is not surprising, therefore, that any treatment tending to reduce the olefine content is accompanied by a corresponding loss in knock rating. Fig 6 illustrates the loss in knock rating (initial octane number was 69.9 by the C.F.R. Motor Method) accompanying acid treatment of a cracked naphtha at two different temperatures. It will be noted that the curves are similar in shape to those in Fig 5, indicating that the low-temperature process conserves a greater proportion of high anti-knock olefines than treatment without cooling

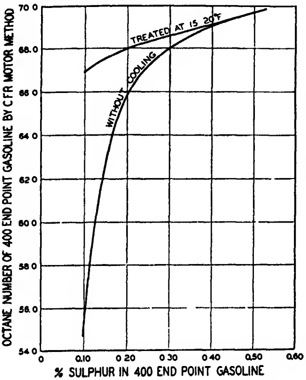

Fig 6 Loss in knock rating by sulphuric acid treatment of a California cracked naphtha

Since Figs 2-6 are based upon a single series of laboratory experiments, it is of interest to show individual results These numerical data, taken from smoothed curves plotted from the experimental data, are given in Table I

It will be noted that the data summarized in Table I and illustrated by the curves are all based upon the use of 98% sulphuric acid However, the general effects of temperature are applicable to other strengths of acid, a curve for estimating the quantities of other strengths required for equivalent treatment is presented in Fig 7

In an earlier paragraph it was stated that the olefines in naphtha react with sulphuric acid to yield acid and neutral esters The acid sulphates are more soluble in sulphuric acid than in hydrocarbons and this reaction is evidenced by treating loss However, the neutral esters are quite soluble in the naphtha and are decomposed with the formation of acidic materials during the distillation step which follows acid treatment Neutralization with caustic soda is generally practised to prevent corrosion of condensing equipment and discoloration of the distillate in storage The effect of treating temperature on this caustic consumption is illustrated by Fig 8 Low treating temperatures also minimize the caustic requirements in the neutralizing step which immediately follows acid treatment and water washing [5, 1934]

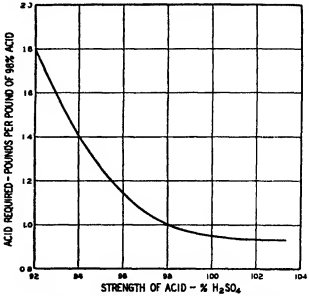

Fig 7 Effect of sulphuric acid strength on acid requirements

Commercial Application of Low-temperature Treatment

The advantages of the low-temperature refining process have been demonstrated in an impressive manner by large-scale application in California refineries Table II summarizes the savings resulting from the installation of the process for the treatment of naphtha obtained by liquid phase cracking of a fuel oil residuum from California crude The examples cover low-temperature treatment at two

Table I

Cold Treatment of a California Cracked Naphtha at 15–20° F compared with Treatment without Cooling Sulphuric Acid Requirements and Gasoline Yields—Single Stage or Laboratory Treatment

Crude Cracked Naphtha		*Crude 400° F End-point Gasoline*	
Per cent sulphur	0 62	Per cent sulphur	0 53
Per cent 400° F end-point gasoline	76 0	Octane number	69 9

Per cent sulphur in finished 400° F end-point gasoline	*0 40*		*0 30*		*0 20*		*0 10*	
Temperature of treatment	*Without cooling*	*15–20° F*	*Without cooling*	*15–20° F*	*Without cooling*	*15–20° F*	*Without cooling*	*15–20° F*
Lb 98% acid per 42-gal barrel of naphtha	4 2	7 0	8 7	11 2	18 7	16 0	58 5	23 6
Treating loss, %	2 6	2 9	4 8	4 3	8 4	5 5	18 9	7 0
Polymerization loss, %	3 8	1 9	6 6	2 8	11 2	3 7	30 9	5 2
Treating yield, %	97 4	97 1	95 2	95 7	91 6	94 5	81 1	93 0
Distillation yield, %	73 1	74 6	71·0	73 9	67 5	73 2	52 5	72 0
Net yield, % from crude naphtha	71 2	72 4	67 6	70 7	61 8	69 2	42 6	66 9
Net yield, % of original gasoline	93 8	95 3	89 0	93 0	81·4	91 0	56 0	88 1
Octane number of finished gasoline	69 0	69 1	68 0	68 6	65 8	68 0	55 2	66 9
Loss in octane number	0 9	0 8	1 9	1 3	4 1	1 9	14 7	3 0

TABLE II

Investments and Savings

Cold Treatment of Cracked Naphtha at 20° F compared to Treatment without Cooling for Same Sulphur Reduction

Equivalent acid requirements		
Lb 98% acid per 42-gal barrel—without cooling	17 9	60 5
Lb 98% acid per 42-gal barrel—treatment at 20° F	10 0	15 0
Savings by cold treatment		
98% acid—lb per 42-gal barrel of naphtha	7 9	45 5
Caustic soda—lb per 42 gal barrel of naphtha	1 48	3 86
Increase in gasoline production—barrel per barrel of gasoline	0 132	0 79
Gain in octane number, C F R Motor Method	2–3	15–18
Equivalent c c tetraethyl lead per gal	0 33–0 50	1 86–2 25
Reduction in A S T M 20% temp —° F	17	31
Refrigeration Plant—1,000 bbl (42's) daily throughput		
Capacity required—tons of refrigeration	56	65
Plant investment, approximate	$14,600	$16,900
Operating requirements per 24 hours		
Labour	One man per shift	
Power—K W H	805	935
Salt water—thousands of gal	197	228 5
Ammonia (losses)—approximate pounds	5 0	5 8

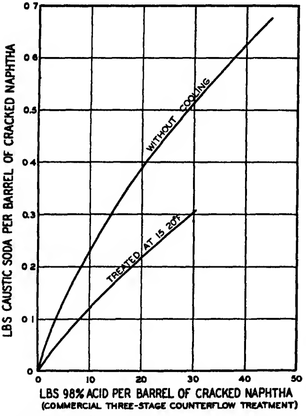

FIG 8 Caustic soda requirement for redistillation after sulphuric acid treatment

different acid rates, actual data for treatment in the absence of cooling being adjusted to conform to the same reductions in sulphur content These figures are given for illustrative purposes only since the exact savings vary with the type of naphtha treated

Table II also includes the approximate initial investment in an ammonia refrigeration plant and the daily operating requirements for lowering the treating temperature to 15–20° F These figures assume a crude naphtha charge of 1,000 barrels daily Fig 9 contains additional data on refrigeration requirements

The type of plant and operating procedure used in commercial low-temperature treatment have been described in detail [5, 1934]

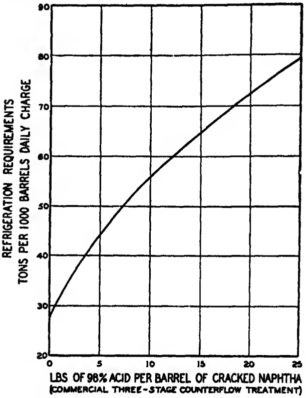

FIG 9 Capacity of refrigeration plant for treatment of cracked naphthas at 15–20° F

The treatment is conducted in three-stage counterflow equipment, with cooling between stages [3, 1934] to control the maximum temperature of the naphtha, usually 15 to 20° F This type of plant is illustrated in Fig 10 Crude naphtha is thoroughly dried, pre-cooled to 0–10° F, and contacted in centrifugal pump mixers with partially spent acid sludge from the second stage The naphtha and sludge layers are separated, the sludge is removed from the system, and the naphtha is again cooled before mixing with sludge from the third treating stage Sludge separated in the second stage is piped to the first stage and the naphtha is further cooled before contacting with fresh acid in the third and final treating stage As the final treatment generates considerable heat, the naphtha-sludge mixture is cooled before passing to the settling tank Treated naphtha from the third settler is piped to a rock-packed separator where last traces of sludge are removed The sludge-free naphtha is passed through a heat exchanger to cool incoming crude naphtha and is then washed with water and finally with caustic before being pumped to the treated naphtha storage tank

As indicated by the curve in Fig 4, the counterflow operation reduces acid requirements by about 35–45% compared with single stage or laboratory treatment. Experience has shown that in the absence of cooling a similar reduction is not obtained due to the rapid loss in treating efficiency of the acid sludge layer caused by secondary decomposition reactions

The chief advantages of temperature control in sulphuric acid treatment of cracked naphthas are thus shown to be reduction in treating and polymerization losses, decreased acid requirements, retention of valuable anti-knock constituents, and decreased caustic consumption Greater reduction in gum content, improved colour stability, elimination of emulsion troubles, &c [5, 1934], are other attractive features of this process

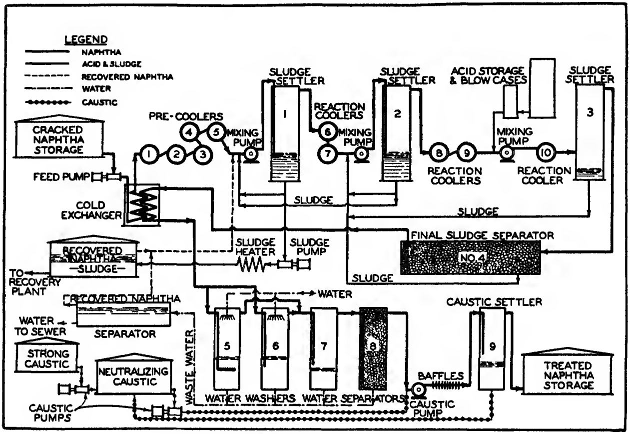

Fig 10 Three-stage plant for treatment at low temperatures

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SULPHUR REMOVAL FROM GASES

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Occurrence of Sulphur in Refinery and Natural Gas

THE sulphur present in refinery gas and in sour natural gas is almost entirely in the form of hydrogen sulphide, H_2S Quite often very small quantities of organic-sulphur compounds, such as mercaptans, are also present, but the amount of organic sulphur does not usually exceed 8 grains per 100 cu ft , and, for all practical purposes, the removal of organic-sulphur compounds need never be considered [15, 1929]

It has been common practice in the manufactured-gas industry to express the hydrogen-sulphide content of the gas in terms of grains per 100 cu ft of gas saturated with water vapour at 60° F and under an absolute pressure of 30 in of mercury This convention has been quite generally adopted for sour natural gas and refinery gas and is used here Under these conditions, 1 % by volume of H_2S in the gas is equivalent to 635 grains of H_2S per 100 cu ft

The hydrogen-sulphide content of natural gas varies between extremely wide limits, and it is impossible to give a really typical figure Most of the natural gas distributed for commercial and domestic use is 'sweet' as it comes from the wells, that is, it contains no appreciable amount of H_2S Sour natural gas may contain any quantity from a trace up to as high as 10,000 grains per 100 cu ft

Refinery-still gas has a hydrogen-sulphide content varying between 100 grains and 5,000 grains per 100 cu ft , the amount depending largely on the sulphur content of the crude oil A fairly typical figure is 1,000 grains per 100 cu ft

Objects of Sulphur Removal

Legal restrictions usually specify that gas offered for sale shall contain not more than 30 grains of total sulphur compounds per 100 cu ft of gas Under some State laws, the requirement is made even more stringent by specifying that the gas must contain substantially no H_2S However, experience has shown that gas containing less than 30 grains of total sulphur will produce no sulphur odour or nuisance due to the formation of sulphur dioxide, when the gas is burned Hydrogen sulphide must usually be removed from sour natural gas or refinery gas sold for city use

Aside from legal restrictions on gas to be sold, there are also several other reasons that make sulphur removal from natural and refinery gas very desirable

The corrosive effect of hydrogen sulphide in gas pipelines, especially when the gas is under pressure and contains moisture and oxygen, is well recognized and has been quite thoroughly investigated Even where the H_2S is present in a quantity less than 12 grains per 100 cu ft , severe corrosion may occur, according to Devine *et al* of the U S Bureau of Mines [8, 1933] As a result of their work, they recommend that the hydrogen sulphide be removed from the gas, and/or that the oxygen be reduced and the humidity be controlled, if it is desired to reduce corrosion in pipeline systems

Where gasoline is recovered from natural gas or refinery gas, there is a distinct advantage in first removing the hydrogen sulphide from the gas, in order to avoid the recovery of sour gasoline, which must be subjected to special treatment Auld [1, 1928] states that the presence of H_2S in natural gas causes the efficiency of a charcoal-process gasoline-recovery plant to decrease to about 50% after 10 days' use, due to the formation of free sulphur in the pores of the charcoal

When gas contains high concentrations of hydrogen sulphide it is highly poisonous, and leakage of such natural gas may cause serious accidents The removal of the H_2S makes such gas relatively non-poisonous

If natural gas containing hydrogen sulphide is used as a fuel for internal combustion engines, the corrosion is usually quite severe, according to Mills of the U S Bureau of Mines [20, 1925]

Historical

Processes for the removal of hydrogen sulphide were first developed early in the period of coal-gas manufacture, since it was found that the combustion of unpurified gas led to the production of disagreeable sulphur fumes harmful both to the consumer and his property These injurious effects led to stringent legal requirements for the removal of H_2S from gas intended for household use

In the earlier days of the manufactured-gas industry lime was used almost exclusively for the removal of hydrogen sulphide The chief objection to lime, apart from rather high operating costs, was the difficulty of disposing of the spent lime without involving a public nuisance as evidenced by odour and contamination of streams

The iron-oxide process for purifying coal gas was introduced about the middle of the nineteenth century From that time it gradually displaced the lime process, until today practically no coal-gas plants use lime for purification The use of iron oxide for removal of H_2S was a notable improvement over the old lime process, since it selectively removes hydrogen sulphide with a reasonably high efficiency, it does not involve the running of an effluent into streams, the fouled iron oxide is easily revivified by air so that it may remove far more sulphur than the theoretical amount for a single fouling, and, with adequate capacity, it requires little supervision or attention

However, in 1920 a new process for H_2S removal, known as the Seaboard process of liquid purification, was introduced by the Koppers Company Since that time a very large percentage of the gas-purifying capacity in the United States, as well as many plants in other countries, have changed to or adopted the Seaboard process or other processes using liquids or solutions instead of the dry iron oxide It has now become rather common usage in the American gas industry to refer to the iron-oxide process as 'dry purification', while the generic term of 'liquid purification' is applied to the several processes for H_2S removal developed since 1920

The many reasons that have led to the rapid adoption of the Seaboard and other liquid-purification processes by plants producing coal gas or carburetted water gas since 1920 need not be detailed here, since they have been well described by Sperr [23, 1921], and in various other later publications

Only in very rare cases is the iron-oxide process adaptable to the economical removal of hydrogen sulphide from refinery or sour natural gas In some instances, where the hydrogen-sulphide content of the gas is low, and where the gas is purified at substantially atmospheric pressure, the iron-oxide process might be used

In nearly all cases, however, the H_2S content of the gas is relatively high and usually the gas is under a considerable pressure Under these circumstances the iron-oxide box system of gas purification is too cumbersome, laborious, and expensive a method to be applied to natural gas and refinery-still gas The design of iron-oxide boxes to withstand pressure leads to very high installation costs, whereas it is relatively simple and inexpensive to install the absorber towers used in liquid purification to withstand any pressure that might be encountered With gas containing large amounts of H_2S the fouling of the iron oxide is very rapid, and it is necessary to shut down the boxes very often, in order to remove the fouled oxide and replace it with fresh material This operation involves considerable labour and is often quite hazardous, due to the pyrophoric nature of iron sulphide

For these reasons, as well as others, there was really no practical process available for the purification of high-pressure refinery and natural gases containing large amounts of sulphur until the introduction of liquid purification in 1920 Since that time, many large liquid-purification plants have been installed

Liquid Purification Processes for Removal of Sulphur from Gases

All liquid-purification processes consist of two essential stages The first step is absorption, where the sulphur-containing gas is contacted with a solution which absorbs the hydrogen sulphide The absorption is carried out in counter-current fashion, with the solution entering at the top of the tower and leaving at the bottom, while the foul or sour gas enters at the bottom, and the clean gas leaves the tower at the top The absorbing tower may contain any one of several types of tower packing or may contain trays of bubble caps, depending on rate of solution flow, gas-pressure, and other conditions

The second step involves regeneration of the solution, freeing it of the sulphur which was taken up in the absorption stage, and thereby rendering it suitable to be returned to the absorption stage, where it again functions as an absorbent to remove hydrogen sulphide from the gas In nearly all cases the process is cyclic and continuous, the same solution being recirculated more or less continuously between the two stages A general review of liquid-purification processes has recently been published by Denig and Powell [7, 1933]

It is in the regeneration stage, commonly known as 'actification', that there is the widest variation in method and equipment between different liquid-purification processes for sulphur removal from gas In the present discussion liquid-purification processes will be classified according to the principle used in regenerating or 'actifying' the foul solution received from the absorption tower

By this scheme liquid-purification processes may be divided into four general classes, as follows

1 Sweep-gas actification
2 Oxidation-by-air actification.
3 Hot actification
4 Miscellaneous (vacuum actification, electrolytic actification, &c)

Under each class various commercial processes will be mentioned, and one typical process of each class will be described in some detail

Sweep-gas Actification as typified by the Seaboard Process

The Seaboard process for the removal of H_2S from gas is not only the earliest liquid-purification process of commercial importance introduced in the United States, as mentioned earlier, but it is also the simplest in operation, and has been the most popular process up to this date, as evidenced by the large number of installations At the present time there are more than 50 Seaboard gas-purification plants in operation in the United States and Canada alone Almost one-third of these plants are removing hydrogen sulphide from refinery-still and sour natural gas

A general description of the Seaboard process and various developments connected with it has been given by Sperr [23, 1921, 24, 1923] The practical application of the Seaboard process to refinery and natural gas specifically has been described by Jacobson [14, 15, 1929] Burrell and Turner [3, 1933] describe the use of the Seaboard process, among others, for the removal of H_2S from natural and refinery gas

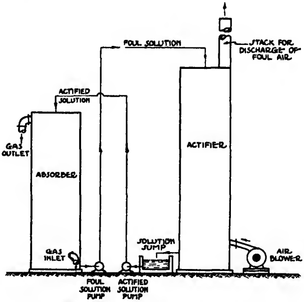

FIG 1 Seaboard process of gas purification flow-diagram

The method of operation of the Seaboard process is illustrated by the flow-diagram in Fig 1 The liquid used in this process is a solution of sodium carbonate (about 3%) This solution enters the top of the absorber and is sprayed on to the packing in this tower The gas, which is passing up through this absorber tower, is thereby contacted with the solution in a counter-current manner, and nearly all of the hydrogen sulphide is absorbed from the gas The spent soda solution, containing the absorbed H_2S, flows continuously out of the bottom of the absorber, and is then pumped to the top of a second packed tower, which is called the actifier Here the spent solution is sprayed on to the packing and passes down through the actifier tower, while a current of air, furnished by a blower at the bottom, passes up through the tower By this sweep-gas action of the air the hydrogen sulphide is largely removed from the solution and the actified solution is then in a suitable condition again to be returned to the absorber Most of the H_2S removed from the gas leaves the plant in the actifier air, which is usually discharged through a high stack

The principal chemical reaction involved in the Seaboard process is as follows

$$H_2S + Na_2CO_3 \rightleftharpoons NaHS + NaHCO_3$$

This is a reversible reaction, subject to the ordinary laws of mass action In the absorption stage it proceeds to the right, in the actification stage, to the left

One of the side-reactions which occurs to a very small extent is the conversion of sodium carbonate to sodium thiosulphate, due to the oxidizing action of the air Fortunately, the loss of sodium carbonate by this irreversible reaction is very small Another side-reaction, which is more or less essential to the successful working of the process, is the conversion of a substantial part of the Na_2CO_3 into $NaHCO_3$ This is caused by the presence of CO_2 in the gas being purified or by the CO_2 released by the formation of sodium thiosulphate mentioned above After a short period of operation the ratio of Na_2CO_3 to $NaHCO_3$ becomes more or less constant due to attainment of equilibrium The presence of $NaHCO_3$ in the solution assists in the removal of H_2S in the actification stage

Experience has indicated that the most economical operation can be obtained when the plant is designed for about 90% removal of the hydrogen sulphide from the gas, if the gas is under ordinary pressure However, if the gas is purified under higher pressure, 98% or higher, removal may be secured economically Where the gas is at ordinary pressure, secondary removal by iron-oxide boxes is usually quite feasible and economical, since the quantity of H_2S to be removed in these 'catch boxes' is small

The Seaboard process is well suited for the purification of gas under pressure in the case of gases not subject to liquefaction, and in several installations gas is being treated up to pressures of 300 lb per sq in or higher Where pressures are high, the absorber is designed somewhat smaller in size, whereas the actifier, where the solution is swept with air at ordinary pressure, is of normal size and design

The cost of operating the Seaboard process varies somewhat, depending on local conditions and different unit costs The table below gives a typical cost analysis

TABLE I

Operating Costs of Seaboard Process

Kind of gas	Refinery-still or natural gas
Capacity of plant	5,000,000 cu ft per day (normal temp and pressure)
Sulphur content	1,000 grains H_2S per 100 cu ft
Sulphur removal	98%
Gas-pressure	60 lb per sq in gauge

	Per day
Labour 6 hr at 50 cents per hour	\$3 00
Power 1,000 K W H at 1 cent	\$10 00
Soda ash 400 lb at 1 2 cents	\$4 80
Maintenance	\$1 00
Total operating cost per day	\$18 80
Cost per 1,000 cu ft of gas	0 376 cent

A view of a typical Seaboard process plant is shown in Fig 2 This is the plant of the Illinois-Missouri Pipe Line Company at Wood River, Illinois It has a capacity of 6,000,000 cu ft of refinery-still gas per day and removes about 98% of the H_2S from gas containing about 1,000 grains per 100 cu ft

Although the Seaboard process is relatively simple and economical in operation, and has been very popular for these reasons, it possesses the disadvantage of discharging the H_2S removed from the gas along with the actifier air This means (1) that there is no by-product recovery of sulphur, and (2) that the actifier air containing the H_2S may be objectionable if discharged directly into the atmosphere However, plants have solved this latter problem by utilizing the actifier air under gas producers, boilers, &c, [17, 1929]

Oxidation-by-air Actification as typified by the Thylox Process

Several different processes utilizing the principle of oxidation-by-air for actification or regeneration of the solution have been developed and put into commercial operation In these processes the solution, after absorbing H_2S from the gas, is contacted with air However, the air, instead of acting as a sweep gas to carry out H_2S, as in the Seaboard process, oxidizes the solution to produce free sulphur, which is carried to the surface of the solution as a finely divided suspension, which may be filtered off and the sulphur recovered as a by-product Not only is a by-product recovered, but also the possible objection of discharge of H_2S into the atmosphere is eliminated, without the extra operation of disposing of the air under boilers, &c

The chief difference between the various processes of this type is in the nature of absorbing solution The Ferrox process (Sperr [26, 1926]) employs iron hydroxide in suspension in a solution of soda ash The Nickel process (Cundall [5, 1926]) employs a nickel catalyst suspended in a soda-ash solution Several purification plants using these processes have been installed by the Koppers Company and have been in successful commercial use for years Both processes are suitable for the removal of hydrogen sulphide from refinery-still and natural gas

The Thylox Process The Thylox process (Gollmar [10, 1929], Jacobson [16, 1929], Colbert [4, 1930], McBride [19, 1933], Denig [6, 1933]) employs a solution for absorption which is free from suspended matter, and which is practically neutral in reaction Gollmar [11, 1934] has described the chemistry of this process The active absorbing compound in the solution is a mixture of various sodium thioarsenates The principal reaction involved in the absorption stage of the process, where the H_2S is removed from the gas, is as follows

$$Na_4As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O$$

The principal reaction occurring in the actification stage, where the solution is regenerated for further use, and where the free sulphur is released, is as follows

$$Na_4As_2S_6O + O = Na_4As_2S_5O_2 + S$$

The flow-diagram in Fig 3 illustrates the operation of the Thylox process The gas to be purified passes up through the absorber where it is contacted with the actified Thylox solution in much the same manner as in the Seaboard process The purified gas leaves the top of the absorber, the foul Thylox solution is pumped from the bottom of the absorber into a tank called the pressure thionizer Compressed air is introduced at the bottom of this tank and bubbles up through the solution, finally

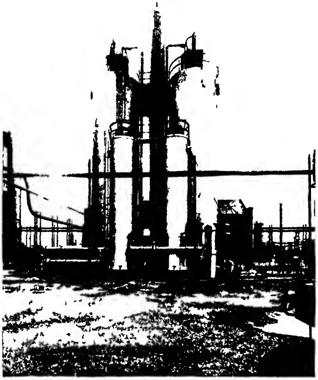

FIG. 2. Seaboard process liquid purification plant of the Illinois-Missouri Pipe Line Company at Wood River, Illinois.

FIG. 4. Thylox liquid purification plant at Racine, Wisconsin. Left to right: thionizer, sulphur slurry tank, absorber.

being discharged into the atmosphere at the top The foul Thylox solution from the absorber enters the pressure thionizer at the bottom and flows slowly upward to near the top, where it is withdrawn again to enter the absorber as an actified or regenerated solution Usually, pressure thionizers are operated in series of two or more, in order to secure more complete regeneration of the solution

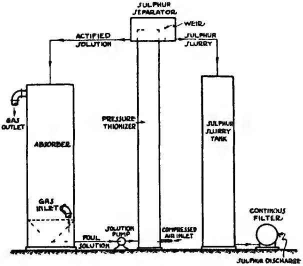

FIG 3 Thylox process of gas purification flow-diagram

The air which bubbles through the solution in the pressure thionizer performs two functions (1) it supplies the oxygen for the regeneration of the solution, and (2) it carries the finely divided sulphur, which is released by the regeneration reaction, to the top of the tower, where it flows over a weir as a froth or slurry This sulphur-bearing froth flows into the slurry tank, from which it feeds to a continuous filter, where the moisture content is reduced to about 50%, and the sulphur is discharged as a white cake or paste

This sulphur paste constitutes a marketable by-product which, credited against the cost of purification of the gas, largely or completely cancels the operating cost in most cases At the present time, several hundred tons per annum of this paste are sold as such or converted into other forms for use as fungicides in agriculture (Jacobson [18, 1931], Sauchelli [22, 1933]) The Thylox sulphur-paste may also be melted into brimstone in autoclaves At the present time several hundred tons per year of this brimstone are marketed for sulphuric acid and paper manufacture

The Thylox process normally shows a somewhat higher sulphur-removal efficiency than does the Seaboard process Removal of 95% or higher of the H_2S in the gas is fairly common, even when only one stage of absorption is provided.

Recently the Thylox process has been modified by using two stages of absorption in series instead of one, whereby the removal of H_2S may be made substantially complete, and no iron-oxide 'catch' boxes are necessary after the liquid-purification plant In this two-stage process the make-up solution of arsenic trioxide and soda ash is added to the secondary stage of absorption, thereby producing a very active medium for the absorption of the last traces of H_2S left in the gas after the usual primary stage of absorption At the present time, a plant to purify completely 45,000,000 cu ft of blue water-gas per day is being constructed for E I du Pont de Nemours and Company at Belle, West Virginia

The cost of operating the Thylox process varies to some extent, since it is dependent on many factors peculiar to individual plants The following table gives a typical cost analysis of the Thylox process for purifying the same gas taken as an example in Table I The ordinary single-stage absorption is assumed in this case

TABLE II

Operating Costs of Thylox Process

Kind of gas	Refinery-still or natural gas
Capacity of plant	5,000,000 cu ft per day (normal temp and pressure)
Sulphur content	1,000 grains H_2S per 100 cu ft
Sulphur removal	98 %
Gas-pressure	60 lb per sq in gauge
	Per day
Labour 12 hr at 50 cents per hour	$6 00
Power 1 200 K W H at 1 cent	$12 00
Steam 15,000 lb at 30 cents per 1,000 lb	$4 50
Soda ash 600 lb at 1 2 cents	$7 20
Arsenious oxide 150 lb at 4 cents	$6 00
Maintenance	$2 00
Total operating cost per day	$37 70
Credit for recovered sulphur 3 tons at $15 00	$45 00
Net operating credit per day	$7 30
Net credit per 1,000 cu ft of gas	0 146 cent

As compared with the relatively simple Seaboard process, the Thylox process shows a considerably higher gross operating cost However, in this typical example, the credit established by the recovery of sulphur more than cancels this cost, so that there is actually a net operating credit As mentioned previously, the Seaboard process does not recover sulphur as a by-product

It is a thoroughly practical procedure to utilize the by-product sulphur of the Thylox process, in the form of brimstone, for the manufacture of sulphuric acid by the contact process, and small contact sulphuric-acid plants may be operated in connexion with Thylox purification plants, if so desired The brimstone contains a small amount of arsenic, which is readily removed in the acid plants, following the sulphur burners

A view of a typical Thylox-process plant is shown in Fig 4 This is the purification plant of the Wisconsin Gas and Electric Company at Racine, Wisconsin It has a capacity of 10,000,000 cu ft of coal gas per day and removes about 98% of the H_2S from gas containing more than 300 grains per 100 cu ft

Hot Actification as typified by the Phenolate Process

Several liquid-purification processes which heat the solution in order to secure actification or regeneration have been developed In this type of actification the solution, after absorbing H_2S from the gas, is heated, usually by direct or indirect steam Indirect steam is usually preferred, since this avoids diluting the solution with water Since the operation involves alternate heating and cooling of the solution in its cycle between the absorption and the actification stages, heat exchangers are used in order to conserve steam

In one sense hot actification is really another form of the sweep-gas principle used in the Seaboard process Instead of air, steam is used as the sweep-gas, or, more properly, sweep-vapour, and necessarily the solution must be near its boiling-point instead of at ordinary temperature One of the chief advantages of hot actification over sweep-gas actification at ordinary temperatures is that the steam may be condensed, thereby allowing almost pure H_2S gas to leave the actifier, instead of the extremely dilute mixture of H_2S in air, as in the Seaboard process The H_2S gas, in this concentrated form, may be burned to produce sulphuric acid, or, if it is not desired to utilize it as a by-product, it may be burned and the products of combustion discharged through a stack

The chief difference between the various processes utilizing the hot-actification principle is in the nature of the absorbing solution

The Espenhahn process [9, 1923] uses a solution of soda ash This process is in practical commercial use and is economical with regard to soda ash, though somewhat high in steam consumption

Many processes using ammonia have been tried for the purification of coal gas during almost the entire period that gas has been manufactured Suspensions of magnesium hydroxide in water (Sperr [25, 1925]) and in soda solutions (Hall [12, 1925]) have been used with very promising results, although as yet these have not been adopted on a large commercial scale Another hot-actification process described recently (Rue [21, 1932]) uses a solution of lime and salt According to Denig and Powell [7, 1933], this process does not appear to be commercially feasible The Girdler process (Bottoms [2, 1931]) is a hot-actification process making use of solutions of certain organic amines The Girdler process is described in detail in another section of this work Several other methods of gas purification making use of the hot-actification principle have been described in the literature and in patents, but lack of space forbids reference to all of them

The Phenolate Process. The Phenolate process of gas purification is one of the more recent developments (1928) of the Koppers Company (Denig and Powell [7, 1933]) The absorbing liquid is a fairly concentrated solution of a phenolate, usually sodium phenolate The foul solution is regenerated by hot actification

The process involves the reaction

$$NaOC_6H_5 + H_2S \rightleftharpoons NaSH + C_6H_5OH$$

If sodium hydroxide alone were used in the purification process, the reaction would proceed vigorously to the right during the absorption stage, but the reverse reaction to the left during the actification stage would be almost nonexistent except by the expenditure of huge quantities of steam The process may be brought into more equal balance between the two stages, which is quite necessary for a cyclic process, by the addition of an auxiliary acidic constituent This auxiliary acidic constituent must satisfy two conditions, among others First, it must be a somewhat weaker acid than H_2S, in order that it will not prevent the reaction of the solution with H_2S in the absorption stage Secondly, its acidity must increase with temperature in much the same ratio as does hydrogen sulphide, in order that it may effectively perform its function of 'crowding out' the H_2S at the high temperature of the actification stage This latter condition is quite necessary and the acids satisfying the requirement are very limited in number, since hydrogen sulphide increases in acidity with increasing temperature very rapidly, as shown by its high negative heat of electrolytic dissociation

Experiments with a large number of substances have shown that phenol and other tar acids are very effective as auxiliary acidic constituents Furthermore, they are relatively inexpensive materials, and are available as common chemical commodities

One of the important characteristics of the sodium-phenolate solution used in this process is its high carrying capacity for H_2S With refinery or natural gases of high sulphur content, the solution will carry 2,000 to 4,000 grains of H_2S per gallon, as it flows from the absorption to the actification stage This means a relatively low rate of solution circulation, and makes the process of special value for gas of this nature, especially when the gas is purified under pressure

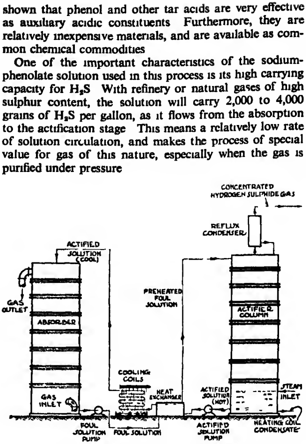

Fig 5 Phenolate process of gas purification flow-diagram

A flow-diagram of the Phenolate process is shown in Fig 5 Both the absorber and the actifier towers are provided with trays of bubble caps The foul solution from the absorber is preheated in the heat exchanger by the hot actified solution leaving the actifier The preheated foul solution then flows into the top of the actifier, and passes down through the actifier from tray to tray until it reaches the bottom Here it is heated to boiling by indirect steam, and steam and some of the phenol vaporized from the solution passes up through the trays, thereby releasing the H_2S from the solution by the combined effect of temperature, the sweep-gas action of the steam, and the 'crowding-out' effect of the phenol The steam and some phenol leaving the top of the actifier are returned to the solution by a reflux condenser, while the hydrogen sulphide passes out in a substantially pure form, to be used for the production of sulphuric acid, &c

The actified solution leaving the bottom of the actifier tower gives off a portion of its heat to the foul solution in the heat exchanger, is further cooled in cooling coils, and then flows into the top of the absorber Here it flows down from tray to tray in a counter-current relationship to the flow of gas undergoing purification It then leaves the bottom of the absorber to again proceed through the same cycle

The usual sulphur-removal efficiency of the Phenolate process is 90% Under high gas-pressures the efficiency may be somewhat higher Also it is entirely feasible to operate two units in series, thereby securing 99% or higher removal of H_2S

The hydrogen sulphide produced as a by-product may be burned under a boiler to furnish steam for the process With gas very high in H_2S the steam so generated is sufficient to operate the process The products of combustion may be utilized in a contact sulphuric-acid plant, and a careful cost analysis has indicated that sulphuric acid may be produced at very low cost, even in a comparatively small unit

Like all other commercial operations, the cost of operating a Phenolate-process plant varies according to conditions in each specific location The following table gives a typical cost analysis of the Phenolate process for purifying the same gas taken as an example in Tables I and II In this case single-stage absorption is assumed, and also credit is allowed for steam generation by combustion of H_2S under a special boiler, as well as credit for the H_2S as a material for sulphuric-acid manufacture The cost without these credits is also shown

TABLE III

Operating Costs of Phenolate Process

Kind of gas	Refinery still or natural
Capacity of plant	5,000,000 cu ft per day (normal temp and pressure)
Sulphur content	1,000 grains H_2S per 100 cu ft
Sulphur removal	90%
Gas pressure	60 lb per sq in gauge

	Per day
Labour 6 hr at 50 cents per hour	$3 00
Power 37 K W H at 1 cent	$0 37
Steam 50 000 lb at 30 cents per 1,000 lb	$15 00
Water 148,000 gal at 1½ cents per 1,000 gal	$2 22
Soda ash 25 lb at 1 2 cents	$0 30
Crude tar acid 50 lb at 7 cents	$3 50
Maintenance	$2 00
Total operating cost per day (without credits)	$26 39
Cost per 1,000 cu ft of gas (without credits)	0 528 cent
Credits	
Recovered H_2S 3 tons at $15 00	$45 00
Steam from combustion of H_2S, 70% boiler efficiency 24,000 lb at 30 cents per 1 000 lb	$7 20
Total credits	$52 20
Net operating profit (with credits)	$25 81
Operating profit per 1,000 cu ft of gas (with credits)	0 516 cent

When compared with the Thylox process, the Phenolate process is more attractive for this particular example The total operating cost is somewhat less, and the credits are higher, due largely to the fact that the heat of combustion of the H_2S may be utilized for steam production, before the products of combustion pass to the contact sulphuric-acid unit In many other situations, especially where the H_2S content of the gas is low and the gas-pressure is substantially atmospheric, the opposite is true and the Thylox process becomes more attractive

The Phenolate process has two disadvantages when compared with the Thylox process First, the recovered sulphur is in the form of H_2S gas, which is best utilized for sulphuric-acid production right at the plant On the other hand, the solid sulphur produced by the Thylox process may be stored or shipped, as desired, either as agricultural sulphur or as brimstone Second, the sulphur-removal efficiency of the Phenolate process is usually somewhat lower than the Thylox process, as far as the gas is concerned However, sulphur losses in the Phenolate process are lower, as far as the processing of the solution is concerned, so that the net sulphur recovery from both processes is about the same

The Phenolate process is a recent development and is not as yet operating in a large commercial installation, but reliable operating and cost data have been obtained from the operation of a plant of 1,000,000 cu ft per day capacity over an extended period Refinery-still gas of high-sulphur content under moderate pressure was purified in this plant

Other Processes

Several methods of solution actification other than those just mentioned have been proposed or used The application of a partial vacuum to the solution, whereby the solution is made to boil at ordinary temperatures, has been described by Hultman [13, 1932] He uses a solution of soda ash, of much the same composition as that used in the Seaboard process Sperr and Hall [27, 1925] use a soda solution, which is actified by a combination of heat and vacuum Thau [28, 1932] has described a liquid-purification process developed in Germany which utilizes a solution of potassium ferrocyanide and potassium bicarbonate In this process the solution is actified by electrolysis, free sulphur being released None of these processes are in use in America

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ORGANIC AMINES—GIRBOTOL PROCESS

By R R BOTTOMS

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THE Girbotol process for the separation of acidic constituents from gaseous mixtures is applicable to the purification of gases in the petroleum industry The process has been employed for two purposes the removal and recovery of hydrogen sulphide from natural and refinery gas, and the separation of carbon dioxide from hydrogen used for hydrogenation processes

Operation of the process is based on the discovery [1, 1933, 2, 1931] that certain organic amines form compounds with hydrogen sulphide and with carbon dioxide the stabilities of which decrease with increase in temperature The early development of the process is described by Bottoms [3, 1931] Acidic constituents are washed from a gas stream by contact with an amine at one temperature and subsequently recovered from the amine at a higher temperature The reversible reaction may in the case of hydrogen sulphide, be represented as follows

$$2R\mathrm{NH_2}+\mathrm{H_2S} \rightleftharpoons (R\mathrm{NH_2})_2\ \mathrm{H_2S},$$

where *R* represents an organic radical The reaction proceeds to the right at low temperatures, and to the left at high temperatures

Operating Cycle

A typical flow diagram of the process is shown in Fig 1 The cycle and equipment employed are almost identical with those of a gasoline absorption plant Gas to be treated passes up through a bubble tower of suitable size called the absorber Amine solution, at atmospheric temperature, enters the absorber and flows down the tower from tray to tray picking up the acid gas Purified gas leaves the absorber at the top

Rich amine solution, saturated with acid gas, flows from the base of the absorber through heat exchangers, where its temperature is raised to 190–200° F, and into the upper part of the reactivator, which also consists of a bubble tower, containing in its base a tubular reboiler section and at the top a reflux condenser The amine solution, flowing down the tower, is heated to 215–220° F by steam rising from the boiling solution in the reboiler section, and the acid gas is expelled and flushed out by ascending vapours The acid gas leaves the reactivator saturated with water vapour at 190–200° F and flows through the condenser, where it is cooled by water and the steam condensed The condensate is returned to the reactivator Hot, lean solution, stripped of acid gas, flows from the base of the reactivator to a pump, thence through the exchangers in counter-current relation to the cold, rich solution From the exchangers the solution passes through water coolers, and finally back to the top of the absorber The operation of the plant is entirely automatic, requiring only casual supervision

Although water solutions of the amines are usually employed, other solvents may be used In certain instances it is possible to circulate an anhydrous liquid amine as the absorbent As explained below, pressure, as well as temperature, affects the reaction equilibrium, and partial reactivation may be obtained by decreasing the pressure on the solution

The Removal of Hydrogen Sulphide from Hydrocarbon Gases

Separation of hydrogen sulphide from hydrocarbon gases is accomplished exactly as described above The gases are treated at high or low pressure with equal success, but gas under pressure is purified more economically because smaller towers are required and larger volumes of hydrogen sulphide are removed per gallon of solution circulated

The process is particularly well adapted to purifying gas containing a high percentage of hydrogen sulphide The rate of reaction in the absorption stage is so rapid that complete stripping may be obtained in a single tower One plant is washing natural gas containing 1,500 grains of hydrogen sulphide per 100 cu ft and effecting better than 98% removal consistently When an aqueous absorbing solution is employed no hydrocarbon constituents are removed from the gas if the physical conditions of temperature and pressure are controlled This makes it possible to apply the process to the purification of wet gas before the extraction of gasoline, and results in lower subsequent treating costs to purify the gasoline

Frequently sour natural gas contains appreciable quantities of carbon dioxide The cost of purifying the gas from hydrogen sulphide would be prohibitive if it were also necessary to remove this carbon dioxide There are, however, certain amines which have a strong selective affinity for hydrogen sulphide, and this impurity may be washed out preferentially For example, the hydrogen sulphide in a gas containing 150 grains per 100 cu ft and 3 5% carbon dioxide may be completely removed with the attendant removal of only 0 3% carbon dioxide

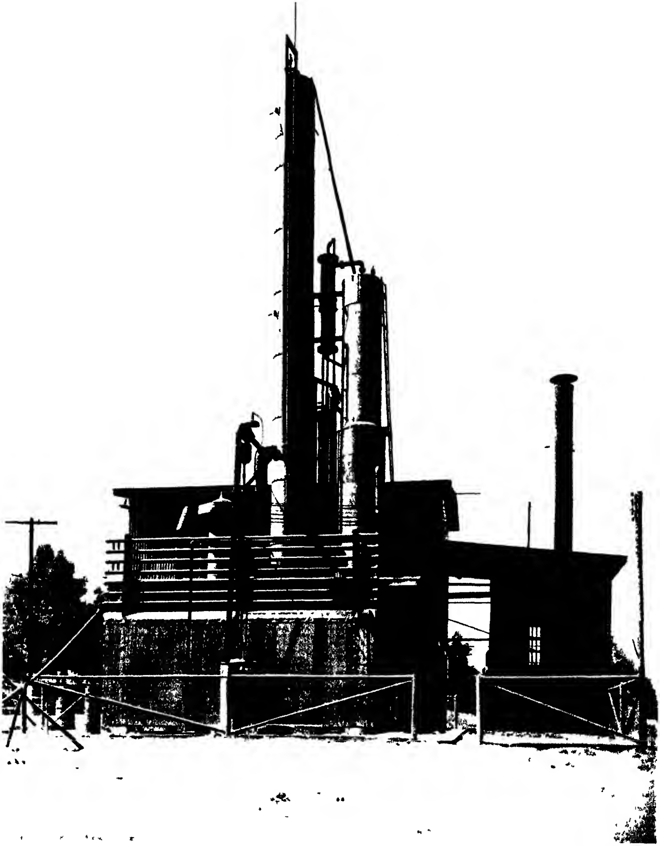
Utilization of Hydrogen Sulphide

Hydrogen sulphide is recovered by the process in concentrated form In instances where quantities are small and the sulphur is of no value, it may be burned in a stack or under a boiler Large refineries, however, especially those treating sour crude, produce great quantities of hydrogen sulphide, and its recovery, either as elementary sulphur or as sulphuric acid, is entirely justified For the production of sulphur, strong hydrogen sulphide from the Girbotol plant may be oxidized, in a Claus kiln (*a*), or by interaction with sulphur dioxide (*b*) produced by combustion of a portion of the hydrogen sulphide

$$2\mathrm{H_2S}+\mathrm{O_2} \rightarrow 2\mathrm{H_2O}+2\mathrm{S} \tag{a}$$

$$2\mathrm{H_2S}+\mathrm{SO_2} \rightarrow 2\mathrm{H_2O}+3\mathrm{S} \tag{b}$$

Many refineries can profitably convert the recovered hydrogen sulphide into sulphuric acid for their own use One million cubic feet of gas containing 460 grains of hydrogen sulphide per 100 cu ft carries sufficient sulphur for 1 ton of sulphuric acid of 1 8354 sp gr In cases where the gas alone does not contain sufficient sulphur for the requirements of the refinery, the deficiency may be made up by operating a sludge acid recovery system in conjunction with the Girbotol process



Girbotol gas purification plant

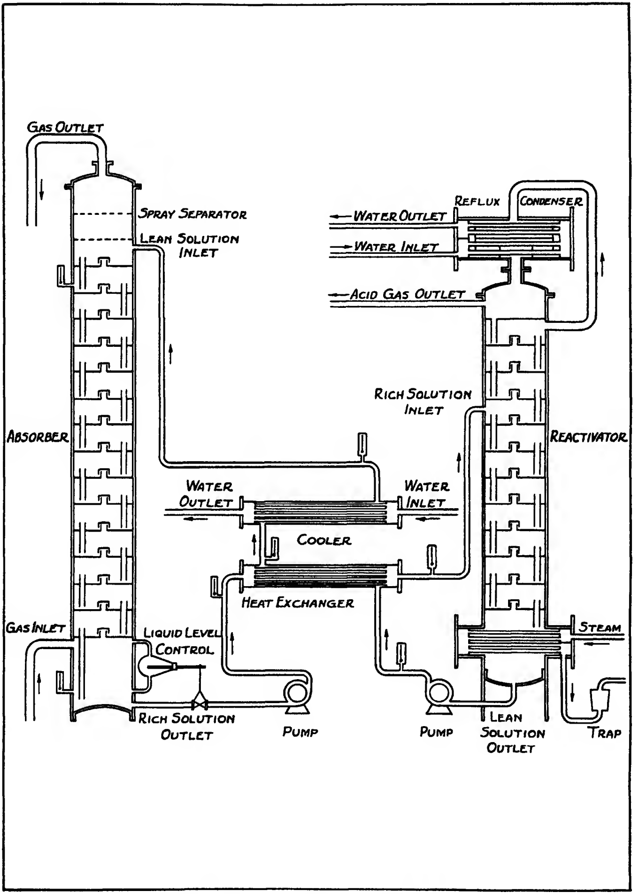


FIG 1 Flow sheet of Girbotol purification process

The Removal of Carbon Dioxide from Hydrogen

Large volumes of industrial hydrogen are now prepared by reacting methane with steam at a high temperature and oxidizing the resulting carbon monoxide to carbon dioxide with an additional quantity of steam at a lower temperature The reactions are

$$CH_4+H_2O \rightarrow CO+3H_2$$
$$CO+H_2O \rightarrow CO_2+H_2$$
$$\overline{CH_4+2H_2O \rightarrow CO_2+4H_2}$$

The resulting gas mixture contains 18–20% carbon dioxide and practically no carbon monoxide

In most instances the Girbotol process will remove the carbon dioxide more economically than will the older, water-wash process Separation with an amine solution may be carried out at atmospheric pressure, whereas the solubility of carbon dioxide in water is so low that the gas must be compressed before it is washed Even though the hydrogen must be subsequently compressed, there is a saving of 18–20% in compression cost with the Girbotol process because of prior removal of carbon dioxide Of greatest importance, the carbon dioxide may be completely eliminated with relatively small volumes of amine solution, while very large volumes of water must be employed for comparable purification Before use, the water must be decarbonated and de-aerated

Amines as Absorbents

Amines are the organic bases, derivatives of ammonia, in which one or more of the hydrogen atoms of the ammonia molecule are replaced by an organic residue There are primary, secondary, and tertiary amines, according to whether one, two, or three organic residues are substituted for hydrogen There are monoamines, diamines, and polyamines, containing one, two, or more ammonia groups There are aliphatic amines, in which the nitrogen atom is joined to a carbon chain, and aromatic amines, in which the nitrogen atom is attached directly to a benzene ring There are cycloparaffin amines, in which the nitrogen is joined to a saturated carbon ring, and amines in which the nitrogen atom is a member of a heterocyclic ring Finally, there is a miscellaneous group of amines such as hydrazines, hydroxylamines, and ureas

The organic residue may be a simple hydrocarbon, or it may contain substituting groups such as hydroxyl or carboxyl Two or more similar or dissimilar residues may be joined to the same nitrogen atom The possible combination and groupings are practically unlimited

Several hundred amines have been studied as absorbents for hydrogen sulphide and carbon dioxide, with the result that certain broad conclusions may be drawn regarding the suitability of the various groups Aliphatic and cycloparaffin amines are absorbents, except those which contain carboxyl or carbonyl groups This includes primary, secondary, and tertiary amines, mono-, di-, and polyamines, containing straight chains and saturated rings, substituted and unsubstituted Hydrazines are absorbents Amines in which the nitrogen atom is a member of or attached directly to an unsaturated ring, such as aniline, are not absorbents Amines which contain a carboxyl or carbonyl group are not absorbents

Not all the amines which will absorb acid gases are usable in the Girbotol process Some few form stable carbonates or hydrosulphides which do not dissociate easily at elevated temperatures Others form insoluble carbonates The great majority, however, behave normally, and the selection of the proper amine for commercial use is a relatively simple process A good amine has the following properties

High percentage of nitrogen The capacity of an amine for acid gases is proportional to its nitrogen content

Complete miscibility with water Both the amine and its acid-gas salts should be freely soluble so that concentrated solutions may be employed

Low vapour pressure The amine should have a high boiling-point to prevent losses into the gas stream

Rapid reaction rate with acid gases The time of contact between gas and absorbent necessary for the removal of acidic constituents is dependent on the reaction rate

High temperature coefficient of the dissociation pressure of the amine-acid gas salts The dissociation pressure of the amine-acid gas salts should be low at absorption temperature to permit complete removal of acid gases It should be high at reactivation temperature so that the acid gases will be easily expelled from the amine

High Stability

Low cost

Amino-alcohols have been found to be the most suitable absorbents The hydroxyl group in the molecule increases the solubility of the compound in water and raises its boiling-point, both desirable effects Of the many amines experimented with, those shown in Table I have been found most satisfactory, and have been employed in commercial installations The amines are listed in the order in which they were developed Triethanolamine was the original

TABLE I

Commercial Amines

Amine	*Structure*	*Nitrogen content, %*	*Boiling-point, °C*	*Strength solution employed, %*	*Acid gas capacity of solution, ft³/gal*
Triethanolamine	$N(CH_2CH_2OH)_3$	9 4	208 (100 mm)	50	5 5
Monoethanolamine	H_2CNH_2 $\vert$ H_2COH	22 9	172	15	4 0
Dapol	H_2CHN_2 $\vert$ $HCOH$ $\vert$ H_2CNH_2	31 1	119 (4 mm)	30	11 0
Methicol	$H_2CN(CH_3)_2$ $\vert$ $HCOH$ $\vert$ H_2COH	11 8	217	15	2 0

amine, which has now been almost entirely replaced by the more efficient monoethanolamine and dapol Methicol is an absorbent which has a strong selective affinity for hydrogen sulphide, where this gas is to be removed from a mixture which also contains carbon dioxide

Absorption of Acid Gases by Amines

Amines form compounds with hydrogen sulphide and carbon dioxide similar to those formed by ammonia These are the normal and acid carbonates and sulphides Some have been isolated as crystalline compounds, others exist only in solution, at normal temperatures Primary and secondary amines also form carbamates, RNHCOONH$_3R$, similar to ammonium carbamate The stability of the salts varies widely with the different amines For a particular amine, the stability is dependent on the temperature and partial pressure of the acid gas over the solution These latter facts form the basis for the Girbotol process

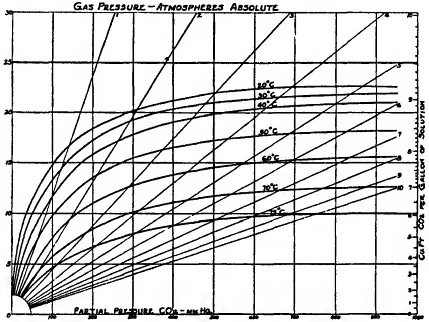


FIG 2 Equilibrium data for carbon dioxide and 30% 'dapol' solution

Equilibrium data for carbon dioxide and 30% dapol solution are shown in Fig 2 Values for hydrogen sulphide are quite similar It is generally true that equilibrium conditions of amine carbonates and sulphides are approximately the same The effects of temperature and partial pressure are shown in the appended curves The capacity of the amine solution increases rapidly with increase in acid-gas content of the mixture being treated, and with increase in pressure, which raises the partial pressure of the acid gas present

The overall rate of absorption of hydrogen sulphide by amines is in all cases high It is governed entirely by the rate of diffusion of hydrogen sulphide from gas to solution and is therefore proportional to the efficiency of contact and the viscosity of the solution The reaction rate of amine and hydrogen sulphide is practically instantaneous The overall absorption rate of carbon dioxide by primary and secondary amines is also high Carbamates are apparently formed instantaneously, and the overall rate is again controlled by the rate of diffusion

Tertiary amines cannot react with anhydrous carbon dioxide The absorption requires two chemical reactions

$$CO_2+H_2O \rightarrow H_2CO_3 \qquad (a)$$

$$2R_3N+H_2CO_3 \rightarrow (R_3N)_2\ H_2CO_3 \qquad (b)$$

The overall rate of absorption of carbon dioxide by tertiary amines is appreciably slower than by primary and secondary amines, and it appears that the rate of reaction (*a*), rather than diffusion, is the controlling factor in the absorption Similar observations have been made by Payne and Dodge [4, 1932] in discussing their own and other investigators' results on the absorption of carbon dioxide by water and alkali media The rate varies with different tertiary amines, but is in all cases slower than with primary and secondary amines

The above observed facts led to the development of methicol and similar amines which will absorb hydrogen sulphide preferentially from carbon-dioxide-bearing gases All amines show a slight preferential absorption for hydrogen sulphide, due, no doubt, to its greater solubility and lower molecular weight and higher diffusion rate in the gas phase, as compared to carbon dioxide But with tertiary amines the selectivity of absorption is marked Fig 3 shows the relative rates of absorption of hydrogen sulphide and carbon dioxide by triethanolamine where the partial pressure of the gas is in each case 760 mm

In Fig 4 the absorption of hydrogen sulphide and carbon dioxide by a 15% methicol solution is shown These represent laboratory data, obtained by bubbling a gas mixture containing 600 grains (approximately 1%) of hydrogen sulphide per 100 cu ft and 3 3% carbon dioxide through the solution, and determining the CO$_2$ and H$_2$S content of the solution at frequent intervals Carbon dioxide is absorbed at a uniformly slow rate Hydrogen sulphide is absorbed rapidly at first, but as the concentration of total gases in the solution approaches equilibrium for the partial pressure existing in the gas phase, the hydrogen sulphide absorption drops off and eventually passes through a maximum Carbon dioxide is the stronger of the two acids, and, after the solution is saturated, it displaces a portion of the hydrogen sulphide In a commercial plant the absorption is carried only to a point corresponding on this curve to 70–80 minutes, to produce good preferential removal

Reactivation

Reactivation is best carried out by raising the temperature of the amine solution The capacity of triethanolamine and dapol at various temperatures is shown in Fig 5 As the temperature of the solution approaches the boiling-point the acid gases are expelled rapidly In the bubble-plate type reactivator employed in commercial plants, steam from the boiling solution in the base continuously sweeps the liberated acid gas up the tower and keeps the partial pressure of the gas over the solution on the lower plates down to a point where rapid reactivation is obtained

The heat required for reactivation is made up of three items

1 The heat necessary to raise the solution from the temperature of the feed plate to its boiling-point
2 The heat required to dissociate the amine-acid gas compound
3 The heat required to vaporize the water which saturates the acid gas as it leaves the feed plates.

Item 2 is determined experimentally for each amine and represents a small proportion of the total requirement Items 1 and 3 can be calculated for any set of conditions It is found in making the calculation that the total heat requirement is dependent on the feed-plate temperature,

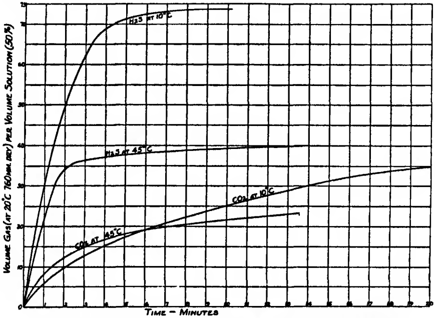


FIG 3 Absorption of carbon dioxide and hydrogen sulphide by triethanolamine

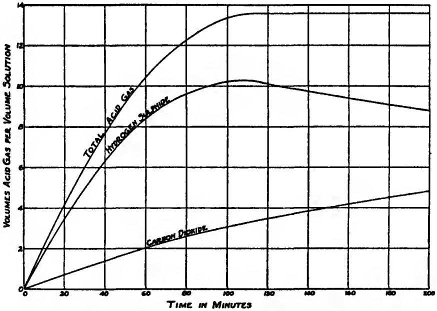


FIG 4 Absorption of carbon dioxide and hydrogen sulphide by 'methicol' solution

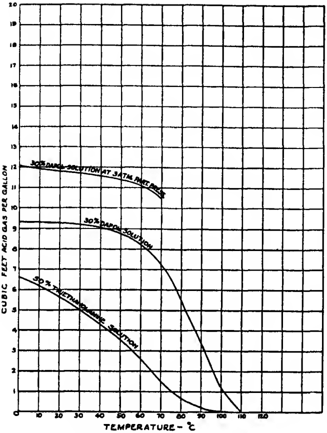


FIG 5 Effect of temperature on acid gases in amine solution

and that there is an optimum feed-plate temperature for each degree of solution saturation This is shown in Fig 6, where the steam requirement for reactivation is plotted against feed-plate temperature at various degrees of solution saturation If the feed-plate temperature is low, two much heat is consumed in heating the solution as it passes down the tower If the temperature is high, too much steam is boiled away with the escaping acid gas The higher the degree of solution saturation, the lower the optimum feed-plate temperature

By applying these facts to plant design, an economical steam rate for the process is obtained

Stability of Amines

The amines now employed in the Girbotol process are entirely stable under plant conditions The usual constituents of industrial gas mixtures, such as hydrocarbons, hydrogen, carbon monoxide, nitrogen, ammonia, are without effect on the amines Oxygen, present in a gas containing hydrogen sulphide, produces a slow accumulation of thiosulphuric acid in the solution In instances of this kind, it is commercial practice to add an inorganic alkali, such as soda ash, to the solution at intervals, in proportion to the thiosulphuric acid present to fix it as the sodium salt The amine itself is not affected by this procedure, and the absorption efficiency of the solution is not impaired until large quantities of sodium thiosulphate have accumulated One plant removing H_2S from natural gas containing 4% air has been in operation for over 2 years without any interference from the small amount of thiosulphate that has accumulated

Strong acids, such as sulphur dioxide, and organic acids and aldehydes, form stable, neutral compounds with the amines, just as does thiosulphuric acid If present they are removed in a scrubber ahead of the Girbotol plant When small quantities of these compounds are absorbed in the amine solution, they are fixed as sodium salts by the addition of soda ash, and the amine is not adversely affected Carbon bisulphide is not absorbed by tertiary amines Primary and secondary amines react slowly with carbon bisulphide to form dithiocarbamates and related compounds

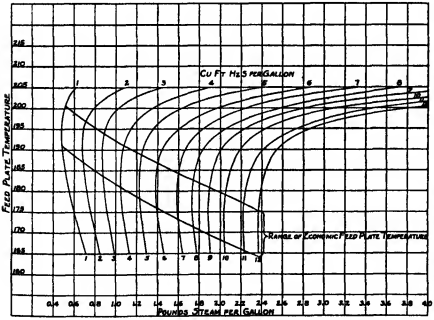


FIG 6 Steam requirements for reactivation

Materials of Construction

Low carbon steel and cast iron are satisfactory materials of construction for Girbotol plants Nickel, monel metal, and the various chrome and chrome-nickel steels are also suitable No copper, zinc, aluminium, or alloys containing them (except monel metal) can be used, because, like ammonia, the amines attack these metals Standard ammonia gasket and packing materials are satisfactory

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SECTION 28

SOLVENT-EXTRACTION METHODS OF REFINING

Theoretical Principles of Solvent Extraction	T G HUNTER
The Application of Triangular Graphs to the Comparative Laboratory Study of Solvent-refining Processes	F E A THOMPSON
General Factors Affecting Solvent-extraction Processes	S W FERRIS
Refining Kerosines by Extraction with Liquid Sulphur Dioxide—The Edeleanu Process	F C HALL
Solvent Treatment of California Lubricating Stocks, particularly with Sulphur Dioxide, Sulphur Dioxide-Benzene	U B BRAY
The Nitrobenzene Method	S W FERRIS
Phenol Extraction of Lubricating Oils	R K STRATFORD
The Chlorex Extraction Process	W H BAHLKE
The Application of Furfural to the Refining of Lubricating Stocks	R E MANLEY and B Y McCARTY
The Duo-Sol Process	H W SHELDON and B W STORY

THEORETICAL PRINCIPLES OF SOLVENT EXTRACTION

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Equilibria in Liquid-liquid Systems of Three Components

For the simplest case of an isothermal system, in which a common solute is distributed between two liquid phases, solute concentrations can be systematized by the distribution law, which takes the form

$$\frac{C_1}{C_2} = K, \tag{1}$$

where C_1 = the concentration of the solute in the first liquid phase,

C_2 = the concentration of the solute in the second liquid phase,

and K = a constant dependent only upon temperature

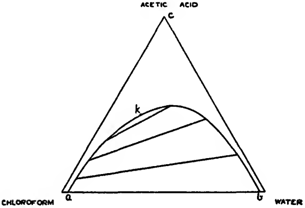


FIG 1.

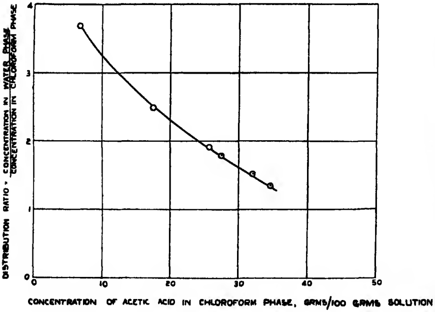


FIG 2

If the solute consists of different substances, the law holds for each single material

In systems where dissociation or association of the solute occurs, however, certain corrections are necessary In the case where the solute is associated in the second solvent, and exists chiefly as double molecules, then the number of single molecules in this second solvent is proportional to the square root of the concentration, and the equilibrium is given by

$$\frac{C_1}{\sqrt{C_2}} = K \tag{2}$$

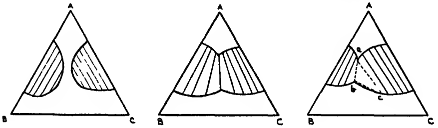
The distribution law is only strictly valid if both liquid phases are mutually insoluble, or do not have their mutual solubility altered by the distributed solute This condition is never realized over a wide concentration range, but at small concentrations the effect is negligible and the distribution law can be applied

Representation of equilibrium in an isothermal ternary system over a wide concentration range by a simple mathematical expression is therefore almost impossible, and the best representation of such a case is a graphical one employing triangular coordinates

The distribution of acetic acid between chloroform and water can be represented in this way by the single binodial curve of the form shown in Fig 1 All ternary mixtures whose compositions are represented by points falling in the triangle outside the area *akb* give rise to single homogeneous solutions All mixtures represented by points falling within the area bounded by the binodial curve *akb* generate two ternary or binary solutions

Chloroform and water, having a limited solubility, give rise to two conjugate binary solutions *a* and *b* As acetic acid distributes itself between the two liquids it brings about an increase in the mutual solubility of the chloroform and water The two phases become closer and closer to each other in composition until at *k*, the critical or plait point, they become identical In Fig 2 the distribution ratio of acid between the two phases has been plotted against the acid concentration in the heavier (chloroform) phase, and shows how this ratio varies as the acid brings about changes in the mutual solubility of the two phases A distribution curve which followed the distribution law exactly would be shown by two straight lines running from *a* to *C* and from *b* to *C* in Fig 1

In a ternary system of which two of the binary systems exhibit limited solubility, two binodial curves are obtained as in Fig 3(*a*) These curves can be made to expand by altering the temperature of the system until they meet If this juncture takes place at two plait points, the two binodial curves merge into each other to form a continuous band, as in Fig 3 (*b*) If, however, the two curves meet in such a way that the two plait points do not coincide, the formation of an area occurs in which three liquid phases are coexistent (*abc* of Fig 3 (*c*)) Where three of the binary systems show partial miscibility similar phenomena occur An interesting industrial example of the formation of three liquid layers is sometimes found to occur in the steam distillation of petrol with a high phenol content produced by the hydrogenation of coal



(a) (b) (c)

FIG 3

If a series of single isothermal binodials for any system at various temperatures were placed one above the other in regular order, they would produce a triangular prism in which temperature was measured upwards The binodial curves would form boundary surfaces of a cone-shaped volume representing the concentration and temperature limits of the conjugate solutions The projection of the isothermal binodial curves at different temperatures on to the base of the prism would produce a plane figure showing the temperature variable in the form of a series of binodial curves

Mathematical Properties of Triangular Coordinates

In the equilateral triangle chosen for the graphic representation of a ternary system each pure component is, of course, represented by a vertex of the triangle A point inside the triangle represents a mixture made up of components *A*, *B*, and *C* in amounts proportional to the perpendiculars from this point to the sides opposite vertices *A*, *B*, and *C* respectively

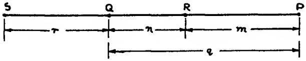


FIG 4

In Fig 4, if the two points *Q* and *P* represent the compositions of two ternary phases defined by the position of two points in an equilateral triangle, then the composition of a third phase formed by mixing these two in the proportion of the lengths *m* and *n* is represented by the point *R* It should be noticed that the amount of *Q* contained in the mixture *R* is proportional to that section (*RP*) of the line *QP* which lies farther from the point *Q* The amount of *P* is proportional to the section (*RQ*) which lies farther from the point *P* This is a purely mathematical deduction, and can be shown by geometrical methods to be independent of the number of components assumed for *Q* and *P*, and of the axes by means of which the position of the points are defined and is true whether the phases are binary, ternary, &c, or whether their composition is defined by the sides of a rectangle, triangle, or space figure These conclusions can be expressed as

$$mQ+nP=(m+n)R \qquad (3)$$

Consider the composition of a phase *S* which lies on the straight line *QP*, but not between the points *Q* and *P* Since the point *Q* now lies between *S* and *P*, its composition can be expressed in terms of *S* and *P* in accordance with equation (3)

$$qS+rP=(q+r)Q, \qquad (4)$$

where *PQ* and *QS* equal *q* and *r* respectively Hence

$$qS=(q+r)Q-rP \qquad (5)$$

The phase *S* cannot therefore be considered a mixture of positive amounts of the two phases *Q* and *P*, and can never actually result from a simple physical mixture of *Q* and *P*, but can be considered mathematically as a mixture of these two phases in negative proportion, which is

$$\frac{-(q+r)}{r}, \text{ or } \frac{-q}{r}-1$$

Therefore every point on the line *QP*, produced indefinitely at both ends, represents a complex which can be expressed mathematically in terms of the compositions of the two phases *Q* and *P*

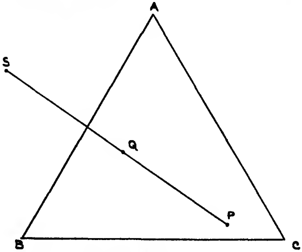


FIG 5

By applying these deductions to any point in the plane of the equilateral triangle *ABC*, but lying outside this triangle, it is obvious that such a point, *S* in Fig 5, can be expressed in terms of the two phases P and Q lying inside the triangle Further, this point can still be expressed in terms of the three components A, B, and C if the use of negative concentration values is admitted

Thus the mixture, complex, or phase represented by point S can be considered as a mixture of the three components A, B, and C, and the concentration of one or more of these components in the mixture is negative, in the above case component C

Computations for Liquid-liquid Systems of Three Components

Computation methods for extraction processes are based on the equilibrium relationships for the particular system employed Simple mathematical computations can be applied where these relationships can be characterized by the distribution law, but where such relationships can only be adequately represented graphically, graphical methods of computation must be employed

Where the two liquids, treated liquid and solvent, are completely immiscible and where the solute is distributed between them in accordance with the distribution law, computations for batch or single-stage extraction processes are purely arithmetical applications of this law, computations for the multiple-contact extraction method, on the other hand, are more complicated, and have been exhaustively discussed in the literature

Calculations for successive extractions with batches of fresh solvent have been put forward by Herz [8, 1909], Smith [14, 1928], Holleman [9, 1932], and Fischer [5, 1929], while a graphical method has been described by Evans [2, 1934] Successive extraction with batches of solvent containing some dissolved solute has been discussed by Underwood [16, 1934] In the multiple-contact method the most efficient extraction is obtained when the solvent is subdivided into batches of equal volume, and this condition has been dealt with fully by several investigators [9, 1932, 14, 1928, 15, 1928, 17, 1928] With a finite volume of solvent available for extraction the limit of the process with the solvent subdivided into many portions has been investigated theoretically by Evans [1, 1934] and Griffin [7, 1934]

When the solute exists in one liquid as single molecules and in the other liquid chiefly as double molecules the distribution equilibrium is given by a formula of the type $K = C_1/\sqrt{C_2}$, and computations for this special case have been derived by Friedrichs [6, 1932] and by Hunter and Nash [11, 1933] A more complicated case of solute association is often found, for example, in the distribution of phenol between benzene and water where the solute exists in one phase partly as single and partly as triple molecules Multiple-extraction calculations for this type of equilibrium have been discussed by Hunter and Nash [11, 1933]

All these computations apply to special cases where some comparatively simple distribution equilibrium is maintained over a limited solute concentration range and where the two solvent liquids are completely immiscible or where their partial miscibility is not materially altered by the presence of the distributed solute Equilibrium relations for the general case where the partial miscibility of the two solvent liquids varies with the concentration of the distributed solute are, as has already been shown, best represented graphically on triangular coordinates A graphical method of computation applicable to this general case has been described by Hunter and Nash [12, 1934], and reviewed together with other computation methods by Evans [2, 1934]

As in the multiple-contact method, computations for countercurrent extraction for the simplest case of two immiscible liquids in which a solute is distributed in accordance with the distribution law have been well established The various mathematical and graphical treatments possible have been exhaustively described by Hunter and Nash [10, 1932], who have also described a graphical method of computation [12, 1934], using triangular coordinates for the general case

Batch or Single-contact Processes

The method of computation for isothermal single-contact processes employs the usual method of interpreting the three-component equilibrium isotherm

Consider a pure liquid B containing a dissolved solute A, which is to be removed by contacting the solution with a second liquid C Let the equilibrium between these three components of the system at a constant operating temperature be represented by the binodial curve in Fig 6 Suppose the composition of the solution of A in B to be treated is given by the point M in Fig 6 Let the ratio of solvent liquid C to the solution to be treated M be R_s/R_m

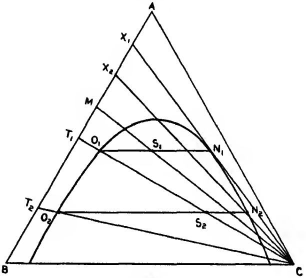


Fig 6

Solution M, in amount R_m, is mixed with solvent C, in amount R_s, in the contacting process The composition of the mixture resulting from this operation must lie on the straight line MC (Fig 6) If this composition is denoted by the point S_1, then in accordance with the rule expressed by equation (3) the ratio of the lengths MS_1 to S_1C must be equal to R_s/R_m The complex S_1 given by the mixing of M and C falls within the area bounded by the binodial distribution curve and must therefore separate into two ternary component phases The composition of these two phases is given by the tie-line passing through S and intersecting the binodial in O_1 and N_1 The points O_1 and N_1, therefore, represent the composition of the two phases resulting from the contacting process, and the composition of the extract remaining when all solvent is removed from it is obtained by joining C to N_1 and producing the line to intersect AB in X_1 Similarly, the composition of the treated solution after removal of solvent is obtained by producing CO_1 to intersect AB in T_1

The point S_1 represents the composition of the complex obtained by mixing the two ternary phases O_1 and N_1 Again, according to the rule denoted by equation (3) the amounts of the extract and treated solutions before solvent removal must be proportional to the lengths of the lines O_1S_1 and S_1N_1, and the amounts of these solutions after solvent has been removed are proportional to the lengths of the lines T_1M and MX_1

The result from a single-stage contacting process can therefore be computed as follows The two points on the ternary diagram representing the composition of the solution to be treated and the treating solvent are joined by a straight line The line so obtained is divided in the ratio of the amounts of solvent to solution to be contacted giving a point S_1 The tie-line passing through S_1 is drawn and intersects the binodial in two points representing the composition of the extract and treated solutions, N_1 and O_1 respectively The amounts of extract and treated solutions are calculated from the length of the lines O_1S_1 and S_1N_1

Multiple-contact Processes

In this process mixing and separation of the two liquids as in the single-contact process is followed by contact of the treated liquid, after separation into two layers and removal of the extract layer, with fresh solvent

Suppose, as in the previous case, we have a solution represented by point M on Fig 6, and treated with a solvent liquid C in the ratio R_e/R_m The treated liquid obtained from this process, after separation of the extract layer, is again treated with fresh solvent in the ratio R_{e_1}/R_{o_1}

By the same construction as before the amounts and compositions of the two phases resulting from the first-stage treatment are ascertained, namely, O_1 and N_1 The phase O_1 is now mixed with fresh solvent C in the ratio R_{e_1}/R_{o_1}, by joining the points O_1 and C, and dividing the line O_1C in this ratio the composition of the complex resulting from this mixture is obtained, that is, S_2 in Fig 6 The tie-line passing through this point gives the composition and amounts of the two phases into which it separates, O_2 and N_2 The composition and amounts of the two resulting complexes when the solvent associated with them has been removed is given by the points T_2 and X_2 and the lengths of the lines X_2T_1 and T_1T_2

By means of these graphical methods the process results which can be obtained by means of single- and multiple-contact processes can be easily computed for simple three-component systems One assumption, however, is involved in this treatment—that each contacting stage in such a process is theoretically ideal, or, expressed otherwise, that complete equilibrium is attained between the two phases resulting from each contacting stage

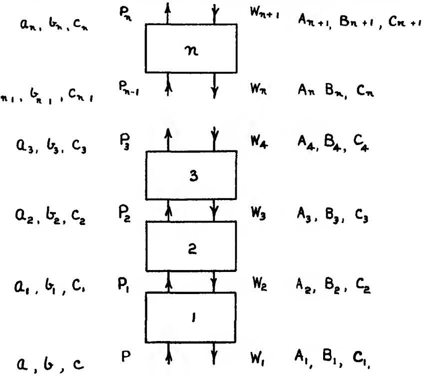


FIG 7

Countercurrent Contact Processes

Consider a substance A dissolved in a liquid B, contacted countercurrently in an isothermal system of n stages with a solvent C, which is purifying B by the extraction of solute A The equilibrium between the three components is again represented by a single binodial curve of the form shown in Fig 1 Let the weight of solution to be treated entering the system per unit time be P, and the weight rate of solution or solvent stream leaving any stage be P and W combined with a suffix describing the number of the stage such stream has just left Further, let the composition of the two liquid streams be described by the letters a, b, and c for the three components of the solution to be treated and by A, B, and C for the components of the solvent, such letters representing the weight fractions of each component present Let the weight fractions of a component in a liquid stream leaving any stage be described by a suffix denoting the number of the stage such stream has just left A diagram of this system complete with the appropriate symbols is shown in Fig 7.

Assuming continuity of operation and taking a total weight balance over each stage of the system we obtain

$$P+W_2=P_1+W_1 \tag{6}$$

$$P_1+W_3=P_2+W_2 \tag{7}$$

$$P_{n-1}+W_{n+1}=P_n+W_n \tag{8}$$

If we call the weight of the solution stream flowing upwards at any point less the weight of the solvent stream flowing downwards at the same point the total upward flow, then at the entrance to the first stage the total upward flow is given by $P-W_1$, and similarly at the entrance to stage 2 and stage n by P_1-W_2, and $P_{n-1}-W_n$ respectively By rearranging equations (6), (7), and (8) we get

$$P-W_1=P_1 \quad W_2 \tag{9}$$

$$P_1-W_2=P_2-W_3 \tag{10}$$

$$P_{n-1}-W_n-P_n-W_{n+1} \tag{11}$$

and

$$P-W_1=P_1-W_2-P_{n-1}-W_n - P_n-W_{n+1} \tag{12}$$

That is, the amount of the total upward flow taken at any cross-section of the system is a constant By taking a material balance of component A at the entrance to each stage it can be shown that

$$P_{n-1}\ a_{n-1}-W_n\ A_n=P_n\ a_n-W_{n+1}\ A_{n+1}, \tag{13}$$

and similarly for components B and C That is, the amount of the total upward flow of any component taken at any cross-section of the system is a constant It follows at once that the composition of the total upward flow through any cross-section of the system is a constant, and can be represented by a point, S The triangular coordinates of the point S, representing the weight fractions of the three components in the material flowing upwards in the system, are therefore

$$S_A=\frac{P_n\ a_n-W_{n+1}\ A_{n+1}}{P_n-W_{n+1}},\quad S_B=\frac{P_n\ b_n-W_{n+1}\ B_{n+1}}{P_n-W_{n+1}},$$

$$S_C=\frac{P_n\ c_n-W_{n+1}\ C_{n+1}}{P_n-W_{n+1}} \tag{14}$$

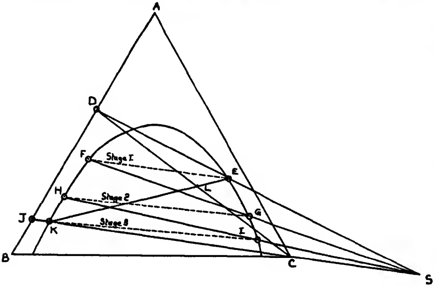


FIG 8

If the total quantity of material flowing upwards (P_n-W_{n+1}) were mixed in negative amount with the exit stream from stage n of the solution to be treated, P_n, the amount of the solvent stream W_{n+1} entering stage n would be obtained, since

$$P_n-(P_n-W_{n+1})=W_{n+1} \tag{15}$$

Similar relations hold for mixing the amount of each component flowing upwards in negative amount with the amount of that component in the P stream For example, with component A we have

$$P_n\ a_n-(P_n\ a_n-W_{n+1}\ A_{n+1})=W_{n+1}\ A_{n+1} \tag{16}$$

This can be rewritten as

$$P_n\ a_n-(P_n-W_{n+1})S_A=W_{n+1}\ A_{n+1} \tag{17}$$

Equation (17) together with two similar equations referring to components B and C show that if the phase whose composition is represented by the point S is mixed in negative proportion with a phase whose composition is that of the treated solution in any horizontal plane through the system, such mixture generates a phase whose composition is that of the solvent in the same horizontal plane

That is, the points representing the composition of any two phases of composition a_n, b_n, c_n, and A_{n+1}, B_{n+1}, C_{n+1}, lie on a straight line passing through point S In accordance with equation (5) the length of the line joining the point a_n, b_n, c_n and the point A_{n+1}, B_{n+1}, C_{n+1} must be proportional to the quantity (P_n-W_{n+1}) and the length of the line joining the point A_{n+1}, B_{n+1}, C_{n+1}, and the point S must be proportional to the quantity P_n

Since the quantity of solvent in the solvent phase will always exceed the quantity of solvent dissolved in the phase being treated, the composition represented by point S must possess a negative concentration of solvent, and therefore be outside the triangle ABC

Computations for the counter-current system just considered usually involve a knowledge of the composition and amount of material to be treated, P, the ratio of solvent to treated material W_{n+1}/P, and the composition of the refined material desired

It is usually required to calculate

(a) the amount of solvent associated with the refined material,

(b) the amount and composition of the extract,

and (c) the number of extraction stages required

In Fig 8 let points D and J represent the composition of the material to be treated and of the desired refined material respectively, and the point C the composition of the solvent employed The amount of solvent associated with the refined material is obtained from the point K where the line joining J and C intersects the binodial curve

Referring for a moment to Fig 7 and taking a material balance over the entire system, we have

$$P+W_{n+1}=P_n+W_1 \tag{18}$$

That is, the complex obtained by mixing solvent and material to be treated can also be obtained by mixing the two exit streams from the system It follows that the line joining the two points representing the composition of the two inlet streams must intersect the line joining the points representing the composition of the two exit streams at a point L Therefore by joining points D and C, in Fig 8, and dividing the line DC in the ratio W_{n+1}/P we locate the point L, such that $DL/LC=W_{n+1}/P$ By joining points K to L and producing KL to intersect the binodial curve at E the point representing the composition of the extract is located and the ratio KL/LE equals W_1/P_n

It will be seen from Fig 7 that the extract is also the solvent stream leaving stage 1, and in an ideal stage, which is the type of stage being considered, the solvent leaving a stage is by definition in equilibrium with the treated material leaving the same stage The composition of the treated material leaving the first stage is therefore located by the tie-line passing through E, and is the point F in Fig 8 We must now locate the point representing the composition of the solvent leaving stage 2 As has been shown above, the point S must lie on the line passing through the points D and E and can be found by the relation

$$\frac{DE}{ES} = \frac{(P-W_1)}{P}$$

The composition of the solvent leaving stage 2 can therefore be obtained from the intersection of the line FS with the binodial at G Drawing the tie-line through G completes the representation of stage 2 Further construction on these lines enables the number of ideal stages (three in the case of Fig 8) required to be calculated Should an auxiliary line passing through point S coincide with a tie-line, no further extraction is possible with the conditions employed

Non-isothermal Processes

Only isothermal processes have been studied in connexion with the three methods of contacting Systems in which the temperature is varied in the different stages employed offer no difficulty, provided the temperature of each extraction stage is known and is maintained constant

In Fig 9 the graphical representation of a three-stage countercurrent process employing a working temperature of 10° C, 20° C, and 30° C in stages *1*, *2*, and *3* respectively is shown The method of solution closely follows that laid down in regard to Fig 8 and is sufficiently obvious not to require further amplification

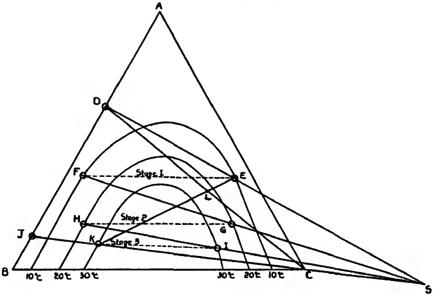


Fig 9

Equilibria in Complex Hydrocarbon-solvent Systems

Where solvent extraction is employed for the removal of undesirable constituents from petroleum products, such as the extraction of aromatics from kerosine by liquid sulphur dioxide and the extraction of the more unsaturated constituents from lubricating oils by nitrobenzene, phenol, or dichloro-ethyl ether, the equilibria involved cannot be represented exactly by any simple means Exact representation can only be obtained by the use of complex methods involving a comprehensive knowledge of the constituents of such petroleum products Even if our present state of knowledge were sufficient to enable exact equilibria relationships to be compiled, it is doubtful if the resultant phase representations would be suitable for purposes of computation, since the major essentials of a successful method of computation must combine simplicity, ease, and speed of calculation with reasonable accuracy, all of which demand the simplest possible representation of equilibrium relationships However, this problem is simplified by our ignorance of the chemical nature of petroleum products, and equilibria characterization on the following lines devised by Hunter and Nash [11, 1933] leads to an approximate but satisfactory solution

In the solvent refining of an oil the solvent tends to split the oil into two fractions, soluble and less soluble, possessing different physical characteristics These two fractions do not represent a sharp separation of the oil into purely soluble and less soluble constituents, but are mixtures of both In certain special cases the nature of the soluble and less soluble constituents may be known as, for example, in the refining of kerosine where the more soluble constituents are aromatic hydrocarbons and the less soluble non-aromatic In this case where the amounts of aromatic and non-aromatic hydrocarbons are readily determined by analysis then the oil may be considered as a simple two-component system, the two components being each complex mixtures of aromatic and non-aromatic hydrocarbons respectively The resulting oil-solvent system may then be treated as a simple ternary system and equilibrium relations represented on triangular coordinates in terms of solvent, aromatics, and non-aromatics, while the already described triangular coordinate graphical method, suitable for the general case in ternary systems where the partial miscibility of the two solvent components is altered by the distributed component, may be used for both multiple and countercurrent extraction computations Such cases where the oil can be analysed in terms of two groups of constituents are, however, relatively rare and unimportant, compared with cases where such analysis is impossible The chemical nature of the hydrocarbon groups present in any lubricating oil, for instance, is not known Such oils are usually considered to be made up of two major groups of constituents generally referred to as naphthenic and paraffinic, where the term naphthenic is to be interpreted as denoting a mixture of hydrocarbon groups relatively poor in hydrogen, and the term paraffinic as a mixture of hydrocarbon groups relatively rich in hydrogen Lubricating oils are then designated naphthenic in character or paraffinic in character by virtue of the numerical value of certain physical properties like the viscosity index (V I) or the viscosity gravity constant (V G C) The number and actual chemical nature of the hydrocarbon groups present in any particular product is still entirely speculative It is known, however, that the groups comparatively poor in hydrogen form the bulk of the undesirable constituents which have to be removed to produce a good lubricating oil It is also known that such constituents possess a high value for the V G C and a low value for the V I, while conversely the desirable or so-called paraffinic constituents have respectively low and high values for these physical properties The degree of refining of a lubricating oil stock may, therefore, be followed and controlled to a certain extent by the use of these or similar physical properties

Therefore with our present state of knowledge, in order to represent the equilibrium relations in an oil-solvent system it is only necessary to record by some suitable means the following information

(1) Amounts of the two phases in equilibrium
(2) Amount of solvent in each phase at equilibrium
(3) A physical property of the oil present in each phase at equilibrium

Items (2) and (3) of this information can be recorded by a single point on a triangular graph of which one vertex represents pure solvent, and one side, opposite to this vertex, is scaled into units representing the required physical property of the solvent-free oil The equilibrium resulting between a lubricating oil and nitrobenzene at 10° C is shown in Table I

TABLE 1

Lubricating Oil Stock A and Nitrobenzene at 10° C

Expt	Ratio of solvent to oil used	Raffinate layer: % original oil in layer	Raffinate layer: V G C of oil in layer	Raffinate layer: % solvent in layer	Extract layer: % original oil in layer	Extract layer: V G C of oil in layer	Extract layer: % solvent in layer
1	6	10 5	0 824	10 7	89 5	0 872	87 0
2	3	35 0	0 836	14 6	65 0	0 882	81 9
3	1	63 0	0 851	17 0	37 0	0 900	70 2

These equilibrium relationships are plotted on the triangular graph, Fig 10 (*a*) The V G C of the solvent-free oil in the raffinate layer from experiment 1, Table I, is given by point *b* on this diagram Now if raffinate oil of this V G C were mixed with an amount of nitrobenzene such that the total mixture contained 10 7% of nitrobenzene we should get the actual raffinate layer obtained Therefore by joining *b* to the apex of the triangle representing 100% of nitrobenzene and locating the point on this line where the nitrobenzene content is 10 7% we obtain the point *d* representative of the composition of the raffinate layer This may be shown in another way By starting with the raffinate layer of composition *d* and removing all the solvent present we would obtain point *b* on the diagram, which is solvent-free oil of V G C 0 824 The composition of the various raffinate and extract layers is therefore easily ascertained and is indicated on this diagram by the points *d, f, h,* and *e, g, i* for the example quoted in Table I Returning again to experiment 1, the compositions of the raffinate and extract layers in equilibrium are given by points *d* and *e* These two solutions are conjugate and hence may be joined by the tie-lines *de* The completed isothermal binodial curve and tie-lines shown on the diagram then represent the equilibrium relations for this lubricating oil-nitrobenzene system at 10° C

This diagram can also be used to determine the amounts of any two phases in equilibrium, given only the quantities of oil and solvent used for the equilibrium experiment In experiment 3 equal volumes of nitrobenzene and oil were employed, so that the resultant mixture contained 50% of nitrobenzene and its composition would be represented by the intersection of the line joining the V G C of the stock, point *c* in the figure, to the 100% nitrobenzene apex and the line representing 50% of nitrobenzene, namely, point *m* on Fig 10 (*a*) This mixture, however, can only exist as two phases whose compositions *h* and *i* are given by the tie-line passing through *m* The amounts of the raffinate phase *h* and the extract phase *i* are then proportional to the lengths of the two lines *mi* and *mh* Therefore, knowing the volumes of solvent and oil used originally, the volumes of the two phases formed can be calculated from this relationship Further, since the volume per cent of solvent in each phase can be read from the figure, the actual volume of solvent-free oil in each phase can be calculated also Such a diagram therefore gives a complete representation of all essential equilibrium relationships In constructing these diagrams the scale employed for the physical property of the solvent-free oil can be chosen to give a suitably sized binodial curve The actual terminal values finally selected become, by the nature of the diagram, equivalent to the physical properties of the soluble and insoluble components of the oil This is an unavoidable assumption made in the actual construction of the figure, but since such terminal values will vary with the desired degree of refining for the same oil, and with solvent and temperature conditions, it is preferable not to consider these terminal values as indicative of soluble and insoluble group properties The physical property chosen for the construction of the diagram is also required by the nature of the diagram to be additive

The equilibrium diagram can be constructed from the experimental results obtained by the single-stage batch extraction of an oil with different volumes of solvent, as in Table I Care must be exercised, of course, to ensure that the two phases are in equilibrium The diagram can also be constructed from multiple-extraction results provided that the compositions of conjugate layers are used and true equilibrium is attained at each extraction stage, that is, each stage is equivalent to an ideal stage In a heterogeneous system undergoing agitation two phases may coexist which are approaching equilibrium with each other In this case the points representing the composition of each phase at any instant during approach to equilibrium may be assumed to lie on the binodial curve, since this curve represents the compositions of all possible heterogeneous solutions, but the tie-line joining two such points would not of course, represent equilibrium

The composition of any phase from either a multiple or countercurrent extraction process would then presumably lie on the binodial curve even if equilibrium is not attained in each extraction stage

A modification of the ternary equilibrium diagram has been described by Kurtz [13, 1935] in which rectangular in place of triangular coordinates are employed This method of plotting suffers from the fact that it does not enable experimental inaccuracies to be detected as readily as when triangular graphs are employed

In Fig 10 several oil-solvent equilibrium diagrams are illustrated The equilibrium between nitrobenzene and three different lubricating oil stocks at 10° C are shown in Fig 10 (*a*), (*b*), and (*c*), using the V G C for the physical property of the solvent-free oil The binodial curves and tie-lines for these three systems were constructed from batch-extraction experiments The data for stocks No 2, Fig 10 (*b*), and No 3, Fig 10 (*c*), were taken from the paper of Ferris, Birkhimer, and Henderson [3, 1931] The individual points indicated on these figures by crosses and circles were obtained respectively by multiple and countercurrent extraction of these oils with nitrobenzene at 10° C, employing actual stages where equilibrium between the two phases of each stage was not always obtained The fact that these points lie for the most part on the binodial curves provides a useful check on the already established shape of the binodials It affords proof also of the assumption that a point representing the composition of a phase from any extraction stage of an agitated heterogeneous system, whatever the stage efficiency, will lie on the binodial Such equilibrium diagrams can therefore be employed to compute graphically the results to be expected from any solvent-extraction process of oil refining.

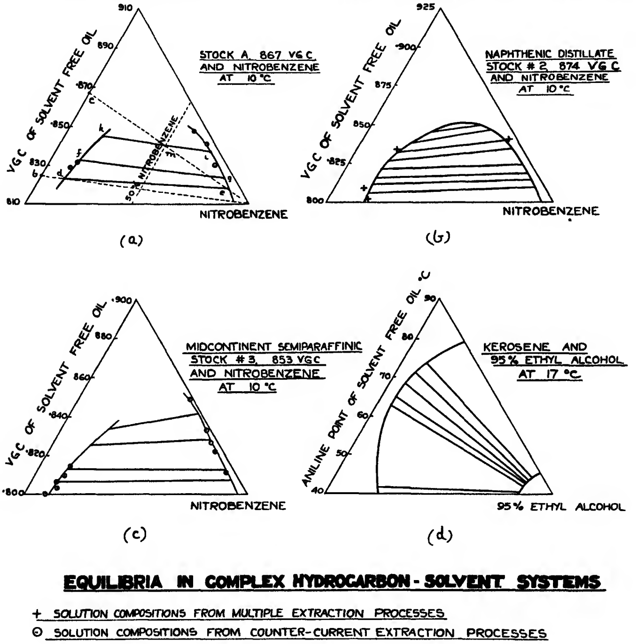


Fig 10

In Fig 10 (*d*) the equilibrium diagram for the system kerosine—95% ethyl alcohol at 17° C is shown, using the aniline point (miscibility temperature of equal volumes of oil and aniline) as the physical property of the solvent-free oil This diagram is similar to that of a ternary system where both components of the binary mixture being treated are only partially miscible with the solvent The diagrams for the lubricating oil-nitrobenzene systems, on the other hand, are all similar to that of a ternary system where only one of the components of the binary mixture being treated is partially miscible with solvent, the other being completely miscible

Computations for Complex Hydrocarbon-solvent Systems

The triangular equilibrium diagram may be employed as a basis for computation in complex oil-solvent systems The actual method of computation is the triangular coordinate graphical method for the general case in ternary systems which has already been described. The only difference in this method is that in the present case instead of phase compositions being expressed in terms of three components they are given in terms of solvent per cent and a physical property of the solvent-free oil.

Computations for a multiple or countercurrent extraction process normally involve a knowledge of the value of some physical property of the oil to be treated, the ratio of solvent to treated oil employed, and the value of the physical property of the refined oil desired. Given such data it is usually required to calculate at fixed working conditions

(1) the yield of refined oil,
(2) the amount of solvent associated with the refined oil,
(3) the amount of extract,
(4) the amount of solvent in the extract and yield of solvent-free extract oil,
(5) the value of a physical property of the solvent-free extract oil,
(6) the number of ideal extraction stages required to give the desired refined oil.

This graphical method enables these results to be computed with reasonable accuracy. Further, if such results are already available from a working unit utilizing a known number of actual extraction stages, then the number of ideal stages obtained by such a computation may be combined with this number and an overall stage efficiency evaluated, where the overall stage efficiency is defined by

$$E' = \frac{N_1}{N_a} \times 100, \tag{19}$$

in which N_a = number of actual extraction stages,
N_1 = number of ideal extraction stages.

Since the method of computation has already been thoroughly described in connexion with simple ternary systems, it will not be necessary to discuss it again here. Instead, the results obtained by applying the method to several oil-solvent systems will be compared with results actually obtained.

The multiple extraction of a naphthenic distillate lubricating oil stock No. 2 with nitrobenzene at 10° C., the equilibrium diagram of which is given in Fig. 10 (*b*), has been described by Ferris and Houghton [4, 1932]. The actual extraction process employed was as follows. 100 volumes of stock were treated with 100 volumes of solvent giving the first raffinate and extract. The first raffinate was then extracted with 120 volumes of nitrobenzene giving a second raffinate, and an extract which was added to the first extract giving the second extract. The second raffinate was finally treated with 173 volumes of solvent to give the third raffinate. The third extract was obtained by adding the second extract to that obtained in the last treatment. The scheme is shown diagrammatically in Fig. 11. The experimental results from this extraction process are given in Table II together with results calculated by the triangular coordinate graphical method using the equilibrium diagram of Fig. 10 (*b*). It will be seen that very satisfactory agreement is obtained except in the third stage. The rather wide divergence here is undoubtedly due to insufficient data to define accurately the lowest part of the binodial curve, where the graphical constructions for the third stage are located. Since the experimental extraction was carried out in the laboratory, it has been assumed in making this comparison that equilibrium has been attained in each experimental stage, whereas it is possible that such stages did not reach complete equilibrium, which would in part be the cause of a certain amount of discrepancy between experimental and calculated data.

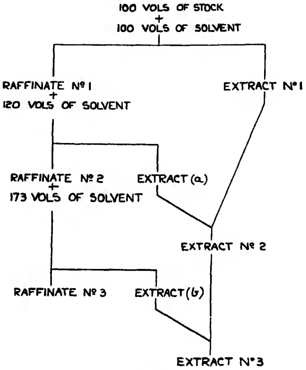


FIG. 11

TABLE II

Multiple Extraction of Stock No. 2 with Nitrobenzene at 10° C.

Extraction stage	Raffinate layer						Extract layer			
	Solvent-free oil, volume % of original stock		V.G.C. of solvent-free oil		Volume % of solvent in layer		Solvent-free oil, volume % of original stock		V.G.C. of solvent-free oil	
	Act.	Calc.	Act.	Calc.	Act.	Calc.	Act.	Calc.	Act.	Calc.
1	49·0	49·7	0·840	0·838	19·5	19·5	50·7	50·6	0·911	0·911
2	27·3	31·0	0·811	0·811	12·5	15·0	72·7	69·3	0·898	0·904
3	15·6	20·7	0·802	0·805	16·6	16·0	84·4	79·6	0·887	0·893

In Table III the experimental results, communicated to the author by S W Ferris of the Atlantic Refining Company, from a three-stage countercurrent extraction process refining different lubricating oil stocks with nitrobenzene at 10° C are compared. The oil stocks treated were a Mid-Continent semi-paraffinic stock No 3, V G C 0.853, the equilibrium diagram of which is given in Fig 10 (*c*), stock *A*, V G C 0.867, the equilibrium diagram of which is given in Fig 10 (*a*), stock *B*, V G C 0.864, and stock *C*, V G C 0.824. The equilibrium diagrams of the last two oils, stock *B* and *C*, are not given as they are very similar to that of stock *A*.

The extraction conditions employed were as follows. The extracting vessels were all approximately the same, being pear-shaped separating funnels 7 in diameter at the top, and 13 in high with a capacity of 3 litres. Air agitation was used, but no attempt was made to systematize stirring. Temperatures were maintained constant in all three stages at 10±0.5° C.

In arriving at the calculated values in Table III, the yields of solvent-free raffinate and extract oil, the volume per cent of solvent in both layers, and the V G C of the extract were computed for the treatment of the given stock with the given volume of solvent to obtain a solvent-free raffinate oil having the V G C shown in column 3. The agreement between actual and calculated results is satisfactory, and the average deviation is of the order of ±10%.

The maximum deviation was found to occur for the experiments where the constructional computation lines were located in that part of the equilibrium diagram which was outside the range of the initial equilibrium experiments. A material balance check on the experimental data used for constructing the equilibrium diagrams also showed that many of these data were only correct to within ±10%. Unless particular precautions are taken, the error in determining those sections of the binodials where one phase is large and the other phase comparatively small may easily be even larger. With very accurate equilibrium diagrams the deviation between the actual and computed data could easily be reduced to less than +3%. The accuracy of the computations is chiefly dependent on the accuracy of the experimental extractions used for constructing the equilibrium diagram.

The number of ideal stages required to reproduce these countercurrent extraction results, as computed graphically, is shown together with the overall stage efficiency in Table IV. The overall stage efficiency is apparently inversely proportional to the solvent-oil ratio employed, and

TABLE III

Three-stage Countercurrent Extraction of Lubricating Oil Stocks with Nitrobenzene at 10° C

Oil stock treated	*Volumes of solvent per 100 volumes of oil stock used*	*V G C of solvent-free oil*	*Roffinate layer*						*Extract layer*			
			Solvent-free oil as volume % of originol stock		*Volume % of solvent in layer*		*V G C of solvent-free oil*		*Solvent-free oil os volume % of originol stock*		*Volume % of solvent in layer*	
			Act	*Calc*	*Act*	*Calc*	*Act*	*Calc*	*Act*	*Calc*	*Act*	*Calc*
Stock 3, V G C 0.853	53.3	0.817	54.8	57.7	14.2	14.0	0.899	0.901	45.2	44.0	49.8	51.0
	100.0	0.811	49.0	50.5	12.5	12.5	0.895	0.897	51.0	49.5	64.8	65.0
	136.4	0.807	44.0	47.5	10.8	12.5	0.889	0.895	56.0	52.5	70.1	71.1
	185.0	0.804	37.7	42.0	12.5	13.0	0.884	0.890	62.3	57.0	74.3	75.5
	375.0	0.799	27.9	23.0	9.0	14.5	0.874	0.879	72.1	72.0	83.7	84.0
Stock *A*, V G C 0.867	65.0	0.845	56.6	59.3	11.1	16.0	0.897	0.898	43.4	41.4	57.0	56.0
	98.0	0.835	52.5	51.4	13.2	14.0	0.902	0.901	47.5	48.2	65.5	65.0
	188.0	0.831	37.9	40.4	11.2	13.0	0.887	0.891	62.1	60.5	74.4	75.0
Stock *B*, V G C 0.864	75.0	0.828	62.7	63.0	14.6	16.0	0.925	0.925	37.3	37.0	63.3	63·0
	150.0	0.814	50.5	56.0		13.8	0.917	0.928	49.5	50.0		76.6
	225.0	0.811	45.7	50.6	13.7	13.3	0.909	0.918	54.3	48.6	80.0	82.0
Stock *C*, V G C 0.828	150.0	0.803	62.5	64.0	13.6	14.3	0.869	0.863	37.5	39.5	78.9	77.5

TABLE IV

Overall Stage Efficiency for Air-agitated Stage

Lubricating oil stock used	*Volumes solvent per 100 volumes of oil*	*V G C of solvent-free raffinate oil produced*	*Number of ideal extraction stages required*	*Number of air-agitated stages used*	*Percentage overall stage efficiency*
Stock 3, 0.853 V G C	53.3	0.817	*	3	
	100.0	0.811	2.42	3	80.6
	136.4	0.807	2.05	3	68.3
	185.0	0.804	1.80	3	60.0
	375.0	0.799	1.53	3	51.0
Stock *A*, 0.867 V G C	65.0	0.845	*	3	
	98.0	0.835	2.43	3	81.0
	188.0	0.831	1.53	3	51.0
Stock *B*, 0.864 V G C	75.0	0.828	2.70	3	90.0
	150.0	0.814	2.45	3	81.6
	225.0	0.811	1.90	3	63.3
Stock *C*, 0.828 V G C	150.0	0.803	2.30	3	76.6

* Number uncertain owing to insufficient tie-line or binodial curve data

100% efficiency is probably approached at solvent-oil ratios which correspond to complete miscibility between the oil stock and the solvent Unfortunately, insufficient data are available definitely to fix the effect of solvent-oil ratio upon the overall efficiency, and these results are further complicated by the variable nature of the air agitation employed

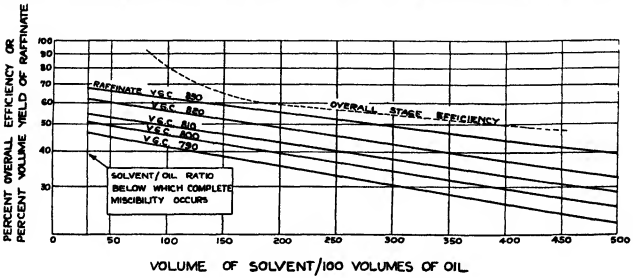


Fig 12

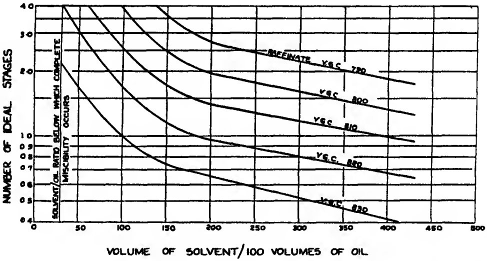


Fig 13

The method of computation is exceedingly useful, particularly for forecasting the most favourable extraction conditions to produce a maximum yield of raffinate of a given V G C The data resulting from such graphical calculations for the countercurrent extraction of stock No 2, with nitrobenzene at 10° C, are shown in Figs 12 and 13 The volume per cent yield of raffinates of varying V G C. are plotted against the solvent-oil ratio Maximum yields of the most desirable raffinate, that is, a raffinate possessing a low V G C, are obtained at low solvent-oil ratios At these low solvent-oil ratios, however, a rather large number of ideal extraction stages is required to give a low V G C The number of actual stages necessary can be computed from the overall stage efficiency The variation of the overall efficiency for an air-agitated stage as tabulated in Table IV has been plotted in Fig 12 The best extraction conditions to give maximum yield of low V G C raffinate reconcilable with a reasonable number of actual stages and the lowest solvent-oil ratio can easily be determined from such diagrams

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THE APPLICATION OF TRIANGULAR GRAPHS TO THE COMPARATIVE LABORATORY STUDY OF SOLVENT-REFINING PROCESSES

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THE increasing use of solvent processes in general refinery practice, particularly in the manufacture of high-grade lubricants, has emphasized the need for some reliable method for comparing the efficiency of different solvents in order to distinguish between the various processes now available Moreover, the number of different solvent processes on the market to-day presents a bewildering problem to the petroleum engineer who attempts a comparison by correlation of the published data and, while it is perhaps only natural that the inventors of each solvent process should exert themselves primarily to demonstrations of the wide range of applications of their particular process to different types of charging stock, the unfortunate result is seen in the scarcity of comparative information regarding the treatment of any one particular charging stock by different solvent processes

In the discussion which follows an attempt has been made to indicate the way in which the efficiencies of the various processes may be compared by the use of the triangular graphical methods developed by Hunter and Nash While this method of treatment is probably not exact in the extreme owing to the complexity of the usual petroleum products used as charging stocks for solvent treatment, it does give a very clear picture of the various factors affecting solvent refining and enables the relative efficiency of the different solvent processes to be assessed with a greater accuracy than is possible by any other means It should be borne in mind that, although comparisons of solvents by actual plant tests are useful, the results will not be strictly comparable if one process is handicapped by less efficiently operated or designed plant, and it is obviously desirable that in selecting a solvent process the choice should be influenced by fundamental solvent efficiency and not based entirely on plant performance, which, in a matter of a few years, may be surpassed by further plant development

History and Development

The Object of Solvent Refining.

Gurwitsch [14, 1926] gives a summary of early investigations on solvent refining, using aliphatic alcohols as selective solvents, but the credit for the development of the first commercially successful solvent extraction process is generally accorded to Edeleanu for his process employing liquid SO_2, which was originally developed for the removal of aromatic fractions from Roumanian kerosines It has, however, been used in one refinery in Great Britain since 1927 for the manufacture of turbine oils, and to-day has become very widely adopted for the production of a large variety of petroleum products such as anti-knock gasoline, turpentine substitutes, special dry-cleaning spirit, high-grade kerosine, transformer oils, turbine oils, and motor lubricants, including cylinder stock

From 1930 onwards the number of solvent processes has increased enormously The phenol process has been developed by R K Stratford and his co-workers [41, 1933] in the Imperial Oil Refinery, Ltd , Sarnia, Ontario, Canada The Texas Company in America have developed the Furfural process described by Fichwald [6] The Atlantic Refining Company, Philadelphia with Ferris and his co-workers have developed the Nitrobenzene process [11, 1932], while the Standard Oil Company of Indiana have sponsored the Chlorex process [29, 1933], to mention only some of the better known of the single-solvent processes The Duo-Sol process employing liquid propane in conjunction with a cresylic acid solvent has been worked out by the Max B Miller Company of New York [23, 1933], while other double-solvent processes include the SO_2-benzole modification of the original Edeleanu process, and the phenol (and/or cresol) plus water processes

While for the majority of solvent processes the object of solvent refining is to produce high-grade lubricating oils, such a definition cannot be applied generally The original Edeleanu process, for example, handled only kerosine fractions and produced high-grade lamp oils, while in its recent application to gasoline treatment the process is operated for the concentrated aromatic fraction obtained in the low-temperature extract, the raffinate being an inferior gasoline to the starting stock In every solvent process, however, the object and effect can be chemically defined as one of separation into components of low hydrogen/carbon ratio (extracts) and high hydrogen/carbon ratio (raffinates) The separation is quantitative in that no loss of hydrocarbon material occurs due to chemical combination with the pure solvent, but is seldom, if ever, complete in the chemical sense since the raffinates and extracts are never pure components but are mutually contaminated to a greater or lesser degree

Composition of Crude Lubricating Oil Fractions and Base Stocks

It is doubtful if any of the hydrocarbon constituents of petroleum lubricating oil has ever been isolated in a state of purity, much less identified, but a good idea of the possible constituents may be inferred from the known constitution of the lighter components of petroleum present in the gasoline boiling range, and also by comparison with high molecular weight hydrocarbons prepared synthetically Such constituents include straight or branched chain paraffins, naphthene hydrocarbons containing saturated 5- and 6-membered carbon rings, such as cyclopentane and cyclohexane *nuclei*, and aromatic hydrocarbons containing benzene or naphthalene, *nuclei*, &c Moreover, these constituents are for the major part in combination, giving large complex molecules containing both paraffinic and aromatic, or paraffinic and naphthenic, or even all three characteristics

Rossini [32, 1935] gives a very good discussion on this subject, while Vlugter, Waterman, and Van Westen [44, 1935] have developed a method for determining the average percentage composition of the lubricating-oil fractions of a crude in terms of paraffinic, naphthenic, and aromatic constituents. They give the following compositions for a Pennsylvanian lubricating oil and a naphthene base oil:

	Pennsylvanian oil	*Naphthene base oil*
% Aromatic rings	8	32
% Naphthene rings	15	29
% Paraffinic side chains	77	39

Mikeska [25, 1936] has attempted a correlation between chemical structure and the common physical properties of lubricating oils by an examination of fifty-two pure hydrocarbons prepared synthetically. His findings throw considerable light on the relationships between viscosity index, viscosity, &c., and structure.

Rossini [33, 1936] in a later paper gives further information on the same subject obtained from a different angle by examination of the products of close solvent fractionation of a lubricating oil stock.

As a general system of classification, the constituents of a lubricating oil fraction are referred to as:

1. **Paraffinic.** Characterized by high hydrogen/carbon ratio and including crystalline wax. The term is used loosely to include all constituents of good viscosity index [5, 1929] or viscosity-gravity constant [15, 1928], which are not readily dissolved by selective solvents.

2. **Naphthenic.** Characterized by low hydrogen/carbon ratio and generally considered to represent those portions of the crude stock which are readily soluble in the selective solvents. The term is somewhat of a misnomer, since undoubtedly a large proportion of the hydrocarbon constituents which are popularly referred to as paraffinic, and which are included in the solvent-refined oils, are in reality naphthenic in structure. Occasionally a further distinction is introduced between *naphthenic* and *aromatic* fractions, in which case the naphthenic constituents are generally rated from about 0 to 50 viscosity index, and the aromatic constituents of very low viscosity indices ranging down to below −350 when they resemble a soft asphalt in appearance.

Results of Solvent Refining

If with a given solvent and a given base stock a series of batch extractions is carried out, using different percentages of solvent but maintaining the same treatment temperature for the whole series, a range of products will be obtained having different characteristics such as specific gravity, viscosity, &c., and it will be found that, while the change in quality of the raffinates is progressive with increasing treatments, the change in quality of the extracted oils is less regular and may even increase to a maximum and then decrease as the percentage treatment is increased, depending upon the solvent used, the treatment temperature, and the base stock. If, however, the series of raffinates and extracts be examined and in each case the specific gravity be plotted against some other characteristic (say viscosity at some given temperature) a smooth curve is obtained which is characteristic of that particular base stock but which is practically independent of the treatment temperature, or the solvent used (i.e. SO_2, phenol, furfural, chlorex, SO_2-benzole, phenol-water, &c.), or the manner in which the solvent is applied, whether in single-batch treatment, multiple-batch or countercurrent treatment. In other words, all raffinates (or extracts) of a given specific gravity obtained from a given starting stock will have the same viscosity independent of the solvent used, the treatment temperature, or the manner in which the solvent is applied. It is not known whether this generalization holds exactly in all cases, but at least it can be taken to apply with sufficient exactness for all practical purposes.

An exception must, however, be made for solvents such as liquid methane, propane, &c., which have been referred to as precipitative solvents, and which act in more or less the reverse manner to the general run of selective solvents as described in a later section, or to combined solvent processes employing these light liquid hydrocarbons. The products obtained by the Duo-Sol process, for example, do not conform to the curves for the single-solvent processes.

That the same general curve applies for batch and countercurrent treatment is significant, since it implies that the products obtained by repeated re-extraction and recycling of intermediate raffinates and extracts during countercurrent treatment exhibit the same gravity-viscosity, &c., relations as the products of the single-batch treatment. See Fig. 1.

Similar general relationships, independent of solvent, treatment temperature, &c., are found to hold for all the usual characteristics such as viscosity index, aniline point, refractive index, &c., and it would appear that even colour and carbon residue may be included in the list if side reactions such as oxidation, asphalt precipitation, or chemical interaction with the solvent impurities are avoided. The effect of solvent refining on these various relationships is discussed in detail below, and gives a very useful introduction to the more general discussions which follow.

Viscosity-Gravity Constant.

The viscosity-gravity constant (V.G.C.) of Hill and Coats [15, 1928] has received very widespread acceptance as a measure of paraffinicity for lubricating oils and has been used by various writers [19, 1933, 21, 1935] as a suitable function for expressing quantitatively the effects of solvent refining. It has the advantage that for oils covering a wide range of viscosities the V.G.C. is additive, since for the raffinates and extracts produced by solvent-treating a given stock, the V.G.C. is a linear function of the specific gravity. On the other hand, the V.G.C. formulae were originally developed by Hill and Coats from data for oils of a limited viscosity range:

Viscosity at 210° F	40 to 400 sec. Saybolt
Viscosity at 100° F	40 to 3,000 sec. Saybolt

Moore and Kaye [27, 1934] have, however, given a modified formula based on kinematic viscosity at 100° F which enables the V.G.C. to be calculated for oils as light as kerosines.

It is found that for extracts of high viscosity the linear relation between specific gravity and V.G.C. no longer holds, while the V.G.C. as determined by the two formulae gives very different results.

Fig. 2 gives a series of curves relating the specific gravity at 60° F with the V.G.C. for the solvent fractions (raffinates and extracts) obtained from a series of starting stocks ranging from a White Spirit Cut of 0.783 specific gravity up to a heavy cylinder stock of 0.962 specific gravity prepared from a mixed base crude, and these curves have been found to hold independently of the solvent used or the conditions of solvent treatment. For example, the curves for medium lubricating base have been found to apply under all of the following conditions:

1. Liquid SO_2 at 30°, 60°, and 100° F.
2. Chlorex at 30°, 60°, 100°, and 125° F.
3. Phenol at 105°, 110°, and 150° F.

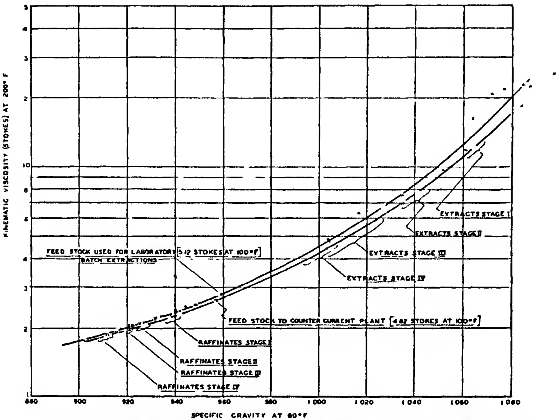


FIG. 1 Relation between specific gravity at 60° F and viscosity at 200° F for raffinates and extracts produced from similar base stocks by (*a*) batch treatments, (*b*) four-stage countercurrent SO_2-benzole

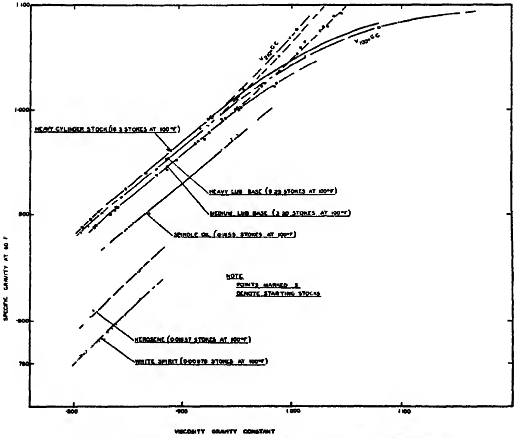


FIG 2. Relation between specific gravity at 60° F and viscosity-gravity constant.

4. SO_2-benzole (80:20) at 60° F
   - ,, (70:30) at 60° and 30° F
   - ,, (60:40) at 60° F
5. Four-stage countercurrent chlorex at 70° F
6. Three-stage countercurrent SO_2-benzole (70:30) at 60° F

The curve for the heavy lubricating base has been verified for treatments with

1. SO_2 at 70°, 100°, and 210° F
2. SO_2-benzole (70:30) at 70° F
3. Chlorex at 70° F
4. Furfural at 130°, 200° and 250° F
5. Three-stage countercurrent chlorex at 70° F

lubricating base are given in Fig. 3. These curves are also perfectly general in that they are independent of the solvent used, the treatment temperature, or the method of treatment, &c., though owing to the relatively large effects which experimental errors in viscosity determination may have on viscosity-index measurements the agreement between the various experimental points is not always good. The curves are similar in shape for practically all stocks, though the actual position of the curves is determined in each case by V.I.-V.G.C. relationship of the starting stock and depends to a considerable extent on the wax content (i.e. degree of dewaxing).

The relation between viscosity index and V.G.C. (or specific gravity), as indicated in Fig. 3, is not linear, and the V.I. of a mixture of two different oils of known quality can therefore only be estimated approximately.

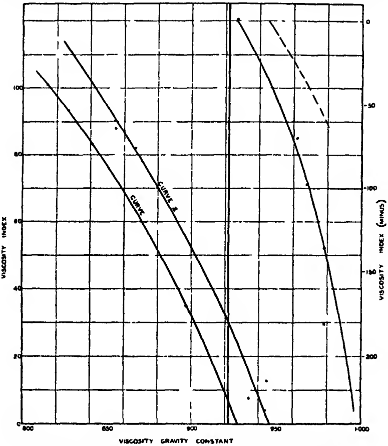


FIG. 3. Relation between V.I. and V.G.C. for solvent fractions from various starting stocks. Curve 1, heavy lub. base distillate, Curve 2, spindle-oil distillate.

Viscosity Index

The viscosity index (V.I.) of Dean and Davis [5, 1929] enables different oils to be compared for viscosity-temperature sensitivity, and this, together with the fact that most oils of high viscosity index show better all-round characteristics than oils of low V.I., has resulted in its becoming the generally accepted standard of quality. While the V.I. is not an infallible standard of quality or stability for comparing oils from totally different stocks, there does exist a definite relationship between V.I. and quality for raffinates and extracts produced from any one given starting stock by various solvent treatments.

The relations between V.I. and V.G.C. for two of the series of solvent fractions plotted in Fig. 2, i.e. the spindle-oil fractions and the raffinates and extracts from the heavy

Viscosity.

Fig. 4 gives typical curves for viscosity *versus* specific gravity for the various solvent fractions (raffinates and extracts) obtained from four different starting stocks (lub. distillates) from the same crude. The shape of the curve in every case is determined by the viscosity and gravity of the starting stock but is unaffected by the solvent used or the conditions of treatment. Values for raffinates and extracts obtained in a laboratory three-stage countercurrent treatment are included on two of the curves. The shape of the curves is not necessarily the same, however, for similar stocks produced from different crudes (compare Figs. 1

and 4), but depends on the nature and relative proportions of 'paraffinic' and 'naphthenic' constituents present in the starting stock

Colour and Carbon Residue.

The effect of solvent refining on colour and carbon residue has been the subject of some controversy, it being maintained that certain solvents, and SO_2 in particular, produced poor-coloured raffinates While the present author has not been able to test a great many solvents in this respect, a carefully conducted series of tests on an asphalt-free mixed base distillate stock indicated that in all probability, if reasonable precautions are taken to avoid secondary reactions such as oxidation or asphalt precipitation (see later section), the relation between colour and other characteristics is also independent of the solvent process, &c The colours of the series of raffinates all produced from the same starting stock were determined by means of a 'Klett' Bio-colorimeter which gives colour values relative to any given standard liquid in terms of the lengths of the two liquid columns (i e length of standard and length of sample under examination)

The results obtained are plotted against V G C in Fig 5 It will be observed that where little or no improvement in V G C occurred the colour of the product was considerably darker than the starting stock, the mere admixture and subsequent removal of solvent in the starting stock produced a marked change in colour due to heat treatment of this stock alone

In dealing with a crude residuum of mixed-base origin, however, it was found that the raffinates produced by SO_2 and certain other solvents were invariably darker than the extracts, due to precipitation of asphaltic matter which remained suspended in the raffinate layers The differences in colour which have been recorded by some observers when using different solvents can be explained by this precipitation of asphalt in certain cases, and is therefore rather to be attributed to abnormalities in the starting stock, due to defective distillation in the production of the original distillate stocks, than to any fundamental difference in the effect of the various solvents on colour removal Stratford [39, 1936] indicates a similar concentration of asphaltic matter in the phenol raffinates and states this to have a serious effect on emulsification difficulties

In Fig 6 the relation between specific gravity and carbon residue (determined by the Ramsbottom method, British

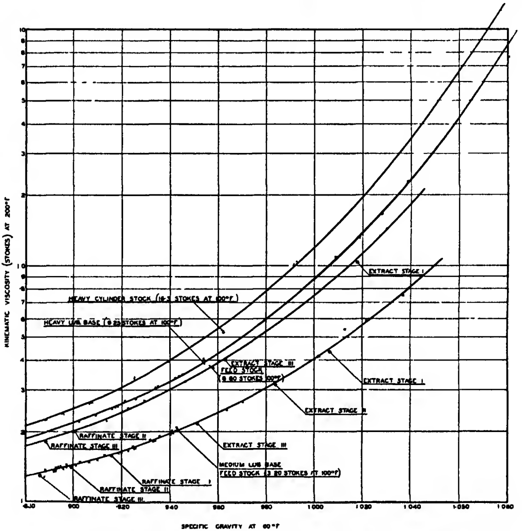


FIG 4 Relation between specific gravity at 60° F and viscosity at 200° F for raffinates and extracts from various distillate base stocks obtained from the same crude

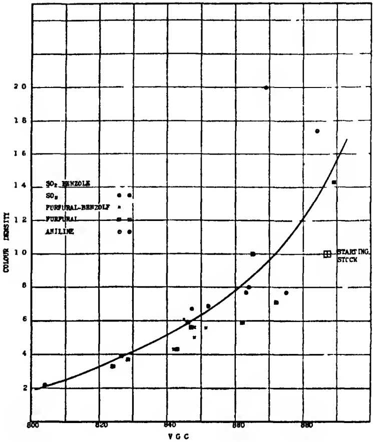


FIG 5 Relation between V G C and colour density for raffinates produced by different solvent processes

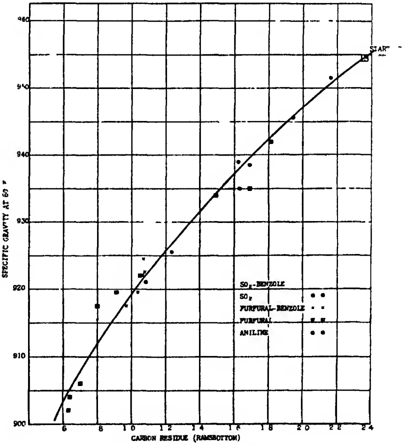


FIG 6 Relation between specific gravity and carbon residue for raffinates produced by different solvent processes.

Air Ministry Specification D T D 109) is given for the same series of oils as was used for the colour-V G C determinations The relationship is also seen to be, within experimental error, independent of the solvent process employed The same remarks regarding asphalt precipitation would, however, be expected to apply as in the case of colour removal, since the presence of hard asphalt would be immediately reflected in an increased carbon residue

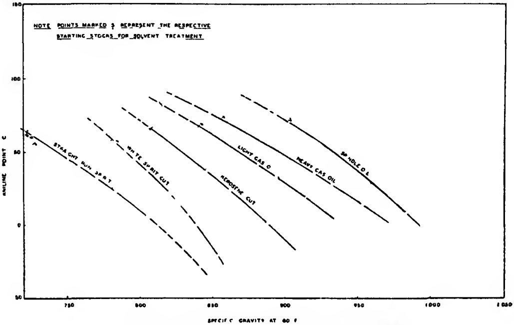


FIG 7 Relation between aniline point and specific gravity at 60° F

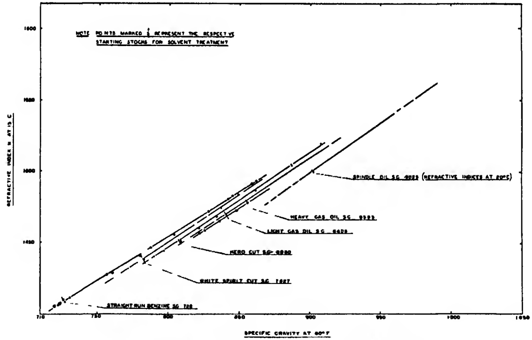


FIG 8 Relation between refractive index at 60° F and specific gravity at 60° F

Aniline Point.

The effect of refining the lighter petroleum distillates for the manufacture of high anti-knock aromatic concentrates, special cleaners' spirits, white spirit substitutes, high-grade lamp oils, or spinning oils has a considerable effect on the aniline point The relationship between aniline point and specific gravity for the raffinates and extracts obtained from a range of light distillates from gasoline up to light spindle oil is shown in Fig 7 This relationship is not linear and the curves for the various stocks, which, with the exception of the spindle oil, are all from the same crude, do not even exhibit a family resemblance, due probably to the decreasing complexity of the lighter fractions of the crude and the presence of certain aromatic constituents (e g benzene, toluene, &c) in fairly large amounts

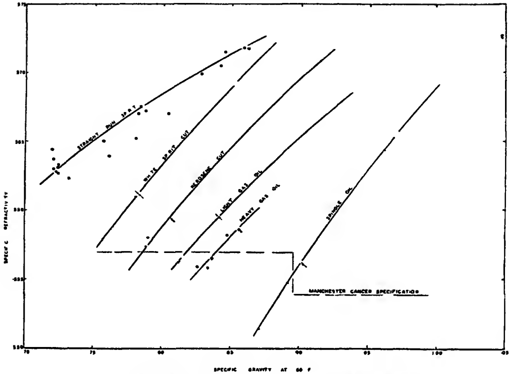


FIG 9 Relation between specific refractivity and specific gravity at 60 F

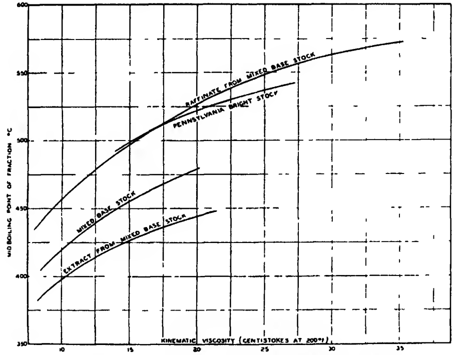


FIG 10 Mid boiling point-viscosity-curves for mixed base and Pennsylvanian oils

Refractive Index.

The relations between refractive index and specific gravity for the solvent fractions (raffinates and extracts) from a given starting stock appear to be linear within experimental limits This is indicated by the curves in Fig 8 for petroleum distillates ranging from 0 728 to 0 9025 in specific gravity (60° F) This linear relationship is of value in enabling *specific refractivities* to be checked by calculation, since small errors in refractive index introduce considerable errors in specific refractivity

Specific Refractivity.

Specific refractivity has recently been specified by the Manchester Cancer Research Board as a measure of the carcinogenicity of Mule spinning oils, and limits have been set for the specific refractivities of oils to be used in the spinning mills. The effect of solvent refining on specific refractivity is illustrated in Fig 9, which also shows the limit for carcinogenicity adopted by the Manchester Cancer Research Board (The curves in Fig 9 have been derived from the curves given in Fig 8 and are seen to deviate considerably from some of the experimental points, especially for the lighter products)

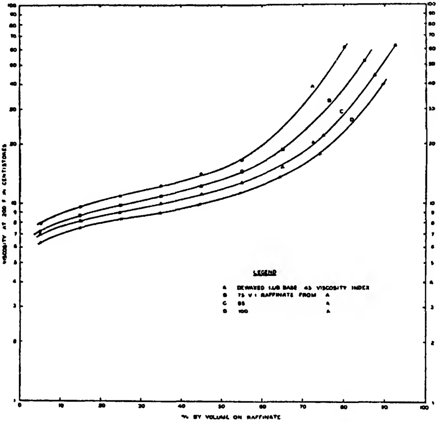


FIG 11

Boiling Range.

The effect of solvent refining on the boiling range of a lubricating oil is illustrated in Fig 10, where the viscosity-mid per cent boiling-point curves are given for a mixed base starting stock of about 45 V I, the raffinate (about 100 V I) produced therefrom by solvent refining, and the corresponding extract (about 10 V I) It will be seen that the boiling range of a given viscosity fraction (measured at 200° F) increases about 10° C for every 10-number increase in viscosity index

Viscosity-Mid Per Cent. Curves or Viscosity-Composition Curves.

Fig 11 gives the viscosity-composition curves for a mixed base stock *A* of 45 V I and raffinates *B*, *C*, and *D* of 75, 85, and 100 V I respectively, obtained from the base stock *A* by solvent refining The curves indicate that while the viscosity of the stock *A* has been reduced in accordance with the general relationship indicated in Fig 4, this drop in viscosity, although more marked in the more viscous fractions of the stock *A*, has also taken place more or less uniformly over all the components present in the stock from the lightest to the heaviest

In Fig 11 the viscosity-composition curve *A* is convex downwards and the curves show a tendency to become flatter with increased solvent refining While this is the case with most stocks, there are exceptions, as are indicated in Fig 12, in which the viscosity-composition curves for a starting stock of South American origin is shown to be convex upwards with the convexity increasing on solvent refining, indicating a preferential absorption of the less viscous fractions

The V I -Viscosity Relationship.

While, as just stated, the effect of solvent refining is to reduce the average viscosity, with preferential removal of the less viscous or more viscous fractions as the case may be, this preferential removal of certain constituents cannot be explained on the grounds that the fractions removed are always of lowest quality as measured by V G C or V I For example, Fig 13 gives the plots of V I versus viscosity for fractions produced by distillation from the starting stock and raffinates indicated in Fig 12, in which the V I of the distillate fractions is seen to fall from about 50 V I in the lightest fractions to about 0 V I in the medium viscosity range, rising again to about 40 in the heaviest fractions On solvent refining, this minimum V I viscosity fraction does not disappear as might be expected, but the curves for the raffinates are found to be roughly parallel to that of the base stock This persistence of form in the V I -viscosity curves resembles the other general relationships in that it is characteristic of the starting stock alone and independent of the solvent process It would therefore appear that the viscosity index as a measure of quality has little or no direct connexion with the mechanism of the selective solvent action

Comparison of Solvent Processes in the Laboratory

Since it has been shown in the previous paragraphs that a raffinate of any given quality (say 100 V I) obtained from a given starting stock will be the same in every respect independent of the solvent process employed, it follows that the best solvent process will be that which gives the greatest yield of raffinate at the lowest cost per ton of product, and for a comparison of solvent processes it is therefore necessary to consider only those factors which affect the yield of raffinate and the operating costs

The yield of raffinate may be determined in several ways, the most obvious method being, of course, to determine the yield by actual measurement Unfortunately, this is seldom possible unless a suitable plant is available of the type required for the particular solvents If, however, the quality of the extract which is likely to be made in producing the required raffinate can be determined, then, knowing the corresponding values for (*a*) raffinate, (*b*) starting material, and (*c*) extract of some property which is known to be additive, the yields of raffinate and extract may be calculated Of the additive properties of petroleum oils, specific gravity is the one which can be most accurately determined and has the advantage of being applicable to all products from gasoline up to heavy cylinder oils, though even specific gravity is not a truly additive function since some slight change in volume occurs on mixing two oils of very different characteristics For all practical purposes such changes in volume may be neglected On the other hand, specific gravity gives no indication of quality unless considered in conjunction with some other characteristic such as viscosity, aniline-point, &c For lubricating oils, viscosity index is the standard which is frequently accepted as giving an indication of quality, but V I as shown in Fig 3 is not an additive function The viscosity-gravity constant developed by Hill and Coats, and calculated from specific gravity and viscosity, has been used with considerable success, and is additive over a wide range of oils from light kerosine up to medium-heavy lubricating oils, but cannot be employed satisfactorily for oils lighter than about 0 760 or heavier than 1 000 in specific gravity In fact, it would seem that no additive property exists which will give an indication of quality and is at the same time

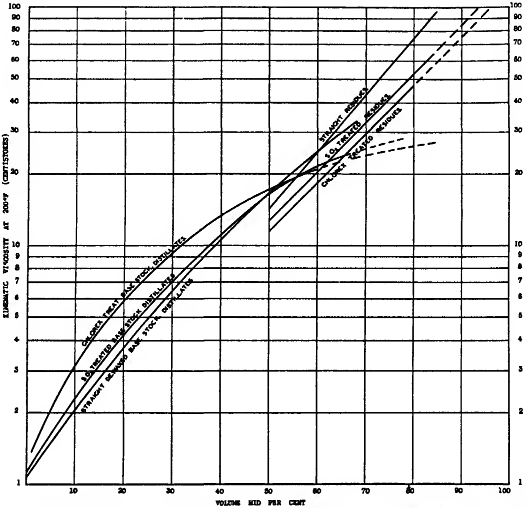


FIG 12 Mid per cent viscosity curves for distillates and residues for South American dewaxed long cut (base stock) and for the corresponding SO_2 and chlorex raffinates

applicable over the whole range of petroleum products Nevertheless, for examination of special products over a limited range of quality, an appropriate standard such as V G C may be chosen, which is both additive and gives the required indication of the degree of refining, though for general purposes the use of specific gravities is most reliable

Having selected some additive function (say specific gravity), the efficiencies of different solvent processes may be compared on a yield basis

Suppose, to take a fictitious case, that under *practical* working conditions with one solvent process *A*, extracts of more than 1 050 specific gravity cannot be obtained from a given starting material, while another solvent process *B* will produce extracts of not more than 0 995 specific gravity Assume also that the starting stock has a gravity of 0 895 and that a raffinate of 0 840 is required The maximum yields of raffinate obtainable by the two processes will therefore be

$$\text{Process } A \quad \frac{1\,050-0\,895}{1\,050-0\,840}\times 100\% = 73\,8\% \text{ by volume,}$$

$$\text{Process } B \quad \frac{0\,995-0\,895}{0\,995-0\,840}\times 100\% = 64\,7\% \text{ by volume,}$$

i e the yield of raffinate is greatest for the process which produces the worst (i e most naphthenic or highest specific gravity) extract

The question of operating costs is considerably more difficult to settle than the question of yields, and for estimating purposes it is necessary to obtain approximate figures for each of the following factors

1 Cost of solvent, since the cost of replacing solvent loss in the process may become a prohibitive item
2 Amount of solvent required per ton of oil treated, and the latent and specific heats of the solvent These will largely determine the steam, fuel, and power requirements of the plant
3 Number of countercurrent stages required for the process, and the settling rates of raffinate and extract layers in the various stages, which will determine size and throughput of the plant and be a major item in the capital cost

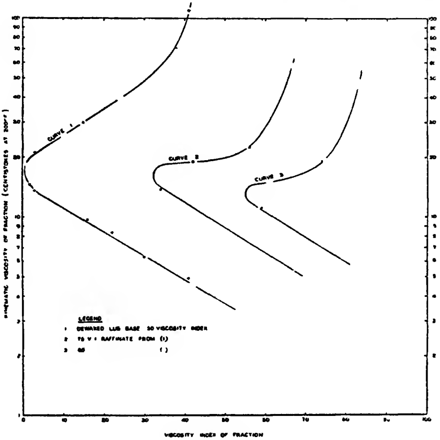


FIG 13

Of these three factors, the first is generally already known, but for the determination of the amount of solvent, and the number of countercurrent stages, it would be necessary to carry out a considerable amount of experimental work on the trial and error principle, using countercurrent apparatus with various conditions of temperature gradient, throughput, and solvent treatment, if some simplified means of obtaining results were not available Moreover, equilibrium conditions are not immediately attained in countercurrent plant, and such experiments are almost invariably costly in time, labour, and materials Fortunately, the results of countercurrent operation, with and without temperature gradient, can be fairly well predicted from the results of laboratory batch treatments using the principles of triangular graphs [16, 1935, 18, 1934] This is fully described in the companion article on 'The Theoretical Principles of Solvent Extract' by T G Hunter, but the following simple illustration will, however, be found helpful in following the present discussions

Triangular graphs are used for the representation of what are known as ternary systems That is to say, if three pure components X, Y, and Z are considered and a mixture M of these components is made in any known proportion, say $x\%$ of X, $y\%$ of Y, and $z\%$ of Z, the composition of that mixture or of any other mixture chosen can be represented by using a triangular graph

Let XYZ (Fig 14) be an equilateral triangle and let the length of the perpendicular from any of the apices X, Y, or Z on to the opposite sides of the triangle $= p$, i e $XP = p$ Then since the sum of three perpendiculars from any point in the triangle on to the three sides is constant and equal to the perpendicular from any of the apices on to the opposite side, one can represent the mixture M above by choosing the point M so that $MA = xp/100$, $MB = yp/100$, and $MC = zp/100$

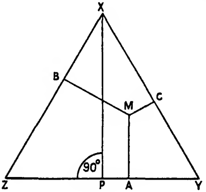


Fig 14

This is the fundamental principle of triangular graphs applied to mixtures of three pure components, but as soon as an attempt is made to apply the principle to hydrocarbon mixtures and solvents the difficulty of estimating the composition of the mixture is encountered However, this may be overcome in the following way Consider the case of the three pure components SO_2, benzene, and hexane (Fig 15) It is a relatively simple matter to separate the SO_2 from an unknown mixture of these three components by fractional distillation, but the quantitative separation of hexane and benzene is extremely difficult, if not impossible However, by determination of specific gravity on the SO_2-free mixture we can estimate the proportions of the two constituents, knowing the gravities of pure benzene and pure hexane Referring to the triangular graphs once more, let X, Y, and Z represent pure SO_2, hexane, and benzene respectively, we now have a simple means of locating the position of the point M representing the mixture, for if we divide the ZY side of the triangle into a scale of specific gravities such that Z represents the gravity of benzene and Y the gravity of hexane, and then join the points S representing the gravity of the SO_2-free mixture M to X, it can be shown that for all the points on the line XS we have

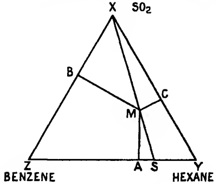


Fig 15

$$\frac{\%\ \text{benzene in the mixture}}{\%\ \text{hexane in the mixture}} = \frac{z}{y} = \text{constant} = \frac{SY}{ZS}$$

Hence the point M must lie on this line and, since the percentage SO_2 in the mixture is easily determined, we may locate M by finding a point on XS from which the perpendicular MA on to $ZY = xp/100$

Consider for a moment what this implies We have determined the amount of SO_2 in a mixture and then calculated the composition of the remaining benzene-hexane mixture by gravity without actually separating the constituents, and from these results we are able to locate the position of the point M representing the mixture Similarly, the composition of any number of mixtures may be determined without separating the pure benzene and hexane components, and it is seen that the fact that Z represents pure benzene and Y pure hexane does not really affect the results so long as a suitable scale of gravities along the side YZ is chosen The same results might, in fact, have been obtained without knowing that such things as benzene or hexane exist

This in effect is the position when triangular graphs are applied to solvent refining of petroleum distillates The amount of solvent in an extract layer, for example, can generally be easily determined, but the composition of the solvent-free extract cannot be determined in terms of 'pure raffinate' and 'pure extract', and it is necessary to select some suitable scale such as specific gravity for the ZY side of the triangle such that, to take the case of the process A given in the previous example,

$$(\text{vol}\ \%\ \text{starting stock}) \times 0\ 895$$
$$= (\text{vol}\ \%\ \text{raffinate}) \times 0\ 840 + (\text{vol}\ \%\ \text{extract}) \times 1\ 050,$$

i e $$100 \times 0\ 895 = 73\ 8 \times 0\ 840 + 26\ 2 \times 1\ 050$$

If instead of specific gravity a V G C scale had been employed, it will be seen from Fig 2 that different values for the V G C would have been obtained for an extract of 1 050 specific gravity depending on whether the V G C had been calculated from the Saybolt viscosity at 210 or 100° F Moreover, in either case the substitution of V G C for specific gravity in the above equation would be less satisfactory, especially in the case of heavier feed stocks

However, except in the case of high-gravity feed stocks yielding very high-gravity extracts, the V G C scale may be used satisfactorily, as is illustrated in certain of the examples which follow

Experimental Procedure

Except in cases where the solvent has an appreciable vapour pressure at the temperature of the extraction, laboratory treatments may be carried out in glass cylinders or separating funnels surrounded by a water bath or air oven to control temperatures Where possible the two layers, raffinate and extract, may be completely separated, measured, and analysed, though this may give rise to errors

Fig 16a

Fig 16b

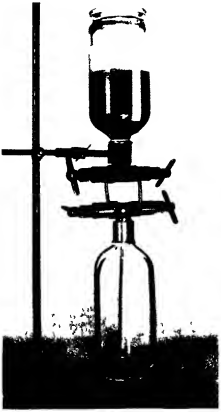


Fig 17

as described below More accurate results are, however, obtained if complete separation of the two layers is not attempted, but if portions only of each layer are analysed, thus avoiding errors due to disturbance of the interface

In the case of solvents such as liquid SO_2 and propane which have an appreciable vapour pressure at the treatment temperature, the experiments must be conducted in pressure-tight equipment such as the apparatus shown in Fig 16, for example, which consists of a glass siphon fitted with needle-valve connexions to the top and bottom of the siphon By means of several such siphons and small suitable interconnexions as shown in Fig 17, it is possible to separate representative samples of the extract and raffinate layers For temperatures above atmospheric the glass siphons are unsatisfactory for pressure experiments unless thoroughly annealed, and may be replaced by suitable steel apparatus (e g small oxygen cylinders), although in such cases, of course, the separation of the two phases is not visible and the amounts of the phases can only be measured by inverting the cylinder and carefully running off the extract layer through a needle valve and glass capillary when the change from extract to raffinate layer can in most cases be easily detected by change in viscosity It should be realized that if the extract layer is withdrawn too rapidly, causing a rapid fall in pressure, the liquid contents remaining in the siphon may boil suddenly or 'bump', causing remixing of the two layers and vitiation of the experiment

TABLE I

Batch Treatment of Light Gas Oil (Mixed Base Origin) with Liquid SO_2

	Treatment				*Tests on SO -free raffinates*							*Tests on SO_2-free extracts*		
Experiment no	*Vol* % SO	*Treat temp*, F	*Vol* % SO_2 *in layers* *Raff*	*Ext*	*Sp gr at* 60 F	*Vis 100 F* cs	*Aniline-point* C	*Pour-point*, F	*Set point* F	*Refractive index* 60 F	*V G C* *	*Sp gr at* 60 F	*Aniline-point*, °C	*Refractive index* 60 F
	Starting stock (untreated)				0 8408	2 90	68 2		9	1 4701	0 835			
1	49 4	70	19 2	77 1	0 8338	2 975	72 0			1 4651	0 828	0 9152	21 6	1 5185
2	103 1		17 2	82 8	0 8249	3 025	76 2	0	3	1 4595	0 819	0 9134	19 6	
3	327 0		14 7	90 5	0 8150		81 5	5	0	1 4532		0 8936	32 7	
4	479 0		16 1	92 3	0 8132		83 6	10	0	1 4519		0 8853	38 5	
9	323 0		15 6	90 6	0 8165	3 115	81 9	5		1 4536	0 809	0 8952	32 4	
10	564 0		16 6	93 0	0 8126	3 150	84 3	5		1 4515	0 804	0 8807	41 9	
11	56 4	30	10 4	82 0	0 826					1 4617		0 957		
12	36 0		9 6	95 4	0 811					1 4519		0 955		
13	295 0	0	5 1	94 0	0 813							0 9505		
14	49 8			78 6	0 8255							0 9735		
15	407 0	70			0 8136		82 9					0 881	42 1	
16†	523 0				0 807	3 15	87 4	10	5		0 800	0 842	64 9	

* V G C calculated by method of Moore and Kaye [27, 1934]

† Raffinate from experiment 15 used as starting stock for experiment 16

Construction of Triangular Graphs.

Having selected the raffinate and extract limits for the triangular graph and marked off the side of the triangle joining these limits into the appropriate scale, the point representing the starting stock can be located In Fig 18, which represents the equilibrium conditions given in Table I, a specific-gravity scale is chosen ranging from 0 810 for the hypothetical 'pure' raffinate *Y* to 0 910 for the hypothetical 'pure' extract *Z* The point 0 841 on the scale now represents the starting material *S*, and the line *SX* therefore represents all mixtures of pure solvent (SO_2) with the starting material The portion *SV* of the line *SX* represents mixtures which are homogeneous (i e simple solutions of SO_2 in the starting stock) and do not separate a second phase but, as soon as the concentration of SO_2 is increased to give a mixture represented by the point *V*, the mixture ceases to be homogeneous and separates into two phases, and two phases are obtained for all mixtures of SO_2 and starting stock represented by points on the portion *VW* on the line When the amount of SO_2 in the mixture is increased above that represented by the point *W*, the raffinate phase disappears and a single-phase solution of the original material in SO_2 is obtained for all mixtures represented by points on the portion *WX* of the line

Any point of the portion *VW* of the line *SX*, therefore, gives a mixture which after stirring to equilibrium, settles into two layers and if each of these layers is analysed for per cent SO_2, and specific gravity of the SO_2-free oil, &c, the position of each layer may be located in the way described above for the mixture *M* of SO_2, benzene, and hexane Moreover, from the properties of triangles, it follows that the points representing *M* the original mixture, *R* the raffinate phase, and *E* the extract phase all lie on the same straight line Moreover, if after stirring the original mixture *M* to equilibrium, and settling, the volumes of the two phases are measured, it is found that these volumes are represented by the relations

$$\%\ \text{raffinate phase} = \frac{\text{length of line } ME \times 100}{\text{length of line } RE},$$

$$\%\ \text{extract phase} = \frac{\text{length of line } RM \times 100}{\text{length of line } RE}$$

By examining a sufficient number of mixtures in this way it is possible to determine the equilibrium curve for the solvent and starting stock at the extraction temperature, and by carrying out similar experiments at various temperatures the equilibrium curves over a whole range of different treatment temperatures may be obtained which will enable the results of operating commercial equipment either at one temperature or with a temperature gradient through the system to be predicted

In determining the equilibrium curves for oil and solvent at the treatment temperatures higher or lower than standard (60° F), all volumes may be calculated back to equivalent volumes at 60° F for convenience, since this does not affect the accuracy of the curves in any way In the case of a solvent such as phenol, which melts at a relatively high temperature, some other temperature, i e 100° F, is found more suitable

Yields of products may be calculated from the gravities of the products and of the starting stock for each extraction, or from measurement of the two phases and the phase analyses

It will be noted in the example chosen that the position of the points representing the extract phases in the experiments 1 and 2 lies outside the triangle This does not affect either the method of construction or the results, but is the result of having chosen the hypothetical extract *Z* with too low a value, in order to obtain a more open graph In Fig 19 a wider scale has been chosen for the same series of treatments to enable the equilibrium curves at 0° F and 30° F to be included in the same triangular graph, with the result that the 70° F curve is more compact, though somewhat less suitable for purposes of estimation The limits chosen for the base of the equilateral triangle are therefore merely a matter of convenience, and for that reason, if several solvents are being compared on the same starting stock, or if the effect of temperature is being investigated for one or more solvents on the same stock, it may be preferable to retain the same limits for the triangle in every case, thus making it possible to compare the resulting equilibrium curves directly by superimposing one curve on the other, even though the scale chosen is not ideally suited to every treatment

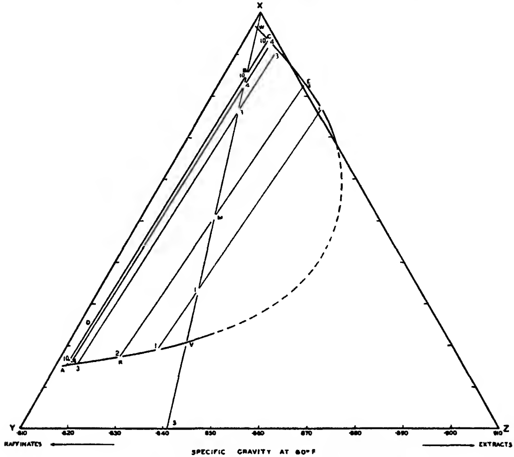


FIG 18 Equilibrium curve for light gas oil and liquid SO_2 at 70° F

Effect of Experimental Errors.

As has already been stated, the ratio of the raffinate layer to extract layer in any treatment becomes rapidly smaller as the treatment is increased Referring to experiment 10 in Fig 18, for example, this ratio is $\frac{BC}{AB} = \frac{10 4}{89 6}$, and the solvent content of these two layers is given in Table I as 16 6% and 93% respectively The effect of only 1% contamination of the raffinate phase with extract phase by imperfect separation would have given the point *D* as the apparent position of the raffinate phase since $\frac{BC}{DB} = \frac{11 4}{88 6}$, and the apparent percentage solvent in the layer would have been increased from 16 6 to 23 4%, approximately Actually, unless extreme care is taken in separating the two layers, the contamination may greatly exceed 1% owing to the film of extract remaining on the walls of the settler as the extract layer is withdrawn However, by withdrawing portions only of the two layers, first the raffinate and then the extract, contamination of the two phases is avoided and, by careful measurement of the volume ratio of the two layers before attempting to separate the phases, an additional check is obtained of the position of the points on the graph

The effect of this form of contamination was discussed at the I P T Symposium on solvent refining in 1936 [36, 1936] and equilibrium curves based on the early work by Ferris, Birkhimer, and Henderson [10, 1931], which show such deviations between the experimental results and the probable correct position of the equilibrium curves are reproduced in Fig 20

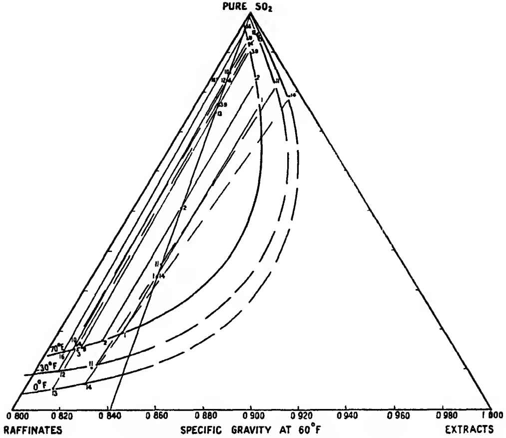


FIG 19 Equilibrium curves for light gas oil and liquid SO₂

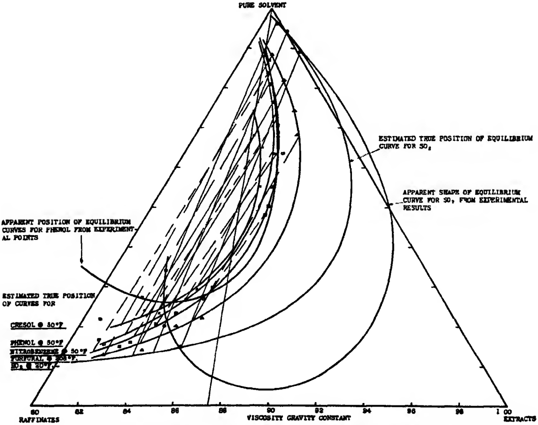


FIG 20 Equilibrium curves for stock 2, with cresol, phenol, nitro-benzene, furfural, and SO_2 plotted from data published by Ferris, Birkhimer, and Henderson, *J Ind Eng Chem* 23, 753 (1931)

Further Consideration of Triangular Graphs as applied to Solvent Refining

The Advantages of using Triangular Graphs.

The advantages of expressing the equilibrium relationship between solvent and oil on triangular coordinates are as follows

(*a*) The quality of the raffinate and extract obtained by any percentage solvent treatment at any temperature may be estimated directly from the graph

(*b*) The yields of raffinate and extract for any required conditions may be estimated

(*c*) The composition of the extract and raffinate layers may be obtained directly This information is essential for plant design and calculation, for example, of heat requirements for solvent recovery from the two phases

(*d*) The efficiency of any continuous or countercurrent plant can be directly assessed, or,

(*e*) If the efficiencies of any particular mixers and settlers are already known, the number of such stages required to equal the ideal conditions of yield and solvent requirements may be estimated

(*f*) The equilibrium relationships between solvent and oil may be readily determined by laboratory batch extractions

(*g*) The construction of the triangular graphs does not depend on the isolation of pure components

The Effect of Temperature on Solvent Refining.

The effect of temperature on solvent refining has already been indicated in the curves for SO_2 extraction of light gas oil, Fig 19, but in Table 11 a series of experimental results for chlorex and medium lub base stock over a range of temperatures from 30 to 125° F are given, and the results are plotted in Fig 21, using a V G C scale for the base or 'oil' side of the triangle

As the temperature of solvent treatment is raised, the area within the equilibrium curve becomes smaller, the difference in composition between the extract and raffinate layers (i e % solvent) is reduced and the slope of the tie lines joining corresponding phase-points also decreases The one effect tends to reduce selectivity since the points at the extremities of the tie lines are brought closer together, the other effect tends to increase selectivity since the less steep the tie line the longer will be its projection on the base of the triangle In general, the net effect of increasing the treatment temperature is to increase the selectivity for the higher grade oils and to reduce the selectivity for the lower grade oils The equilibrium curves in Fig 21 illustrate the much greater range of effectiveness of the solvent for the low-grade oils of high V G C at low temperatures They also indicate that at temperatures much above about 115° F no separation into two layers is possible with any percentage of chlorex for batch treatments of this particular stock, since the *SX* line lies outside the equilibrium curve for this temperature, though as the series of experiments at 125° F indicate, equilibrium curves (isotherms) for higher temperatures may be obtained by treating the raffinates produced at lower temperatures

Further consideration of the curves in Fig 21 indicates that for every treatment temperature there exists a definite limiting quality of raffinate and extract which may be obtained By drawing a tangent to the equilibrium curve for any temperature to intersect the base line of the triangle, a point of intersection is obtained which gives the limiting quality of the extract obtainable at that temperature The highest quality of raffinate which can be produced from a given base stock by any solvent varies with

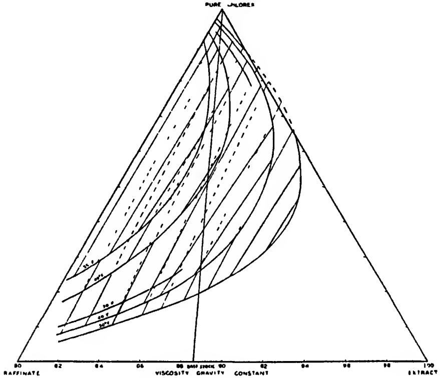


Fig 21

TABLE II

Batch Treatments of Medium Viscosity Lubricating oil Base (Mixed Base Origin) with Chlorex

Expt no	Chlorex treatment		Oil charge		Volume % separation at temp of expt		Volume % oil in layers estimated at 60°F		Volume % yield on charge		Tests on solvent free raffinate					Tests on solvent free extracts					VGC Products*		Remarks
	Vol % at 60°F	Treat temp, °F	Source	VGC	% raff	% ext	% raff	% ext	% raff	% ext	Sp gr at 60 F	Viscosity (stokes) 100°F	Viscosity (stokes) 200°F	VI	VGC	Sp gr at 60°F	Viscosity (stokes) 100°F	Viscosity (stokes) 200°F	VI	VGC	In	Out	
	Starting stock		(untreated)						100		0.945	3.20	0.207	44	0.886								
1	51	62	Starting stock	0.886	73.8	26.2	79.8		88.7		0.9325	2.50	0.185	58	0.870								
2	100		„ „	„	45.4	54.6	83.3		75.3		0.920	1.91	0.166	70	0.856								
3	200		„ „		27.2	72.8	85.2		67.8		0.907	1.55	0.1505	79	0.840								
4	500		„		11.3	88.7	89.2				0.8975	1.248	0.141	93	0.831								
5	251	„			22.5	77.5	83.6		61.2		0.905	1.515	0.149	80	0.838								
6	50.6				73.2	26.8	77.7		86.0		0.934	2.58	0.1855	53	0.872								
7	500	„	„		7.8	92.2	86.6		40.0		0.895	1.23	0.1365	90	0.825								
8	206	40	„	„					71.0		0.910	1.61	0.152	76	0.844								
9	400	„	„ „	„					62.0		0.898	1.37	0.143	84	0.830								
10	850	„	„						50.0		0.890	1.23	0.140	95	0.821								
11	233	72	„	„	20.8	79.2	83.6	15.8	58.2	41.8	0.904	1.457	0.149	85	0.838	1.002	20.28	0.420	−70	0.953	0.886	0.885	
12	233	104	„ „		16.0	84.0	70.0	22.5	37.0	63.0	0.903	1.479	0.149	83	0.836	0.970	6.18	0.270	12	0.914	0.886	0.885	
13	233	35			23.2	76.8	87.5	12.6	69.0	31.0	0.909	1.595	0.153	79	0.843	1.025	51.1	0.585	−274	0.985	0.886	0.887	
14	141	30	C C extract	0.969	15.0	85.0	78.3	34.8	27.3	72.7	0.953	4.02			0.895	1.037	105.0	0.758	−476	1.000	0.969	0.969	Sp gr of charge 1.014 at 60° F
15	608	62	C C raffinate	0.844	10.6	89.4		5.5	63.1	36.9	0.886	1.13	0.1383	104	0.816	0.951	4.23	0.2345	37	0.891	0.844	0.844	0.910 „
16	75	125	Raffinate 12	0.836	82.1	17.9	63.3				0.902	1.393	0.1463	88	0.835						0.836		Insufficient extract layer for analysis
17	500	62	Starting stock	0.886	8.7	91.3	89.5	9.8	47.5	52.5	0.893	1.20	0.138	96	0.826	0.992	12.55	0.348	−38	0.944	0.886	0.888	
18	250	100	Raffinate 5	0.838	23.8	76.2	78.8	11.5	64.8	35.2	0.886	1.15	0.1352	97	0.816	0.940	2.875	0.199	54	0.878	0.838	0.838	
19	119	60	Extract 17	0.944	13.2	86.8		42.0								1.000	18.0	0.410	−73	0.953	0.944		
20	67.4	30	„ 19	0.953	46.0	54.0	66.0				0.988	11.07			0.937						0.953		raffinate „ „
21	39.8	60	Starting stock	0.886	86.3	13.7	76.6				0.940	2.90	0.195	48	0.880						0.886		„ extract „
22	125.5	100	„ „	„	12.5	87.5		42.3								0.949	3.63			0.890	0.886		„ „ „
23	251	125	Raffinate 18	0.816	25.0	75.0	75.7	12.3	67.7	32.3	0.876	1.035	0.128	100	0.804	0.907	1.51	0.1563	89	0.841	0.816	0.816	„ raffinate „ „
24	50	60	Starting stock	0.886	27.2	72.8	78.5	32.7	86.5	13.5	0.933	2.53	0.1865	57	0.870	1.022	51.7	0.594	−267	0.981	0.886	0.885	
25	310	125	Raffinate 24	0.870	0.5	99.5			Not separated												0.870		
26	504	100	Starting stock	0.886	5.1	94.9	80.0				0.888	1.18	0.1377	98	0.819	0.964	5.39	0.2505	15	0.9075	0.886	0.885	
27	66	60	Extract 12	0.914	61.4	38.6			Not separated		Chilled to 30° F stirred, and then separated (Expt 28)										0.914		
28	66	30	„ 12	„	56.0	44.0	80.3				0.940	3.46			0.886						0.914		extract „ „

* VGC products in = VGC of charge
„ „ out = vol % raff × VGC raff plus VGC ext × vol % extract

the temperature since it is determined by the slope of the tie lines, and it is obviously impossible to obtain any further improvement in quality once a stage has been reached for which the tie line joining corresponding raffinate and extract phases will, if produced, pass through the solvent apex of the triangle, since the quality of the raffinate and extract (which are obtained from the graph by producing this same line to cut the base of the triangle) would obviously be the same The only difference between the two phases at this stage would be in composition (i e % solvent in the two layers) From Fig 21 it may be estimated from the slopes of the tie lines that the limiting quality of raffinate obtainable from this medium base lubricating oil at the different temperatures would be as follows

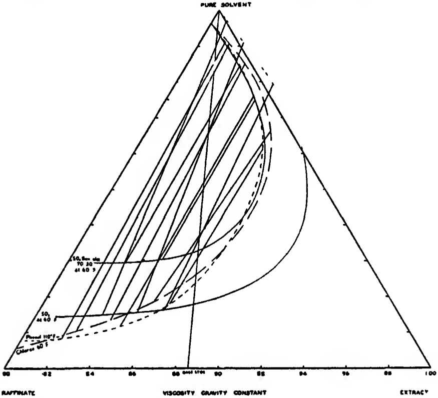


FIG 22

Treatment temperature	*Quality of raffinate*	
30° F	0 820 V G C	96 V I approx (from Fig 3)
60° F	0 809 ,,	104 ,, ,, ,,
100° F	0 805 ,,	107 ,, ,, ,,
125° F	0 796 ,,	110 ,, ,, ,,

It will be obvious that these limiting qualities of raffinate could not be obtained by any single batch treatments, and could, in fact, only be approached at these temperatures either by exhaustive batch extraction or heavy countercurrent treatment

Comparison of Different Solvents.

For a comparison of different solvent processes it is necessary to prepare in every case equilibrium curves covering the whole range of practical working temperatures, and to determine by graphical means the volume yield of raffinate and the number of countercurrent stages required for the various conditions of per cent solvent treatment and temperature gradient The procedure adopted in such cases is described in the article by Hunter in this section A very brief outline of the procedure is, however, given in a later part of this article

It is obviously impossible to construct on one graph all the equilibrium curves for the several solvents to be examined, but comparisons may be simplified by employing the same limits for the triangular graphs in every case, when the quality of the various raffinates and extracts obtained under various conditions may, to a large extent, be gauged by eye from the relative displacements of the curves to the right and left of the triangles Those sections of the curves which are of greatest practical significance are (*a*) the portions in the bottom left-hand section of the triangle near the raffinate apex, which give the qualities of the raffinates and percentage solvent in the raffinate layers, and (*b*) those portions near the top right side of the triangle which give the corresponding data for the extracts

Fig 22 gives equilibrium curves for the medium lubricating oil base with SO_2, 70% SO_2—30% benzole blend, chlorex, and anhydrous phenol under approximately optimum practical temperature conditions for the production of maximum gravity extracts, i e maximum raffinate yields The superiority of the SO_2 process over the other three solvents in producing extremely naphthenic extracts is obvious, and since, for any efficient solvent process, the *yield* of raffinate is determined solely by the quality of the extract produced, it follows that, for the range in which it is effective, SO_2 is an extremely efficient solvent Moreover, the market requirements for lubricating oils of medium quality (70 to 80 V I about) are greater than for high-class lubricants of 90 to 100 V I, and while SO_2 will produce the former in greater yields than the majority of other solvents, plant costs and operating difficulties may make it generally less suitable for the production of the latter In this respect the choice of solvent may be influenced by the sales commitments of a refinery which does not participate in the market for high-grade lubricants

The Relation between Solvent Structure and Selective Solvent Action.

The connexion between the chemical constitution of selective solvents and their selective solvent action is not clear Ferris, Birkhimer, and Henderson [10, 1931] attempt a correlation between selective solvent action and various physical properties, and the effect is popularly attributed to the presence of polar groups in the solvent molecule No satisfactory method of measuring the potential selective action of a solvent, other than actual comparative tests, appears to have been developed as yet

Ferris [9] has shown that the effect of halogenation on the selective solvent action of the aliphatic oxy and hydroxy compounds is considerable Not only is the specific gravity of the solvent very substantially increased, giving improved separation rate between oil and solvent, but the selectivity is considerably increased These results are brought out in Table III

Composition of Base Stock

The effect of changes in feed stock with a given solvent process are indicated by the equilibrium curves in Figs 24 and 23 drawn on a V G C and specific-gravity basis, re-

TABLE III

The Effect of Halogenation on Solvent Selectivity for Aliphatic Oxygenated Compounds

Solvent	*Sp gr solvent*	*Ratio vol solvent to vol of oil stock*	*V G C of oil stock*	*V G C of undissolved oil produced (raffinate)*	*V G C of dissolved oil (extract)*	*Vol undissolved oil (raffinate) per vol of solvent employed*
Ethyl acetate	0 900	1	0 836	0 833	0 880	0 912
Ethyl chloracetate	1 159	1	0 836	0 831	0 884	0 869
Ethyl acetate	0 900	3	0 836	0 825	0 871	0 247
Ethyl chloracetate	1 159	3	0 836	0 824	0 875	0 240
Acetone	0 792	1	0 874	0 869	0 932	0 834
Chloracetone	1 162	1	0 874	0 858	0 950	0 787
Acetone	0 792	2	0 874	0 855	0 921	0 328
Chloracetone	1 162	3	0 874	0 843	0 924	0 192
Propyl alcohol	0 804	3	0 874	0 864	0 884	0 128
2,3-Dibromo propyl alcohol	2 083	3	0 874	0 836	0 941	0 190

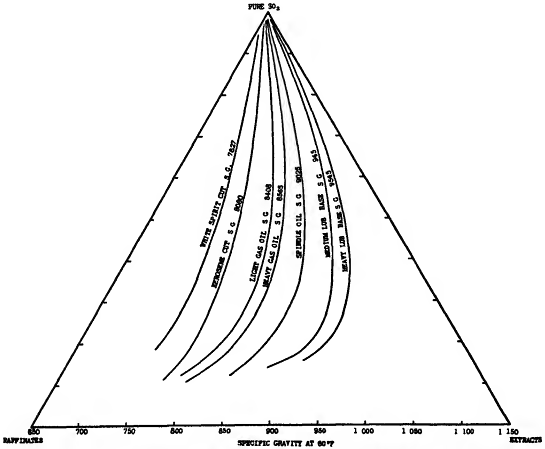


FIG 23. Equilibrium curves for liquid SO_2 at 70° F with various gravity distillates from the same crude

spectively, and covering distillates ranging from white spirit cut to heavy lubricating oil distillate prepared from the same crude stock It will be observed that neither on a V G C nor on a specific-gravity basis can one general curve be drawn which applies to all the different boiling fractions from a given crude Moreover, since the shape of these curves also changes for distillates of the same boiling range, if produced from different crude stocks, the difficulty of obtaining any satisfactory correlation from the various unrelated articles on solvent refining, which have appeared from time to time in the technical literature, is apparent

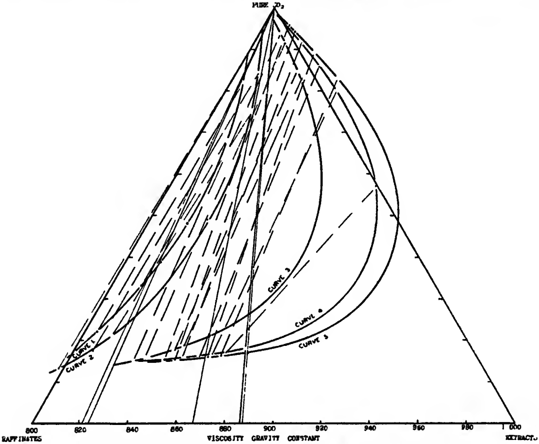


FIG 24 Equilibrium curves for liquid SO_2 at 70° F with various petroleum distillates

	Stock	Sp gr at 60° F	V G C
Curve 1	White spt cut	0 7827	0 824
,, 2	Kerosine cut	0 8080	0 821
,, 3	Spindle oil	0 9025	0 867
,, 4	Medium lub base	0 9450	0 886
,, 5	Heavy lub base	0 9545	0 887

It might appear on the face of things that comparison of the results obtained for different stocks from the same crude, or, as is more generally the case in refinery practice, estimation of the results to be obtained when processing a slightly different feed stock, is a matter of considerable uncertainty, unless the equilibrium curves for the actual stock are available A very simple modification of the triangular graph is possible, however, which enables such comparisons to be easily obtained as subsequent examples illustrate This modification consists (see Figs 36 and 39) in substituting a scale of *change in gravity* (the starting stock being taken as zero, and raffinate and extracts being fixed by decrease and increase in gravities, respectively) in place of the usual gravity or V G C scale for the base of the triangular graph

Solvent Extraction Processes (Single-solvent Processes)

In the present discussion it is not proposed to give a detailed comparison of the various single-solvent processes at present operated on a commercial scale, but merely to indicate the limitations imposed on any solvent process by the solvent itself

The following five solvents which differ widely in characteristics have, therefore, been selected as being representative of the majority of commercial single solvents available to-day, and these will be considered in some detail

1 Liquid SO_2
2 Furfural
3 Anhydrous phenol
4 Chlorex
5 Liquid propane

The requirements of the ideal solvent have been variously defined, but in general the major requirements are agreed to be the following five essentials

1 Good selectivity or ability to separate the stock into paraffinic and naphthenic constituents of widely differing characteristics
2 Chemical stability under conditions of storage and in use
3 The raffinate and extract phases produced must be capable of sharp separation by reason of gravity differential either by gravity settling or by the use of centrifuges

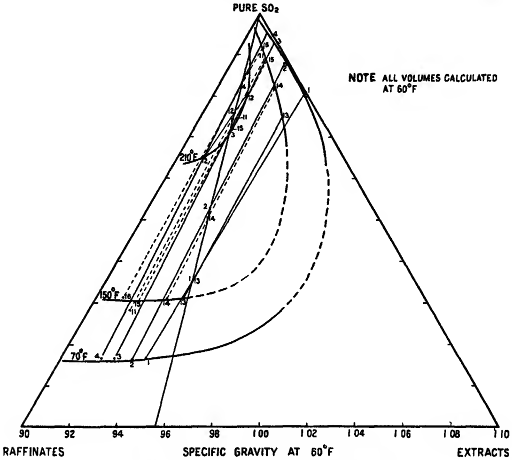


FIG 25 Equilibrium curves for liquid SO_2 and heavy lubricating oil base at 70°, 150°, and 210° F

4 The solvent should be readily and completely recoverable from the separated raffinate and extract phases
5 The solvent should be non-corrosive to the usual materials of construction

It is frequently claimed in addition that the solvent should possess adequate solvent power for the naphthenic constituents and low solvent power for the paraffinic constituents, and should be relatively insoluble in the paraffinic material It is doubtful, however, if any selective solvent can be found which does not behave in such a manner The requirements that the solvent should be non-toxic is an advantage but not an essential, since satisfactory safeguards against poisoning of operatives are relatively simple, and, moreover, the 'toxic' solvents in use to-day are relatively innocuous compared to some of the products handled daily in the chemical industry with absolute safety

Liquid Sulphur Dioxide (SO_2)

Under normal conditions of temperature and pressure SO_2 exists as a gas, and its use in the liquid state as a selective solvent involves the use of pressure equipment for all except low-treatment temperatures

As has been previously stated, liquid SO_2 is not generally suitable for the manufacture of high-grade lubricating oils, but this is mainly a result of its physical characteristics which limit its practical applications However, pure SO_2, if used in a suitable-type pressure equipment, is equal to most other selective solvents in producing high yields of high V I oils, but the temperature gradient required is rather wide (about 100° to 0° C)

Fig 25 illustrates the equilibrium curves for liquid SO_2 with a similar mixed-base heavy lubricating oil stock to that used for preparing the furfural curves in Fig 26 and has been constructed from the experimental results given in Table IV A study of these equilibrium curves for SO_2 indicates that, while at low temperatures, 70° F and under, very high gravity extracts are obtainable, the solubility of the raffinates increases rapidly in the SO_2 solvent as the treatment temperature is increased, and at 210° F , for example, where the slope of the tie lines is suitable for the production of high V I raffinates of low specific gravity, the miscibility (equilibrium) curves necessitate working with high percentages of solvent to obtain phase separations From the curves of Fig 25, therefore, it follows that if a raffinate of 100 V I (*c* 0 890 specific gravity) is to be

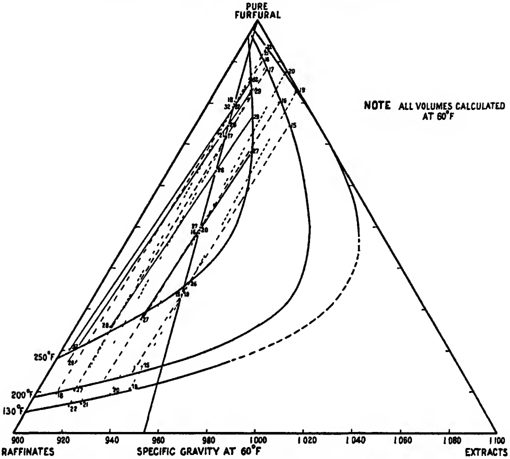


FIG 26 Equilibrium curves for heavy lubricating oil base and furfural at 130° to 260° F

TABLE IV

Batch Treatments of Heavy Lubricating Oil Base (Mixed Base Origin) with liquid SO_2

	Treatment						Tests on solvent-free raffinates					Tests on solvent-free extracts				
Expt no	Vol % SO_2 at 60°F	Treatment temp °F	Volume % SO_2 in layer		Volume % yield on charge		Sp gr at 60°F	Viscosity (stokes)		V I	V G C	Sp gr at 60°F	Viscosity (stokes)		V I	V G C 100°F
			Raff	Ext	Raff	Ext		100°F	200°F				100°F *	200°F		
Starting stock (untreated)					100		0 9565	8 70	0 370	41	0 890					
1	54 6	70	16 8	80 4	91 2	8 8	0 9428	6 14	0 319	56	0 8735	1 099				
2	110 5	,	16 3	87 9	87 8	12 2	0 9371	5 12	0 299	64	0 8675	1 093				
3	247·0	,,	16 6	92 7	81 6	18 4	0 928	4 25	0 275	71	0 856	1 083				
4	471 0	,	16 8	94 7	77 2	22 8	0 9212	3 61	0 265	82	0 848	1 076				
9	301 0	145			68 6	31 4	0 9243	3 82	0 269	78	0 852	1 027				
10	320 0	210	67 5	78 0	29 3	70 7	0 9312	4 77	0 293	69	0 861	0 9669	11 92	0 415	25	0 903
11	288 0	145	28 1	89 6	69 9	30 1	0 9254	3 96	0 266	73	0 854	1 0286	221 1	1 30	−175	0 982
12	303 0	210	65 3	79 7	37 4	62 6	0 9326	5 04	0 307	71	0 861	0 9708	14 24	0 458	22	0 911
13	54 0	150	31 9	75 0	96 7	3 3	0 9537	8 19	0 360	44	0 888	1 0396	310 0			1 004
14	99 9	,	31 0	81 6	87 6	12 4	0 9441	6 24	0 321	54	0 874	1 0316		1 44		
15	258 0	,	31 0	88 9	70 9	29 1	0 9277	4 20	0 274	71	0 856	1 0268		1 27		
16	455 0	,,	33 6	91 7	60 8	39 2	0 9176	3 37	0 248	79	0 846	1·0171	118 6	1 01	−121	0 965

* Viscosities at 100° F determined by the Ball and Bucket Viscometer of Beale and Docksey [*J I P T* 22, 42 (1936)]

produced at 210° F with a good yield, the conditions necessary involve the following

1 Raffinate phase represented by point on the 210° F curve
2 An extract outlet temperature chilled to about 70° F with the extract phase represented by a point on the 70° F curve, and
3 A point on the starting-line representing the overall treatment, and, as explained previously, this point must also lie on the line joining points 1 and 2 The slope of this line 1–3–2 would be small and it would intersect the starting-line relatively near to the solvent apex of the triangle, from which it follows that, (*a*) the number of equivalent perfect countercurrent stages would be large, and (*b*) the treatment necessary would be heavy, resulting in the one case in increased capital cost and in the second in increased operating costs Moreover, the whole plant would be required to operate at a pressure in excess of the partial pressure of SO_2 in the hottest section of the plant, which would add to construction costs

That pure SO_2 is capable of producing high V I raffinates if employed at suitable treatment temperatures may easily be demonstrated by treating a high-grade raffinate (say 95 V I) with hot liquid SO_2

The possibility of producing good yields of high-quality (97 V I) raffinates directly from certain mixed base lubricating stocks by SO_2 alone, using a suitable temperature gradient, has, in fact, actually been demonstrated to be a commercial proposition

Relatively little work has, however, been done on the use of liquid SO_2 at high temperatures, and the statement has been made that at high temperatures liquid SO_2 reacts chemically with certain of the hydrocarbon constituents of the feed This, however, appears doubtful, since no indication of any such reaction has been observed by the writer at temperatures up to 210° F , except small effects attributable to dissolved oxygen and moisture which result in the formation of sulphuric acid and sulphuric acid sludges It is interesting in this connexion to note that the use of mixtures of liquid SO_2 and olefines (e g propylene) having from 2 to 5 carbon atoms per molecule has been patented [37] for lubricating oil treatment at temperatures up to and above that of complete miscibility of the oil and mixed solvent

In lubricating oil manufacture liquid SO_2 finds its chief application in the production of medium-grade lubricants and high-grade turbine oils, but the majority of SO_2 plants are, however, engaged in kerosine refining, for which the treatment averages 50 to 100% by volume at temperatures around 10° F to 20° F A further application of the SO_2 process, discussed below, is the low-temperature extraction of naphthas for the production of extracts of high aromatic content and high octane number

Furfural.

The operation of the furfural process on various stocks has been previously described in the literature [24, 1933, 3, 1935, 46, 1936, 45, 1936] Table V gives the results of a series of experimental batch treatments of the same heavy lubricating base used in the SO_2 experiments detailed in Table IV These results have been used to construct the equilibrium curves of Fig 26

A comparison of Figs 25 and 26 indicates that both furfural at 130° F and SO_2 at 70° F produce extracts of similar quality (gravity, V G C , &c) except at high percentage solvent treatments when the SO_2 extracts, owing to the greater curvature of the furfural equilibrium curves, will be more naphthenic It is, therefore, to be expected that the furfural process operating with an extract outlet of 130° F will produce raffinate yields comparable to those produced by an SO_2 process operating with an extract outlet temperature of 70° F In the case of furfural, however, while the slope of the tie lines changes rapidly with increase in temperature, the solubility of the raffinates in the solvent increases much less rapidly than in the case of SO_2 for a comparable change in slope of the tie line For example, the slope of the furfural tie lines at 250° F is approximately the same as the slope of the SO_2 tie lines at 210° F , but whereas a 0 900-gravity raffinate if treated with SO_2 at 210° F would require the addition of about 180% of solvent before showing any separation of an extract phase, a raffinate of the same gravity treated with furfural at 250° F would show separation of an extract phase if treated with more than about 22% of solvent

Furfural is therefore an example of a single-solvent process having good selectivity for low-grade oils at 130° F and producing very high gravity extracts, thus ensuring good raffinate yields Moreover, by employing a temperature gradient and operating with a high-temperature raffinate outlet (*c* 250° F) good yields of high V I oils may be produced This relatively high range of operating temperature gives the furfural process an added flexibility in that waxy stocks can be treated without difficulty, a point which is further discussed below

Furfural, being an aldehyde, is oxidized fairly readily to give acidic products and is also stated to polymerize to gummy oil-soluble constituents For this reason the raffinates and extracts from the furfural process are frequently slightly contaminated by traces of gummy materials which are, however, removed by the subsequent acid or contact clay treatment This tendency to oxidize has apparently been successfully eliminated in the modern commercial equipment which gives very low solvent losses over prolonged periods of operation

Anhydrous Phenol.

Fig 27 gives the equilibrium curves over a temperature range of 105° F to 150° F for anhydrous phenol with the same medium viscosity lubricating base as used to construct the equilibrium curves for chlorex in Fig 21 Temperatures much below 110° F cannot in practice be employed with this solvent without danger of crystallization of the solvent, this, therefore, limits the naphthenicity of the extracts ob-

TABLE V

Batch Treatment of Heavy Lubricating Oil Base (Mixed Base Origin) with Furfural

	Treatment		*Phase separation*						*Tests on solvent-free raffinates*					*Tests on solvent-free extracts*				
					Volume % oil in layers		*Volume % yield on charge*			*Viscosity (stokes)*					*Viscosity (stokes)*			
Expt no	*Vol % at 60°F*	*Treatment temp , ° F*	*Vol % raff*	*Vol % ext*	*Raff*	*Ext*	*Raff*	*Ext*	*Sp gr at 60°F*	*100 F*	*200° F*	*V I*	*V G C*	*Sp gr at 60°F*	*100° F **	*200° F*	*V I*	*V G C 100°F*
Starting stock (untreated)							100		0 9545	9 25	0 3864	43	0 887					
15	50 5	200	70 6	29 4	83 9	25 4	90 5	9 5	0 944	6 75	0 3415	57	0 875	1 054				
16	95 8	„				19 7								1 047				
17	257 0		20 6	79 4	89 9	12 0	68 0	32 0	0 917	3 465	0 254	79	0 843	1 034				
18	403 0		13 1	86 9	90 2	9 3	61 5	38 5	0 900	2 95	0 236	85	0 834	1 027				
19	49 8	130	67 9	32 1	89 3	17 2	91 9	8 1	0 942	6 55	0 337	58	0 872	1 095				
20	98 0	.	47 9	52 1	89 7	12 9	87 0	13 0	0 934	5 30	0 303	64	0 862	1 091				
21	259 0	„	23 1	76 9	92 4	8 1	79 8	20 2	0 922	4 02	0 270	73	0 847	1 075				
22	398 0	„	15 6	84 4	93 3	6 4	72 8	27 2	0·9175	3 515	0 256	79	0 843	1 055				
26	57 6	250	99 7	0 3	63 5				0 956	9 48	0 3928	43	0 889					
27	99 1		44 7	55 3	72 4	32 2	67·0	33·0	0 935	5 13	0 299	64	0 865	0 994	45 7	0 750	−27	0 933
28	175 7	.	23 3	76 7	74 2	23 3	52·0	48 0	0 9195	3 64	0 261	78	0 846	0 9925	44 0	0 743	−24	0 931
32	380 0	„	9 1	90 9	79 8	14 05	37 0	63 0	0 904	2 63	0 226	90	0 826	0 9855	30 85	0 664	1	0 922
33	380·0	„	8 9	91 1														

* Viscosities at 100° F determined by the Ball and Bucket Viscometer of Beale and Docksey [*J I P T* 22, 42 (1936)]

tainable with anhydrous phenol A comparison of Figs 21 and 27 indicates that the extracts obtainable with phenol at 110° F are comparable in quality with chlorex extracts produced at 70° F, but are considerably less naphthenic than those produced by liquid SO_2 at 70° F, for example

High yields of raffinate cannot be obtained with anhydrous phenol, though, as explained in a later section, this limitation of the anhydrous phenol process is overcome in the newer installations by operating a combined phenol-water system

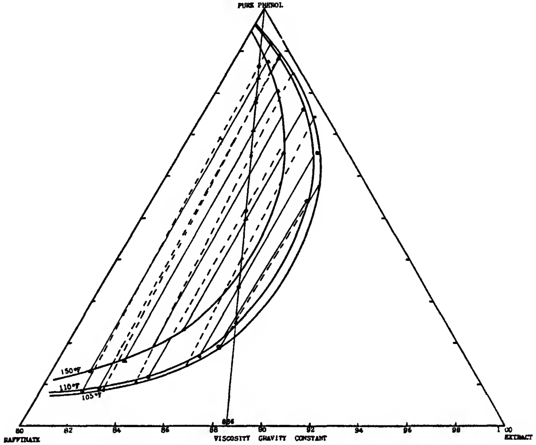


FIG 27 Equilibrium curves for medium heavy lubricating oil base (V G C 0 886) and anhydrous phenol

Phenol has the advantage of being a stable solvent readily recoverable from the raffinate and extract phases and, unlike SO_2 and furfural, is not oxidized by the small amounts of dissolved moisture or oxygen generally present in the majority of feed stocks

Chlorex.

This is an example of a single-solvent process operating at moderate treatment temperatures and possessing good selectivity for high-grade oils, which explains its early popularity for treatment of dewaxed stocks of Pennsylvania quality, while the high gravity of the solvent which favours rapid separation of the extract and raffinate phases and its relative insolubility in water considerably reduces the size and complexity of plant required for chlorex treatments The solvent suffers from several disadvantages, however, in that it is relatively expensive and decomposes slowly with the formation of free mineral acidity Moreover, highly naphthenic extracts cannot be produced by the chlorex process without operating at temperatures considerably below 70° F which introduces practical difficulties caused by (*a*) increased operating costs due to refrigeration, and (*b*) reduced separation rates and throughputs For these reasons chlorex does not compare favourably with solvents such as furfural, SO_2, &c, for the production of high yields of medium-grade (or high V I) raffinates

Equilibrium curves for chlorex and a medium-heavy lubricating oil base have already been given in Fig 21, and comparative results for SO_2 and chlorex at 60° F in Fig 22

Liquid Propane.

Liquid propane, as generally employed for deasphalting and deresinating, is definitely a selective solvent, although obviously not of the same type as liquid SO_2 for example, and it will be as well, since there are many solvents which behave similarly to liquid propane, to consider briefly the characteristic effects of the two types of selective solvent action

J W Poole [31, 1936] has suggested classifying solvents as 'Extractive' and 'Precipitative', and the results of treating, say, a lubricating oil base stock with these two types of solvents may be summarized as follows

(*a*) **Precipitative Solvents.** The raffinate or 'paraffinic' phase contains the bulk of the solvent, while the extract or naphthenic phase consists principally of the high specific-gravity constituents of the feed stock, associated with only a relatively small amount of the solvent Liquid propane as employed in propane deasphalting is a solvent of this class, as are also the butyl alcohols, &c [51] (*b*) **Extractive Solvents.** The raffinate phase consists principally of the low specific gravity constituents of the feed stocks associated with relatively little solvent, while the bulk of the solvent is associated with the high specific gravity constituents of the feed stock in the extract phase All the commercial single-solvent processes belong to this type, e g SO_2, SO_2-benzole, furfural, phenol, nitrobenzene, &c

The 'precipitative' effect of the light paraffin hydrocarbons on the high-gravity constituents of petroleum fractions is greatest in the case of liquid methane but decreases rapidly for the other members of the series, as the results in Table VI published by Bray, Swift, and Carr [2, 1934] indicate

TABLE VI

Properties and Yields of Oil and Asphalt produced from Poso Creek Residuum (topped to 66 Sec Saybolt Universal Viscosity at 100° F on Overhead Stream) by Extraction with Low-molecular-weight Hydrocarbon Solvents

	(10 volumes of solvent at 80° F)										
			Properties of extracted oil					*Properties of asphaltic residue*			
				Viscosity Saybolt Universal at							
Solvent	*Yield of oil (% by vol residuum)*	*Yield of asphalt (% by vol residuum)*	*Gravity A P I at 60 F*	*100°F*	*210°F*	*Carbon residue (%)*	*Colour N P A*	*Specific gravity at 60°F*	*Melting-point (° F)*	*Penetration at 77° F*	*Ductility at 77° F*
Ethane	11.0	89.0	24.2	255		0.077	3½	0.98		soft	0
Propane (boiling-point, −42° to −40° F)	75.0	25.0	17.5	2,100	94	2.35	opaque	1.063	176	2	0
Propane, 50% Butane, 50% (boiling-point, −42° to +36° F)	87.3	12.7	15.8	4,000	119	4.2	opaque		275	0	0
Butane 50% isobutane, 50% normal butane (boiling-point, 14° to 31° F)	89.2	10.8	15.7	5,000	139	5.3	opaque	1.107	295	0	0
Butane (boiling-point, 30° to 36 F)	88.8	11.2	15.2	4,600	139	5.12	opaque		307	0	0
Pentane (boiling-point, 82° to 100° F)	95.20	4.8	14.5	10,000	192	6.23	opaque		320	0	0
Hexane (boiling-point, 140° to 156° F)	98.0	2.0	13.8	15,000	208	7.09	opaque		325	0	0

Of these light liquefiable hydrocarbons, liquid propane is the most suitable for lubricating oil manufacture Liquid methane and ethane possess insufficient solubility for many of the useful hydrocarbon constituents present in the base oil, and liquid butane, pentane, &c, dissolve too much naphthenic and asphaltic material at normal temperatures The lighter hydrocarbons may be employed in the cold fractionation of crude petroleum as described by Pilat [13, 1935, 30, 1936], but such a process does not appear to have been used to any great extent in practice, and is, in any case, merely the more general application of the principles employed in propane deasphalting

In the production of viscous lubricating oil distillates from asphaltic crudes, the oil and asphalt are unavoidably subjected to rather drastic heat treatment even under the best conditions of high-vacuum distillation, and some cracking and thermal decomposition of the high-molecular-weight hydrocarbons takes place In propane deasphalting the separation of the undesirable asphaltic matter is accomplished under relatively low-temperature conditions where no undesirable thermal decomposition is possible, and the asphalt-free oils obtained by this procedure are considerably better in viscosity index, &c, than the best distillate produced by high-vacuum distillation from the same crude stock Part of this advantage, however, lies in the fact that liquid propane exerts some selective action on the naphthenic constituents normally included in the heavy distillates, so that while from a given crude residuum the same yield of asphalt may be produced by distillation and by propane deasphalting, the oil produced by the distillation process will include naphthenic constituents which are absent in the propane-deasphalted oil, and the latter will include very high-boiling paraffinic material normally lost in the asphaltic (or pitch) residue produced by distillation

Whereas in the case of extractive selective solvents such as SO_2 chlorex, &c, the various components of the feed stock are separated mainly on a basis of chemical composition or quality, in the case of precipitative solvents the separation appears to be effected largely on a molecular weight basis, and to a lesser extent on molecular structure

For any given series of hydrocarbons subjected to some specified conditions of treatment with a precipitative solvent, the separation into raffinate and extract (or 'oil' and 'asphalt' phases) appears to take place at some definite point in the molecular-weight scale depending on the treatment temperature, though the position of this point in the molecular-weight scale depends also upon the constitution of the hydrocarbon series, so that the greater the degree of paraffinicity the higher will be the average molecular weight of the constituents retained in solution in the raffinate phase, and the higher the position of the point of separation between 'oil' and 'asphalt' on the molecular-weight scale

When methane is forced into a propane solution of an oil mixture which has been freed of asphalts and highly aromatic colouring substances, aromatic components of much lower molecular weight are precipitated together with higher molecular-weight oils of paraffinic characteristics This is shown by the following figures for (*a*) a 66% distillate (taken off under 0.2 mm pressure) from a lubricating oil fraction precipitated by methane at 70/100 atm, (*b*) the precipitated fraction itself, and (*c*) the 34% residue [30, 1936]

If a crude residue or heavy lubricating oil fraction is subjected to repeated extractions or precipitations with propane the separated 'asphalt' phases will decrease in molecular weight with each step in the treatment Table VII shows the results of treating a Pennsylvania Bright

TABLE VII

Propane Fractions of Pennsylvania Bright Stock

Precipitated fraction	% on charge	A P I gravity	Viscosity (Saybolt) 100° F	Viscosity (Saybolt) 210° F	V I	V G C	Pour-point, ° F	Carbon residue (Canradson)
Charge	100	26.6	2,337	150.9	100	0.807	25	1.69
1 and 2	3.68		Insufficient for analysis					
3	10.24	25.3	4,023	218.4	102	0.811	25	2.48
4	12.84	25.4	3,543	199.8	102	0.812	25	2.47
5	9.52	25.6	3,495	197.4	101	0.811	25	2.51
6 and 7	8.05	25.7	3,093	180.6	100	0.811	25	2.31
8	12.30	26.6	2,076	138.8	98	0.809	25	1.55
9 and 10	37.00	27.5	1,485	112.6	97	0.806	30	1.19

TABLE VIII

Batch Propane Treatments of a Dewaxed Asiatic Crude Residuum

Propane treatment (on charge)		% propane by weight in layer		% volume yield on charge		Analyses of propane-free products					
						Oil					Asphalt
% by wt	% by vol	Oil phase	Asphalt phase	Oil	Asphalt	Sp gr at 60° F	Viscosity (stokes) 100° F	Viscosity (stokes) 200° F	V I	V G C	Sp gr at 60° F
Charging stock (untreated)				100		0.999					
150	300	70.5	23.0	56	44	0.942	14.1	0.513	50	0.861	1.073
184	368	75.0	21.1	59	41	0.941	12.4	0.483	52	0.860	1.081
286	571	82.8	21.1	59	41	0.938	10.97	0.452	60	0.857	1.087
478	955	88.5	21.0	65	35	0.942	13.52	0.498	47	0.862	1.098

	Extract precipitated by methane	66% distillate cut from extract	34% residue from extract
	(b)	(a)	(c)
Sp. gr. at 60° F	0.9275	0.9315	0.9190
Viscosity at 50° C	15.27° E	9.02° E	40.70° E
Viscosity index	44	19	71

Stock with liquid propane at increasing temperatures, given by Wilson, Keith, and Haylett [48, 1936].

For representing the equilibrium relationships between liquid propane and heavy lubricating oil distillates or residuums the triangular graph is again to be recommended. Fig. 28 illustrates the equilibrium relationship at 70° F for liquid propane and a dewaxed Asiatic crude residue, plotted on a weight basis with a specific-gravity scale for the base of the triangle, from the experimental results given in Table VIII which show that the asphalt phase contains appreciable quantities of propane. The asphalt phase is in effect a true homogeneous solution of propane in asphalt, even though under certain conditions and with certain types of starting stocks the asphalt phase may separate as an apparently solid granular mass.

A comparison of Fig. 28 with any of the equilibrium diagrams for the solvents previously described shows that the shape of the curves is similar but that the propane curve is reversed in curvature, being convex towards the low-gravity apex of the triangle, whereas for the extractive solvents the equilibrium curves are convex towards the high-gravity apex. It follows that in propane extraction or deasphalting, the asphalt phase corresponds to the raffinate phase of solvents such as phenol, and steadily 'improves' with increasing solvent treatment (i.e. the asphalt phase steadily increases in specific gravity with increasing propane treatment compared with the steady decrease in gravity of phenol raffinates with increasing phenol treatment). The oil phase in propane deasphalting corresponds, on the other hand, to the extract phase of extractive solvents such as phenol, and in a similar way, depending on the treatment temperature and starting stock, may first improve in quality up to a certain point and then deteriorate with increasing solvent treatment, and just as the yield of extract from a phenol process, say, increases continuously with increasing treatment, so the yield of oil is always increased by increasing the propane treatment. This is clearly brought out in Table VIII, where the quality of the oil obtained with 286% by weight of propane is considerably superior to that obtained either by higher or lower treatments.

The effect of treatment temperature on precipitative solvents, e.g. in propane deasphalting, is different from its effect on the extractive solvent processes in that the area enclosed within the equilibrium curves is *increased*, with the result that the specific gravity of the deasphalted oil produced at the higher temperatures tends to decrease. On the other hand, as in the case of the extractive solvents, the slope of the tie lines is steeper for the larger curves, and since the asphalt phase corresponds to the raffinate phase in the other type of solvents, the yield of asphalt is increased and the gravity decreased by operating on the larger curves obtained at higher temperatures.

Double-solvent Processes

The double-solvent processes may, generally speaking, be subdivided into two classes:

(*a*) Blended solvents, such as the phenol-water process or the Edeleanu SO_2-benzole modification of the original SO_2 process, which function mainly as the single-solvent process but with modified selectivity.

(*b*) Two solvent processes, such as the Duo-Sol process, the mechanism of which is not at present completely understood but in which one solvent is an 'extractive' solvent and the other a 'precipitative' solvent as explained above.

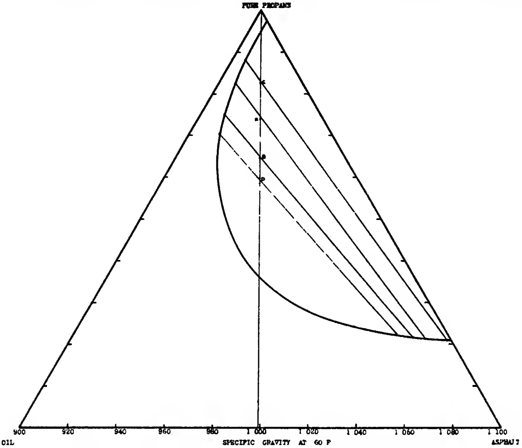


FIG 28 Equilibrium curves for liquid propane and dewaxed crude residue at 70° F

The Duo-Sol Process.

This process has been developed by the Max B Miller Company of New York, and has been frequently described in the literature [42, 1935, 26, 1935] Two solvents are employed (*a*) Selecto, which is essentially commercial cresylic acid, and (*b*) liquid propane

As an efficient single solvent, cresylic acid is limited owing to its relatively low miscibility temperature with the average mixed-base feed stock and to its high solubility for even the moderately high-grade oils It has, however, high selectivity for high-grade oils at the usual treatment temperature, but compared with other single solvents, the raffinate yields obtained with cresylic acid are low

The effect of treating with cresylic acid and propane, as compared with treating with cresylic acid alone, is illustrated by Tuttle [42, 1935] for a dewaxed Oklahoma City residuum in Table IX

In the operation of the Duo-Sol process the liquid propane and the selecto are fed to opposite ends of a countercurrent system, and the raw-oil feed stock is injected at an intermediate point somewhat nearer the propane inlet than the selecto inlet end of the system The system thus comprises in effect a stripping section in which the outgoing raffinate is stripped by the selecto of the naphthenic constituents contained therein, and a rectifying section in which the extract is freed from paraffinic constituents by washing or refluxing back with propane

In practice only part of the fresh propane is fed to the last stage of the system, the remainder being injected with the fresh feed of raw oil This arrangement has been found to give greatest overall economy (yields and quality) [48, 1936, 38]

TABLE IX

Treatment of Dewaxed Oklahoma City Residuum

	Single solvent	*Duo-Sol*
Total solvent used in batch treatment		
% selecto	300	300
% propane		300
Yield of raffinate	68 65	77 77
Composition of raffinate		
Paraffinic oil	59 63	65 29
Naphthenic oil	9 02	12 48
Ratio $\frac{\text{paraffinic oil in raffinate}}{\text{paraffinic oil in extract}}$	2 48	3 49

The operation of the Duo-Sol process is dependent on the effect of two different types of solvent (precipitative and extractive), and will be better understood when the similarity between distillation and solvent refining is discussed It should be mentioned, however, that the principle involved will be found to apply equally to a considerable number of other solvents, as, for example, the following

Precipitate solvents		*Extractive solvents*
Liquid propane, propylene, &c	and	Furfural, nitrobenzene, chlorex, SO_2, &c (32)
Sec-butyl alcohol	and	Cresol, furfural, liquid SO_2, &c

Certain of the above combinations of solvents are covered by existing patents [37], but in general it may be stated that the process depends on the satisfactory combination of a precipitative with an extractive solvent

The advantages of the Duo-Sol process are chiefly (*a*) its ability to produce high-grade, good-coloured oils directly from asphaltic stocks and crude residuums, thus avoiding the high-vacuum distillation necessary to separate the lubricating oil fractions from the pitch, and (*b*) the very high yields of viscous lubricants obtainable by the Duo-Sol process, which probably slightly exceed those obtainable by any other practicable combination of vacuum distillation and solvent refining

On the other hand, if low carbon residue values are required on the high viscosity-finished lubricants, then it becomes necessary to sacrifice part of the advantages in yield, since it is necessary to reject even the high-boiling paraffinic hydrocarbons together with the naphthenic and asphaltic constituents in order to meet this specification

The SO_2-Benzole Processes.

The effect of employing an SO_2-benzole blended solvent instead of pure SO_2 as a selective solvent is illustrated by the series of equilibrium curves in Fig 29 for the same medium-heavy lubricating base used in Figs 21, 22, and 27 The addition of benzole to a selective single solvent has a similar effect to that obtained by increasing the treatment temperatures for the single solvent, although the two effects are not identical, i e as the proportion of benzole in the solvent is increased the slope of the tie lines decreases, making it possible to obtain higher quality raffinates, but the equilibrium curves contract towards the left of the triangle, so that the extracts produced are less naphthenic, and raffinate yields are reduced accordingly For example, while it is impossible under any conditions of treatment to produce 100 V I (0 816 V G C) raffinate from this medium-heavy lubricating base with SO_2 alone at 60° F , the effect of various benzole concentrations in the feed solvent is indicated in Table X, which gives the maximum yield of 100 V I raffinate and the number of perfect countercurrent stages estimated for maximum raffinate yield

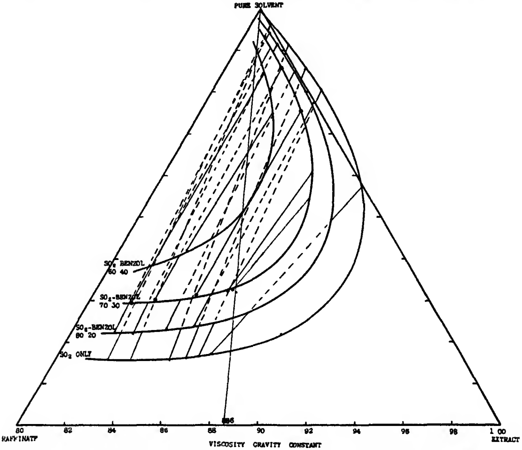


FIG 29 Equilibrium curves for medium-heavy lubricating oil base (V G C = 0 886) and various SO_2-benzole blends at 60° F

TABLE X

SO_2-benzole ratio in solvent	60 40	70 30	80 20
Number of perfect countercurrent stages required to produce 100 V I raffinate (estimated)	1¾	2¾	3¼
Volume per cent of solvent required at 60° F	240	215	200
Yield of 100 V I raffinate obtainable	33 6	54 2	60 4
Quality of extract produced			
V G C	0 922	0 970	0 994
V I	0	−185	−350

The effect of adding benzole to a selective solvent is general and applies to all single solvents of the 'extractive' type (e g SO_2, chlorex, furfural, &c), and the advantage of employing a benzole-blended solvent is that it enables any given high-quality raffinate to be obtained at a lower treatment temperature than would be necessary if the unblended (benzole-free) solvent were used alone At the same time, however, unless lower temperatures are maintained at the extract outlet from a benzole-blended solvent-treating system, the extracts obtained will be lower in specific gravity and hence yields will be reduced

As a general rule, therefore, for maximum yields it is preferable to employ an extended temperature gradient with a pure solvent than to employ a benzole-blended solvent, as the following figures illustrate

Treatment of Heavy Lubricating Base (Mixed Base Origin) in Eight-stage Countercurrent Plant

Treatment vol %	*Solvent composition* Vol % SO₂	Vol % benzole	*Temperature gradient* Raff out	Extr oil	*Raffinate* V I	Yield vol %	Extract sp gr
250–300	75	25	55° C	0° C	96	63	1 048
500	100		80° C	0° C	94	70 3	1 066

When an oil is treated with an SO_2-benzole mixture the SO_2 and benzole do not maintain a fixed ratio throughout the treating system, but the solvent in the raffinate phases is found to be richer in benzole and the solvent in the extracts poorer in benzole than the original SO_2-benzole blend used as fresh solvent feed This phenomenon is general and is illustrated by the figures in Table XI, which give the approximate phase analyses for various batch extractions using furfural-benzole blends to facilitate solvent rectification

TABLE XI

Approximate Composition of Solvent in Furfural-Benzole Treatment of Lubricating Oil Stock (Treatment in each case approximately 200% solvent by volume at 130° F)

Composition of charge solvent Furfural benzole	90 10	80 20	70 30
Composition of solvent in raffinate layer Furfural benzole	75 25		45 55
Composition of solvent in extract layer Furfural benzole	92 8	83 17	75 25

Although in the original modification to the Edeleanu process pure benzene was employed, this is seldom used in practice Crude benzole cut approaches pure benzene closely in solvent effect, and even this may be replaced if desired by an aromatic extract of suitable boiling range obtained from solvent treatment of a kerosine or heavy naphtha fraction, though as the aromatic content of the extract substitute decreases, so does the solvent effect decrease compared with pure benzole

Analysis of a typical motor benzole used in commercial SO_2-benzole plant is given in Table XII

TABLE XII

Specific gravity at 60° F	0 8737
I B P , ° C	77
Distillation	
Temp at 2%, ° C	80
" 5 "	81
" 10	81 5
" 50 "	84 5
" 70	87
" 80 "	94
" 90 "	104
F B P , ° C	149
Total distillate, %	99

The Phenol-Water Process.

Anhydrous phenol possesses very similar characteristics and limitations to anhydrous cresol, but whereas in the case of cresol the effects of the solvent have been modified in the Duo-Sol process by introducing liquid propane into the oil-cresol system, which influences the physical properties of the oil being treated but does not affect the properties of the solvent, in the phenol-water process the introduction of water into the phenol-oil system modifies the solvent treatment effects by modifying the properties of the *solvent* only Fig 30 gives the equilibrium curve for anhydrous phenol at 110° F with a heavy lubricating base of mixed-base origin, based on the experimental results given in Tables XIII and XIV

The results of adding water to anhydrous phenol extract are superimposed on the same curve by calculating phase and mixture compositions in terms of oil and total solvent (phenol plus water) To obtain these experiments the primary extract layer produced by treatment with anhydrous phenol is separated and then mixed with a definite amount of added water, but if the amount of water which is added to the anhydrous phenol extract layer exceeds a definite quantity a third aqueous layer makes its appearance From the International Critical Tables the limiting proportion of water which can be added to anhydrous phenol

TABLE XIII

Phenol Treatment of Heavy Lubricating Oil Base

Expt no	*Treatment* Temp , ° F	Total % solvent	% water in solvent	*% solvent in layer* Raff	Extr	*Yield on charge* Raff	Extr	*Raffinate* Sp gr at 60° F	Sp gr at 100° F (calc)	Visc 200° F	Visc 100° F	V I	V G C	*Extract* Sp gr at 60° F	Sp gr at 100° F	Visc 200° F
Charge								0 9565	0 9435	0 370	8 70	41	0 890			
1	110	52 8	5	9 86	82 2	91 1	8 9	0 9450	0 9320	0 320	6 25	53	0 876	1 0740	1 0620	6 57
2	"	102 5	"	13 5	86 3	85 3	14 7	0 9380	0 9250	0 296	5 14	62	0 869	1 0640	1 0520	4 87
3	"	266 0	"	13 7	90 2	73 2	26 8	0 9234	0 9105	0 256	3 64	76	0 851	1 0470	1 0350	2 68
4	"	540 0	"	10 1	93 0	63 2	36 8	0 9109	0 8980	0 230	2 76	87	0 840	1 0346	1 0226	1 10
5	"	57 2	10	9 7	87 2	94 6	5 4	0 9488	0 9358	0 3477	7 22	53	0 878	1 0910	1 0790	
6	"	173 5	"	12 0	91 2	85 7	14 3	0 9373	0 9245	0 290	4 80	66	0 865	1 0718	1 0598	6 165
7	"	48 0	nil	16 2	63 3	85 0	15 0	0 9422	0 9290	Repeated (Expt 17)				1 0377	1 0257	
8	"	96·0	"	16 4	76 7	74 4	25 6	0 9300	0 9170	0 271	4 28	68	0 860	1 0333	1 0213	1 80
9	"	245 5	"	19 4	85 8	61 6	38 4	0 9153	0 9020	Repeated (Expt 18)				1 0224	1 0104	
10	"	501 0	"	15 2	90 8	50 6	49 4	0 9019	0 8890	0 205	2 27	90	0 824	1 0124	1 0004	1 17
11	"	99 5	"	16 2	77 5	74 2	25 8	0 9297	0 9169	0 270	4 27	67	0 859	1 0337	1 0217	1 93
12	"	116 2	"		79 0	73 0	27 0	0 9277	0 9149	0 268	4 06	71	0 857	1 0344	1 0224	1 89
17	"	52 1	"	16 3	67 6	83 1	16 9	0 9405	0 9277	0 307	5 64	59	0 870	1 0353	1 0233	2 02
18	"	249·0	"	16 5	86 0	61 0	39 0	0 9137	0 9010	0 232	2 89	84	0 842	1 0235	1 0115	1 52

TABLE XIV

Addition of Water to Extracts from Phenol Treatment of Heavy Lubricating Oil Base

	Treatment			% phenol + water in layer		Yield on extract		Analyses of pseudo-raffinates								Analyses of enriched extracts		
Expt no	Temp , ° F	% water on extract layer	% phenol and H_2O in mixture	Raff	Extr	Raff	Extr	Sp gr at 60° F	Sp gr at 100° F	Visc 100° F stokes	Visc 200° F stokes	V I	V G C calc 100° F	V G C estimated* 100° F	V G C estimated* 210° F	Sp gr at 60° F	Sp gr at 100° F	Visc 200° F stokes
Charging stock (extract Expt 11)																1 0337	1 0217	1 93
14	110	50 5	85 0	34 7	95 9	82 6	17 4	1 0261	1 0141	292	1 585	−155	0 977	0 974	0 964	1 0698	1·0578	
15		10 1	79 5	18 0	90 2	53 7	46 3	0 9931	0 9811	49 54	0 780	− 28	0 931	0 932	0 932	1 0808	1 0688	
Charging stock (extract Expt 12)																1 0344	1 0224	1 89
13	110	24 8	83 0	16 4	93 6	77 8	22 2	1 0181	1 0061	201 80	1 375	−122	0 963	0 964	0 957	1 0659	1 0439	
16	"	4 95	80 2	21 4	84 9	28 9	71 1	0 9720	0 9600	28 94	0 546	−45	0 913	0 916	0 916	1 0609	1 0489	

Remarks

Expt 14 = Aqueous layer obtained above raffinate and extract layers

Pseudo-raffinate layer	12 5% by vol
Enriched extract layer	75 0% by vol
Aqueous layer	12 5% by vol

* V G C estimated from Sp gr – V G C curves See Fig 2

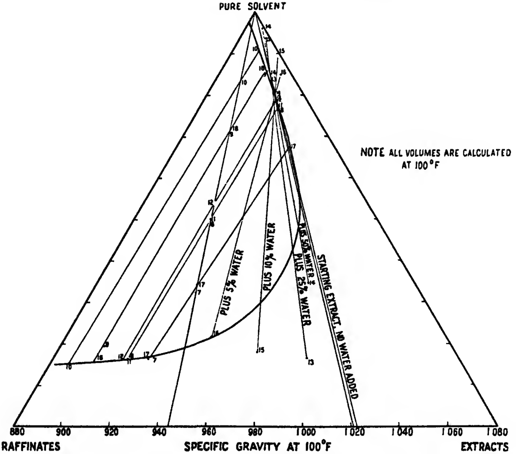


FIG 30 Equilibrium curve for anhydrous phenol and heavy lubricating oil base at 110° F , with results for aqueous dilution of phenol extracts

without causing phase separation is approximately 34 5% by weight of the phenol-water mixture at 110° F , and proportions in excess of this cause the formation of conjugate phases containing approximately 10 2% and 65 6% phenol by weight respectively (See Fig 31)

In experiment 14 (Table XIV) the amount of water added has exceeded the minimum required to form two conjugate phases and 48 c c of aqueous layer (containing approximately 10% phenol by weight) have separated The concentration of phenol in this new phase is, however, too low for the layer to exert any appreciable solvent action on the hydrocarbon constituents of the original mixture, with the result that the layer appears colourless and may be rejected

It is seen from Fig 30 and Tables XIII and XIV that as the amount of water added to the primary extract is increased, the quality of the pseudo-raffinate which separates rapidly deteriorates until the point is reached beyond which the addition of water to the primary extract layer results in the formation of a third phase If the amount of water added is increased beyond this quantity, then the dilute aqueous phenol in equilibrium with the extract and pseudo-raffinate will remain constant in composition but slowly decrease in amount, and the quality of the pseudo-raffinate and extract phases will approach each other until, in the limit, the amount of aqueous phenol is insufficient to cause the separation of a pseudo-raffinate and the bulk of the phenol will have been transferred to the dilute aqueous layer

Fig 31 also illustrates why the addition of water to furfural extracts cannot be expected to yield extracts of greatly increased naphthenicity, since the amount of water which may be added without causing the formation of the third aqueous layer is very limited

Table XIII also gives the results of treating the heavy lubricating base directly with phenol-water mixtures, and illustrates the highly naphthenic extracts obtainable by this means On the other hand, the selectivity of aqueous phenol for the high-grade oils is poor, so that direct treatment with aqueous phenol is uneconomical for the manufacture of high-grade oil despite the high yields obtainable, owing to the large volume of solvent required These limitations have been overcome by, in effect, treating with anhydrous phenol and adding water to the extract A tower contactor is used, operating under a temperature gradient, and water is injected at a point near the base The process is fully described elsewhere [39, 1936]

Analogy between Solvent Extraction and Distillation.

In the *World Petroleum Congress* of 1933 Saal and Van Dyck [35, 1933] contributed an excellent article on the analogy between distillation and solvent extraction, in which they pointed out that by making suitable transformations in the controlling variables extraction problems could be simplified by consideration of the known principles of distillation practice

The extent of this analogy is not widely appreciated, but it may be stated that in general the principle laws governing the transformation of liquids and liquid mixtures into vapour, i e partial pressure of hydrocarbon mixtures, vapour pressure-temperature relationships, &c, will be found to have their equivalent in the laws governing solvent extraction of hydrocarbon mixtures In distillation the variables which determine the system are heat content and volume which may be controlled by adjustment of operating temperature and pressure In solvent extraction, on the other hand, the variables are heat content and quantity of solvent (which determines the volume of the system), and these may be controlled by adjustment of the amount of solvent employed and the operating temperature In comparing distillation and solvent extraction processes, however, there is a kind of interchange between the role of heat content and volume, so that heat in distillation is the analogy of amount of solvent in extraction, pressure in distillation corresponds to treatment temperature in extraction, while change in distillation temperature (which for the distillation of mixtures determines heat content) corresponds in effect to variation in the amount of solvent used in extraction

In an equilibrium flash distillation the supply of heat to the system results in an increase in the amount of vapour phase and in the vapour-liquid ratio at constant pressure The supply of solvent to an extraction system results in an increase in the extract phase and in the ratio of extract phase to raffinate phase, from which it follows that the extract phase in extraction corresponds to the vapour phase in distillation, and that an increase in paraffinicity of a hydrocarbon mixture on solvent extraction corresponds to an increase in boiling-point of a liquid residue on distillation of a hydrocarbon mixture

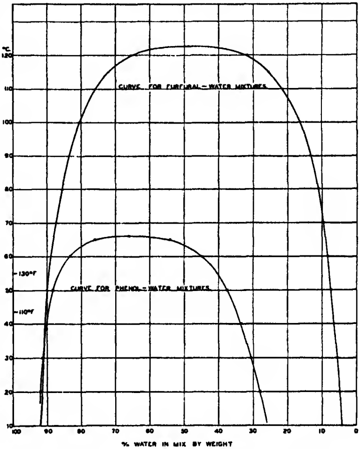


Fig 31 Miscibility curves for phenol-water and furfural-water mixtures

In solvent extraction problems, therefore, the asphaltic constituents of greatest molecular weight must be considered analogous to the most volatile constituents of a distillation system, and by the same reasoning liquid propane is seen to correspond in distillation to an exceedingly high-boiling hydrocarbon

Varteressian and Fenske [43, 1937] give an excellent comparative discussion on treatment of distillation and solvent extraction problems

It has been shown, for example, in Fig 21 that at temperatures above about 115° F no separation into two layers is possible with any percentage of chlorex for mixtures of this solvent and base stock This corresponds to the distillation of binary mixtures in which, at pressures above the critical pressure for the mixture, it is impossible to form a second liquid phase from mixtures containing more than a certain proportion of that component Moreover, as pointed out in the same section, it is impossible to obtain raffinates above a limiting quality at any given temperature, depending on the treatment temperature and solvent used This limiting quality corresponds in the case of distillation to the maximum boiling still residue which may be obtained at a given distillation temperature when the still temperature is below the boiling-point of the heaviest constituent

A consideration of various well-known phenomena by analogy with known distillation practice is instructive In SO_2 extraction, for example, at any given temperature the limiting quality of raffinate obtainable is relatively low If instead of SO_2, SO_2-benzole mixture is used as extracting agent, the limiting quality is improved, since benzole, being a hydrocarbon completely miscible in SO_2, acts as a vapour in distillation and the system becomes analogous to the increased volatility obtained by introducing steam or a light-boiling liquid into a distillation system at a fixed temperature, thereby reducing the partial pressure of the system A further interesting illustration is afforded by the Burmah Oil Company, patent No E P 459,595, which covers the improvement in aromaticity of SO_2 extract from spirits and light distillates by extracting the separated extract phase with a paraffinic lubricating oil Here the analogy with distillation may be explained as follows the separated extract phase (free from raffinate) represents a vapour system of fixed heat content The paraffinic lubricating oil corresponds to a high-boiling liquid, and its addition to the vapour system causes a readjustment of heat with partial condensation of the higher boiling constituents, i e separation of the more paraffinic fractions The system is analogous to the common absorption process in gasoline recovery

Propane deasphalting and the Duo-Sol processes owe their effectiveness to the fact that liquid propane in solvent extraction is analogous in distillation to a very high-boiling liquid of high sensible heat content, the addition of which to a system of fixed heat content results in a readjustment of heat and the volatilization of the lowest boiling constituent

One further case remains to be considered the addition of water to phenol, cresol, &c, extraction systems As before pointed out, the effect of adding water to a phenol extract is to produce a separation of pseudo-raffinates up to a certain point beyond which a third phase, consisting mainly of water, makes its appearance A little consideration will show that the effect of water is similar to the addition of a low-boiling immiscible liquid, such as water, to a distillation system, i e the added liquid immediately vaporizes at the expense of the less volatile constituents in the vapour phase

It is clear, therefore, that since in this system the water is playing the part of an inert liquid and merely exerts its effect by reason of its equivalent heat capacity, the effect obtained by adding water to phenol extracts will be greater than by treating with aqueous phenol, as is known to be the case in actual practice

In fractional distillation it is well known that optimum separating conditions are obtained by maintaining a constant molal reflux down the column in the case of countercurrent solvent extraction at constant temperatures, however, the solubility of the raffinate in fresh solvent is much less than the oil concentration in the extract phase leaving the other end of the system, so that the molal concentration in the solvent phase is not constant throughout, but increases steadily through the system By increasing the temperature at the raffinate end of the system and maintaining a temperature gradient so that the concentration in the solvent (extract) phase is constant throughout the system, the advantages of operating with a constant molal reflux will be obtained as in distillation This argument, however, requires modification, for whereas in distillation the shape of the vapour-liquid equilibrium curve does not as a rule change greatly with increasing temperature, in solvent extraction processes the selectivity of the solvent changes appreciably with temperature, so that although a temperature gradient is definitely advantageous in solvent extraction, the optimum operating conditions may not require a constant concentration in the extract phase throughout the entire system

In all cases it must be emphasized that while the analogy to the better-understood distillation processes may be found of considerable assistance in deciding the mechanism of an extraction process, theories based on distillation practices should not be too quickly adopted without first studying the equilibrium conditions for the solvent and base stock under all the possible conditions

Correlation of Plant and Laboratory Results

Mathematical analyses of continuous countercurrent liquid-liquid extraction processes have been discussed in the literature by Hunter and Nash [16, 1935, 17, 1936, 18, 1932], Saal and Van Dyck [35, 1933], Evans [7, 1934], Cannon and Fenske [4, 1936], and others, but none of these references give sufficient data to compare actual plant operations with the predicted results based on laboratory batch extractions Rushton [34, 1937] claims that actual countercurrent operation does not give results which are in line with laboratory predictions, in illustration his actual laboratory data for countercurrent operation are given in Table XV, together with the smoothed results required to fit the equilibrium curve determined by batch extractions As Rushton states, it is not necessarily true that the extracts and raffinates for single-stage batch and multi-stage countercurrent operation should all fall on the same equilibrium line for a system when there is decided mutual solubility On the other hand, the experimental evidence given in support of these statements is inconclusive and exception must be taken to the method adopted in determining the batch equilibrium at any temperature by first heating to complete immiscibility and then cooling to the separation temperature Moreover, Rushton's experimental results for two-stage countercurrent operation show far greater divergence from the batch equilibrium curve than do his three-stage results, which would hardly be expected if the same equilibrium curve did not apply for batch and countercurrent treatments

Several attempts have been made by the present writer to correlate countercurrent plant operation with the results predicted by laboratory batch extraction of the same feed stock, and the conclusions reached may be summarized as follows

1 The results obtained with three- and four-stage countercurrent plant working under equilibrium conditions of mixing and separating show that a very close approximation to the actual plant conditions may be predicted from the equilibrium curve constructed from laboratory batch extractions

2 A definite discrepancy, however, exists between actual and predicted results for countercurrent operation, which is shown by the steeper slope of the tie lines for the various countercurrent stages This discrepancy is small in the case of light oils (spirits, kerosines, and light gas oils) but is appreciable in the case of the more complex lubricating oil fractions of petroleum

TABLE XV

Experimental and Smoothed Data from Equilibrium Batch Countercurrent Extractions

		Laboratory data					*Smoothed data*			
		Raffinate		*Extract*			*Raffinate*			
Stages	*Solvent ratio*	*V G C*	*Vol %* NO_2	*V G C*	*Vol %* NO_2	*E/R*	*V G C*	*Vol % yield*	*Extract V G C*	*E/R*
1	0 5	0 844	19 8	0 897	71 4	0 36	0 844	88 7	0 897	0 35
	1 0	0 834	17 1	0 893	75 8	1 38	0 834	72 8	0 893	1 25
	1 5	0 827	15 5	0 889	79 0	2 40	0 827	62 9	0 889	2 36
	2 0	0 821	13 2	0 883	81 1	3 79	0 822	54 8	0 884	3 61
	2 5						0 818	48 4	0 880	5 41
	3 0	0 817	12 8	0 875	83 5	7 04	0 815	41 7	0 875	7 42
2	1 0	0 822	13 7	0 889	70 9	1 57	0 826	66 2	0 897	1 59
	1 5						0 818	56 7	0 892	2 75
	2 0	0 815	13 7	0 886	79 3	4 11	0 814	50 7	0 887	4 22
	2 5						0 810	44 5	0 882	6 00
	3 0	0 812	12 7	0 881	81 2	8 43	0 808	40 0	0 878	8 45
3	1 0	0 821	13 6	0 899	70 6	1 83	0 821	62 8	0 899	1 82
	1 5						0 814	54 4	0 893	3 03
	2 0	0 810	11 5	0 890	77 7	4 33	0 809	48 7	0 889	4 45
	2 5						0 804	42 5	0 884	6 45
	3 0	0 800	10 5	0 880	83 0	8 83	0 800	37 5	0 880	8 90

3 The various raffinate and extract-phase analyses for the different countercurrent stages are found to fit in with the graphical constructions for countercurrent operation described below, as can be seen in Fig 43, which gives results for a three-stage countercurrent plant operating on SO_2 and light gas oil

Estimation of Number of Countercurrent Stages required from the Equilibrium Curve.

The equilibrium curves may be used to obtain an estimate of the number of ideal or perfect countercurrent stages required to obtain a given quality raffinate with a given amount of solvent The method employed was developed by Hunter and Nash [18, 1932, 1934], and a simplified graphical construction is given in a review by Evans [7, 1934], but in order to assist the discussion the principle of the graphical construction may be summarized as follows with the aid of Fig 32 The reader is referred to the two articles just mentioned for the proof of the construction

Fig 32 shows in diagrammatic form the graphical relationships for a countercurrent process equivalent to three ideal stages (*a*) under isothermal conditions and (*b*) under a temperature gradient of 30° F at the extract outlet end of the system to 100° F at the raffinate outlet Points *D*, *J*, and *M* represent the composition of the base oil and solvent-free raffinate and extract respectively, and *C* the composition of the pure solvent feed The composition of the extract and raffinate layers (or phases), leaving the opposite ends of the plant, are represented by the points *E* and *K* respectively *L*, the intersection of *CD* and *EK*, gives the overall composition of the feed to the system and the percentage solvent treatment $= DL/CL \times 100\%$ The point *S* is located by the intersection of the lines *JKC* and *DE* Since in the ideal stage equilibrium is attained, the point *F* (raffinate phase leaving the first stage in equilibrium with the final extract *E*) is located at the opposite end of the tie line through *E* *G* is located as the intersection of the line *FS* with the equilibrium curves for the temperature prevailing in the next stage, and *H* by the tie line through *G*, and so on Similarly, if the actual results obtained on any countercurrent plant under given conditions of solvent treatment, temperature, &c , are known, and if the equilibrium curves for the same solvent and feed stock are available, an estimate might be made of the average or overall stage efficiency of the process plant (See Principles of Solvent Extraction by Hunter in this section)

However, since the slope of the equilibrium tie line in countercurrent processes does not correspond with the slope of the tie line for the same quality raffinate or extract produced at the same treatment temperature by single-batch treatment of the feed stock, the efficiency of each stage must be separately determined by laboratory mixing and separation of the products entering the countercurrent stage Such laboratory-determined tie lines are included in Fig 43 for laboratory treatments 31 and 32 obtained by treatment of the raffinates from stages 1 and 2 respectively

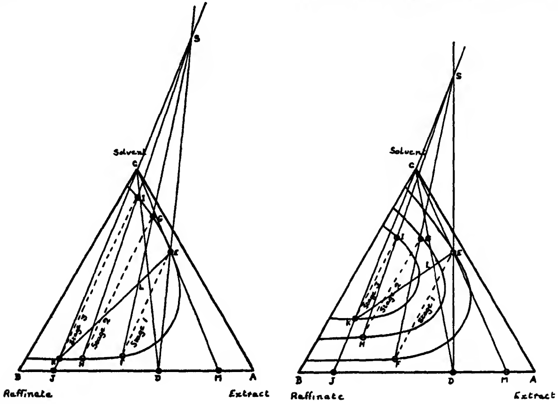
While it must be agreed, therefore, that actual countercurrent plant operation cannot be predicted exactly from equilibrium curves based on batch extraction, it must be re-emphasized that the specific gravity-viscosity relationships, &c , for countercurrent operation do not differ within practical limits from similar quality products prepared by batch extraction, this has been fully discussed in an earlier section The discrepancy between actual and predicted results for plant stages, &c , appears to be the same for all solvents, but this has only been examined by the present writer for the limited number of solvents, e g furfural, chlorex, SO_2-benzole

Pre-chilling and Pre-dilution of Feed Stock by Solvent Injection.

In order to assist the pumping of the cold oil in the case of the more viscous feed stocks, part of the solvent is sometimes injected with the fresh feed in actual practice

The effect of such pre-dilution to reduce feed-oil viscosity will be the same in any solvent process and can be seen by reference to Fig 32 The feed to stage 1 is now a mixture of oil and solvent, i e a point on the line *DC* near to *D* On joining this new point to *E* and producing the line to cut the line *CJ*, the new position of the point *S* will be found to be farther from the triangle so that point *G* will be nearer the point *E*, and so on, with the result that more stages will be required to reach the desired quality raffinate *J*

Taking a figure of 25% for the amount of solvent injected with the fresh feed, an estimate, made on the lines described above, of the reduction in the number of ideal stages indicated a loss equivalent to 0 6 of a perfect stage in one instance for a plant operating on a feed stock of high viscosity



(a) (b)

FIG 32

Mixer Efficiency.

The ease with which equilibrium is attained on mixing any oil and solvent makes it possible to obtain very good mixer efficiencies, and in general plant practice the mixer efficiency is high, as shown by the following actual results

(*a*) Sample of mixture entering settler, immediately settled at mixer temperature and the two phases separated and analysed

	% oil in layer by wt	*Sp gr of solvent-free oil*
Raffinate	73 0	0 9377
Extract	8 2	1 0718

(*b*) Sample of mixture entering settler, repeatedly shaken at mixer temperature to ensure equilibrium, settled at same temperature and the two phases separated and analysed

	% oil in layer by wt	*Sp gr of solvent-free oil*
Raffinate	74 0	0 9372
Extract	8 7	1 0723

Settler Efficiency.

The amount of entrainment in various plant settlers is generally the chief cause of inefficient plant operation, and since, as has been shown, the mixing efficiency in most plants is almost perfect, it follows that the efficiency of the various stages must be mainly determined by the separation in the settlers

While the amount of entrainment which takes place in the settlers will be an entrainment of one phase in another, the effect of this entrainment on the quality of the products may be appreciated by comparison of specific gravities for the solvent-free raffinate and extract leaving each stage with the corresponding gravities for the uncontaminated products The average figures given below have been taken from an actual plant test and show that in this instance the effect of entrainment was greater in the extracts than in the raffinates, and was most marked at the raffinate outlet end of the system

TABLE XVI

Settler no	*1*	*2*	*3*	*4*
Raffinate (Solvent free)				
Gravity of uncontaminated raffinate entering settler, obtained by perfect separation of mixer sample	0 9376	0 9273	0 9201	0 9120
Actual gravity of raffinate leaving settler	0 9399	0 9277	0 9210	0 9119
Extracts (Solvent free)				
Gravity of uncontaminated extract entering settler, obtained by perfect separation of mixer sample	1 0643	1 0425	1 0214	1·0044
Actual gravity of extract leaving settler	1·0616	1·0356	1·0129	0 9785
Composition of solvent-free raffinate and extracts from each settler in terms of the uncontaminated solvent-free constituents				
Raffinate				
Vol % incoming R O	98 2	99 6	99 1	100
,, ,, ext	1 8	0·4	0·9	
Extract				
Vol % incoming R.O	2 1	5·4	8·4	28
,, ,, ext	97 9	94·6	91·6	72

The Oil Variable

The effect of change in quality of the oil feed stock has been previously discussed, but the object and results of treating various petroleum fractions may be better appreciated by the following illustrations

Production of Aromatic Extracts of High Anti-knock Value from Gasolines.

The relation between chemical constitution and anti-knock value for hydrocarbons of the gasoline boiling range has been studied in considerable detail [12, 1932, 28, 22, 1934], while the critical solution temperatures with aniline which have been determined for the same series of hydrocarbons [8, 1937] give some indication of the effect of solvent treatment of mixtures of these hydrocarbons A consideration of these results would indicate that of the high anti-knock hydrocarbons, the aromatics and naphthenes would be preferentially removed in the solvent extract, but the isoparaffins, possessing higher C S T values than the pure paraffins, would be lost in the low anti-knock raffinate

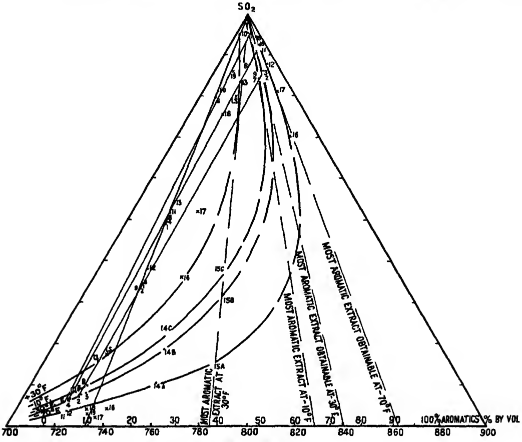


FIG 33 Equilibrium curves for straight-run benzine and liquid SO_2

For the production of extracts of high aromatic content and anti-knock value, considerably lower treatment temperatures are required than are generally employed for the solvent treatment of heavier petroleum fractions such as lubricating stocks Similar results may, of course, be obtained with any selective solvent which is not unsuitable on other grounds, such as freezing-point, boiling-point, or viscosity at low temperatures, but the results of SO_2 extraction on a straight-run benzine of 9 5 % aromatics by volume (32 5% at 100° C and 185° C end-point) are shown in Figs 33 and 34, which are self-explanatory Various alternative methods of producing fractions of high aromatic content from straight-run benzines and gasolines by solvent refining have been examined, such as

(*a*) Direct treatment of the gasoline at low temperatures

(*b*) Preliminary treatment at intermediate temperatures with subsequent re-extraction (cooling) of the primary extracts

(*c*) Preliminary solvent treatment of the gasoline alone with subsequent separate treatment of the extract phase by a paraffinic higher boiling fraction, i e addition of a paraffinic lubricating oil

(*d*) By the use of extract reflux to the extract phase

It is seen from the curves in Fig 33 that the most aromatic extracts are produced by treatment at the lowest temperatures, and in this actual series of experiments the most aromatic extract was produced by treatment with about 60% SO_2 at −70° F, giving an extract on benzine charge of 7% by volume, containing approximately 93% by volume of aromatics

The effect of adding a paraffinic lubricating oil to a benzine extract is shown in Table XVII This results in a further separation of paraffinic light material which is included with the bulk of the added lubricating oil in the new raffinate layer, the new extract layer contains, in addition to a small amount of lubricating oil extract, benzine extract of considerably increased aromatic content In the

TABLE XVII

Effect of adding Paraffinic Lubricating Oil to Primary Extract

	Composition of layer or mix			Analyses of spirit				Analyses of lub oil			
	Lub oil %	Spirit %	SO_2 %	Sp gr	Aromatics (vol) %	Aniline-point, °C	Ref index	Sp gr	V 100	V 200	V I
Charge	38 7	12 4	48 9	0 777	37	60 1		0 884	0 715	0 0965	93
Raffinate	71 1	19 0	9 9	0 740	17	52 4	1 415	0 884	0 696	0 0949	93
Extract	1 5	7 4	91 1	0 836	71			0 939 (calc)			

actual experiment the aromatic content of the benzine extract increased from 37 to 71% by addition of the lubricating oil fraction and chilling the mixture to +30° F, whereas to obtain a further separation of raffinate from the primary extract and a corresponding increase in aromatic content or specific gravity without the addition of the paraffinic lubricating oil, this primary extract would have to be cooled down to about −20° F, i e about 50° F lower operating temperature

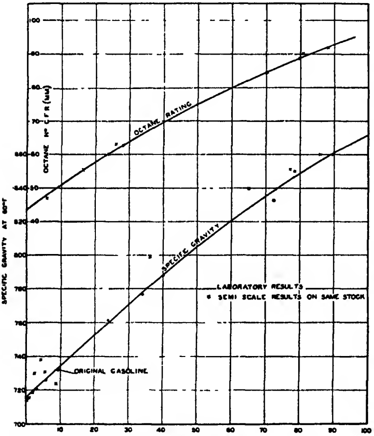


FIG 34 Relation between specific gravity and aromatic content for SO_2 raffinates and extracts from straight-run benzine

This method of procedure is fully described in a patent application of the Burmah Oil Company and by patents held by the Royal Dutch Shell Company of The Hague (B P 444,104), and has the advantage of economies in refrigeration if highly aromatic extracts are required by the SO_2 or other low-temperature process.

In certain cases appreciable improvement in aromaticity of the extract may be obtained as previously described by refluxing solvent-free extract to the extraction end of the treating system This applies particularly to solvents which give an equilibrium curve of marked convexity in the upper portion of the triangle (compare furfural and SO_2 equilibrium curves) The following example [50] is illustrative

Aromatic gasoline (I) with final boiling-point of 110° C and 15% aromatics by volume is extracted at −20° C with two-thirds of its volume of furfural An extract layer (II) is obtained from which an extract (III) is obtained by distilling off the furfural, containing 55% aromatics and amounting to 14% of the original gasoline by volume If the extract layer (II) is washed with 75% by volume of the extract (III), two layers are again formed, an upper raffinate layer (IV) containing 30% by volume of aromatics and the new extract layer (V) showing an increased aromatic content of 75% by volume

Treatment of Kerosines and White Spirits.

For the treatment of these products, liquid SO_2 is an ideal solvent, on account of the greater ease with which it may be separated by distillation from the hydrocarbon products, compared with other solvents The results of solvent treatment of white spirit and kerosine cuts with liquid SO_2 shows the same general relationships as the other petroleum fractions such as lubricating oils, spindle oil, light and heavy gas oils, and straight-run benzines It is interesting to observe, however, that in the case of white spirit, kerosine, and, to a lesser extent, light gas oil the viscosity of the raffinates *increases* with the degree of refining, while the viscosity of the extracts *decreases*, and in this respect the lighter petroleum products behave in the reverse manner to the heavier distillates

Fig 35 illustrates the equilibrium curves for a white spirit cut from mixed base crude with liquid SO_2 at 0, 30, and 70° F (experimental results summarized in Table XVIII)

Fig 36 gives the equilibrium curves for a white spirit cut (sq 0 7827) and kerosine cut (sq 0 8080) plotted in such a way that the results for stocks of intermediate gravities may be estimated This method of plotting has been found exceedingly useful in comparing results on feed stocks which only differ slightly in specific gravity

Solvent Extraction of Crude Residues containing Asphaltic Constituents.

The action of the single-solvent processes on crude residuums or on feed stocks containing asphaltic constituents as impurities is anomalous in that the asphaltic material present in the feed stock is not removed with the extract

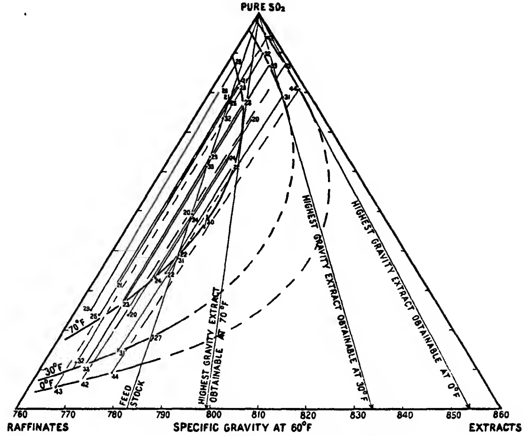


FIG 35 Equilibrium curves for SO_2 and mixed base W S cut

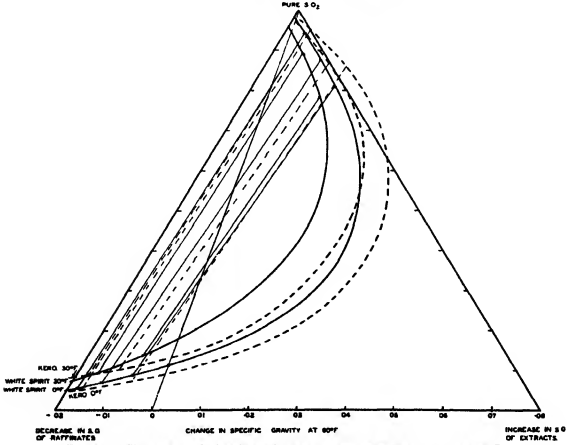


FIG 36 Equilibrium curves for liquid SO_2 white spirit cut and kerosine cut at 0° F and 30° F

TABLE XVIII

SO$_2$ *Treatments of White Spirit Cut from Mixed Base Crude*

Expt no	Treatment		Composition of charge (vol %)		% SO$_2$ by vol in layers		Tests on raffinates							Tests on extracts						
	Vol % SO$_2$	Temp, °F	SO$_2$	W S	R O	Ext	Sp gr at 60° F	Density $D_{15\cdot6}$°C	Visc (Stokes) 100° F	V G C	Aniline point, °C	Ref ind $N_{15\cdot6}$° C	$\frac{N_{15\cdot6}-1}{D_{15\cdot6}}$	Sp gr at 60 F	Density $D_{15\cdot6}$°C	Visc (Stokes) 100° F	V G C	Aniline point, °C	Ref ind $N_{15\cdot6}$° C	$\frac{N_{15\cdot6}-1}{D_{15\cdot6}}$
		Starting stock					0·7827	0·7819	0·00976	0·826	56·1	1·4388	0·5612							
K 20	97·4	70	49·3	50·7	23·6	72·9	0·7749	0·7741	0·01003	0·816	63·1	1·4333	0·5597	0·8051	0·8043	0·00923	0·848	36·9	1·4536	0·5640
21	363·0	„	78·5	21·5	31·6	82·9	0·7670		0·01071	0·805	70·3			0·7898	0·7890	0·0095	0·832	50·1		
22	64·0	„	39·0	61·0	34·2	61·2	0·7807	0·7799	0·00982	0·824	57·9	1·4375	0·5610	0·7960		0·0095	0·840	45·3		
23	177·8	„	63·8	36·2	26·4	77·3	0·7713	0·7706	0·01024	0·811	66·2			0·7966	0·7958	0·0093	0·840	43·6	1·4428	0·5564
24	92·6	„	48·1	51·9	33·3	63·5	0·7780	0·7772	0·00993	0·819	60·6	1·4351	0·5598	0·7932		0·0094	0·836	47·2		
25	345·5	„	77·5	22·5	23·9	81·1	0·7670		0·0106	0·807	70·2			0·7874		0·0096	0·829	52·0		
29*	411·0	„	80·5	19·5	25·0	86·9	0·7639	0·7632	0·01087	0·803	73·5	1·4263	0·5586	0·7747	0·7739	0·0104	0·814	63·7	1·4331	0·5596
31	61·8	30	38·2	61·8	15·0	78·4	0·7760	0·7752	0·00992	0·820	62·3	1·4341	0·5600	0·8331	0·8323	0·0087	0·876	7·4	1·4714	0·5664
32	273·5	„	73·2	26·8	11·9	89·6	0·7675	0·7668	0·01035	0·806	69·4	1·4282	0·5584	0·8202	0·8194	0·00892	0·866	21·4	1·4632	0·5653
33	157·3	„	61·3	38·7	10·7	86·4	0·7698	0·7690	0·01018	0·811	67·7	1·4299	0·5590	0·8286	0·8278	0·00871	0·872	14·0	1·4683	0·5657
42		0			7·62	86·7	0·7705	0·7698	0·106		64·5	1·4310	0·5599	0·8500	0·8492	0·0084		−13·6	1·4842	0·5702
43		„			5·9	93·8	0·7655	0·7648	0·0103		69·7	1·4274	0·5588	0·8380	0·8372	0·0086		0·4	1·4747	0·5669
44		„			9·6	80·7	0·7765	0·7757	0·0099		61·9	1·4337	0·5591	0·8550	0·8522	0·0084		−21·0	1·4851	0·5692
Cutting-points																				
K 27		70	41·0 42·0	59·0 58·0			0·7827 (starting stock, white spirit cut)													
		30	17·5 19·0	82·5 81·0			0·7827 („ „ „)													
K 30		70	46·0 49·0	54·0 51·0			0·7893 (blended extracts except runs K 21 and K 25)													
		30	20·0 23·0	80·0 77·0			0·7893 („ „ „)													
K 40		30	25·5 27·5	74·5 72·5			0·7945 (blended extracts except runs K 22 and K 24)													

* Starting stock for K 29 was 0·7698 sp gr blend of raffinates from Experiments K 21, K 23, and K 25

but remains to a large extent in the raffinate layer Very little information has been published to date on this subject, but Stratford [39, 1936] states with reference to the phenol process 'certain of these oils emulsified to a serious extent at the raffinate end of the treater The real reason for the emulsification, however, was found to be the entrainment of asphaltic material with the distillate during the crude preliminary distillation', indicating that the asphaltic constituents are not completely removed with the extract during phenol refining Again, apart from the Duo-Sol process, the nitrobenzene process appears to be the only solvent-refining process which claims to be able to produce good coloured raffinates from asphaltic stocks

If an asphaltic residue is extracted with any of the usual single solvents, it is found that, contrary to what might possibly be expected, the raffinate layer is generally black, while the extract layer is dark green in colour Moreover, the asphaltic constituents are found to be largely concentrated in the raffinate layers, suggesting either (*a*) that selective solvents exert a precipitating action on the asphaltic constituents with the precipitated asphalt remaining in the raffinate or oil phase (possibly due to interfacial tension phenomena or preferential wetting of the asphalt by the oil), or (*b*) that certain asphaltic constituents are semi-paraffinic in nature and are selectively removed with the other paraffinic constituents of the stock according to the normal mechanism of the solvent action

The significance of these observations has been studied by the present writer and shown to take place independently of the presence of wax by an examination of various dewaxed and undewaxed asphaltic crude residues using the following solvents at various temperatures

1 Liquid SO_2
2 Furfural
3 Chlorex
4 Nitrobenzene
5 *sec* -Butyl alcohol
6 *ter*-Butyl alcohol

The results obtained indicate clearly that although solvents may be classified generally as 'precipitative' or 'extractive' as discussed in an earlier section, the 'extractive solvents' such as SO_2, chlorex, and furfural also exert a definite precipitating action on the asphaltic constituents of the feed stock, but the precipitated asphalt remains suspended in the raffinate layer or forms a third viscous layer lying between the main raffinate and extract layers The precipitating action of the various 'extractive' solvents on the asphaltic constituents of the feed stock, however, varies with the solvent and appears to be negligible in the case of nitrobenzene For this reason the raffinates obtained by the nitrobenzene process are low in asphalt content and therefore of better colour than the raffinates obtained by the other 'extractive' solvent processes operating on certain feed stocks

The separation of a viscous asphaltic layer within the main raffinate layer may in most cases be readily demonstrated by centrifuging at the treatment temperature when a third phase makes its appearance as a heavy black layer lying between the raffinate and extract phases proper

The mechanism of this precipitating action of the extractive solvents is difficult to understand, but it must be concluded that although the main effect of these solvents is 'extractive', a 'precipitative' effect is also present The representation of this state of affairs on a triangular graph has already been given for propane by P C Keith [20, 1934]

The results of solvent treatment of an asphaltic residue feed stock may be indicated on triangular coordinates as in Fig 37 by separating the extract phase and evaporating the solvent from the two layers, the asphaltic matter suspended in the raffinate layer being redissolved in the oil In the case of SO_2 treatments precipitation of asphalt is heavy and increases to a marked degree as the temperature falls during evaporation of the solvent In such cases the raffinates and extracts, after complete removal of the SO_2, may be redissolved in CS_2 to give a homogeneous solution which on distilling off the CS_2 leaves the asphalt in solution in the oil, or as a stable suspension which shows no separation on centrifuging

Table XIX gives the results obtained on a 30% crude residue of mixed base origin, and these results are plotted in Figs 37 and 38 It will be seen that secondary and tertiary butyl alcohols behave as 'precipitative' solvents similar to liquid propane for which they could be used as a substitute in solvent refining They show sparing solubility for the asphaltic constituents and produce raffinates of relatively low asphalt content Settling rates are low, however, and centrifuging appears to be essential, but, on the other hand, the high capital cost of pressure equipment and compressors required for the propane deasphalting process is avoided The use of these solvents is described in E P 450,511, but unless used in conjunction with other solvents in a similar manner to the Duo-Sol process these solvents would not appear to be suitable for the manufacture of high V I raffinates, and yields in any case would be low

As determined in the experimental work here quoted, 'Hard Asphalt' is a measure of the extract produced by a 'precipitative' solvent (petroleum ether) under standardized conditions of oil solvent ratios and temperature, while 'Soft Asphalt' is a measure of the extract produced by an 'extractive' solvent (acetone) under conditions which are not standardized as to oil solvent ratio. Neither the hard nor the soft asphalt contents can therefore be regarded as absolute measures of any particular type of petroleum constituents and must, from the nature of things, vary with the paraffinicity of the stock, particularly in the case of the soft asphalt content It is not to be expected, therefore, that the hard or soft asphalt contents on 'products in' for any experiment should equal the corresponding figures for 'products out', but a constant relationship between specific gravity, say, and hard asphalt content would be expected for the raffinates and extracts from a given feed stock if only two phases were formed The absence of any such general relationship which applies for all the 'extractive' type of solvents, e g SO_2, chlorex, furfural, and nitrobenzene (see Fig 38), indicates that the precipitative effect is a function of the solvent employed and not, as in the specific gravity-viscosity relationship, &c , obtained for solvent extraction of distillate stocks, a function of the oil stock alone independent of the solvent used

It follows, therefore, that any asphaltic matter present in the feed stocks to the Edeleanu, furfural, phenol, or similar processes will result in the production of asphaltic raffinates No advantage would appear to be gained by treating crude residues, and, therefore, every care should be taken in the primary distillation process to avoid entrainment of asphalt in the raw stocks for solvent treatment Such raffinates would be difficult to refine to low colour by high-temperature clay treatment and would probably require a very light initial acid treatment to coagulate the asphalt

TABLE XIX

Solvent Treatments of 30% Crude Residue (Mixed Base Origin)

	Treatment		Vol % solvent in layer		Analysis of raffinates											Analysis of extracts										
						Viscosity (Stokes)					Wax			% asphalt			Viscosity (Stokes)					Wax			% asphalt	
Solvent	Vol %	Temp, °F	R O	Ext	Sp gr at 60°F	100°F (calc)	140°F	200°F	V I	V G C	% by wt	M P °F	Carbon residue Ramsb	Hard	Soft	Sp gr at 60°F	100°F (calc)	140°F	200°F	V I	V G C	% by wt	M P, °F	Carbon residue (Ramsb)	Hard	Soft
Charging stock					0.9665	16.3 (detd)	3.02 (calc)	0.562	49	0.899	5.53	128	7.07	2.60	4.58											
SO₂	544·0	125	28.2	94.9	0.9407	10.7	2.48	0.546	84	0.862	7.4	128	7.30	4.19	13.2	1.0265	95	9.84	0.972	−84	0.984	1.74	128		3.56	nil
	135.5	,,	24.1	89.9	0.9550	12.5	2.68	0.546	72	0.883	6.23	128	7.15	3.59	4.73	1.048	480	28.68	1.885	−210	1·017	1.11	132		6.31	nil
	75.9	,,	25.2	86.5	0.9595	13.6	2.82	0.562	68	0.888	6.35	128	7·09	3.36	5.65	1.0564	740	36·05	2.11	−302	1.030	1·04	131		5.32	nil
	264.0	,,	26.8	92.5	0.950	11.5	2.51	0.52	72	0.875	6.37	125	7.15	3.86	10.7	1.0389	220	15.93	1.273	−181	1.002	1.63	129	8.43	3.0	nil
Chlorex	103·0	70	19.0	78.2	0.9468	8.2	2.005	0.456	84	0.875			6.33	2.87	11.8	1.0287	400	27.35	1.935	−138	0.976			10.8	3.31	0.36
	228·0	,,	21.1	87.4	0.939	5.6	1.77	0.442	108	0.868			6.32	2.96	9.9	1.0261	320	24.5	1.873	−98	0.972			10.30	2.35	nil
Furfural	109.9	70	45.3	92.4	0.9568	13.3	2.865	0.577	73	0.886			7.02	3.13	6.25	1.108									11.9	nil
	224.5	130	28.9	92.2	0·9470	8.2	2.025	0.465	86	0.875			6.34	2.38	9.30	1.0793									9.1	nil
Nitrobenzene	95·9	30	22.9	65.0	0.9226	3.25	0.997	0.278	98	0.853			3.63	0.49	9.80	1.0237	970	70.67	4.97	4	0.956			12.38	9.70	7.75
	115.5	30	31.5	70.5	0.9316	3·90	1.133	0.302	92	0.862			3.92	1.01	8.9	1·0273			5.18					11.38	8.2	4·40
sec-Butyl alcohol	255·0	70	86.4	18.3	0.934 (calc)	3.80	1·01	0.2515	66	0.876			3.26	0.24	0.10	0.9761		5.11						9.00	3·09	12·0
ter-Butyl alcohol	284·0	70	87.3	32.9	0.9367	3.205 (detd)	0.88 (calc)	0.226	67	0.873			2.06	0.13	0.03	0.9815	35	6.27	1.02	70	0.913			9.55	4.50	13.6

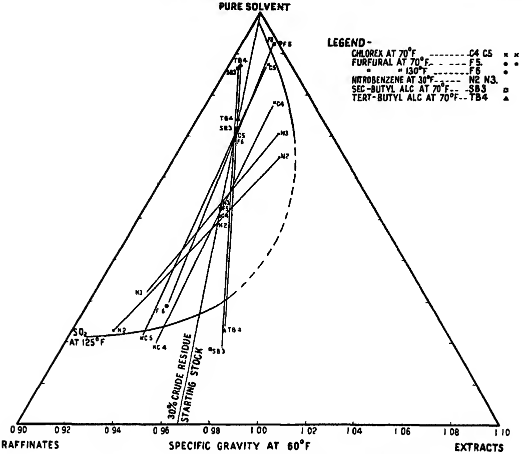


Fig 37 Solvent treatments of 30% crude residue (mixed base origin)

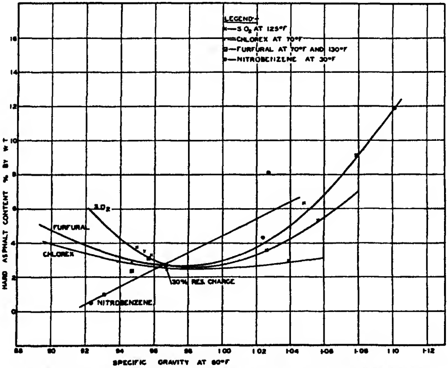


Fig 38 Hard asphalt gravity curves for raffinates and extracts from 30% crude residue

Treatment of Blended Feed Stocks.

The effect of treating a blended feed stock, e g naphtha lubricating base oil blend, may occasionally call for consideration Considerable experimental evidence exists indicating that the effect of applying a given solvent treatment (say 100% solvent at 75° F) to a blended feed stock is the same as that obtained by treating the components of the blend separately under the same conditions with the same percentage of solvent at the same treatment temperature

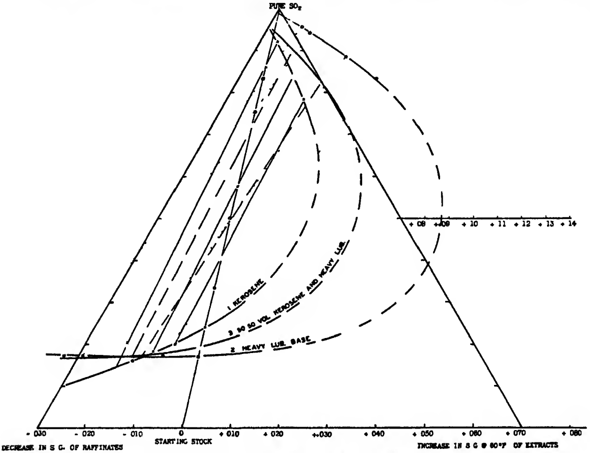


Fig 39 Equilibrium curves at 70° F for SO_2 and (1) kerosine cut, (2) heavy lub base, (3) 50 50 blend of kerosine cut and heavy lub base

The treatment of blended feed stocks has been examined in a variety of cases, and while absolute agreement is difficult to obtain owing to the difficulty experienced in separating the components of the blend from the experimental raffinates and extracts, the results agree within reasonable experimental limits with those to be expected The following blended feed stocks are illustrative

(1) 70% 182° C end-point straight-run benzine (sp gr 0 727)
    30% lubricating oil base (sp gr 0 890)
(2) 50% kerosine cut (sp gr 0 808)
    50% medium-heavy lub base (sp gr 0 956)
(3) 90% white spirit cut (sp gr 0 7827)
    10% SO_2 extract ex medium-heavy lub base (sp gr 0 9845)
(4) Waxy lubricating oil base (*c* 15% wax)

Fig 39 gives the equilibrium curves for case (2) above using liquid SO_2 at 70° F. compared with the curves for SO_2 treatment at 70° F of the components of the blend The results are plotted using a very wide scale for the base of the triangle, and show the blend to be intermediate, both as regards position of the equilibrium curve and slope of the tie lines, to the results for treatment of the separate constituents

Table XX gives comparative data for the treatment of various stocks neat and in blend with other crude fractions using liquid SO_2 at various temperatures In certain pairs of results the agreement is not good owing to the experimental difficulties in separating the small amount of product by distillation, after solvent refining

In considering the solvent refining of waxy or dewaxed lubricating oil stocks, it has been found that the presence of wax does not affect the solvent action, apart from introducing mechanical difficulties in separation if treatment temperatures fall below the wax crystallization point Waxy stocks may be treated as blended stocks composed of dewaxed oil plus wax, and if a certain treatment (say 100% of solvent at 140° F) is required to produce a given V I raffinate from a dewaxed stock, for example, then the waxy stock will require to be treated with the same percentage solvent to produce an equal specific-gravity raffinate of similar pour-point after dewaxing the waxy raffinate This is clearly brought out in Fig 40, where the same lubricating oil distillate has been treated with various solvents before and after dewaxing; the raffinates from the waxy stock being subsequently dewaxed to approximately the same pour-point as the raffinates from the dewaxed distillate.

TABLE XX

SO_2 *Treatment of Miscellaneous Stocks Neat and in Blend*

		SO_2 *treatment*		*Analysis of refined oils*				*Analysis of extrocted oils*			
Feed component	*Composition of feed stock*	*Temp , °F*	*Vol % on charge*	*Sp gr at 60° F*	*Visc (Stokes) 200° F*	*Aniline point, °C*	*Refractive index*	*Sp gr ot 60° F*	*Aniline point, °C*	*% oromotics by vol*	*Refractive index*
Light benzine	In blend 30 70 with lub base	−10	93 5					0 822	−3 5	61	1 4650
" "	Neat	−10	93 5					0 822	−10	61	1 4675
" "	In blend 30 70 with lub base	−30	71 3	0 723		60 8	1 4062	0 841	< −25	74	1·481
" "	Neat	−30	71 3	0 722		63 0	1 4065	0 841	< −25	74	1 4795
" "	In blend 30 70 with lub base	+30	121					0 788		40	1 4460
" "	Neat	+30	118					0 781		36	1 4410
Kerosine	In blend 50 50 with lub base	70	259	0 794		75 3	1 442	0 835	47		1 468
"	Neat	70	259	0 796		74	1 4435	0 838	43		1 471
Lub base oil	In blend with kerosine as above	70	259	0 9236	0 259			1 084			
" "	Neat	70	259	0 9264	0 280			1 085			
Kerosine	In blend with lub base oil as above	70	96 6	0 799		71 2	1 446				
"	Neat	70	96 6	0 799		71 8	1 4455				
Lub base oil	In blend with kerosine as above	70	96 6	0 9353	0 290						
" "	Neat	70	96 6	0 9385	0 316						
White spirit cut (0 7827)	In blend with lub oil extract	70	302 5	0 7669	0 0092		1 4295	0 7885			1 4426
" "	Neat	70	302 5	0 7665	0 0101		1 4285	0 7890			1 4435

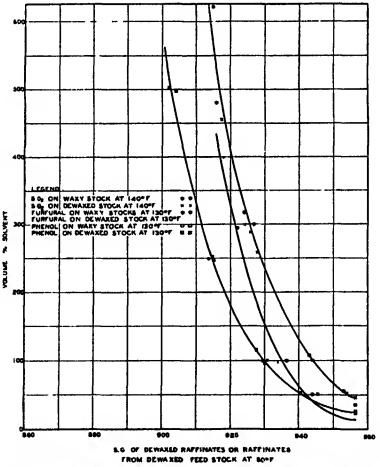


FIG 40 Relation between specific gravity at 60° F of dewaxed raffinate and vol % solvent for batch treatment of waxy and dewaxed feed stocks

The Solvent Refining of Waxy versus Dewaxed Base Stocks.

In the manufacture of lubricating oils from waxy stocks there are, as before stated, possible economic advantages in placing the solvent-refining process before the dewaxing process if low pour-point products are required, since the average cost of solvent dewaxing per ton of input to the modern dewaxing processes is approximately double the cost of solvent refining per ton of feed

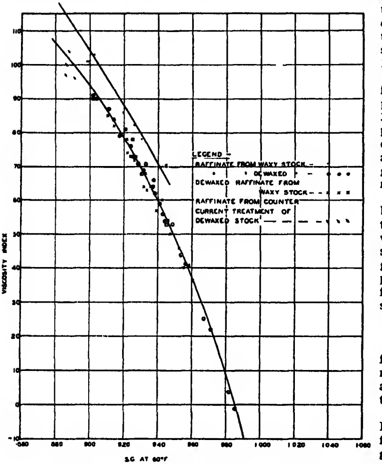


FIG 41 Sp gr-V I curves for raffinates and extracts from waxy and dewaxed feed stocks, and dewaxed waxy raffinates

The solvent refining of waxy stocks presents no practical difficulties if the treatment temperatures are sufficiently high to prevent the separation of crystalline wax, and in general this temperature is not very different from the set point of the stock, i e about 100° F On the other hand, as has been shown, in the solvent refining of mixed stocks the effect of treatment on the mixture is the same as the effect of treating each constituent of the mixture separately at the same temperature with the same percentage of solvent It follows, therefore, that those conditions which give maximum yield of raffinate will be the same whether the stock is dewaxed before or after solvent refining (leaving out of account the factors affecting the dewaxing process) This introduces possible difficulties in the case of solvents such as SO_2, SO_2-benzole, chlorex, &c, in which the extract end of the system must be cooled to temperatures of about 30° F. to 60° F in order to produce high-gravity extracts and good yields of refined oil

The modified phenol process (with water injection into the extract) or the furfural process, for example, can both be applied to waxy as well as dewaxed feed stocks without difficulty, since these processes generally operate at temperatures above the set point of the waxy distillates obtainable from most crudes But in order to equal the yields obtainable with, say, the furfural process operating on waxy or dewaxed stocks at a minimum temperature of 130°F, it would be necessary for the final extract leaving, say, an Edeleanu plant to be chilled to about 30° F to 60° F, and these conditions would hardly be suitable for the treatment of waxy distillate with a set point of about 115° F In this case the temperature of the feed oil and of the raffinate stages of the system would probably have to be operated at 120° F to 140° F

The possibility of taking a primary extract from a treatment at 140° F, say, and chilling the primary extract phase to lower temperatures (say 30° F) does not appear to have been fully explored The raffinates obtained are known to be definitely waxy, but with the amount of solvent associated with the phase it is possible that no great practical difficulties would be experienced in pumping these materials

The quality of the raffinates produced either by treatment of a dewaxed base stock or by treatment of a waxy stock with subsequent dewaxing of the waxy raffinate appears to be the same, and Fig 41 shows that the same specific gravity-viscosity index curves hold for raffinates produced directly from dewaxed feed stocks and for dewaxed raffinates produced from waxy feed stocks

Production of High-quality Diesel Fuels

The production of high anti-knock gasolines for spark-ignition petrol engines has already been indicated in discussing the production of high aromatic extracts by low-temperature solvent treatment

For the production of high-grade, high-speed Diesel fuels solvent extraction is also likely to find extended application Woods [49, 1936] gives results for SO_2 batch treatment of two cracked Diesel fuels and states that 'solvent treating a cracked Diesel fuel (produced by cracking gas oil for naphtha production) offers a ready means of producing a high-grade Diesel index and low pour-point Diesel fuel, but large treating losses are a drawback to this method' In comment it must be said that the method of solvent treatment employed by Woods was one known to be inefficient in yields, and considerably higher yields could have been obtained by countercurrent operation with a temperature gradient (i e low-temperature extract outlet)

The effect of SO_2 treatment on a light straight-run distillate gas oil is shown in Fig 43 and has already been discussed in the section on correlation of plant and laboratory results above This work was, in fact, carried out for the production of a high-quality, high-speed Diesel fuel, and in Fig 42 the relation is plotted between specific gravity of the starting stock and of various raffinates and extracts obtained therefrom, and 'cetene number' on the Sunbury-Delft correlation scale [1, 1936]

The yield in this case was actually 65% (a corresponding treatment at 30° F. extract outlet temperatures increased

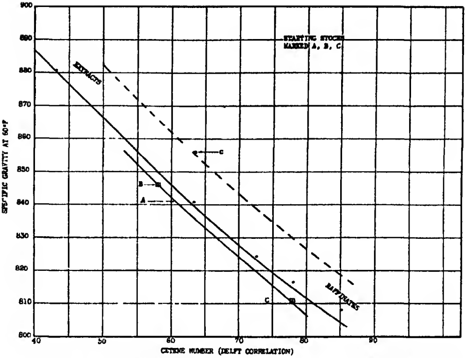


Fig 42 Relation between specific gravity at 60° F and cetene number for raffinates and extracts from gas-oil feed stocks tested in the C F R Diesel and Gardner 'L W' engines

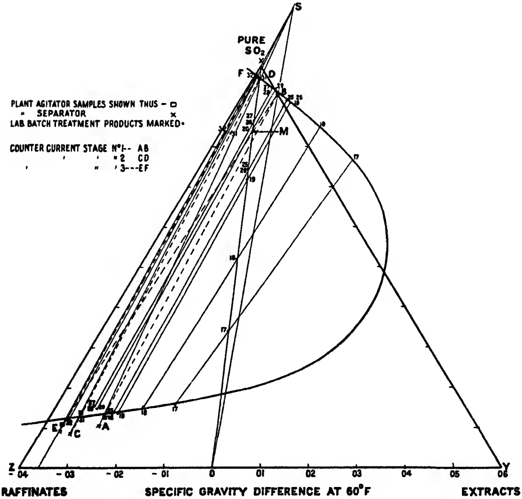


FIG. 43. Equilibrium curve for light gas oil and SO_2 at 60° F showing tie lines for actual plant stages

this yield to approximately 71% by volume on charge) While it must be admitted that the actual plant treatment in this case was heavy (500% SO_2 by volume), the finished product was of very high quality and was in fact specially prepared for use as a high ignition secondary standard for testing Diesel fuels generally

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GENERAL FACTORS AFFECTING SOLVENT-EXTRACTION PROCESSES

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DISTILLATION accomplishes the first separation of the extremely complex crude oil into fractions containing fewer chemical constituents. In the lowest boiling portions of the crude this process is capable of producing highly purified materials, such as propane or butane, but as the molecular weight of the distillate increases the chemical make-up of fractions even of extremely narrow boiling range rapidly becomes more complex. In those fractions containing lubricating oil, where the molecules contain upwards of 20 carbon atoms, the number of possible isomers is incalculably large and it is probable that the best distillation cut obtainable would still contain scores of individual chemical compounds.

The role of selective solvents in petroleum refining is to bring about a further separation of the compounds having much the same molecular weight and boiling-point and therefore being substantially inseparable by the process of distillation.

Character of Lubricating Oils

It has been stated that the chemical composition of a lubricating oil distillate (or residual) is extremely complex. Beyond this statement exact knowledge is lacking, and it is only possible to draw certain analogies between the known composition of petroleum fractions of low boiling range and the supposedly similar composition of those of high boiling ranges. On this basis it is to be presumed that lubricating oils are composed chiefly of hydrocarbons, of both chain and ring configurations. The straight-chain paraffin hydrocarbons of high molecular weight are of high melting-point (i.e. waxes), and are usually removed from lubricating oil at some stage in the refining process. It is probable, however, that the highly branched paraffins are liquid. Cyclic compounds are also presumably present and since little or nothing is actually known of their structure the cycles may contain almost any number of carbon atoms up to the total number present in the molecule and of course more than one cycle may be present in a single molecule.

Since chemical classification of lubricating oils is at present out of the question, it becomes necessary to classify them on the basis of physical properties. The two indices most commonly used are viscosity-gravity constant [4, 1928], and viscosity index [2, 1929].

The former index is based upon the relationship between specific gravity at 60° F. and Saybolt viscosity at either 210° F. or 100° F. Paraffinic oils, exhibiting a low specific gravity for a given viscosity, have low V.G.C. values, while naphthenic oils, with high specific gravities for a given viscosity, show a high V.G.C. Viscosity index, however, depends upon the rate with which viscosity changes with temperature and is usually determined from the viscosity at 210° F. and the viscosity at 100° F., although viscosities at other temperatures may be used. The numerical values in the two systems run in opposite directions, inasmuch as paraffinic oils, changing relatively slowly in viscosity with changing temperature, exhibit high V.I. values, whereas naphthenic oils, which change rapidly in viscosity with changing temperature, exhibit low V.I. values.

It is impossible to say which of these two indices is the more accurate as an expression of paraffinicity or naphthenicity. In one very important respect, however, the viscosity index is a more critical value than the viscosity gravity constant, inasmuch as the temperature-viscosity relationships of lubricating oils have a direct bearing upon their behaviour in use. Particularly with motor oils it is desirable that the lubricating oils have a sufficiently low viscosity at low temperatures to permit easy starting, yet it is necessary, in order to avoid metal to metal contact, that the viscosity at high temperatures be reasonably high. In expressing the results of solvent extraction, however, and especially in attempting to compare the relative efficiencies of several solvents, or to compare different procedures with the same solvent, it is much easier to express the quality of the oil fractions in terms of viscosity-gravity constant, because A.P.I. gravity may be determined readily and accurately, and the effect of small errors in viscosity upon the viscosity-gravity constant is not large. Viscosity index, on the other hand, demands extreme accuracy in viscosities, errors of the order of 0.2 sec. result in wide variations of viscosity index, particularly when the viscosity at 210° F. is 50 sec. or less. It is for this reason that most of this discussion is based upon viscosity gravity constant rather than viscosity index.

Qualitatively, the two indices give the same results in comparing the characteristics of lubricating oils, but close correlation is not found, and indeed is scarcely to be anticipated in view of the different bases of comparison. Fig. 1 indicates the degree of comparability, using the 'H' and 'L' series of oils upon which Dean and Davis based the V.I. system, and the five series of distillates which Hill and Coats used in the derivation of V.G.C. The V.I. values are, however, according to the modified Davis Lapeyrouse and Dean formula [1, 1932], which somewhat improved the values in the low viscosity ranges. That the V.I. values are still erratic, however, when the viscosity at 210° F. is below 55 sec. is shown by the solid symbols. It has been the experience of the writer that any conclusion based on V.I. values involving viscosities in this range should, to put it mildly, be viewed with some suspicion.

Among naturally occurring oils Pennsylvania has long been a standard of the paraffinic type, whereas Gulf Coastal oils represent the naphthenic type. Between these two extremes lie the vast number of mixed base crudes.

Before the advent of commercial extraction plants, coastal lubricating oils were characterized by the admittedly unfortunate properties of low viscosity index (rapid change of viscosity with temperature) and relatively poor resistance to oxidation, and the excellent characteristic of very low carbon-forming tendencies.

Oils of the Pennsylvania type, on the other hand, were of high viscosity index and good stability, but were inferior to coastal type oils in the matter of carbon deposition

Solvent refining, however, has made it possible to produce, from substantially any lubricating stock, an oil combining the desirable characteristics of both types

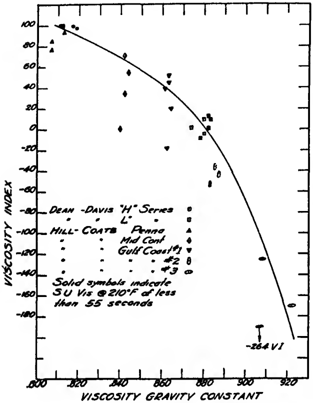

FIG 1 Comparison of two indices of paraffinicity

Definition of Selective Solvents

A very large number of organic compounds and a lesser number of inorganic compounds may be used as selective solvents for lubricating oils Their efficiencies, of course, vary over rather wide limits

Considering all materials which might be used as selective solvents they may be divided into the three following classes

1 Compounds which form one homogeneous phase with oil
2 Compounds which form two phases with oil but with substantially all the oil in one phase and none in the other
3 Compounds which form two phases with oil with substantial amounts of oil in each phase

The last group may be used as selective solvents

The matter of temperature in this connexion is, however, an extremely important one For example, di-ethyl ether, carbon tetrachloride or carbon di-sulphide would fall into the first class mentioned above at any ordinary temperature inasmuch as they are all completely miscible with oil, or in other words each has very high solvent power for oil It does not necessarily follow, however, that none of these materials would form two phases with oil if taken to some extremely low temperature Such temperatures are, for the time being, at any rate, not of particular interest

Similarly with the second class Water, methyl alcohol, or glycerine would be examples, inasmuch as when any of these compounds is mixed with oil very little of the oil dissolves in the solvent layer At some elevated temperature oil would presumably dissolve and then the material might be acting as a selective solvent The third class, then, includes those compounds which at some reasonable temperature form two layers with oil 'Reasonable temperature' may of course be only roughly and arbitrarily defined, say between the temperatures of −20° F and +400° F

A selective extraction, therefore, consists merely in mixing the selective solvent with the oil, providing intimate agitation (or heating and subsequently cooling), and then allowing the mixture to stand at a suitable temperature in order that the two phases may form layers, which are then separated The layer containing the major portion of the solvent, and usually consisting predominantly of solvent, is called the extract layer and contains dissolved in it the naphthenic portion of the oil The other layer, containing the major portion of the oil in which some solvent is dissolved, is known as the raffinate layer and the oil contained therein is the paraffinic oil

To complete the extraction the solvent is removed from each of the layers, usually by distillation The two solvent-free fractions are then known as extract and raffinate, respectively

History of Solvent Extraction

At this point it might be well to refer briefly to the history of solvent extraction in the petroleum industry Some 25 or 30 years ago kerosine was probably the most valuable single product of petroleum and, accordingly, the burning quality of kerosine was a matter of great importance Lazar Edelaneau found that if kerosine were brought into contact with liquid sulphur dioxide two layers were formed, and that furthermore certain constituents of the kerosine were dissolved in the layer which was primarily liquid sulphur dioxide After the separation of the two layers and removal of sulphur dioxide from each, the undissolved portion was found to burn much more satisfactorily than the original kerosine would have burned The process was found to be economically feasible and a number of commercial plants were installed This probably represents the first real application of solvent refining in the petroleum industry

Subsequently, other solvents were applied to various petroleum fractions The purpose was to remove constituents which occurred in small concentrations For example, gums or resins which were dissolved in gasolines or lubricating oils were extracted to remove some small amount of materials in order that subsequent finishing such as acid treatment or clay filtration would be rendered more satisfactory

It was apparently a long while, however, before it began to be realized that the extracts removed with various solvents were naphthenic in character, i e definitely more naphthenic than the original lubricating stock Even after this was clearly realized, it was still a considerable time before it was discovered that fractions of satisfactory lubricating properties could be recovered from Gulf Coast oils, and contrariwise, that naphthenic fractions could be recovered from Pennsylvania oils, leaving the Pennsylvania raffinate more paraffinic than it was originally

One explanation for this relatively slow development of the use of selective solvents is that sulphur dioxide, the first commercially used solvent, was scarcely capable, when used at low temperatures, of demonstrating the facts just set forth While it is perhaps the most selective of solvents, in that the fraction separated from a stock is very much more naphthenic than the stock itself, it is definitely low in solvent power, i e having removed by means of sulphur dioxide a certain small fraction from the oil the remainder is less soluble in sulphur dioxide, and only by the use of comparatively large amounts of this solvent at low temperatures can any considerable portion of a lubricating stock (unless the stock be very naphthenic in character) be removed Several of the other solvents, however, possess much higher solvent power at convenient working temperatures, i e it is possible to remove easily from a given stock almost any desired proportion Of course, it was only after the removal of a very large proportion of Gulf Coast stock that the remainder was found to exhibit the characteristics of Pennsylvania lubricating oil

Necessary Properties of a Commercial Solvent

As developed above, almost any material which will form two layers with lubricating oils at some reasonable temperature and which will dissolve a portion of the oil, leaving the remainder undissolved, can be considered to be a selective solvent, but only relatively few of these can be employed successfully for that purpose To be valuable commercially the solvent must be capable of producing the desired fractions from the lubricating stock at hand at a reasonable cost In general, the highest possible yield of the paraffinic product is desired, and the amount of solvent required should be a minimum The solvent then must fulfil the following requirements

1. Stable chemically under any conditions encountered in any of the steps of the process, or in storage
2. Capable of effecting a sharp separation between paraffinic and naphthenic constituents
3. Of sufficiently high solvent power that a given separation may be effected with a reasonably small amount of solvent
4. Easily and completely separable from the lubricating stock employed by a feasible method such as distillation

Many otherwise interesting solvents must, of course, be eliminated from consideration on the basis of instability The solvents employed are usually many times as expensive as the oil, hence, if any reaction occurs between solvent and oil the cost of the solvent thus destroyed is prohibitively high Likewise if the boiling-point of the solvent be as high or nearly as high as that of some of the constituents in the lubricating oil, separation by distillation is manifestly impossible There are, of course, other methods of separation such as crystallization or salting out by the addition of another solvent, but at present no such method seems to be commercially competitive with distillation

Another requirement is that the cost of the solvent be reasonably low, but such statements must necessarily be qualified because in the first place if losses in process are kept at a very low figure, and they may be, the price of the solvent is more a matter of capital expenditure than operating cost Very high efficiency on the part of the solvents, therefore, may justify the use of an expensive solvent. Furthermore, the current cost of any given material must, unless it be low, be taken as only tentative, inasmuch as many hitherto costly materials have been manufactured very cheaply once a sizeable outlet has been found

The solvents which will be discussed below are substantially non-reactive and may be separated from lubricating stocks by distillation The comparisons, therefore, will be principally upon the basis of items 2 and 3 above, which are closely inter-related It is obviously desirable to secure the maximum possible yields of the desired products from any lubricating stock which is processed, but the major cost of solvent extraction consists of the cost of distillation of solvents and the cost of the solvent lost Hence, it is of importance to effect the desired separation with as small a quantity of solvent as possible High yields can in some cases balance the cost of using a larger volume of solvent and, conversely, if a separation can be effected by the use of a small amount of solvent lower yields may well be tolerated Which of these two alternatives is to be chosen will rest largely upon whether or not there is an excess of the lubricating stocks available

Quality as used above refers to the measure of paraffinicity such as V I or V G C, but, as will be developed more fully, there are certain differences in raffinates of the same paraffinicity obtained from a given stock with different solvents One difference outstanding, which is an important matter to the refiner, is the concentration of colour bodies, inasmuch as the majority of oils which are solvent refined must meet colour specifications, and it is obviously desirable to remove as much colour in the solvent extraction as possible, in order that the finishing cost may be minimized

The various methods of applying solvents to lubricating stocks (batch, multiple batch, stage countercurrent or pseudo-countercurrent and continuous countercurrent) will be discussed more fully in the section which deals with theoretical considerations While all commercial installations employ multiple stage countercurrent or continuous countercurrent, batch extractions are obviously easier to carry out in the laboratory, and for that reason much of the data presented below is for batch treatments The differences in results obtained by the various modes of application are pointed out, but wherever conclusions are drawn from batch treatments, the same findings would result from countercurrent extractions

Temperature of Miscibility

Since two phases are necessary in solvent extraction, miscibility relationships are the first point to be considered. Fig 2 presents miscibility curves for a number of selective solvents with a given stock It is obviously necessary to carry out the extraction at temperatures below the miscibility temperature for the mixture of stock and solvent which is being employed This temperature will, as shown on Fig 2, vary considerably for different solvents Thus, with this particular stock, pyridine with equal volumes of solvent and stock could not be employed above 42° F Cellosolve, however, could be used at 130° F and furfuryl alcohol would give a separation at 300° F

The miscibility temperatures with a given solvent also vary with the characteristics of the stock (Fig 3) With stocks of a given degree of paraffinicity the miscibility temperature increases as the molecular weight increases With stocks of given molecular weight, the miscibility temperature increases as the paraffinicity increases, that is, as the value of the viscosity gravity constant decreases or the value of the viscosity index increases

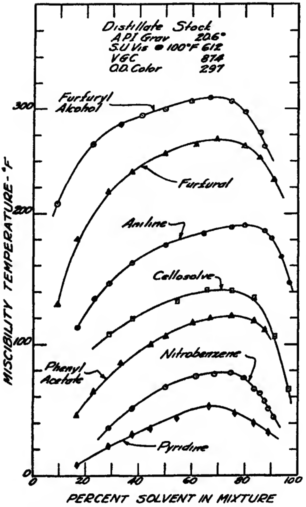

Fig 2 Miscibility curves (one stock, several solvents)

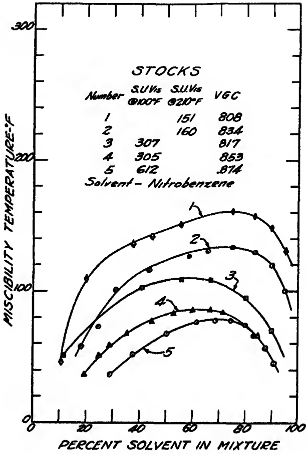

Fig 3 Miscibility curves (one solvent, several stocks)

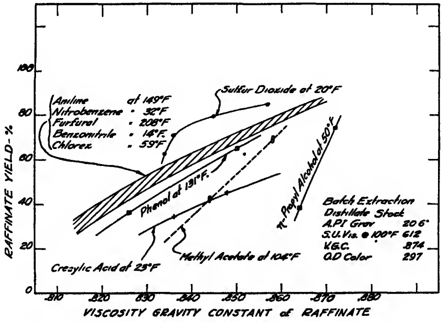

Fig 4 Raffinate yield

Representation of Extraction Results

As stated in a previous contribution, ternary diagrams contain substantially the whole story of solvent extraction They are therefore of very great value in analysing the performance of extractions and particularly in predicting the results of multiple or countercurrent extraction when only batch data are available, or in estimating, without the necessity of actual experiment, the result of modifications in the extraction process, such as various types of recycling, the use of temperature gradients, and the like But for the very reason that they compress so much information into a small space, it is not easy to consider one factor at a time by the use of such diagrams For that reason the remainder of the discussion will be confined to consideration of simpler charts presenting fewer variables

Factors Affecting Yield

As already indicated, other factors may be more important, when everything is reduced to the basis of a cost analysis, than yield But cost analyses are complicated affairs and yields are simple figures, so that, justly or unjustly, yields frequently come in for first consideration and on that basis they will be accorded first treatment here

In Fig 4 the yield of raffinate is plotted against the viscosity gravity constant of raffinate using a number of solvents on the same stock Sulphur dioxide stands out as resulting in the highest yields But the downward trend of the curve at about 0 835 V G C indicates that more paraffinic material could be obtained only with great difficulty, if at all Sulphur dioxide is unquestionably highly selective in the removal of those compounds which it is capable of dissolving This may be due to a peculiarity of structure of sulphur dioxide or it may be largely attributable to the fact that miscibility temperatures of sulphur dioxide and oil are usually high, or to the fact that it is employed at a relatively low temperature that is far below its miscibility temperature, which condition is favourable to maximum yields of raffinate of a given quality

The yields obtained with five solvents, namely aniline, nitrobenzene, furfural, benzonitrile, and chlorex, are so nearly similar that all the points fall within the band indicated The selectivity of these solvents may be classed as good Phenol and cresylic acid, however, show relatively lower selectivity, as also does methyl acetate Normal propyl alcohol is a definitely non-selective solvent, at least in so far as separation, as indicated by V G C, is concerned It should be noted that in Fig 4 each of the solvents is used at a temperature where the yields obtained are reasonably close to the maximum which the particular solvent will give It is to be concluded, then, that a number of solvents have the power of effecting a sharp separation between naphthenic and paraffinic constituents Some, however, are definitely non-selective

The data presented in Fig 4 were obtained by batch extractions That is, each point represented the result of mixing the stock oil with the solvent, separating the two layers and removing solvents from each There are a great many other methods of applying the solvents, but notice should be taken here of three They are

(1) **Multiple extraction.** The raffinate from a batch extraction is again treated with fresh solvent without removing from the raffinate the solvent which it contains after the first extraction This procedure may be continued as many times as desired In other words, instead of applying all of the solvent at once it is applied in increments

(2) **Batch countercurrent** Several extracting vessels are employed with separations being effected in each The raffinate and extract layers are transferred—in opposite directions—from one treater to another The result is that each batch of solvent is employed as many times as there are treaters in the system, initially upon the raffinate which has already been several times treated and is about to be removed, finally upon the fresh incoming stock

(3) **Continuous countercurrent** Solvent and stock pass countercurrently through a tube or tower treater Settling chambers are provided at each end to allow the phases to separate With a tube of any considerable length, this type of treatment may, theoretically, be considered to be equivalent to a very large number of stages, inasmuch as the composition of both the extract phase and the raffinate phase at any point in the tower differs from the composition at any other point Actually, however, the number of batch countercurrent stages to which a continuous countercurrent tower is equivalent depends upon much the same factors as those which govern the height of the equivalent theoretical place in a distillation fractionating tower That is, the efficiency of a countercurrent solvent extraction tower will depend upon the degree of contact between the two phases

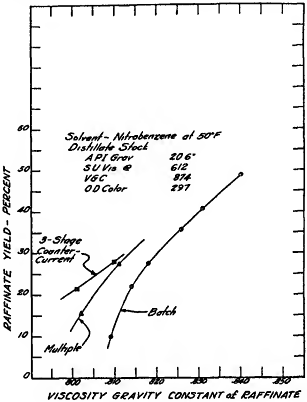

FIG 5 Effect of type of extraction on yield

Both multiple and batch countercurrent extraction produce higher yields of a raffinate of a given quality from a given stock than does batch extraction at the same temperature with the same solvent This is demonstrated in Fig 5. It will be noted that the differences become larger as the quality of the raffinate becomes higher Except in special cases, therefore, all commercial installations operate either on the batch countercurrent or the continuous countercurrent principal.

The temperature of extraction is a factor which may very readily be controlled, and therefore it is of first importance to study the effect of variations of temperature Fig 6 presents several pairs of points obtained in batch extractions of the same stock used for Fig 4, where the batch extractions were carried out at different temperatures The two points are connected in each case by a line and the temperature of extraction is indicated at each point The amount of solvent used in each of the extractions is indicated along the line It will be noted that raising the temperature of extraction very definitely lowers the yield of a raffinate of given quality With a given volume of a given solvent, however, the quality of the raffinate which will be obtained does not vary markedly

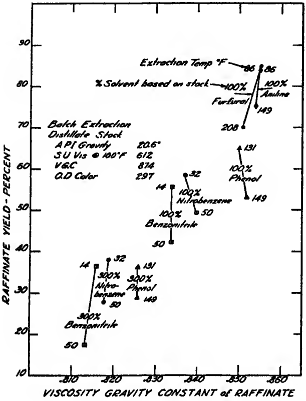

FIG 6 Effect of extraction temperature on yield

Figure 7 presents a larger amount of data on each of two stocks, the lower set of curves being for batch extraction and the upper set for three-stage countercurrent extraction Again, it is clear that the best yields of a given product are obtainable at lower temperatures of extraction

Summing up the factors which affect yields

1. The maximum yield obtainable is to some extent controlled by the chemical composition of the solvent, but a number of solvents are sufficiently selective to give satisfactorily high yields
2. Stage countercurrent (or continuous countercurrent) extraction will improve the yields obtainable with batch or multiple extraction This is applicable to any solvent.
3. Yields of raffinate of a given quality vary with temperature of extraction, the highest yields resulting from low temperatures of extraction.

Amounts of Solvent Required

Any discussion of selective solvents is apt to contain, oft repeated, the two words 'selectivity' and 'solvent power', but unfortunately they are not always used with the same meaning The present author has no desire to correct the usages of others or to propose his own usage as the only correct one It is necessary, however, to digress long enough to make clear in exactly what manner the two words are employed herein

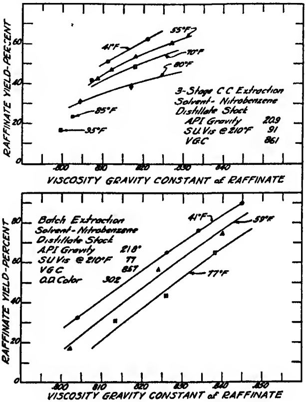

FIG 7 Effect of extraction temperature on yield

A solvent which exhibits high selectivity is capable of effecting a sharp separation between the naphthenic and paraffinic constituents of the lubricating stock to which it is applied That, of course, means that the yield of a raffinate of a given quality is high On that basis one may say that a given solvent is highly selective only if certain reservations are kept in mind For example, nitrobenzene and furfural are certainly highly selective solvents, *if employed at the proper temperatures* At sufficiently high temperatures, however, the yields of raffinate of given quality would suffer sufficiently that neither, at those temperatures, could be called highly selective On the other hand, isobutyl alcohol and propyl alcohol are capable of effecting but very little separation between the two classes of constituents at any temperature and therefore are unquestionably non-selective Every solvent has a maximum selectivity for oils of a particular V.G.C range which varies with the temperature of extraction. A solvent of high selectivity, then, is capable of effecting a good separation at some temperature, a solvent of poor selectivity is incapable of accomplishing that at any temperature

Solvent power, however, is the ability of a solvent to dissolve a relatively large quantity of oil regardless of the quality of the oil dissolved Benzene certainly possesses very high solvent powers for oils Whether or not it is selective is beyond the point Glycerin possesses substantially no solvent power for oil Among those materials which may be used as selective solvents there is an extremely wide variation in this property of solvent power

This is illustrated by Fig 8, where the data used resulted from the same experiments as those of Fig 4, which showed that five solvents at different temperatures gave very similar yields of raffinate The amounts of solvent which it was necessary to employ to obtain these yields, however, varied over wide limits For example (Fig 8), to obtain 0 823 V G C raffinate, nitrobenzene or benzonitrile required about 200% solvent (that is, two volumes solvent per volume stock) furfural and chlorex about 400%, and aniline 550%. These figures, it will be recalled, are for batch extraction Phenol and cresylic acid, which showed in Fig 4 relatively low selectivity, exhibit, however, solvent power much better than furfural, chlorex, or aniline Sulphur dioxide, which exhibited very high selectivity, is extremely low in solvent power inasmuch as it required 1,000% of sulphur dioxide to effect the same improvement in qualities which can be obtained with about 100% of nitrobenzene or benzonitrile at similar temperatures

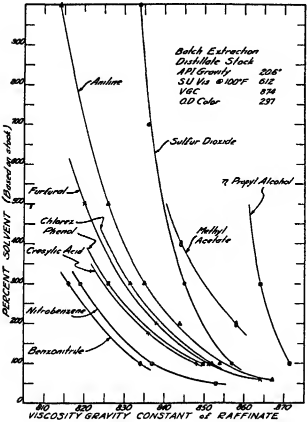

FIG 8 Amount of solvent required

Re-examination of Fig 6 will show the effect of temperature on solvent power when a given quality stock is being treated For example, when 100% benzonitrile was applied to 0 874 V G C. stock about 44% of material was removed in the extract (at 14° F.) When, however, the same amount of benzonitrile was applied at 50° F. about 58% of material was removed, but the quality of the raffinate was the same in the two instances, therefore, while the solvent power was greater at the high temperature, the solvent power increased at the expense of selectivity This will be found true for the other solvents used on this stock and is shown on Fig 6

Fig 9 (same extractions as those of Fig 7) shows that for batch extractions with nitrobenzene the quality obtained is but slightly affected by the temperature of extraction. For moderate improvement in quality this is also true of countercurrent extraction, but for the production of raffinates of high quality, increase in extraction temperature results in better quality It should be noted carefully, however, that the matter of yields, that is, selectivity, does not enter into Fig 9, and, as just pointed out, increase in solvent power, with a given type of extraction, is usually at the expense of selectivity

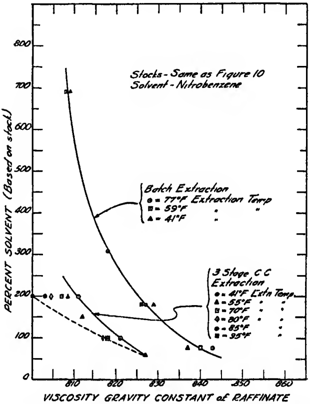

FIG 9 Effect of extraction temperature on amount of solvent required

As would be anticipated, the application of a solvent in multiple or countercurrent manner, rather than batch, allows an improvement in the solvent power This is illustrated for nitrobenzene in Fig 10, but the data would be similar for other solvents The percentage improvement in solvent power which can be effected by using countercurrent extraction instead of batch is much the same for all solvents That is, while the amount of aniline or sulphur dioxide required to produce a given quality would be reduced by countercurrent extraction, neither the aniline nor the sulphur dioxide countercurrent curves would approach the nitrobenzene curves of Fig 10 In other words, if Fig 8 were reconstructed on the basis of countercurrent extractions instead of batch extractions the result would be to lower all the curves but not to bring them together.

Summarizing

1. Solvent power seems to be largely a function of the chemical nature of the solvent
2. Solvent power may be increased by increasing the extraction temperature, but only at the expense of selectivity

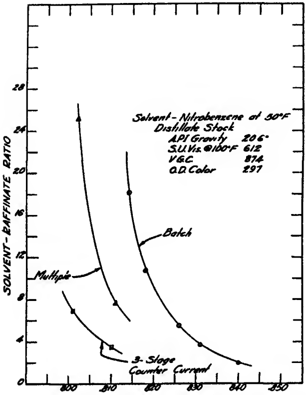

FIG 10 Effect of type of extraction on amount of solvent required

Solvent-Raffinate Ratio

Broadly speaking, the expense of solvent extraction may be split into two items first, the loss in value of that portion of the lubricating stock which is extracted out as naphthenic material and is probably used as fuel oil or cracking stock instead of lubricating oil, and secondly, the cost of the refrigeration, steam, &c, involved in the heating, cooling, and handling of the solvent oil mixtures and in the redistillation of the solvent itself The item of distillation of solvent is a very large one, therefore, other things being equal, the cost of a solvent extraction is very largely a matter of the amount of solvent employed

The two factors of yield and amount of solvent involved can be very conveniently expressed by the 'solvent-raffinate ratio' which is merely the volumes of solvent employed divided by the volume of raffinate produced It expresses the gallons of solvent which it is necessary to cycle through the plant and redistill in order to produce one gallon of raffinate Fig 11 plots the solvent-raffinate ratio against the V G C of the raffinate for the same extractions represented by Figs 4 and 8 The first thing to be noted is that once more five solvents fall rather closely together in a band, but they are not the same five solvents which fell together in Fig 4, wherein yield, representing selectivity, was plotted against V.G C Nitrobenzene and benzonitrile, inasmuch as they exhibited good selectivity and good solvent power as well, i e were capable of producing high yields of raffinate when only relatively small amounts of solvent were used, fall together considerably below the band, being replaced by phenol and cresylic acid On a yield basis these two last-named solvents were somewhat low, but their high solvent power places them, on the solvent-raffinate ratio basis, with those solvents which showed better selectivity but low solvent power, namely aniline, chlorex, and furfural It will be noted that the very low solvent power of sulphur dioxide has more than offset its high selectivity

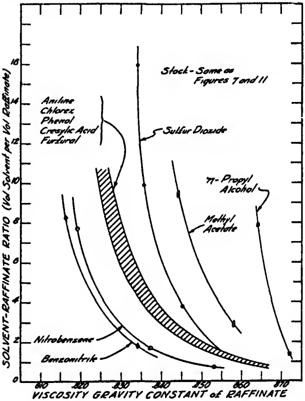

FIG 11 Solvent-raffinate ratio

Inasmuch as countercurrent extraction results in better values both of selectivity and solvent power than does batch or multiple extraction, it is not surprising that low values of the solvent-raffinate ratio are encountered with countercurrent extraction as compared with batch (Fig 12) Once more, however, it should be pointed out that the proportionate change from batch to countercurrent is similar for all solvents In other words, Fig 11 on a countercurrent basis would indicate the same findings pointed out above, but all of the solvent-raffinate ratio values would be decreased

Figure 13 presents solvent-raffinate ratio values obtained at various temperatures, using the same data as that shown in Figs 7 and 9 The upper curve is for 3-stage countercurrent extraction, while the lower curve is for batch extraction It will be noted that there seems little to choose between the various temperatures, that is, the gain in solvent power brought about by raising the temperature has been substantially neutralized by the loss of selectivity If one refers back to Fig 7, however, it will be noted that the yields suffered very badly at 80° F., for example, as compared to 55° F , so that, even though the solvent-raffinate ratio was not markedly changed, one would seldom, if ever, operate on this stock at 80° F , but would choose some temperature probably not above 55° F

It must be emphasized, however, that this independence of solvent raffinate ratio on temperature holds only for *reasonable* temperatures If extractions be carried out too close to the miscibility temperatures of the mixtures involved, then the selectivity, instead of being slowly decreased, is well-nigh destroyed, yields of high-quality raffinate become very small or it becomes impossible to separate highly paraffinic fractions, and, naturally, the solvent-raffinate ratios approach infinity

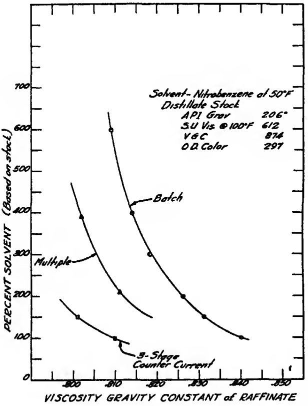

FIG 12 Effect of type of extraction on solvent-raffinate ratio

It seems fair to say that selective solvents may be compared most accurately upon the basis of their respective solvent-raffinate ratios when producing raffinate of a given quality from a given stock with a given type of extraction Solvent-raffinate ratio is dependent upon both selectivity and solvent power It has been brought out that selectivity varies with temperature, becoming better at low temperatures Solvent power may be varied by varying the temperature, but selectivity is affected If such temperatures of operation be chosen for various solvents that the yields are reasonably high in each case, the amount of solvent then required appears to depend largely upon the chemical composition of the solvent If, then, various solvents are used under such temperature conditions that the yields will be satisfactorily high, the amount of solvent used and, therefore, the value of the solvent-raffinate ratio, will depend very largely upon the chemical composition of the solvents, and cannot be varied to any considerable extent

If the solvent-raffinate ratio is to be low, solvent power

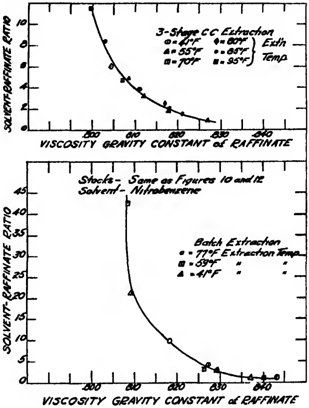

FIG 13 Effect of temperature on solvent-raffinate ratio

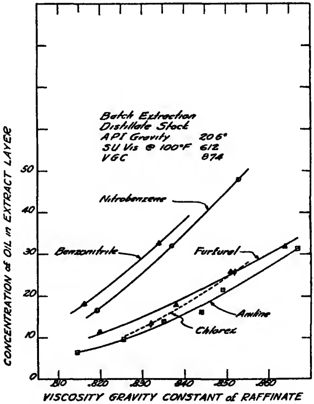

FIG 14 Concentration of oil in extract layer when selectivity is high

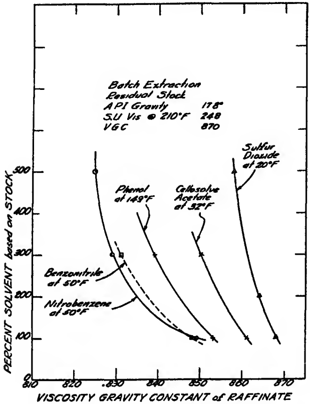

FIG 15 Action of solvents on residual stocks

must be high, and selectivity good It has been pointed out that solvent power may be increased by raising the temperature of extraction, but that selectivity is cut down High solvent power obviously connotes a high concentration of oil in the extract layer, and a consideration of the information presented above leads to the conclusion that, for each solvent (with a given type of extraction) there is a fairly definite upper limit of oil concentration in the extract layer *above* which selectivity is poor This limit appears to depend upon the nature of the solvent Fig 14 shows the concentration of oil in the extract layer for the five solvents which, in Fig 4, showed substantially the same selectivity Again, while these are batch extractions, countercurrent operation would merely increase all the concentrations to a roughly proportional extent

Extraction of Residual Stocks

The comparisons thus far have been on the basis of distillate stocks This is partly because more data were available, but largely because it is difficult to apply many of the solvents mentioned to residual stock. Sometimes this is because the specific gravity differential, between the raffinate and extract phase respectively, is so low that separation of the phases is either impossible or very difficult. Part of the difficulty, however, seems to lie in the fact that a number of solvents, while perfectly capable of extracting the naphthenic constituents from clean distillates, are markedly deficient in solvent power when applied to residual stocks This is illustrated by comparing Fig 15 with Fig 8 For example, while 300% of sulphur dioxide was capable of reducing the viscosity-gravity constant of the distillate from 0 874 to 0 845, a similar amount applied to the residual stock (Fig 15) reduced the V G C only from 0 870 to 0 862 Similarly, 300% of phenol on the distillate (Fig 8) yielded a raffinate of 0 826 V G C, but with the residual stock the raffinate was reduced only to 0 839 Benzonitrile and nitrobenzene, solvents which exhibited high solvent power on the distillate, are capable, however, of effecting considerably greater reductions in viscosity-gravity constant of the residual stock as seen in Fig 15

Colour Removal

If solvent extraction of lubricating stocks, with the resultant degradation in value of part of the stock, is to be anything but a costly process for producing high quality, it must do more than merely remove the naphthenic constituents The one apparent way in which solvent extraction can, as it were, pay for itself, is to reduce the normal cost of finishing stocks by removing a large part of the colour bodies from the stock together with the naphthenic constituents In their ability to remove colour, solvents differ more strikingly than perhaps in any other respect This is demonstrated by Fig 16, the stock being the same distillate employed for many of the experiments previously referred to It will be noted that nitrobenzene reduces the optical density colour [3, 1934] from about 300 to about 40, i e to about 13% of its original value Phenol and furfural reduce approximately to 30%, while sulphur dioxide stops at about 60% Isobutyl alcohol and methyl acetate, on the other hand, have actually concentrated the

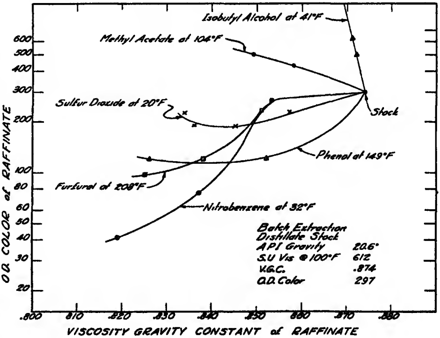

FIG 16 Colour removal from distillate stocks.

colour in the raffinate If one is to place confidence in the ancient dictum that like dissolves like, it would appear that the majority of colour bodies in petroleum products are cyclic in character, for it will be noted that the three materials which remove considerable colour in Fig 19 are cyclic, whereas the two which do not remove colour are of chain structure

Extracting colour from residual stocks is still more difficult as illustrated in Fig 17 Nitrobenzene is still capable of reducing the colour to about 30% of its original value, and benzonitrile is nearly as good, but phenol is considerably poorer, while sulphur dioxide and methyl acetate are practically incapable of extracting colour

In one respect it may be said that the colour of a raffinate is a matter of more concern to the refiner than the colour of an ordinary raw lubricating stock, inasmuch as the cost of the raffinate has been increased by the solvent extraction which has been applied to it and, the more colour to be removed, the more of the costly raffinate is to be lost before the oil is finished

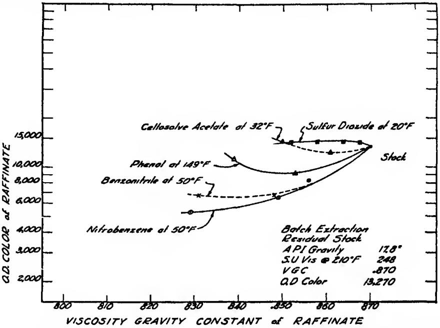

Fig 17 Colour removal from residual stocks 'O D Colour' — 1 000 log(1/T), where T is the optical transmission of a 1 mm layer of the oil for light of 530 millimicrons wave-length Such colours are additive with respect to volumes and may be taken as proportional to the concentration of 'colouring matter

Sulphur Removal

Among other things removed by selective solvents from lubricating oils are the sulphur compounds, and in this respect most solvents act similarly In fact, as Fig 18 shows, if the V G C of the raffinates be plotted against their sulphur content, for a considerable number of solvents applied to the same stock, the points fall in a band which is relatively narrow Perhaps this means that the sulphur compounds present in lubricating oils are of different structure from the colour bodies, since they are removed by either cyclic or chain solvents If this line of reasoning be pursued farther (which may well be too far!), the indications are that the naphthenic constituents (i e compounds of high V G C and low V I) are not of cyclic character alone, but include molecules of chain configuration

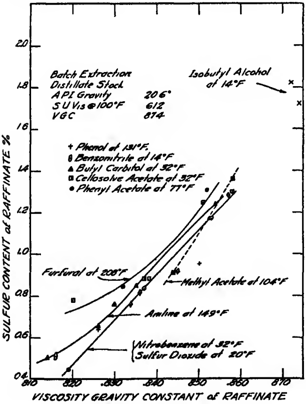

Fig 18 Sulphur removal by solvents

Effect of Extraction on Viscosity

It is somewhat surprising to find that so many diverse compounds act similarly in removing naphthenic constituents from lubricating oils They do not, however, effect the reduction of naphthenicity in precisely the same manner This may be illustrated by Fig 19, where the viscosity of the raffinate, using a number of solvents, on the same distillate, are plotted against the V G C of the raffinate The open characters represent raffinates which were obtained by cyclic compounds, whereas the solid ones represent raffinates obtained by non-cyclic solvents The tendency, apparently, is for cyclic compounds to effect a greater reduction in viscosity, for a given reduction in V G C, than that effected by non-cyclic compounds

This tendency is more strikingly shown in Fig 20, where the stock extracted was a residual stock In this case some of the cyclic compounds were able to reduce viscosity from 278 to slightly over 140, whereas sulphur dioxide, cellosolve acetate, and methyl acetate scarcely affected it, in fact, in some cases the raffinate was more viscous than was the stock

Effect of Wax in Solvent Extraction

The wax contained in various lubricating stocks has very

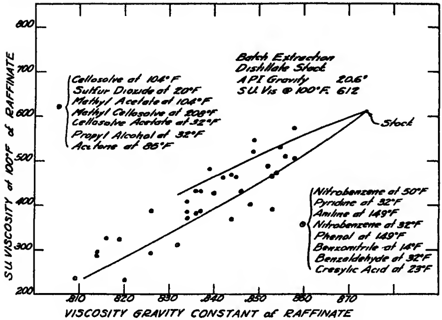

FIG. 19. Effect of extraction on the viscosity of distillates.

little effect on the operation of solvent extraction. If the wax concentration be excessively high, and if the extraction be carried out at low temperatures, the amount of solid wax may be sufficient to introduce some mechanical difficulty in the separation of the layers, but it appears to have little influence on the equilibrium between extract and raffinate phases. In any event, whether the extraction be carried out at such a temperature that the wax is liquid, or at such a temperature that the wax is for the most part solid, the wax is concentrated in the raffinate fraction with the result that the pour-point of the raffinate is usually higher than that of the stock. The wax must be removed from the raffinate before the oil is, for most purposes, marketable, but this may be done by conventional methods. The operation of most of the well-known dewaxing processes seems to be little affected, if at all, by solvent extraction, although it is usually easier to dewax the refined oil than the original stock, particularly in the case of residual stocks.

Dewaxing may, of course, be carried out before solvent extraction, and if the predewaxing be sufficiently complete it is obvious that no subsequent dewaxing of the raffinate is necessary. In general, if a stock be dewaxed before solvent extraction to 0 or −10 A.S.T.M. pour, there will be experienced little if any increase in pour in the raffinate. If, on the other hand, predewaxing be carried only to about 30 pour, a noticeable rise in the pour of the raffinate is usually found.

Whether dewaxing is to be carried out before or after solvent extraction is in the final analysis dependent upon economic factors. If dewaxing be accomplished after solvent extraction there is a smaller charge to the dewaxing plant but, on the other hand, the amount of wax which has to be removed is substantially the same as if the stock were charged. If the stock be dewaxed before solvent extraction, the oil which is lost to the wax is of stock value, whereas if the raffinate be dewaxed, the oil lost to the wax, which is in general of the same amount as that which would be lost if the stock were dewaxed, is now more costly than the stock inasmuch as the expense of solvent extraction has been added to it.

Effect of Variation in Stock

Variations in the properties of stocks charged to solvent extraction plants result in variations in yield which, qualitatively at any rate, are precisely those which would be anticipated. It would be expected that a stock of 0.830 V.G.C. would yield more material of 0.810 V.G.C. than would a stock of 0.860 V.G.C., and this is the case. This type of prediction is, however, only approximate inasmuch as it cannot be assumed that the chemical make-up of two stocks are identical merely because their boiling ranges and V.G.C. values are identical. The vast majority of stocks are, however, made up along much the same lines. A coastal stock contains constituents varying from extremely paraffinic to extremely naphthenic, and the proportion of those materials present increases from paraffinic to naphthenic, whereas a Pennsylvania stock, while containing much the same type of material, contains more paraffinic, intermediate quantities of semi-paraffinic, and small quantities of naphthenic material. There do occur,

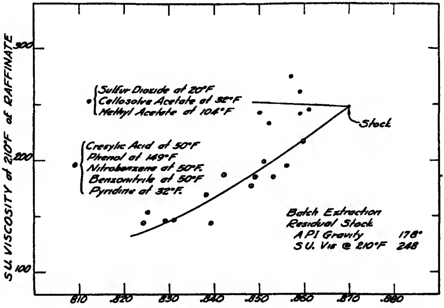

FIG. 20. Effect of extraction on the viscosity of residual stocks.

however, 'trick' stocks which give surprisingly high yields of paraffinic oils in view of their V G C These stocks appear to be made up of considerable quantities of paraffinic materials, together with considerable quantities of extremely naphthenic materials, resulting in a rather high V G C The constituents in a stock of this character, however, may be very readily and easily separated

Mixed Solvents

The discussion so far has been confined to extraction with single solvents It has been brought out that the number of these is large, although their excellence is by no means the same It follows, therefore, that there are a large number of mixed solvents possible

No effort will be made to cover the field of mixed solvents exhaustively Notice will be taken, however, of several types of mixed solvents, although it should be emphasized that the author does not insist that all mixed solvents can be embraced in the types which he discusses, nor indeed does he insist that his classifications are necessarily entirely accurate Since no data will be presented, the remarks must be taken solely as the opinion of the author, particularly if they seem in any respect to disagree with the statements of those particularly concerned with mixed solvent processes, upon which separate papers will be found

Class I. Mixtures of Two Selective Solvents

Materials which are themselves selective solvents may be mixed and used together provided there is no reaction between the solvents The results of such mixing (or at any rate most of the results) are in accord with what one would expect For example, if aniline be admixed with nitrobenzene, and the mixture used as a selective solvent, the normal extraction temperature will be raised to a point somewhere between that for nitrobenzene alone and that for aniline alone The amount of solvent required to effect a given separation will be more than that required with nitrobenzene alone but less than that required with aniline alone

Class II. Mixtures of Selective and Non-selective Solvents.

It was pointed out above that it is substantially impossible to say that any given material cannot, under some set of conditions, be used as a selective solvent One does not ordinarily think, however, of methyl alcohol as a selective solvent, inasmuch as it dissolves little or no lubricating oil, and, on the other hand, since benzene dissolves all constituents of oil, one does not consider it a selective solvent Either one of these, however, may be used in combination with numerous materials which are selective solvents in the ordinary sense of the word, with reasonably good results For example, if a given selective solvent operates at an extremely low temperature and if it is desired to raise that extraction temperature, that may be accomplished by using methyl alcohol in admixture with the selective solvent Again this is what one would expect, inasmuch as the miscibility temperature between oil and methyl alcohol is very high Similarly, or perhaps one should say contrariwise, benzene may be admixed with solvents of the character of SO_2 It has been brought out that SO_2 is notably deficient in solvent power, and is incapable of dissolving out those materials of intermediate V G C which it is necessary to remove in order to leave a raffinate of high quality When benzene is mixed with SO_2, solvent power is, as one would expect, increased, and extraction can, with this mixture, be carried far beyond the point where SO_2 alone at usual temperatures and pressures would go

Class III. Selective Solvents plus Low-boiling Paraffins.

Extraction with most recognized selective solvents can be carried out in the presence of low-boiling paraffin hydrocarbons such as propane, butane, or low-boiling naphthas This combination process has been referred to as a double solvent in the sense that the selective solvent such as nitrobenzene or cresylic acid is considered a solvent for naphthenic material, whereas the paraffinic material (propane, &c) is considered as a solvent for paraffinic material Excellent yields of paraffinic material can be obtained by the use of this type of mixed solvent

Colour removal from residual stocks is also excellent with this type of mixed solvent It would seem that the action of paraffinic constituents when used with selective solvents and applied to residual stocks is largely one of colour precipitation, inasmuch as the amounts used in admixture with a selective solvent are of the same order as those amounts required for direct colour precipitation, i e four volumes or more per volume of stock

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REFINING KEROSINES BY EXTRACTION WITH LIQUID SULPHUR DIOXIDE—THE EDELEANU PROCESS

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THE process for the refining of kerosines and similar light distillates with liquid sulphur dioxide was introduced and developed by Dr Edeleanu, the basic principles being described in a paper to the International Petroleum Congress in 1907 [12]

Investigating the reason for the poor burning qualities of Roumanian kerosine distillates he was able to attribute this to the relatively high proportion of aromatic (and unsaturated) hydrocarbons present Reduction in the aromatic content by sulphuric acid treatment necessitated excessive quantities of acid, very high refining losses, and the disposal of large amounts of acid tar Edeleanu found that, of a variety of solvents tried, liquid sulphur dioxide showed a remarkably high solvent action for aromatic and unsaturated hydrocarbons, while paraffins and napthenes were practically insoluble A process was therefore devised for the extraction of kerosine distillates with liquid sulphur dioxide [9, 1908–13] It was found to be successful as a refining process on a small scale in 1909 at the Vega refinery in Roumania, and was eventually extended to large-scale plant operation The first commercial plant was erected shortly afterwards, using a batch process Its success led to the gradual adoption of this process for the treatment of kerosine stocks from a variety of different crudes, the aromatic content of which depreciated the value of the kerosine as an illuminating oil Continuous operation was first adopted in a commercial installation in 1924, and in 1930, in illustration of the progress made, the Union Oil Company of California put into operation an Edeleanu plant with a maximum throughput of 7,000 bbl per day of Californian kerosine distillate [23, 1930]

The Edeleanu process for the selective solvent refining of light distillates has been successfully extended to the treatment of lubricating oil stocks, using in particular the double solvent sulphur dioxide-benzene, and was the forerunner of the multiplicity of solvent refining processes now in operation or under development

General Considerations

The selective solvent action of liquid sulphur dioxide (commonly referred to as liquid SO_2, or 'SO_2') is entirely analogous to that of other selective solvents utilized in lubricating oil manufacture The relatively low solubility of high molecular weight hydrocarbons in liquid SO_2 necessitates the use of higher temperatures or the addition of benzole for treating heavy (lube oil) stocks The solvent power, high volatility (simplifying the recovery of solvent from the kerosine), high specific gravity, and low viscosity (facilitating phase separation) of liquid sulphur dioxide make it an ideal solvent for kerosine refining

Addition of liquid sulphur dioxide to a normal kerosine stock leads to the separation of an SO_2-extract phase (lower layer) when the concentration exceeds 10–15% Further addition of SO_2 increases the volume of this phase, and with 100% of solvent present (by volume) it will contain 10–20% of extracted hydrocarbons and have a density of 1 3–1 4 The raffinate phase (upper layer) under these conditions contains 10–15% SO_2 and has a density of approximately 0 9 Owing to the low solubility of the saturated hydrocarbons, the addition of a large excess of SO_2 would normally be necessary for complete solution of the kerosine stock

Aromatic and unsaturated hydrocarbons are completely miscible with liquid sulphur dioxide at its boiling-point (− 10° C), under these conditions saturated hydrocarbons (paraffins and naphthenes) are practically insoluble [21, 1918–23] However, the presence of the soluble aromatic or unsaturated hydrocarbons increases the solubility of the saturated hydrocarbons in the extract phase, the effect being comparable with the intentional addition of benzole, to increase the solubility, in treating heavy oils Light distillates with more than 50% aromatics (e g Borneo spirits) are completely miscible with liquid SO_2 at its boiling-point, although the solubility decreases at lower temperatures, and effective separation is in general restricted to distillates containing less than 30–35% aromatics With increasing temperature the solubility of hydrocarbons in liquid sulphur dioxide increases, with a corresponding decrease in the selectivity of the solvent Some degree of separation between naphthenes and paraffin hydrocarbons is obtained with liquid SO_2, but Leslie concludes that its selectivity in this respect is inferior to that of aniline and other solvents [18, 1934]

The reason for the preferential solubility of aromatic and unsaturated hydrocarbons in liquid sulphur dioxide is not understood Locket, however, has shown that aromatic hydrocarbons are associated in SO_2 solution, due probably to induced dipoles in the solvent molecules, in contrast to the non-association of saturated (naphthene) hydrocarbons [19, 1932]

The more or less pronounced segregation of aromatic and unsaturated hydrocarbons from the paraffins and naphthenes by extraction with SO_2 is evidenced by the lower specific gravity and refractive index, lower carbon/hydrogen ratio and higher stability of the raffinate in comparison with the extract

Liquid sulphur dioxide has in addition a pronounced solvent action on sulphur and nitrogen containing compounds in the crude oil, SO_2 extraction representing a most important desulphurizing process for kerosines The effect of sulphur dioxide on sulphur reduction in kerosine distillates is illustrated in Tables III–IV The desulphurizing action is particularly pronounced upon cyclic sulphur compounds, such as the thiophens and thiophanes present in cracked naphthas [20, 1929] Nitrogen compounds are likewise removed, the work of Bailey, for example, on the nitrogen compounds of Californian distillates, being carried out upon the SO_2 extract obtained from the treatment of Californian kerosines [4]

Treatment of Kerosine Stocks

The selection of a refining process is naturally dependent on the type of stock available and the ultimate use of the product, in addition to economic considerations. SO_2

extraction, removing as it does the aromatic, unsaturated, and sulphur containing compounds, is particularly applicable to kerosines for wick-fed lamps, in which these constituents are generally undesirable. In the case of highly paraffinic low sulphur crudes, such as Pennsylvanian, a conventional light acid treatment is adequate for the kerosine distillate. On the other hand, with crudes containing higher proportions of aromatic compounds, particularly of high sulphur content, the acid treatment required to give kerosines of reasonable burning qualities, with the associated refining losses, is excessive. The SO_2 process is particularly applicable in such cases, giving as it does a product of characteristics surpassing that from heavy acid refining. The absence of acid sludge disposal problems, of heavy treating losses, and of troubles associated with over treatment, and the production, instead, of a clean by-product (Edeleanu extract) of definite value to the refiner, are factors in favour of sulphur dioxide extraction as opposed to conventional acid treatment.

The treatment of kerosine stocks with liquid sulphur dioxide is carried out at approximately −10° C (14° F) using 50–100% by volume of SO_2. Heavier distillates, such as transformer oils, generally necessitate a higher temperature of extraction and increased proportion of SO_2.

The marked reduction in the tendency to smoke of a kerosine with decreasing proportion of aromatic constituents is illustrated by the following data, giving the smoke-point (I.P.T. Serial Designation K. 36) of mixtures of a paraffinic kerosine with varying amounts of an aromatic SO_2 extract [15, 1927].

Aromatic extract, %	*Paraffinic oil, %*	*Smoke-point*
40	60	10
30	70	14
20	80	20
10	90	26
0	100	32

The general effect of extraction with sulphur dioxide on the physical properties of a typical kerosine, using 100% by volume of SO_2 at −10° C (14° F), is illustrated in Table I [6, 1930].

TABLE I

	Original stock	*Raffinate*	*Extract*
Gravity, ° API	38·7	42·1	22·1
Sp. gr.	0·831	0·815	0·921
Sulphur, %	0·11	0·03	
Colour	light brown	24 Saybolt	dark brown
Yield, %		85·8	14·2

The distillation characteristics of the original kerosine were as follows: IBP 436° F., 10% 462° F., 50% 504° F., 90% 578° F., FBP 609° F.

Table II compares the burning qualities for kerosines of varying origin after a 2% acid treatment and after extraction with sulphur dioxide, a normal Pennsylvanian kerosine being included for purpose of comparison [11, 1932].

Owing to the partitioning effect of the more soluble 'extract' constituents between the raffinate oil and the liquid SO_2, their complete removal by solvent extraction is impossible. For detrimental sulphur compounds, therefore, a finishing treatment is generally desirable which, in addition, further improves the burning quality and colour stability. A light acid wash is commonly used, the effect of which on the sulphur content is illustrated in Table III. With mercaptan sulphur present, a final treatment with plumbite solution or hypochlorite is necessary to give a product of negative Doctor test. The incomplete removal of mercaptan sulphur from a straight run Iranian kerosine by a 100% SO_2 treatment is shown by the data in Table IV [26, 1929].

TABLE II

Kerosine	*Refining*	*Sp. gr.*	*Illuminating power in Hefner units Kosmos 14 burner* Initial	1 hr	8 hrs	*Smoke test*
Moreni	Sulphuric acid	0·818	7·3	6·7	5·1	bad
"	Sulphur dioxide	0·805	13·5	12·8	10·8	good
Grosny	Sulphuric acid	0·815	10·0	10·0	8·9	unsatisfactory
	Sulphur dioxide	0·806	15·4	15·0	11·8	good
Californian	Sulphuric acid	0·810	9·4	9·1	8·1	bad
	Sulphur dioxide	0·798	14·7	14·3	12·6	good
Peruvian	Sulphuric acid	0·817	11·2	10·7	8·9	unsatisfactory
"	Sulphur dioxide	0·807	14·3	13·8	12·1	good
Pennsylvanian W.W.	Sulphuric acid	0·7915	14·3	14·1	9·9	good

TABLE III

	Specific gravity		*Sulphur content, %*		
Kerosine	*Original*	*After SO_2 treatment*	*Original*	*After SO_2 treatment*	*After SO_2 and final ⅛–1% H_2SO_4 wash*
Mexico	0·774	0·763	0·25	0·07	0·01
"	0·807	0·790	0·82	0·23	0·10
"	0·818	0·793	1·14	0·14	0·03
Texas	0·827	0·826	0·12	0·04	0·01
Iran	0·795	0·781	0·14	0·08	0·06
Shale oil	0·797	0·781	0·27	0·08	

TABLE IV

	Original kerosine	*Raffinate*	*Extract*
Sp. gr. 60° F.	0·800	0·7875	0·870
Mercaptan sulphur, %	0·038	0·027	0·083
Total sulphur, %	0·22	0·07	0·76

Treating Plant

The earliest commercial plants were designed on the batch system, comprising the distillate cooler, SO_2 cooler, mixer, raffinate, and extract evaporators, together with heat exchange and condensing equipment. A counterflow mixing tower [1, 1926] was later designed, and incorporated in the first industrial plant for continuous operation in 1924. Improvement in heat exchanger design and the use of multiple stage high-pressure evaporation for SO_2 recovery [3, 1926] considerably improved the overall efficiency of the process. The early batch process utilized 600 lb. of steam for treating 1,000 lb. of kerosine distillate with 75% (volume) of sulphur dioxide. The later continuous plants have a steam consumption of the order of 340 lb. plus electric power consumption of 2 KWH., while the SO_2 loss per cycle has been considerably reduced.

A flow diagram of the continuous process for distillates and light oils [11, 1932] is given in Fig. 1. The raw kerosine distillate free from water enters the vacuum tank for degasification and then passes through the distillate precooler to the distillate cooler. The cold raffinate coming from the mixing tower passes through the precooler in countercurrent flow to the warm stock. In the distillate cooler the incoming stock is cooled to the final extraction temperature by evaporative cooling with liquid SO_2

The cold kerosine is pumped via a spreader into the lower section of the counterflow mixing tower where it is contacted with cold liquid sulphur dioxide The towers are usually about 30 ft high by 3 ft diameter, packed with contacting rings, and are fitted with visible level indicators The liquid SO_2 withdrawn from storage is passed through a precooler (in counterflow to the cold extract) and a final SO_2 cooler before entering the upper section of the tower

In the mixing tower the raw kerosine distillate travels upward, the heavier SO_2 extract travelling down The extract settling in the tower is continuously withdrawn from the bottom by the extract pump, the cold raffinate being similarly withdrawn from the top The cold extract, containing something like 15% of extracted hydrocarbons, after passage through the SO_2 cooler, proceeds to the extract preheaters 1 and 2 and then to a 4-stage evaporator at a pressure of 150 lb and temperature of 170° F In the evaporator the pressure is reduced to approximately 0 47 in of mercury in the final stage, practically complete recovery of the SO_2 being secured The hot extract finally passes via the first extract preheater to storage

The cold raffinate from the tower, containing 10–15% of SO_2, is similarly dealt with, as shown on the flow diagram, finally entering a three-stage evaporator, for recovery of the SO_2, at a temperature of *c* 150° F

The vaporized sulphur dioxide from the evaporation stages is passed through a gas cooler to condense and separate light hydrocarbons, and through drying towers before compression

Water Removal The absence of water in the system is important in minimizing corrosion In the presence of water, moreover, the sulphur dioxide is liable to oxidation to sulphuric acid, with increased corrosion and possible reaction with kerosine to form acid sludge Dry SO_2 may be regarded as chemically inert towards the hydrocarbons present in the kerosine under plant conditions Water in the entrant stock may be removed by passage through a rock salt packed tower, or by pretreatment with a small proportion of SO_2 [2, 1926] The sulphur dioxide itself, while vaporized, is passed through drying towers during a portion of the cycle Any water present tends to segregate in the extract phase and is removed with the SO_2 during evaporation The SO_2 from this may therefore be separately treated (by drying or rectification from the sulphurous acid) for water removal [13, 1930–3]

Laboratory Plant. Small-scale equipment for the laboratory (batch) treatment of distillates with liquid sulphur dioxide was designed by Edeleanu and later modified by Hess The diagram given in Fig 2 is self-explanatory, the size of the equipment may vary, but the capacity of the mixing vessel is generally 2 litres A continuous countercurrent extraction apparatus for liquid SO_2 has been used by the U S Bureau of Standards Two designs have been described by Leslie [17, 1932], one in glass for use at low temperatures, with a capacity of approximately 0 5 litre of hydrocarbon fraction per hour, and another in metal for use at higher temperatures and pressures

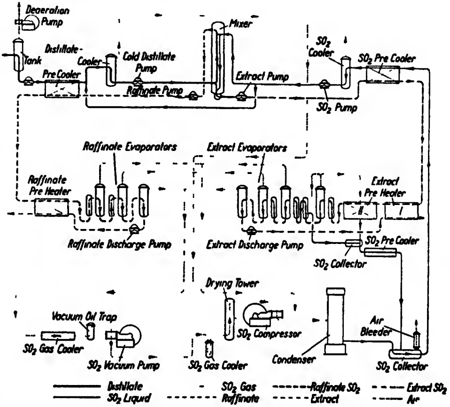

FIG 1 Flow diagram of continuous process for the extraction of kerosine with sulphur dioxide (*Reproduced by permission of L Edeleanu, 'J Inst Petr Technologists'*, **18**, 913 (1932))

Economics. The economics and design of sulphur dioxide treating equipment has been discussed in some detail by Cattaneo [8, 1930] The use of multiple effect evaporation in reducing heat requirements is dependent on individual factors, particularly size of plant and SO_2/kerosine treating ratio For 50% (volume) treatment multiple stage evaporation is generally unnecessary, for 75% SO_2 treatment one high-pressure stage is sufficient, while for 100% treatment and over at least two stages (triple effect) are required Multiple effect evaporation is thus of particular importance in reducing heat requirements and operating costs for lubricating and transformer oil treating, where relatively high volumes of SO_2 are necessary In later practice it is customary to use steam for compressor and vacuum pump operation and for heating the evaporation equipment, while the centrifugal pumps for crude stock, raffinate, extract and liquid SO_2 are electrically operated

The loss of sulphur dioxide is of the order of 2–6 lb per ton of distillate treated (below 0 5% per cycle) and make up may be added through absorption of gaseous SO_2 by the ingoing raw distillate.

Consumption figures and operating costs naturally vary according to the type of kerosine treated, product required, and the size and location of the plant Brandt gives the following figures for a plant treating 3,800 bbl (500 tons) per day of kerosine with 75% (volume) of sulphur dioxide [6, 1930]

Electric power	7,320 K W H per day
Steam (exhaust)	232,200 lb per day
Water (recooled and reused)	70,000 gal per day
Sulphur dioxide	2,500 lb per day

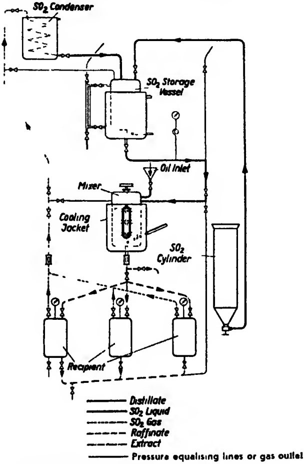

FIG 2 Laboratory apparatus for sulphur dioxide extraction (*Reproduced by permission of L Edeleanu, 'J Inst Petr Technologists'*, 18, 903 (1932))

The operating costs for the same plant are given as 6 7 cents per barrel of distillate treated

Utilization of Extract

The extract from the sulphur dioxide extraction of kerosines contains a high proportion of aromatic hydrocarbons with varying quantities of unstable unsaturateds and sulphur and nitrogen containing compounds, depending on the nature of the stock treated Brandt gives the properties of a typical extract from Californian kerosine distillates as follows

Viscosity at 100° F = 65 sec Saybolt Universal, flash-point = 145° F, gravity °API = 24 5, sp gr = 0 907, distillation I B P 324° F, 10% 390° F, 50% 456° F, 90% 522° F

The extract may be used directly as Diesel fuel of low ignition quality, or as cracking stock for production of aromatic high anti-knock gasoline (cf Bray [7]) Edeleanu has described the high-temperature pyrolysis of an SO_2 extract (topped to 200° C) to give 57 2% 'tar', 9 6% coke, and 33 2% gas The tar contained 22 4% of benzene-toluene-xylene fractions and 23 7% of high-boiling liquid aromatics [10, 1923] Sulphur dioxide extracts are also particularly amenable to hydrogenation cracking for the production of aromatic solvent naphthas ('hydro-solvents')

The aromatic content of the extract can be utilized directly, although the impurities present (sulphur, nitrogen, and unsaturated derivatives) may necessitate particular attention to refining The lower boiling cut (below 225° C, 435° F) will yield white spirits or solvent naphthas of normal specification characteristics, with markedly high solvent power The same cut may also be blended with gasoline for increasing the octane rating, so that the disposal of the extract for fuel or cracking stock is concerned only with the heavier residual fraction

The use of Edeleanu extracts as the aromatic component in condensation reactions with chlorinated hydrocarbons, or with olefine gases, for the synthesis of lubricating oils, is suggested in a number of patents by the German I G Farbenindustrie [14, 1928–9] The extract, containing as it does the nitrogen compounds of the distillate, may be used as a source of these (through subsequent acid extraction) for the production of inhibitors (acid pickling) or insecticides

Further Applications of the Sulphur Dioxide Process

The application of the SO_2 process to heavier stocks (transformer and lube oils), involving the use of higher temperatures of treatment and the addition of benzene, is discussed elsewhere Applied to suitable gas oils, SO_2 treatment yields a Diesel fuel of exceptionally good ignition characteristics, the high ignition quality Reference Fuel, for example, specified under IPT Serial Designation F O 39 (T) (tentative method of engine test for Diesel fuels) is prepared by sulphur dioxide extraction of a straight run Iranian gas oil Woods has concluded that solvent treating of cracked gas oils (produced by cracking gas oil for naptha making) offers a ready means of producing Diesel fuel of high Diesel index and low pour-point, although the treating losses (as extract) are high [25, 1936] It was found that straight run stock did not respond so well to solvent treating as the cracked stock

In the treatment of naphthas, the sulphur dioxide process has been used in the extraction of high antiknock blending fuels and aromatic solvent naphthas The higher solubility of naphthas in liquid SO_2 necessitates a lower temperature of extraction (0 to −60° F) than in the treatment of kerosine distillates, although a suitable temperature gradient in the counterflow tower appreciably lowers the refrigeration requirements Alternatively by addition of a paraffinic heavy oil (a lubricating oil e g) as a 'diluent', separation of a highly aromatic extract can be effected at higher temperatures [5, 1925]

For the production of high anti-knock motor fuel blends, Edeleanu proposed to treat only the heavy ends (165–225° C) of the naphtha cut The extract is reblended with the lighter straight run fraction while the raffinate is used as a narrow cut kerosine or as reforming stock The highly branched *iso*paraffin hydrocarbons, of good anti-knock properties, are not, of course, extracted by solvent treatment The extraction of high octane number blending stock from Mid-Continent, Sumatra, and S Texas naphthas by liquid sulphur dioxide is illustrated in Table V, from data recently presented by Saegebarth, Broggini, and Steffen [22, 1937]

Sulphur dioxide extracted fractions of this character are

TABLE V

Extraction of Straight-run Naphthas with Liquid Sulphur Dioxide

	Mid-Continent			*Sumatra*			*South Texas*		
	Original	*Extract*		*Original*	*Extract*		*Original*	*Extract*	
Extraction temperature ° F		0	−40		0	−40		0	−40
SO_2, vol %		40	40		85	55		70	70
Extract yield, vol %		12 5	9 6		30 0	22 0		46 5	35 9
Specific gravity	0 767	0 841	0 858	0 765	0 821	0 844	0 794	0 830	0 850
Octane number (C F R motor)	below 41	83	89		82	90	58	80	88
Unsats +aromatics, %	9 5	70 7	84 3	19 8	61 6	78 7	31 2	63 1	80 2
Initial boiling-point ° F (° C)	225 (107 5)	243 (117)	251 (121 5)	190 (88)	202 (94 5)	207 (97)	232 (111)	239 (115)	241 (116)
End-point, ° F (° C)	397 (203)	412 (211)	414 (212 5)	321 (160 5)	318 (159)	324 (162)	382 (194 5)	398 (203 5)	390 (199)
Aniline-point								+9 (−12 8)	- 2 7 (−19 3)
Kauri-butanol value	34 4	71 7	82 8		75 8	88 9	46 1	68 8	81 0

of particular value as lacquer solvents, evidenced by the low aniline point and high kauri-butanol number Working on an E Texas heavy naphtha, Woods obtained a 16 1% yield of extract, using 150% SO_2 at −20° F The 275–365° F fraction of this had the following characteristics sp gr 0 855, colour 25 Saybolt, aniline point −15° F, dimethyl sulphate value 95%, kauri-butanol value 73 [24, 1936] The properties of two industrially available lacquer solvents produced through sulphur dioxide extraction of Californian naphtha are summarized in Table VI [16, 1936]

TABLE VI

Product	'Solvsol 19–27'	Solvsol 30–40'
Sp gr , 15° C	0 792	0 844
Initial boiling-point, ° F (° C)	190 (88)	300 (149)
End-point, ° F (° C)	270 (132)	400 (204 5)
Colour	water white	+27 Saybolt
Sulphur, %	trace	0 06
Copper strip	negative	negative
Aniline-point, ° F (° C)	+43 (+6 1)	+20 (−6 7)
Kauri-butanol value	64 0	68 0

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SOLVENT TREATMENT OF CALIFORNIA LUBRICATING STOCKS, PARTICULARLY WITH SULPHUR DIOXIDE, SULPHUR DIOXIDE-BENZENE

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PROBABLY on account of the fact that California lubricating stocks as derived directly from the crude contain a very large proportion of unstable, undesirable material, the first commercial solvent-treating plant for lubricating oils was erected and operated in California With the lubricating stocks available carrying such a large proportion of the less desirable, and hence such a small proportion of the more desirable types of hydrocarbons, the California refiner is faced with a greater problem than most other refiners when it becomes necessary to produce motor oils of the highest quality In recent years both technologists and motorists have become aware of the need for oils of greater stability in the crank-case and better viscosity-temperature characteristics, and consequently have shown a preference for oils of greater paraffinicity as indicated by viscosity index (V I) or viscosity-gravity constant (V G C) However, in even the most paraffinic crudes available in California, asphaltic or naphthenic base constituents predominate, and it is therefore not surprising that much of the earliest work on solvent refining was done in California and that the chain of progress along this line has been continuous with no indication that it will be terminated for some time to come

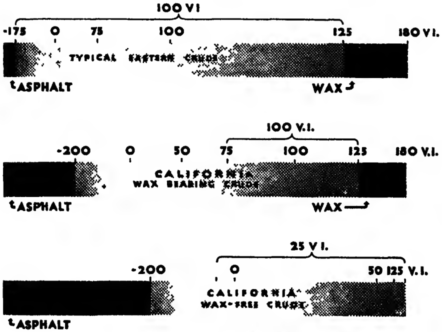

FIG 1 Composition of typical long residua

In order to illustrate the problem confronting California refiners, Fig 1 shows the composition or make-up of typical long residua containing all the lubricating fractions having a viscosity greater than about 100 sec Saybolt Universal at 100° F. The figure shows the composition of residua obtained from Pennsylvania, 'wax-bearing' California, and 'wax-free' California crudes, on the basis of viscosity index of the various lubricating components Strictly speaking, the use of viscosity-gravity constants is to be preferred in place of viscosity indices for designating the various fractions, but since the charts are intended to convey only a generalized picture which has been developed as the result of a large amount of experimental work, the use of viscosity indices is considered permissible

Three facts are immediately apparent from the charts namely, (1) that all the crude residua are composed of essentially the same classes of hydrocarbon compounds if we accept viscosity index as a criterion of composition, (2) that the distribution or proportion of the various classes of hydrocarbons is widely different in the respective crudes, and (3) that in the elimination of low V I material from left to right in the chart by means of selective solvents of increasing solvent power, the V I of the oil remaining is the weighted average V I of the remaining lubricating components

When the fractionation on a V I basis during solvent extraction is imperfect, which is always more or less the case in actual practice, some of the highest V I components are lost along with the undesirable low V I components, and it is then necessary to remove materials of higher minimum V I from the raffinate than would otherwise be necessary in order to obtain a raffinate of the required weighted average V I With crudes containing small or only moderate amounts of components having better than, say, 100 V I, it is imperative from the standpoint of economic yield to preserve as much as possible of the highest quality components In other words, with California stocks particularly, the fractionation or cutting in the V I scale of the components of the stock should be sharp, with a minimum overlap in composition between extracts and raffinate

Directing attention again to Fig 1, it will be seen that it is readily possible to obtain a highly paraffinic oil averaging 90–100 V I from the wax-bearing California crude, but it is practically impossible to produce such an oil from the 'wax-free' California crude (The 'wax-free' California crudes in reality contain a very small amount of wax as to be expected from theory, but the wax is often sufficiently high in boiling-point to be left in the asphalt during the conventional distillation of such lubricating stocks)

For the California refiner to produce economically motor oils of highly paraffinic properties, it is therefore necessary to utilize the wax-bearing type of crude, of which there is an abundance in the Santa Fé Springs, Kettleman Hills, Ventura, and Elwood fields The problem of removing both asphalt and wax is therefore encountered As a solution to this phase of the lubricating problem, the use of liquid propane as a refining agent was conceived and developed [2, 1933–4] It is interesting to point out that when the lubricating stocks are produced entirely as overhead distillates for the sake of reducing carbon residue, and improving the efficiency of the solvent extraction as explained below, the S A E 50 and heavier distillates contain materials insoluble in liquid propane, and are actually 'deasphalted' on contact with liquid propane, with the precipitation of brownish, low API gravity material having a tarry or asphaltic consistency Consequently, in the following discussion where reference is made to lubricating stocks from California wax-bearing crudes, it is to be assumed, unless otherwise stated, that the stocks in question have been propane deasphalted and dewaxed prior to treatment with selective solvents

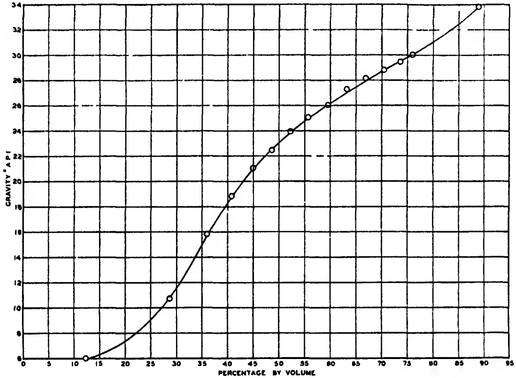

FIG 2 Analytical solvent fractionation of dewaxed S A E 20 Santa Fé Springs distillate

To illustrate more accurately the composition of a typical California stock from wax-bearing crude, Fig 2 is reproduced from data obtained in careful analytical extractions of a dewaxed Santa Fé Springs distillate stock which produces a S A E 20 grade motor oil [1, 1935] The API gravity of each cut is plotted against the midpoint of the volume percentage of that cut to give a composition curve analogous to an ordinary Engler distillation curve Instead of gravity, any other physical or chemical property such as V I or V G C of each cut may be plotted against volume per cent, but for ordinary viscosity grades of motor oil, gravity plots are both conveniently constructed and readily understood With Fig 2 in mind, it is easy to visualize the concept of a point of cutting or fractionation in order to produce a raffinate of specification quality The higher the quality specified for the raffinate, the higher must be the cutting-point on the API gravity scale

It has been found desirable in our experience to differentiate between 'activity' (or 'effectiveness') and 'selectivity' of the refining solvent The activity or effectiveness is considered to refer to the indicated point of cutting in the composition scale of the stock, whereas the selectivity refers to the degree of fractionation obtained with the solvent at the cutting-point In other words, effectiveness or activity of the solvent determines where the solvent appears to cut, and selectivity denotes how well the solvent separates the materials into two groups on either side of the cutting-point Obviously, both the activity and selectivity factors of the solvent must be considered in planning an extraction procedure to produce specification oil from a given stock, and attention will therefore be given to the readily available means of controlling activity and selectivity which have been found particularly useful with California stocks

Control of Activity of Solvent.

The principal methods of controlling the activity of a given solvent are (1) temperature, (2) use of a common solvent such as benzene, carbon tetrachloride, &c, and (3) the use of an antisolvent such as water, alcohol, &c By raising the temperature while using a constant volume solvent ratio, the solvent tends to cut higher and higher in the gravity scale, but the selectivity or sharpness of cutting on a V G.C or V I basis will be impaired with increase in temperature It should be pointed out, however, that increasing the volume ratio of solvent at a given temperature has been found by practical experience to raise the apparent cutting-point, with the result that it appears possible to remove selectively at any reasonable temperature all materials below any specified gravity by simply using a sufficient volume of solvent Furthermore, the fractionation will generally be better and the yield of specification raffinate greater if the lower temperature and larger amount of solvent are used On the other hand, practical considerations usually preclude the use of inordinately large amounts of solvents at low temperatures, and a compromise must generally be reached between yield of raffinate and volume of solvent required

TABLE I

Miscibility Temperatures for 50-50 Mixtures of 0 820 Viscosity-Gravity Constant Raffinates and Sulphur Dioxide-Benzene

Raffinate	*Gravity, ° API at 60° F*	*Viscosity-gravity constant*	*Viscosity, Say Univ, sec at 210° F*	*Temperature of miscibility ° F for C_6H_6—SO Ratio indicated*		
				10/90	*25/75*	*40/60*
No 1	29 6	0 820	45	169 8	136 0	106 0
No 2	27 4	0 821	60		151 0	115 0
No 3	25 1	0 821	130	199 0		122 5

The same considerations hold true for the cases where solvent activity is increased by the addition of a common solvent such as benzol or an antisolvent such as water or alcohol Modification of sulphur dioxide with benzol [3, 1933] constitutes an important example of this type of control of solvent activity As to be expected, an equivalent relationship exists between adding a common solvent or antisolvent at a constant temperature, on the one hand, and raising the temperature, on the other The data in Table II illustrate this relationship for sulphur dioxide-benzene, in which case it is found that a change of 1% in benzene content of the solvent at a constant temperature is roughly equivalent to changing the temperature from 2 to 2 5° F at a constant benzene content Obviously, any combination of temperature control and solvent modification can be employed

Control of Selectivity of Solvent.

As indicated above, one of the most important means of increasing selectivity or efficiency of fractionation at any required point of cutting in the gravity scale is the use of lower extraction temperatures and more solvent Since changing the temperature with the composition of the solvent remaining the same is roughly equivalent to maintaining the temperature constant and varying the composition of the solvent, as by employing a smaller or greater proportion of the common solvent such as benzol, it is apparent that for a given extraction temperature, efficiency of fractionation can be improved by employing a smaller proportion of common solvent, which in turn will necessitate a larger consumption of total solvent based on the stock being treated In other words, the underlying principle may be stated more generally by saying that selectivity and, hence, yield of raffinate of a given quality are improved by employing conditions which correspond to less activity for the solvent and which therefore necessitate the use of larger quantities of solvent Obviously, with certain solvents such as phenol or nitrobenzene, solidification points of the solvents limit the use of low temperatures in the application of this principle, but with sulphur dioxide and mixtures of sulphur dioxide-benzene, a practically unlimited range of possibilities is available

A further means of increasing the efficiency of the fractionation by means of solvents, which is unusually valuable in the refining of California stocks from which oils of fairly good quality must be removed in order to produce specification raffinate, is the device of splitting the lubricating fractions of the crude into two or more cuts by distillation prior to solvent extraction The advantage of this procedure over that of extracting a long residuum or combined lubricating distillate of wide boiling range was predicted by the writer on the theoretical basis that solubility of hydrocarbons in a given solvent is a function of both hydrocarbon constitution and molecular weight Specifically, at a given temperature, a low V I, low API gravity compound of high molecular weight may have the same solubility in the solvent as a high V I, high API gravity compound of considerably lower molecular weight, with the result that if these two compounds are present in the same mixture, it will be impossible at that temperature to separate them by means of the solvent in question

TABLE II

Characteristics of Overhead Cuts and the Bottoms from Vacuum Distillation of the SO_2—C_6H_6 *Extract from Kettleman Hills Long Residuum Pretreated with* SO_2

Sample	*Vacuum, mm Hg*	*Temp of dist, ° F*	*Recovery volume, %*	*Grav, °API at 60° F*	*Flash / Fire C O C ° F*	*Carbon residue, %*	*Pour-point, ° F*	*Acid no*	*Colour, N P A*	*Viscosity Say Univ, sec at*		*V I*	*V G C*
										100° F	*210° F*		
SO_2—C_6H_6 extract*			35 83†	21 9	420 485	1 9	25	0 27	opaque	1,600	96 97	64	0 852
Cut no 1	2 5	410–525	26 80	27 6	355 405	0 01	25	0 32	2¾	158	43 5	91	0 834
Cut no 2	2 5	525–585	27 42	23 7	445 520	0 05	15	0 22	4 –	674	64 5	60	0 847
Cut no 3	1 0	585–750+	25 98	21 0	465 585	1 05	15	0 19	opaque	3,125	126	47	0 854
Bottoms			19 55	13 6					opaque				

* Corresponding final raffinate tested 26 7° API, 85 sec viscosity at 210° F, 0 817 V G C, and 90 V I

† This percentage is based on the dewaxed residuum Other percentages shown are based on the composite sample

Fig. 3 represents idealized diagrams for two solvents of greatly different selectivity, showing the effect of both molecular weight and chemical constitution (represented by viscosity-gravity constant) on the temperature required to obtain a definite solubility in the solvent. If it is assumed that all components above about 0.840 viscosity-gravity constant must be removed as extract in order that the remaining raffinate shall have a specified average viscosity-gravity constant, it will be apparent that upon providing adequate treating conditions to remove the highest molecular weight components of 0.840 viscosity-gravity constant, a substantial loss of low molecular weight components of acceptable and desirable characteristics is experienced upon treating a wide boiling-range stock with Solvent A. An improvement in this situation is experienced by employing Solvent B with which molecular weight is not so important a factor. A greater improvement, however, is obtained by first splitting the stock into two or more cuts of restricted molecular weight (boiling-point) range, and then applying either solvent to each of the cuts separately.

That valuable high-grade components may be lost in the extract when treating a long residuum was definitely proved by treating with sulphur dioxide to give a 70 V.I. raffinate and then re-treating this raffinate with sulphur dioxide-benzene to raise its V.I. to 90. The sulphur dioxide-benzene extract was distilled with the results given in Table II, which show a marked concentration of high-grade material in the low-boiling fraction. Similar distillations of extracts obtained with the same solvent treatment on relatively narrow boiling cuts from the same stock showed marked reduction in loss of low molecular weight highly paraffinic material in the extracts.

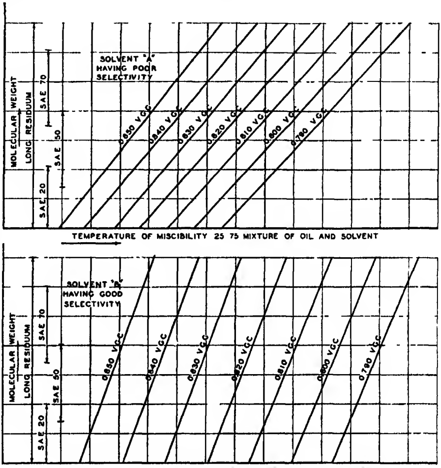

FIG. 3. Idealized solubility curves illustrating miscibility as a function of molecular weight and paraffinicity.

In this connexion it should be stated that when the selective solvent extraction is carried out in the presence of propane, the effect of the propane is to retard the solution of the highest V.I. components in the selective solvent while permitting the extraction to be carried out under conditions sufficiently severe to accomplish the removal of the highest molecular weight components of low quality. In effect, then, propane gives the benefits of steeper slopes and/or greater distances apart for the curves shown in Fig. 3, and makes it possible to obtain efficient solvent fractionation of even a wide boiling-range oil.

Comparison of various Solvents on Representative California Stocks.

To facilitate the choice of solvents for use in refining California stocks, strictly comparable extraction experiments are desirable. In a series of experiments, multiple-batch extractions were performed employing a definite treating schedule to determine the quality and yield of raffinate obtained with a fixed volume of solvent (370 vol. %), and then applying sufficient additional solvent, if necessary, to produce a raffinate of approximately a predetermined quality of 0.808 V.G.C. The extractions were begun in each case at a temperature approximately 50° F below the miscibility temperature of the first dump of solvent and the stock. Further details of the treatments and the results obtained are shown in Table III.

It is apparent from the data in Table III that of the solvents shown, chloroaniline, phenol, and a mixture of phenol and cresol are the most selective, as indicated by high yields, and are also the most effective, as shown by the small amounts of solvent required to obtain a given quality. Chlorex, furfuraldehyde, and croton aldehyde all require larger amounts of solvents and give lower yields of a given quality oil under the conditions tested. Sulphur dioxide, followed by sulphur dioxide-benzene, obviously makes the poorest showing of the solvents recorded, but on account of its low solvent cost per pound, ease of recovery, flexibility, and previous refinery experience with sulphur dioxide, the sulphur dioxide-benzene combination is successfully employed on a commercial scale in the only refinery in California operating on stocks from wax-bearing crude,

TABLE III

Extraction of S.A.E. 30 Dewaxed Santa Fé Springs Distillate with v us Selective Solvents

Solvent	*Sample*	*Volume % solvent*	*Temp., F**	*Yield, % by volume*	*Grav., °API at 60° F*	*% carbon residue*	*Pour-point, ° F*	*Colour, N.P.A.†*	*Viscosity Say. Univ., sec. at*		*V.I.*	*V.G.C.*
									100° F	*210° F*		
	Stock				19.8	0.24	−10	nearly opaque	1,181	73.5	23	0.874
Chloroanilines O M P	Extract 1	100	45	28.20	10.9							
	" 2	80	44	13.42	14.8							
"	" 3	70	45	6.99	16.9							
"	4	70	79	6.22	21.3							
	" 5	50	80	3.69	23.3							
"	Raffinate	370		40.99	29.9	0.01	5	2	407	58.0	95	0.804+
Phenol	Extract 1	100	120	31.73	12.1							
"	" 2	80	121	13.65	14.5							
"	" 3	70	120	6.67	17.5							
"	" 4	70	155	5.98	21.3							
"	5	50	155	4.07	22.8							
"	Raffinate	370		37.80	29.6	0.02	5	2−	412	57.5	92	0.807
Cresol-phenol 60/40	Extract 1	100	70	32.42	11.8							
"	" 2	80	72	13.18	14.1							
"	" 3	70	71	7.35	17.0							
	" 4	70	71	4.12	19.5							
	" 5	50	71	2.51	21.2							
"	Raffinate	370		40.23	29.6	0.01	5	2	423	59.0	95	0.806+
Furfural	Extract 1	100	178	21.04	6.9							
"	" 2	80	176	9.57	9.0							
	3	70	180	6.96	13.3							
	4	70	210	6.56	17.0							
"	5	50	210	4.29	18.6							
"	Raffinate	370		51.25	27.8			4½		61.5		0.817+
"	Extract 6	50	210	4.06	21.1							
"	" 7	50	210	3.57	22.6							
"	Raffinate	470		43.37	28.8	0.03	5	3+	474	61.0	91	0.811
Croton aldehyde	Extract 1	100	30	27.00	11.1							
" "	" 2	80	30	14.31	13.6							
" "	" 3	70	34	7.00	16.3							
"	" 4	70	64	7.23	21.1							
	5	50	65	3.43	22.5							
" "	Raffinate	370		40.76	28.4	0.01	0	3	487	60.5	86	0.814
Sulphur dioxide	Extract 1	100	92	16.60	7.1							
" "	" 2	100	92	8.42	8.5							
" "	" 3	100	92	4.44	11.3							
" "	4	100	92	3.00	13.5							
" "	" 5	70	92	2.03	14.5							
" "	" 6	70	92	1.59	15.7							
" "	" 7	70	92	1.44	17.4							
" "	" 8	70	92	1.10	18.1							
Sulphur dioxide-benzene 70/30	" 9	70	92	3.35	21.8							
" "	" 10	70	92	5.11	23.9							
" "	" 11	70	92	6.56	25.0							
" "	" 12	70	92	5.53	25.6							
"	13	70	92	4.92	26.2							
" "	Raffinate	1,030		35.83	29.1	0.02	5	2	470	61.5	94	0.808+
Chlorex	Extract 1	100	50	22.32	8.6							
"	" 2	80	50	10.46	11.3							
"	" 3	70	52	6.06	14.8							
"	" 4	70	82	6.30	15.9							
"	" 5	50	83	3.94	19.2							
	Raffinate	370		50.00	28.2	0.03	5	5½	461	59.5	89	0.815
"	Extract 6	50	82	2.00	22.0							
"	" 7	50	130	2.79	25.6							
"	" 8	50	130	5.67	26.2							
"	" 9	50	130	4.98	26.7							
"	Raffinate	570		32.45	29.5	0.03	5	4¾	425	59.7	94	0.807

* Extractions begun at temperature 45–50° F below miscibility temperature for equal volumes of stock and solvent, except in the case of the sulpher dioxide, sulphur dioxide-benzene experiment wherein a lower temperature was employed

† Colour after treating with 2 g of Death Valley clay per 100 ml at 325° F

namely, that of the Union Oil Company at Oleum, California.

Before proceeding with the detailed discussion of the use of sulphur dioxide and sulphur dioxide-benzene in California, it is well to point out clearly (1) that with any of the solvents shown in Table III it is probably possible to approach the same ultimate yield of specification oil as defined by the composition of the stock, provided a sufficient volume ratio of solvent can be used at an appropriate temperature, and (2) that the data in Table III are of value mainly in rating the various solvents in the order of the amounts of solvents required for a given yield of specification oil. For every solvent there can be determined a yield versus solvent ratio curve for countercurrent treatment in a tower or with an adequate number of stages, and it is reasonable that the multiple-batch data given in Table III indicate which of the different solvents will necessitate use in larger volume ratios to give the same yield of specification oil. Thus it is apparent that sulphur dioxide and sulphur dioxide-benzene will be required in probably the largest amounts of any of the solvents listed, but with sufficiently large amounts of sulphur dioxide and sulphur dioxide-benzene the results from the standpoint of yield for a given V.I. or V.G.C. are satisfactory. The foregoing generalizations are more strictly true on distillate than on residual stocks.

Commercial Solvent Treatment of Stocks from California Wax-free Crudes.

The first commercial scale solvent-treating plant for lubricating oils was put into operation at Avon, California, by the Associated Oil Company in 1927–8 for the treatment of low cold-test distillates [4, 1935]. Similar plants were subsequently placed into operation by the Shell Oil Company at Martinez, California, and the Union Oil Company at Oleum, California. The Standard Oil Company of California also has operated an Edeleanu plant, but only for the production of oils for special uses. These plants employ liquid sulphur dioxide and, as originally constructed and operated, represented an extension of the Edeleanu process for treating kerosine to the treatment of lubricating oils. The temperatures employed originally required refrigeration, although the temperatures were not as low as those used in kerosine treatment.

If the distillate stocks are contaminated with asphaltic entrainment or undergo deterioration in storage before treatment, it is desirable to give the stocks a light acid treatment of about 15 lb. of 98% acid per barrel, followed by wet neutralization and dehydration by blowing. This preliminary acid treatment of dirty stocks facilitates the solvent treatment by eliminating emulsion difficulties and enables the operators to establish interfaces in the treaters. After treatment the oils may be redistilled under vacuum or may be finished by clay treatment.

In refining lubricating stocks from California low cold-test crudes, it is not considered economical to cut in the API gravity scale at a point higher than about 14° API at 60° F. This gives a raffinate of about 0.862 V.G.C. (approximately 22.5° API on an S.A.E. 30 oil) and 25 V.I. from a San Joaquin Valley distillate having a V.G.C. of 0.910 and a V.I. of −35 before treatment. In attempting to refine to a materially lower V.G.C., by cutting at a higher point in the API gravity scale, the loss of stock is probably out of proportion from an economic standpoint to the additional improvement in quality obtained.

Table IV gives the data for typical refinery treatments of San Joaquin Valley distillates. Approximately 250–300 vol. % of sulphur dioxide is employed on each grade of stock. The yields of raffinate and extract are about 65% and 35%, respectively, on the average. The extracts are very viscous, have gravities of 7–10° API, and are usually utilized as fuel.

Finished motor oils of this type are distinctly superior to acid-treated oils produced from the same stock, apparently

TABLE IV

Sulphur Dioxide Extraction of Lubricating Distillates from California Low Cold-test Crude

Lubricating Distillates

Grav., ° API at 60° F	*Flash, C.O.C., ° F*	*Fire, C.O.C. ° F*	*Pour point, ° F*	*Sulphur, %*	*Carbon residue %*	*Viscosity, Say. Univ., sec at 100° F*	*Viscosity, Say. Univ., sec at 210° F*	*V.I.*	*V.G.C. (visc. at 210° F)*
18.4	350	400	flows at 0	0.77	0.05	217	43	−10	0.907
15.3	430	480	10 (vis.)	0.80	0.33	2,449	84	−55	0.909
14.6	475	525	20 (vis.)	0.80	0.53	12,000	179	65	0.902

Raffinates, vacuum re-run and blended to various S.A.F. Grades

S.A.E. grade	10	20	30	40	50
Gravity ° API at 60° F	23.5	22.5	22.0	21.4	21.0
Colour N.P.A.	3½	4	4½	5	5½
Conradson carbon residue, %	0.02	0.04	0.06	0.11	0.18
Pour-point, ° F	−15	−15	−15	−5	−5
Flash, C.O.C., ° F	365	390	400	420	435
Fire, C.O.C., ° F	415	440	460	485	500
Acid no., mg. KOH/g	0.03	0.04	0.04	0.04	0.05
Sulphur, % by weight	0.37	0.44	0.48	0.50	0.53
Oxidation stability					
Indiana, hr. for 10 mg	15	20	22	20	25
Indiana, hr. for 100 mg	50	55	55	51	55
Sligh no.	15	10	8	6	6
Viscosity, Saybolt Universal					
sec. at 100° F	262	453	670	1,210	1,976
sec. at 210° F	46.0	52.5	59.0	73.0	91.5
Viscosity index	35	25	21	18	19
Viscosity-gravity constant (visc. at 210° F)	0.861	0.862	0.862	0.862	0.860

on account of the more complete removal of the low-gravity components As to be expected, however, the stability of the Edeleanu-treated low cold-test distillates is inferior to that of higher API gravity oils when the latter oils are refined to a point of equal freedom from low-gravity components

The use of sulphur dioxide modified with benzene to give increased activity of the solvent does not appear to be justified in the refining of stocks from California 'wax-free' crudes, on account of the fact that further improvements in V I and V G C over what can be obtained readily with sulphur dioxide only are accompanied by a large sacrifice in yields Recently, however, the use of higher temperatures, not requiring refrigeration, has been practised with sulphur dioxide alone with only a few per cent loss of yield

Considerable attention has been given to the use of phenol in refining lubricating distillates from low cold-test crudes A commercial plant has been erected and operated at Richmond, California, by the Standard Oil Company of California employing phenol for the treatment of non-waxy distillates Details of the operations have not been published, but, from the specifications of the oils marketed, the extraction is controlled to give oils of approximately the same quality as those produced in the other refineries operating in California with sulphur dioxide on the same type of stocks Typical inspection tests on phenol-treated oils of this type are shown in Table V

TABLE V

Phenol-treated Motor Oils from Low Cold-test Distillates

S A E grade	30	40
Gravity, ° API at 60° F	22 6	21 8
Colour, N P A	3½	3½
Conradson carbon residue, %	0 09	0 14
Pour-point, ° F	−15	−15
Flash, C O C , ° F	405	425
Fire, C O C , ° F	445	485
Acid no , mg KOH/g	0 03	0 03
Oxidation stability		
Indiana, hr for 10 mg	28	32
Indiana, hr for 100 mg	51	56
Sligh no	5	6
Viscosity, Saybolt Universal		
sec at 100° F	579	901
sec at 210° F	57	66
Viscosity index	32	22
Viscosity-gravity constant (visc at 210° F)	0 859	0 861

Commercial Solvent Treatment of Stocks from Wax-bearing Crudes.

As seen from Fig 1, in order to produce oils competitive with the best Pennsylvania oils it is necessary to utilize stocks from the wax-bearing crudes With the aim of producing the highest type lubricating oils from California crudes, the Union Oil Company constructed, in 1933–4, a propane deasphalting and dewaxing plant at Oleum, California, and made the necessary changes in its older Edeleanu plant to permit the use of benzol in the refining of the deasphalted and dewaxed stocks with sulphur dioxide The existence of a sulphur dioxide plant for refining of motor-oil stocks from non-waxy crudes was a factor in choosing the sulphur dioxide-benzene method of refining for use on the propane deasphalted and dewaxed stocks

For the twofold purpose of reducing the carbon-forming tendency of the finished motor oils to a minimum and obtaining greater efficiency in the solvent extraction of the lubricating stocks, all grades of motor oil are produced as distillate oils This production of narrow-cut distillate oils entails a sacrifice of 5–15 points in V I for a given viscosity and gravity, but gives the advantage of low carbon formation In the Pacific coast area, at least, a few points in V I have little practical importance, but carbon formation is of major importance because of its effect on the anti-knock requirement of the fuel

The practice followed at Oleum is to distil selected Santa Fé Springs residuum under high vacuum with added steam to obtain normally three side cuts which are designated by the S A E grade which they will produce when refined to approximately 0 808 V G C or 90–95 V I , namely, S A E 20, S A E 50, and S A E 70 As necessary, the controls on the column are changed to produce S A E 10 stock Each of these cuts is then separately propane extracted and dewaxed Upon mixing with propane, the S A E 10 and 20 stocks precipitate little or no resinous material On the other hand, the S A E 50 distillate precipitates about 2–5% of resinous, pseudo-asphaltic material when dissolved in propane, and the S A E 70 stock gives 20–30% of propane insolubles, depending on the viscosity of the stock The dewaxing is accomplished by internal refrigeration by evaporation of propane and filtering at −45° F in 2 vol of propane After dewaxing, the respective stocks are processed separately through the sulphur dioxide-benzene extraction plant

The procedure in the sulphur dioxide-benzene operations is to give the stock two different and distinct extractions first, with sulphur dioxide only to produce an intermediate raffinate of about 0 830 V G C and 70–75 V I , and second, with 80–20 sulphur dioxide-benzene to give a raffinate of about 0 808 V G C and 90–95 V I The extract from the first extractions with sulphur dioxide only is a heavy tar of 7–9 5° API , while the extract from the second extraction with sulphur dioxide-benzene has a V G C of about 0 855–0 865 and a V I of 30–45, depending on the S A E grade of the stock Treatment with sulphur dioxide-benzene throughout in one operation gives closely the same results from pilot plant and laboratory tests, but has the disadvantage of losing the intermediate grade extract oil along with the lowest grade extract It should be pointed out, however, that as produced commercially, the intermediate grade extract oil has a wide range of composition, due to deficiencies in the solvent fractionation, and that as the efficiency of the fractionation is improved to give higher yields of first-grade oil, the yield of intermediate grade extract becomes very small and of poorer quality

The temperature employed in the first-stage treatment, using sulphur dioxide only, ranges from 110–145° F , depending on the molecular weight of the stock On account of the fact that over the lower range of API gravities sulphur dioxide is very selective, only four treaters consisting of mixers and settlers are employed in the first extraction Likewise, it appears logical to carry the refining as far as practical with pure sulphur dioxide until further increase in temperature causes too great a loss in selectivity The solvent-feed stock ratio by volume in this phase of the treatment is approximately 2 50

The temperatures employed in the second-stage treatment, using 80–20 sulphur dioxide-benzene, are somewhat lower than those in the first-stage treaters, but are also regulated in accordance with the molecular weight of the stock. Due to the poorer selectivity of the sulphur dioxide-benzene mixture, eight treaters are employed in the second-stage treatment The solvent-feed stock ratio employed in this second phase of the treatment varies from 2 75 to 3 50

As with any selective solvent, there appears to be a definite relationship in countercurrent treatment with a given number of treaters between yield of oil of a given quality and the total volume of sulphur dioxide and sulphur dioxide-benzene employed, the temperature required to give the specified quality raffinate being fixed by the volume ratio of solvent This relationship for dewaxed Santa Fe Springs lubricating distillates appears to be fairly well described by the curve for sulphur dioxide, sulphur dioxide-benzene treatment shown in Fig 4 It is known from analytical fractionation of the original stock, and from analysis of the extracts produced in commercial practice, together with the yield of corresponding raffinate, that the available material of 0 808 V G C in the stock is very close to 50% Therefore the yield curve will approach 50% asymptotically at very high solvent ratios and correspondingly low temperatures A number of points from pilot and commercial plant runs define the lower portion of the curve It will be observed that very high solvent ratios are required to obtain the highest yields, but on account of the low price of both sulphur dioxide and benzene and the ease of solvent removal, the operations with sulphur dioxide-benzene have proved practical With a given plant circulating the maximum amount of solvent per day, it is obvious that another curve can be constructed from Fig 4 to give the production of specification oil per day as a function of the quantity of stock being treated The shape and location of this curve and other factors will determine the most economical or profitable throughput for the plant

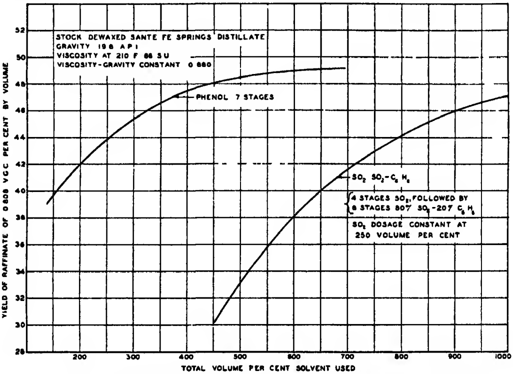

FIG 4 Yield V S solvent dosage to obtain a predetermined viscosity-gravity constant of 0 808

Table VI illustrates the results obtained in treating the four grades of stocks processed through the Oleum plant All raffinates are finished by a light contact clay treatment

An interesting feature in the sulphur dioxide-benzene extraction process is the use of sulphur dioxide to strip the desolventized raffinate and extract of the last traces of benzene This, of course, requires that practically pure sulphur dioxide be available for this operation

Possible Use of other Solvents on California Stocks.

With increasing demands for viscosity index and stability, it is expected that additional lubricating-oil solvent-refining capacity on the Pacific coast will be designed to operate on stocks from wax-bearing crudes, rather than on stocks from the non-waxy crudes Of the various solvents shown in Table III, phenol has appeared sufficiently attractive to be given considerable attention in a seven-stage experimental continuous countercurrent treater The cost of the solvent, ready availability, stability, relatively non-toxic properties, and overall efficiency as a selective solvent make phenol attractive In Fig 4 is also shown the yield-volume per cent solvent curve for phenol obtained in the seven-stage continuous treater operating on the same stock as that used in determining the curve for sulphur dioxide-benzene The marked reduction in solvent requirement is readily apparent Regardless of the increased yield of raffinate and the use of lower solvent ratios, the results as far as the qualities of the raffinates are concerned are essentially the same as for extraction with sulphur dioxide, sulphur dioxide-benzene when operating on the same distillate stocks, except for slight changes in viscosity

In concluding the discussion of solvent treatment of California distillate lubricating stocks, it is desired to point out that, as far as existing data go, it appears that the quality of the final raffinate of a given viscosity-gravity constant is essentially the same regardless of the solvent-treating path employed in arriving at that point In other words, the materials of proper qualities are fixed by the composition of the raw stock, and while some variations

TABLE VI

Sulphur Dioxide, Sulphur-benzene Extraction of Propane Dewaxed Santa Fe Springs Vacuum Distillates

	S.A.E. 10				S.A.E. 20			
	Dewaxed stock	*Sulphur dioxide extract*	*Sulphur dioxide-benzene extract*	*Final raffinate**	*Dewaxed stock*	*Sulphur dioxide extract*	*Sulphur dioxide-benzene extract*	*Final raffinate**
Gravity, ° API at 60° F	20·3	9·5	25·1	30·6	19·6	8·5	23·2	30·0
Colour, N.P.A.	7	opaque	opaque	4	8		opaque	4½
Conradson carbon residue, %	0·11		0·06	0·01	0·17		0·10	0·02
Pour-point, ° F	flows at 0		0	5	flows at 0		0	0
Flash, C.O.C., ° F	405		400	405	440		435	440
Fire, C.O.C., ° F	470		455	465	510		500	510
Acid no., mg. KOH/g	0·27		0·03	0·01	0·18		0·05	0·02
Sulphur, % by weight				0·12				0·16
Oxidation stability								
Indiana, hr. for 10 mg.				35				60
Indiana, hr. for 100 mg.				70				120
Sligh no.				5				3
Viscosity, Saybolt Universal								
sec. at 100° F	365		220	182	735		508	287
sec. at 210° F	49·5	202	46	46	61	210	56	51
Viscosity index	21		71	96			46	93
Viscosity-gravity constant (visc. at 210° F.)	0·883	0·946	0·845	0·809	0·881	0·955	0·856	0·808

	S.A.E. 50				S.A.E. 70			
	Dewaxed stock	*Sulphur dioxide extract*	*Sulphur dioxide-benzene extract*	*Final raffinate**	*Dewaxed stock*	*Sulphur dioxide extract*	*Sulphur dioxide-benzene extract*	*Final raffinate**
Gravity, ° API at 60° F	18·1	8·2	20·2	28·4	17·4	7·0	18·4	27·0
Colour, N.P.A.	opaque		opaque	5½	opaque		opaque	7½
Conradson carbon residue, %	1·60		0·70	0	3·55		1·8	0·12
Pour-point, ° F	15 (visc. pour)		0	10	45 (visc. pour)		35 (visc. pour)	15
Flash, C.O.C., ° F	520		515	520	610		605	615
Fire, C.O.C., ° F	600		600	600	710		700	710
Acid no., mg. KOH/g	0·05		0·03	0·01	0·02		0·02	0·02
Sulphur, % by weight				0·18				0·21
Oxidation stability								
Indiana, hr. for 10 mg.				100				200
Indiana, hr. for 100 mg.				160				
Sligh no.				1				trace
Viscosity, Saybolt Universal								
sec. at 100° F	4,600		3,400	914				2,630
sec. at 210° F	141	483	125	81	402		364	150
Viscosity index	20		32	90				92
Viscosity-gravity constant (visc. at 210° F.)	0·876	0·946	0·861	0·805	0·864		0·858	0·804

* After hot contact treatment with 2–4% of bleaching clay.

in degree of fractionation will exist between the use of different solvents or the same solvent under different conditions, these variations in fractionation will have a greater effect on yield of raffinate of specified V.I. or V.G.C. than on the quality of the raffinate.

Solvent Extraction of Insecticidal Spray Oils and Transformer Oils.

Spray oils for insecticidal purposes and transformer oils are usually produced in California by treating appropriate cuts from the gas-oil fractions obtained in the distillation of low cold-test or asphalt-base crudes. In the distillation of this type of crude (Poso Creek, McKittrick, Midway-Sunset, Coalinga, &c.) for the production of 'naphthenic' lubricating distillates, the gas-oil fractions may be fractionated directly to give one or more grades of spray-oil stock, or the gas-oil cuts may be re-run as a separate operation, depending upon the choice of the refiner. Generally, two or three stocks of different boiling range and viscosity are produced and refined to meet certain specifications, and blending then permits compliance with other specifications. Alternatively, the refiner may process a wide boiling-range cut and then re-run to produce several cuts to comply with specifications. The net results are essentially the same, and again the sequence of operations is a matter of choice for the refiner according to his particular conditions.

While it is possible to produce high-grade spray oils and transformer oils from naphthenic distillates by sulphuric acid treatment alone, followed by wet neutralization, the amounts of acid required to obtain unsulphonated residue tests above 90 are very large, amounting to as much as 250 lb. per barrel in some cases. Therefore, in producing oils of high unsulphonation values, it is more economical first to extract the raw distillate with sulphur dioxide and then to apply a finishing treatment with sulphuric acid to bring the unsulphonated residue test up to specifications.

Transformer oil is conveniently made by utilizing the raffinate of the lowest boiling spray-oil stock, although it is not infrequent to cut at the stills a transformer-oil stock of a particular boiling range and then extract this stock with sulphur dioxide The raffinate in either event is given a finishing treatment with sulphuric acid, aqueous alkali, and clay, or it may be finished by simply alkali-washing and clay-treating if the solvent extraction is carried far enough As a further alternative, the refinery may re-run the transformer-oil raffinate with the addition of caustic soda to the still charge An important point in the finishing treatment of transformer oil is to dry the oil as thoroughly as possible before it leaves the refinery and to see that it is not allowed to pick up moisture during handling Each refiner usually has a preferred method for drying transformer oils

TABLE VII

Refining of Spray Oils and Transformer Oils from Non-waxy California Crudes

Light Stock

	Stock	*Sulphur dioxide raffinate*	*Raffinate after acid treatment*	
Amount sulphuric acid, lb per barrel			75	10
Finished oil			light spray	transformer
Gravity, ° API at 60° F	22 8	28 1	29 8	28 5
Colour, N P A	8		1	4
Pour-point, ° F	- 50	50	50	- 50
Viscosity, Say Univ at 100° F, sec	59	57	54	56
Unsulphonated residue (de Ong), %	60	80	92–93	85
Acid no	1 6	0 03	0 01	0 03
Engler distillation, ° F				
Initial	526	532	535	534
10%	565	573	578	576
50%	615	621	624	622
90%	690	690	694	692
Max	730	730	731	730

Medium Heavy Stock

	Stock	*Sulphur dioxide raffinate*	*Raffinate after acid treatment*
Amount sulphuric acid, lb per barrel			90
Finished oil			medium heavy spray
Gravity, ° API at 60° F	21 4	28 1	29 0
Colour, N P A	8	7	1½
Pour-point, ° F	−40	−40	−40
Viscosity, Saybolt Univ at 100° F, sec	106	90	84
Unsulphonated residue (de Ong), %	63	80	92–93
Acid no	1 73	0 05	0 01
Engler distillation, ° F			
Initial	570	595	605
10%	628	630	642
50%	685	691	708
90%	765	765	770
Max	790	800	803

The specifications to which spray oils are refined usually emphasize (1) boiling range, (2) viscosity, and (3) unsulphonated residue test Boiling range and viscosity are considered important in connexion with penetration of oil into the foliage and the time the oil remains before evaporating High unsulphonated residue requirements are the outgrowth of serious damage to citrus trees, and to deciduous fruit trees in summer, caused by poorly refined 'red oils' employed a decade or so ago These 'red oils' were poorly fractionated as regards boiling range and were given only a light acid treatment primarily for colour Such oils produced from California naphthenic crudes therefore contained large amounts of unsaturated and aromatic materials of a very reactive nature which resulted in the injuries experienced Drastically refined oils of the white oil or medicinal oil type were found to be relatively free from plant injury, and it then became the custom to require spray-oil stocks to be refined to a point approaching white oils in quality As a ready means of ensuring this high degree of treatment, the unsulphonated (de Ong) residue test was adopted and subsequently an unsulphonated residue test in excess of 90% has been required in practically all specifications for high-quality spray oils Unsulphonated residue tests on the older 'red oils' ranged from about 55–68%, depending on the crude method of distillation, and degree of refining employed In the enthusiasm for high unsulphonated residue tests, oils of less than 90 de Ong test have been held in disfavour and oils of 70–90 unsulphonated residue have not been given due consideration

The use of sulphur dioxide extraction in the production of spray oils and transformer oils is practised by the Associated Oil Company, the Union Oil Company the Standard Oil Company of California, and the Shell Oil Company of California The operations are similar to those described above for the heavy lubricating fractions, except that lower temperatures are usually employed in order to conserve yield at, of course, the expense of larger solvent dosages

Table VII illustrates the effect of sulphur dioxide extraction followed by sulphuric acid treatment on two typical spray-oil distillates from California low cold-test crude The lighter distillate also serves as a transformer-oil stock

With the recent installation of dewaxing equipment to permit the refining of distillates from California wax-bearing crudes, it is possible to produce unusually high de Ong spray oils by sulphur dioxide extraction only as illustrated in Table VIII

TABLE VIII

Refining of Spray Oils from Santa Fé Springs Crude

	Dewaxed distillate	*Sulphur dioxide raffinate (clay treated)*
Gravity, ° API at 60° F	26 3	33 8
Colour, N P A	6	1
Viscosity, Saybolt Univ at 100° F, sec	56	82
Pour-point, ° F	- 5	25
Unsulphonated residue (de Ong), %	70	96
Acid no	0 10	0 03
Distillation, ° F		
Initial	550	562
10%	585	594
50%	617	624
90%	672	680
Max	716	730

Solvent Extraction of Reforming Stocks.

The heavier gasoline fractions from California refining crudes contain 12–18% of aromatics, consisting mainly of benzene, toluene, xylenes, ethyl benzene, &c Relatively narrow boiling fractions rich in these aromatic components find valuable use in the paint and lacquer industry and in the blending of high anti-knock fuels such as aviation gasoline. It has therefore been found economical to solvent extract heavy naphthas for the recovery of these aromatic fractions and then to utilize the raffinate in a low octane gasoline or as reforming stock for the production of high anti-knock gasoline

Comparable cracking runs on a heavy naphtha with and without having been previously solvent extracted will give generally 2–4 points higher octane number on the reformed gasoline when the stock has not been solvent extracted before cracking This lower knock rating of the reformed naphtha raffinate can, of course, be remedied by more severe cracking at the expense of less yield of gasoline and greater loss to fixed gases Whether or not Edeleanu treatment of reforming stocks will prove more or less profitable in the future is a question which it is difficult to answer, particularly in view of the development of other processes for the production of aromatics such as the high-temperature gas-polymerization processes

TABLE IX

Solvent Extraction and Reforming Heavy Naphtha

	Heavy naphtha	*Sulphur dioxide extract*	*Sulphur dioxide raffinate*	*Reformed raffinate*
Extraction temp , ° F	15			
Amount sulphur dioxide, vol %	100			
Cracking temp maximum, ° F				980
Gas produced, cu ft per bbl charge				342
Gravity, ° API at 60° F	52 1	41 6	55 5	57 2
Engler distillation, ° F				
Initial	174	212	184	96
10%	222	239	216	178
50%	265	275	251	246
90%	325	324	308	336
Max	381	370	384	435
Sulphur %	0 03	0 04	0 01	0 01
Aromatics, %	18 3	52 2	2 2	29 6
Octane no , A S T M motor method	58	78	56	68 5

The results of solvent extracting and reforming a heavy naphtha are shown in Table IX

In the refining of kerosine by the Edeleanu process attention has been directed to the extract as a possible cracking stock The fractions of the extract boiling below about 425° F , however, find valuable utilization as indicated above, and therefore only the heavier fractions of the kerosine extract are available for use as cracking stocks This type of stock gives high octane-rating gasoline, as illustrated in Table X, but the quantity available is usually quite small in comparison to other cracking stocks

TABLE X

Reforming Heavy Fractions of Kerosine Extract

	Kerosine extract bottoms	*Gasoline produced*
Cracking temperature, maximum, ° F		940
Gas produced, cu ft per bbl charge		245
Gravity, ° API at 60 F	19 6	35 8
Engler distillation, ° F		
Initial	432	106
10%	450	202
50%	476	362
90%	515	401
Max	571	422
Sulphur %	0 74	0 51
Octane no , A S T M motor method		81

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THE NITROBENZENE METHOD

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Introduction

NITROBENZENE as a selective solvent is distinguished by the fact that it is one of the few known compounds, and the only one of those commercially used as selective solvents, which combine good selectivity and high solvent power, i e it is capable of effecting a sharp separation between paraffinic and naphthenic constituents, when used in relatively small quantities It is further substantially unique in its ability to extract residual stocks as well as distillate stocks, and to remove from any of these stocks enough of the colour bodies that the raffinate may be finished by means of clay, without the use of acid or other decolorizing chemicals It is capable of sharply removing naphthenic material from stocks of any sort from extremely naphthenic ones to extremely paraffinic materials such as Pennsylvania When applied to stocks of the latter type its unusual properties allow the paraffinic stock to be advantageously extracted with very small amounts of solvent

Operation of Process

In the remainder of this article the word 'nitraffin' will be used instead of 'raffinate' and the word 'nitrene' instead of 'extract' The derivation of these terms is apparent, nitraffin being the paraffinic portion resulting from a nitrobenzene extraction, and nitrene the naphthenic portion

By reason of the fortunate physical properties of the solvent, which will be discussed below, the operation of the nitrobenzene process is essentially simple Charge oil is mixed with the requisite quantity of nitrobenzene, the mixture brought to extraction temperature and continuously charged to the counter-current extraction vessels, where it separates by gravity into two layers, the lower containing the naphthenic constituents in solution and the upper being the paraffinic portion of the oil in which some nitrobenzene is dissolved The layers are continuously withdrawn and each is passed over steam coils in a vacuum evaporator, in which all but 1% of the nitrobenzene is removed The oil is then passed through a vacuum stripping-tower where the remainder of the solvent is removed by open steam

Fig 1 shows the general arrangement of apparatus, the flow of materials, and the flow of heat Charge chillers are of the scraper type in order that wax-bearing and highly viscous stocks may be handled The 5-stage counter-current extractor is a conventional series of settling and mixing tanks, except that the first-stage mixer is omitted In order to decrease wax concentration and improve heat transfer, the incoming charge is mixed with second-stage nitrene in the chiller, and this serves also for agitation

The evaporators are of the cascade type, consisting of closed steam coils placed in a vertical series of shallow trays Each evaporator consists of several units, with each unit communicating throughout its length with a corresponding condensing unit Pressures of 30 mm of mercury in the first several units and 10 mm in the remaining units are maintained by means of a 3-stage steam-jet vacuum pump Temperatures within the evaporator vary from about 215° F at the top to 325° F at the bottom, while the temperatures in the vacuum strippers are of the order of 350° F The strippers operate at a pressure of 65 mm of mercury in order that the steam may be condensed with ordinary cooling water The small amount of nitrobenzene dissolved in the water is recovered by distilling the condenser water under 100 mm pressure, taking about 10% overhead, and leaving the remaining 90% practically free of nitrobenzene The 10% overhead separates into two layers (nitrobenzene and nitrobenzene-saturated water), the latter of which is recirculated to the still (Note this recovery still is not shown in the diagram) Each cycle recovers 95% of the nitrobenzene in the water

Fig 2 is a photograph of the nitrobenzene plant at the Philadelphia Refinery of The Atlantic Refining Company It was designed to handle 3,000 bbl (50's) per day of nitrobenzene, the amount of oil charged being dependent upon the ratio of oil and solvent With 150% nitrobenzene based on the charge, the oil capacity would be 2,000 bbl per day, &c The plant was promptly brought not only to capacity, but considerably beyond

Physical Properties of Nitrobenzene

The physical properties of nitrobenzene are given in Table I A number of these contribute in no small measure to the simplicity and ease of running of the process

Its high density and low viscosity combine to make separation of the phases easy and rapid No centrifuges are necessary in the extraction step, even when small amounts of solvent are employed

TABLE I

Properties of Nitrobenzene

Colour	yellowish—nearly colourless when pure
Odour	bitter almonds
Density	1 207 at 60° F
Boiling-point	411 5° F (210 9° C)
Melting-point	42 3° F (5 7° C) dry 41 4° F (5 24° C) wet
Refractive index	1 5529
Pensky-Martens flash	208° F
Solubility in water	0·2%
Fluidity	50 rhes (68° F), viscosity 0 021 poise
Sp ht	0 33–0 38 B Th U /lb /° F (1 4–1 6 joules/g /° C)
Latent ht of fusion	40 6 B Th U /lb = (94 25 joules/g)
„ , evaporation	142 6 B Th U /lb = (331 joules/g)
Thermal conductivity	0 09 B Th U /sq ft /ft /° F /hour
Coefficient of expansion	0 00048 c c /c c per ° F

The amount of heat required in redistilling the solvent after extraction is minimized in the first place by the fact that small proportions of solvent are employed, but this is further decreased by the fact that its latent heat of evaporation is relatively low when compared with several other extracting solvents

Being entirely stable towards air and having a high flash-point, no storing precautions such as inert gas blanketing are required

Its low solubility in water is fortunate in two respects First, nitrobenzene works as well when saturated with water as it does in the anhydrous condition, therefore, no

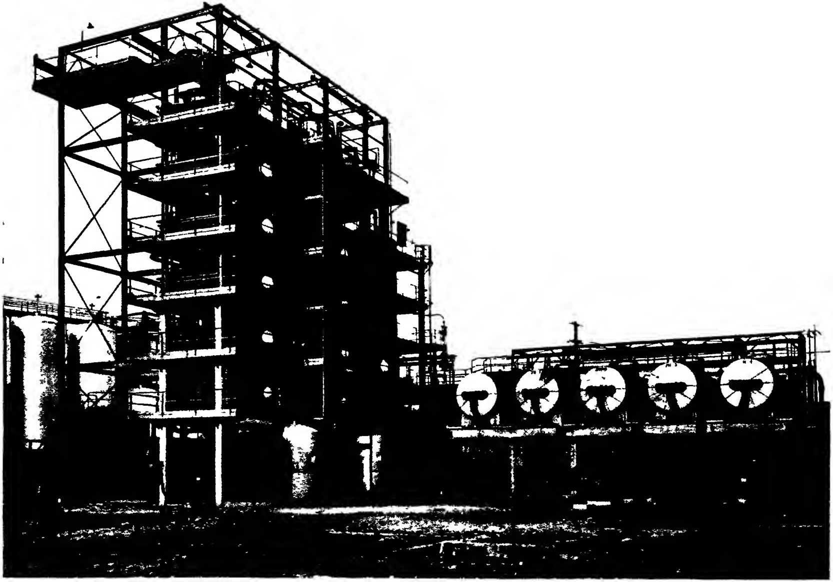

FIG 2 Nitrobenzene plant at Philadelphia, Pennsylvania

concern need be had as to whether the charge stocks are water-free or not Secondly, open steam may be employed in stripping the last traces of nitrobenzene from the oil, after which the major portion of the nitrobenzene so removed separates into a layer which may be returned to the extract The small amount remaining in the water-layer may be removed from the water by distillation, substantially all of the nitrobenzene being distilled in the first 10% overhead

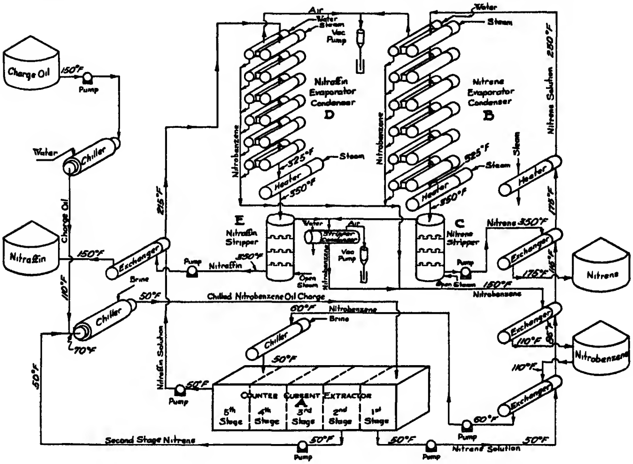

Fig 1 Flow chart

There are no corrosion problems in connexion with the nitrobenzene process Neither the liquid nor vapour causes any excessive corrosion on ordinary metals such as steel brass, copper, or Admiralty

No discussion of nitrobenzene would be complete without reference to the matter of toxicity It is an undeniable fact that nitrobenzene has somehow acquired a very unfortunate reputation in this regard, nor has this reputation been ameliorated during the several years that it has been competitive as a selective solvent with other materials which either are, or are reputed to be, less toxic Furthermore, the very number of excellent characteristics of nitrobenzene have quite naturally increased the tendency to point the finger of accusation at this one characteristic

As a matter of fact, neither makers nor users of nitrobenzene have found reason to be particularly concerned about the toxicity of the material In some 9 years of laboratory, semi-plant and full-scale experience with nitrobenzene as a selective solvent not a single case of serious poisoning has been encountered If one considers the fact that laboratory and semi-plant operation involves the use of nitrobenzene in open containers and, in the laboratory, the manual transfer of nitrobenzene solution from one open container to another, and the fact that this type of work is indoors, it will be apparent that hazards are greater in small equipment than in large equipment, which is not only outdoors but is totally enclosed Still further, successful operation of any selective solvent plant demands that the loss of the solvent be kept to a very low figure, and those precautions which it is very necessary to adopt in order to keep this figure low are the best precautions which could possibly be adopted to eliminate any health hazard

Hamilton, in *Industrial Poisons in the United States* [1, 1929], says ‘In American dye works D N B (di-nitrobenzene) is often the only substance that causes real alarm ’ It may well be, therefore, that most of the difficulties encountered with nitrobenzene have, in fact, been due to di-nitrobenzene, because commercial grades of nitrobenzene frequently contain several per cent of the di-nitrobenzene The grade used for extraction, however (oil of mirbane), is, and must be kept, free of di-nitrobenzene

From the standpoint of availability and price nitrobenzene is in an excellent position It is available in satisfactory quality from a number of manufacturers, and in unlimited quantity Being produced in a single step from benzene, its price is, and probably will remain, definitely lower than those materials which require two steps in their manufacture

Production of Paraffinic Oils

At present the most important function of a selective solvent as applied to lubricating oils is to produce a paraffinic fraction by the removal of naphthenic constituents Instead of exhaustive data on one or two typical stocks, somewhat condensed information is presented on several One purpose of this is to emphasize again the fact that nitrobenzene is capable of producing a paraffinic fraction of quality as high as is desired, or at any rate as high as is contained by the stock, from fractions of almost any character, whether that fraction be a distillate or a residual stock Furthermore, the amount of solvent required to effect this result is always relatively low

The data on distillate stocks are recorded in Table II, and those on residual stocks in Table III

It cannot be assumed, merely because the viscosity gravity constants of distillates are the same, that the composition of those two distillates are identical, because the proportions of the various constituents whose average properties result in the viscosity-gravity constant may differ Those differences are, however, not extreme, and therefore the approximate yield of material of any desired quality may be predicted This is illustrated in Fig 3 For

TABLE II

Extraction of Distillate Stocks*

Description	% nitrobenzene†	Temp of extraction, °F	Nitraffin yield‡	S U viscosity at 100° F	at 130° F	at 210° F	API grav	V G C	V I	O D colour
Barbers Hill				627		59 5	22 0	0 863	33	318
	160	41	48 1	321		52 7	28 8	0 816	93	20
Barbers Hill					792	110	20 4	0 861	39	1,410
	175	59	47 8		349	78 3	27 6	0 813	92	137
Mid-Continent						69	22 1	0 858		
	100	41	59 2			56 6	29 2	0 811		
Hobbs				599			20 0	0 880		
	125	41	30 5	269			31 5	0 804		
Barbers Hill						115	20 8	0 857		676
	100	41	70			88	26 1	0 822		68
	150	59, 68, 77	51 4			83	27 3	0 813		54
Dewaxed Mid-Continent				361			25 3	0 845		
	150	41	51 8	224			31 8	0 805		
Winkler				538			20 9	0 875		
	150	41	29 5	274			30 8	0 808		

* Three-stage counter-current † Volume per cent based on stock ‡ Per cent of stock by volume

TABLE III

Extraction of Residual Stocks*

Description	% nitrobenzene†	Temp of extraction, °F	Nitraffin yield‡	Properties S U visc at 210° F	API grav	V G C	O D colour
Barbers Hill Residuum				898	14 4	0 880	112,600
	100	59, 86, 113	44 6	233	23 2	0 826	8,640
	150	59, 86, 113	41 3	209	24 4	0 818	8,092
	200	59, 86, 113	36 2	210	25 0	0 814	9,609
Barbers Hill Residuum				543	14 5	0 887	69,500
	150	59	41 2	143	25 8	0 814	6,920
	200	59	36 6	145	26 1	0 812	6,860
Winkler Residuum				498	13 3	0 898	
	175	41	32 2	181	25 0	0 816	
Barbers Hill Residuum				443	17 1	0 868	27,744
	80	60, 88, 115	56 0	194	23 2	0 829	10,336
	150	60, 88, 115	50 9	166	25 2	0 816	8,956
Hobbs Residuum				275	14 6	0 895	
	150	41	21 1	105	28 7	0 798	
Oklahoma Residuum				142	20 2	0 858	
	100	41	58 5	101	26 5	0 816	
	150	41	55 0	99	27 2	0 810	

* Three-stage counter-current. † Volume per cent based on stock ‡ Per cent of stock by volume

example, a stock of 0 840 V G C may be expected to yield about 60% of 0 815 nitraffin, whereas a stock of 0 870 V G C would yield about 40% of similar quality As with any solvent, the yields from a given stock may be varied to some extent by controlling the temperature of operation with nitrobenzene, and this must also be borne in mind when predicting on the basis of Fig 4

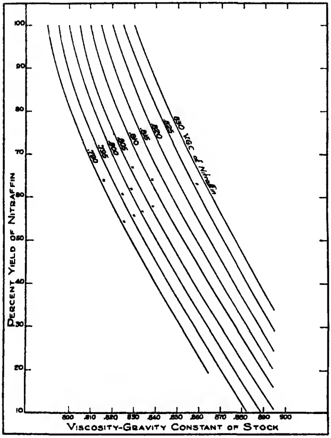

FIG 3 Variation in yield with character of stock

Colour Removal

Naphthenic constituents and colour bodies do not seem to be identical, because a considerable number of solvents are capable of sharply separating naphthenic constituents, but nitrobenzene is one of the very few which simultaneously removes to a large extent those bodies which impart colour to the oil This is particularly true in the case of residual stocks Data on this point are included in Tables II and III These and some additional data are presented in Fig 4 (confined to distillate stocks) and Fig 5 (confined to residual stocks) As will be brought out later, the matter of colour removal is of very great importance in determining the expense involved in finishing the solvent raffinate to marketable colour

Effect on Carbon Residue

Nitrobenzene extraction always results in markedly decreasing the carbon residue of an oil Data are given in Table IV It is to be noted that the carbon residue of the Coastal residuum was reduced from 6 4 to a figure lower than most steam-refined Pennsylvania stocks Extraction was also effective on Pennsylvania stocks Clay finishing of the nitraffins will result in further reduction

TABLE IV

Reduction of Carbon Residue

Stock	*% nitro-benzene*	*% yield*	*S U viscosity at 210° F*	*Carbon residue*
Barbers Hill District			59 5	0 28
	160	48 1	52 7	0 06
Barbers Hill District			110	0 76
	200	54 2	79	0 18
Barbers Hill residuum			444	6 4
	200	44 5	179	1 8
Penna residuum			143	2 14
	100	82 6	124	0 94
Penna residuum			220	3 2
	100	82 7		1 5

Effect on Stability

Nitrobenzene extraction makes possible the production of oils of unusual properties, particularly with respect to stability For example, fractions, some more paraffinic than the stock and some more naphthenic than the stock, have exhibited unusually high electrical resistivities, and certain fractions the remarkable characteristic of a high electrical resistivity which slowly increases during a test which was devised to break it down The test referred to is exposure to air at 212° F for 72 hours or longer

A stability test which is at present much in use is the Indiana oxidation test Whether the criterion be the amount of sludge deposited, or the rate of viscosity increase during the exposure to air, nitrobenzene-treated oils are extremely stable The stability of the raw raffinate is not always high, but the improvements effected by clay treatment are strikingly large, even though the amounts of clay used be very small It appears that nitrobenzene very largely removes those compounds responsible for instability, leaving, however, very small amounts which are readily adsorbed on clay

Finishing

By reason of the large proportion of colouring matter which is removed during nitrobenzene extraction, nitraffins, whether from distillate or residual stocks, may be finished to a marketable colour by clay treatment alone In no case is acid treatment required When handling residual stocks, therefore, the cost of the nitrobenzene extraction may be partly, if not entirely, offset by this factor, inasmuch as acid treatment always results in considerable quantities of sludge having a negligible value, whereas nitrenes make excellent cracking stocks

Table V gives comparative data on the clay percolation of 4 nitraffins and 3 Pennsylvania products The distillate nitraffins gave yields more than twice as large as those obtained from Pennsylvania neutrals and finished to lighter colour The nitraffin from Barbers Hill residual, although it was originally much darker than the Pennsylvania cylinder oil, gave yields slightly higher than the Pennsylvania oil

TABLE V

Comparison of Clay Decolorization of Pennsylvania Oils and Nitraffins

	Tests before filtering				Colour after filtering		% colour removed	Filter-yields	
	S U visc at 100° F	S U visc at 210 F	Colour					Tons clay per bbl finished oil	Bbl finished oil per ton clay
			N P A	O D	N P A	O D			
Pennsylvania 153 Oil	150		4¾–5	111	2¾–3	22	80	0.0199	50
Nitraffin from Reduced M C Pressed Dist	162		2¼	19	1½ 1¾	3.7	80	0.0089	112
Pennsylvania 183 Oil	180		5¼ 5½	151	2¾ 3	22	85	0.0267	37
Nitraffin from Reduced M C Pressed Dist	231		3¼	31	1¾–2	5.7	82	0.0104	96
Pennsylvania Cylinder Oil		145	5 DD	5,340	7–7½	385	93	0.4324	2.3
Nitraffin from Barbers Hill Crude Residuum		159	3¼+DDD	9,640	7	344	96	0.4073	2.5

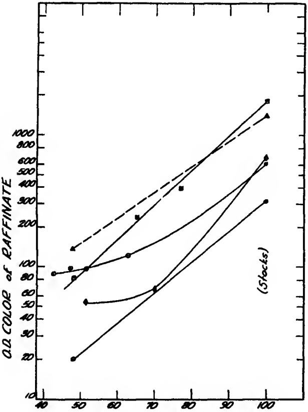

FIG 4 Colour removal from distillates

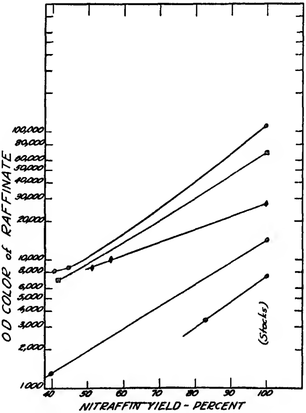

FIG 5 Colour removal from residual stocks

Extraction of Pennsylvania Stocks

When, a few years ago, solvent extraction was brought to the fore, one of its most striking accomplishments was the production, from stocks of other than Pennsylvania origin, of oils resembling in viscosity and gravity characteristics those produced from Pennsylvania crude Of late, however, considerable interest has been shown in the solvent extraction of Pennsylvania stocks themselves in order to remove the relatively small proportions of naphthenic materials which are present and to impart, among other characteristics, better stability In the extraction of Pennsylvania stocks the unique characteristics of nitrobenzene are sharply emphasized By reason of its high solvent power, its high selectivity, and particularly its ability to retain that selectivity even when the extract is rich in dissolved oil, nitrobenzene is able to bring about real improvements in the quality of Pennsylvania lubricating stocks when applied in amounts ranging from 20 to 50% by volume of solvents based on the stock, solvent proportions which are, in the light of most solvent experience, extremely low Results of such extractions on typical Pennsylvania stocks are given in Table VI

Table VI

Extraction of Pennsylvania Stocks

	*% nitro-benzene**	*Temp of extraction, ° F*	*Nitraffin yield†*	*S U viscosity* *at 100° F*	*at 130° F*	*at 210° F*	*API grav*	*V G C*	*V I*		*Carbon res*	*O D colour*
									A	B		
Steam-refined Cylinder Stock					825	143	26.3	0.815	98		2.14	2,929
	40	70	92.5		683	127	27.1	0.806	102		1.45	1,700
	50	50	96		713	130	27.0	0.807	101		1.73	2,500
	100	41	88.3		610	120	28.2	0.800	104		1.05	1,372
	100	70	82.6		646	124	28.3	0.798	104		0.94	1,157
Unfiltered Neutral Stock				174	93.8	44.4	30.0	0.822	92		0.04	53
	20	41	92.8	169	89.6	44.3	30.9	0.817	96	113	0.03	20
	25	41	92.3	168	89.6	44.4	30.7	0.818	98	117	0.02	35
	40	41	87.0	157	86.3	43.9	31.6	0.813	100	114	0.03	44

* Volume per cent based on stock

† Per cent of stock by volume

A– from visc at 100 and visc at 210

B—from visc at 130 and visc at 210

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PHENOL EXTRACTION OF LUBRICATING OILS

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Introduction

In order to improve the quality of lubricating oils and at the same time eliminate or reduce the cost of acid sludge disposal, a programme of research was started at Imperial Oil Ltd, Sarnia, Canada, in 1928, in an attempt to find a satisfactory solvent to displace sulphuric acid

A review of the literature at that time disclosed two patents dealing with the use of phenol Schick [3] in May 1926 was granted a German patent covering the use of phenol plus a large number of diluents for the refining of mineral and other oils In September of the same year, J P Fraser [2] obtained a British patent for a complete treating and recovery process for the refining of kerosine distillates using phenol containing about 5% to 15% of water

An attempt at Sarnia to use phenol as outlined by either of the above inventors gave comparatively poor results, and it was not until about a year later that the use of substantially anhydrous phenol resulted in the production of lubricating oils superior in many respects to those that could be obtained by ordinary refining methods

Reasons for Selecting Phenol

At the commencement of the investigation it was realized that any solvent planned to replace sulphuric acid should be able to treat a large variety of distillates to different degrees of improvement In other words, it should at least equal the flexibility of sulphuric acid At the same time the operation should be cheap and the solvent so stable that the loss in handling would be very low

During the preliminary development work a large number of solvents were investigated as to their selectivity, solvent power, and general commercial applicability It was found that phenol was about half-way between very selective solvents such as sulphur dioxide, furfural, &c, and solvents that are not so selective but have greater solvent power such as nitrobenzene, cresols, &c Because phenol is one of the most stable of the solvents investigated, particularly towards heat, is very easily removed from the oil and is cheap, and because the treating conditions for most oils are only slightly above ordinary temperatures, it was finally decided to concentrate on the investigation of phenol

Properties of Phenol

Phenol (C_6H_5OH) forms large colourless crystals which melt at 42° C (107 6° F) and boil at 183° C (361 4° F) It is an extremely stable compound towards heat, having been used for a number of years as a diluent in certain hydrogenation experiments [1] Phenol occurs naturally in coal tar or can be manufactured synthetically from benzol by several well-known methods Therefore the supply of phenol is unlimited

The Action of Phenol as a Selective Solvent

The majority of lubricating oils contain a number of components which are detrimental to their use as lubricants The nature and quantity of these components vary greatly with different crudes and different fractions from the same crude The purpose of any refining operation is to remove these undesirable substances as completely as possible, and at the same time to leave the desirable components in the oil

There are three important factors which have a direct bearing on the improved character and yield of the raffinate obtained by phenol treating They are

(1) Temperature of treating
(2) Proportion of phenol to oil
(3) Method of contacting phenol and oil

(1) Temperature of Treating The temperature at which treatment can be made is confined within the limits at which miscibility occurs between the oil and the phenol and the temperature at which the phenol crystallizes out of the phenol-oil mixture As a general rule, an increase in temperature gives a greater improvement in the raffinate, but lowers the yield

(2) Proportion of Phenol to Oil. The quantity of phenol usually varies between 1 2 volumes to 1 volume of oil Increasing the proportion of phenol to oil gives somewhat the same results as are obtained by increasing the temperature, although at times a greater improvement in viscosity index can be obtained by increasing the temperature than can possibly be obtained by increasing the proportion of phenol

It is necessary to run a number of experiments in order to determine the optimum conditions of temperature and quantity of phenol for any given oil For light stocks in particular it has been found that the lowest possible treating temperature produces the best yield for a given improvement in the raffinate The higher the viscosity and the viscosity index of the oil being treated the higher the temperature at which treatment can be made without adversely affecting the yield

(3) Method of Contacting Phenol and Oil The treatment of oil with phenol can be carried out either by single batch, multiple batch, or by continuous countercurrent extraction The quantity of solvent necessary to produce a given improvement in the oil by countercurrent treating is approximately one-half that which is required for a batch treatment While it is true that multiple batch treatments can give results approaching those obtained by countercurrent treating, nevertheless neither the yield nor the improvement in stability, colour, &c, are ever as good as with countercurrent treating

General Results of Phenol Treating

The results obtained from the phenol extraction of lubricating oils may be summarized as follows

Phenol can be used either to replace sulphuric acid in the finishing of lubricating oils or to make further improvements which cannot be realized with acid even in excessive amounts It has been calculated that for the former purpose the actual cost of phenol treating is about the same as with acid, with the advantage that the extract is suitable for cracking purposes or as a fuel oil, while the sludge from acid treating is difficult of disposal

The use of phenol to improve the viscosity index, stability to oxidation, Conradson carbon residue, &c , of the oil is important, as cheap, low viscosity index oils can be changed to high-quality oils by solvent extraction As a rule there is a limit to the extent to which an improvement can be made without incurring excessive loss in yield, and this is usually between forty and fifty points in viscosity index It has been found that there is no way of accurately predicting the yields for a desired quality of oil from different crudes, as the possible improvement varies with the crude as well as with the width of cut

The use of phenol as an extracting agent improves lubricating distillates in the following respects

(1) **Viscosity Index.** Phenol has been used successfully in the treatment of oils with viscosity indices below zero as well as for oils with viscosity indices of 100, and also for treating oils with viscosities as low as 80 Saybolt Universal at 100° F and as high as 200 Saybolt Universal at 210° F

(2) **Conradson Carbon Residue** In general the Conradson carbon residue of lubricating oils is reduced between 60% and 95% by phenol treatment The extent of the improvement is governed by the width of cut as well as the viscosity of the oil

(3) **Flash-point** Phenol-treated oils in general have the same flash-point as the stock from which they are prepared and as the viscosity is reduced more by phenol treatment than is the case with acid, the flash of the oil is higher for a given viscosity than can be obtained from the same stock by acid treating

(4) **Gravity and Colour** The improvement in API gravity is very great with solvent extraction, and it has been frequently found that an oil will continue to improve in gravity by additional treatment with phenol even after there is no further improvement in viscosity index Phenol is an excellent solvent for volatile colouring matter in lubricating oil and, while it removes a great deal of colour from the residual oil, it does not appreciably improve the cast or bloom of the oil

(5) **Reduction of Sligh Oxidation Number** Phenol treatment of a lubricating oil greatly improves its stability towards oxidation as measured by the Sligh test and many other oxidation tests The Sligh number is frequently reduced over 90% For example, a Colombian stock of 146 Saybolt Universal viscosity at 210° F before treatment showed a Sligh number of 87 5, and after phenol extraction gave 0 8 The same stock after acid and clay treating gave a Sligh number of 4 5, indicating the superiority of phenol over acid treating

(6) **Sulphur Reduction** The sulphur content is reduced between 60–80%, depending upon the stock and the treating conditions

(7) **Steam Emulsification Number.** By treating an oil with phenol, followed by proper finishing, very low steam emulsification numbers are obtained

Finishing of Phenol-treated Oils

By careful preparation of the stocks to be charged to the phenol plant, it has been possible at Sarnia to simplify and cheapen the finishing operations for the various lubricating oils For example, a distillate from Colombian crude suitable for the production of S A E no 30 oil was treated with 125% phenol at 115° F to give about a 65% yield of raffinate which requires only 2–3% of Filtrol clay to finish to a satisfactory oil with a colour of 13–14 Robinson.

In order to produce an S A E no 40 stock, only 4% of Filtrol was necessary after phenol treating At Port-Jérôme, France, oils of similar quality are obtained without the use of either acid or clay, simply by distillation of the raffinate in a re-run flash coil, from which the oils are pumped directly to finished storage

Only solvent extracted oils that are very dirty or very high in viscosity require acid in order to obtain good colour and bloom, and in every case the quantity used should be very small

Results of Phenol Treating Lubricating Oils from Various Crudes

During the last few years a large variety of oils representing almost every type of crude have been treated with phenol at Sarnia to various degrees of refinement It has been found that while a general inspection of any oil will give a rough idea as to its reaction to phenol, nevertheless there is no way of definitely predicting what improvement can be expected in any specific case, as lubricating oil fractions vary a great deal in their manner of responding to solvent extraction The oils that have been treated varied as follows

(1) Very low and very high viscosity index oils
(2) Narrow- and wide-cut oils
(3) Very clean and very dirty stocks
(4) Heavy residual and light overhead cuts
(5) Waxy and dewaxed oils

Among the American oils studied have been fractions from Mid-Continent, Panhandle, Oklahoma City, Coalinga, Ventura, Coastal, and Pennsylvania, also Iranian and Peruvian crudes These different stocks have been treated not only for the purpose of replacing acid, but also to produce the greatest possible quality improvement

It has been found possible when treating high or intermediate viscosity index oils to first treat the stock lightly with phenol and then re-treat the raffinate with more phenol In this way an oil of very high quality can be obtained, and at the same time an oil of intermediate quality is produced which can be used for many purposes The extract from the solvent treatment of lubricating oils can either be cracked for the production of high octane number gasoline, used for fuel oil or asphalts, or worked up into various specialities

In order to illustrate the flexibility of the process, the following examples of different treatments are given in Table I

TABLE I

California Low Viscosity Index Distillates

	Stocks			
	70 viscosity untreated Coalinga 125% phenol at 90° F		*150 viscosity untreated Coalinga 100% phenol at 100° F*	
Treatment inspection	*before*	*after*	*before*	*after*
Viscosity at 210° F	69	59	139	92
Gravity, ° API	15 9	26 2	14 2	21 3
Viscosity index	−50	+74	−60	+31
Conradson carbon residue	0 215	nil	0 704	0 103
Pour/solid, ° F	25/20	−5/−10	45/40	5/0
Robinson colour	transparent green	17½	transparent green	3½
Yield, %		24 7		36 2

It can be seen from Table I that a great improvement in gravity, viscosity index, and colour has been obtained, and in both cases the Conradson carbon residue has been lowered 85% or better

It will be noted that with these particular oils the cold test of the raffinate has been lowered This peculiarity has been found to occur with a number of distillates which received light solvent treats, notably distillates from Peruvian crude It will also be evident from this table, as well as from succeeding tables, that solvent treating lowers the Saybolt Universal viscosity at 210° F and that the greatest drop occurs with high viscosity oils In the case of California distillates the yields are very low, but at the same time there is an improvement of between 90–120 points in viscosity index, and this is far greater than can be obtained by conventional methods The colour improvement is so great for stocks such as these that little, if any, further treatment is necessary except possibly a small quantity of clay in order to improve the cast

TABLE II

Coastal and Colombian Distillates

	Stocks			
	60 viscosity Coastal 100% phenol at 115° F		*Extra-heavy Colombian 115% phenol at 125° F*	
Treatment inspections	*before*	*after*	*before*	*after*
Viscosity at 210° F	64	60	146	99
Gravity, ° API	20	25 8	17 4	25 8
Viscosity index	22	74	28	77
Conradson carbon residue	0 125	0 029	1 845	0 295
Pour/solid, ° F	−10/−15	0/−5	30/25	45/40
Robinson colour	blue opaque	9¼	green opaque	¾
Yield, %		64 7		53 3

Table II gives the treatment of Coastal and Colombian distillates The same drop in viscosity with solvent extraction can be noted, together with a remarkable reduction in Conradson carbon residue, particularly with the heavy stock The pour test and solid point of these oils has been increased slightly by phenol treating, and this has been found to happen with low cold test oils or oils that have been dewaxed by ordinary methods Those that have been dewaxed by benzol-acetone or chlorinated solvents do not increase in cold test upon solvent extraction

Both the Coastal and Colombian distillates show a very marked colour improvement, indicating that there is very little, if any, entrained material

After phenol treatment of the Coastal oil the API gravity was 25 8 for a viscosity of 60 Saybolt Universal at 210° F, while with the Colombian the gravity is the same with a Saybolt Universal viscosity of 99 at 210° F The viscosity indices for both these distillates are approximately the same

Such a comparison indicates that the viscosity-gravity constant as used in the literature is not as satisfactory as the more empirical but more practical viscosity index, which has a direct relationship to the viscosity at low temperature

Table III gives results typical of Mid-Continent undewaxed stocks As a general rule, phenol treating removes a large proportion of the volatile colouring matter from an oil If the distillate contains entrained asphaltic material, or if a residual oil is treated with phenol, very little visible improvement is obtained A great deal of colouring material is of course removed from the oil, but a very inert black material remains which necessitates other finishing operations before the oil can be improved in colour This point is illustrated in the case of the Oklahoma residual mixture Contacting such stocks with clay does not give satisfactory colour improvement, particularly if only moderate quantities of clay are used

TABLE III

Mid-Continent Undewaxed Stocks

	Stocks			
	100 wax slops 3–100% batch treatments at 210° F		*Oklahoma City crude mix 150% phenol at 140° F*	
Treatment inspections	*before*	*after*	*before*	*after*
Viscosity at 210° F	98	78	144½	111
Gravity, ° API	22 6	28 5	19 8	25 8
Viscosity index	74	107	71	103
Conradson carbon residue	1 330	0 179	5 595	2 866
Pour/solid ° F	70 65	100	70/65	70/65
Robinson colour	blue opaque	red	black	greenish black
Yield, %		65 4		67 8

The Conradson carbon residue is more difficult to lower when treating residual stocks than is the case with distillates In the Oklahoma City crude mixture the Conradson carbon residue is reduced from 5 595 to 2 866 This can be explained in two ways

(1) Because the inert black material remaining in the residual oil produces Conradson carbon

(2) Very high molecular weight hydrocarbons, even though they are not asphaltic in character, decompose and produce carbon under the conditions of the Conradson carbon test

This demonstrates why the Oklahoma City residual, which is a wide cut, has not shown as great a reduction in Conradson carbon residue as do many of the other stocks illustrated in the article

Limitations of the Phenol Process

While no operating difficulties have been encountered in treating residual stocks with phenol, at the same time difficulties have been found in finishing these oils after the solvent operation This is because of the type of colour material left in the oil, which cannot be removed with clay except by employing excessive quantities to contact the oil If the oil is acid treated, hardly any sludge is formed, with the result that coagulation does not take place and the acid cannot be satisfactorily removed Some other step is necessary to produce high-coloured, high-viscosity oils directly from residual stocks In this connexion propane has been employed successfully in experimental treats

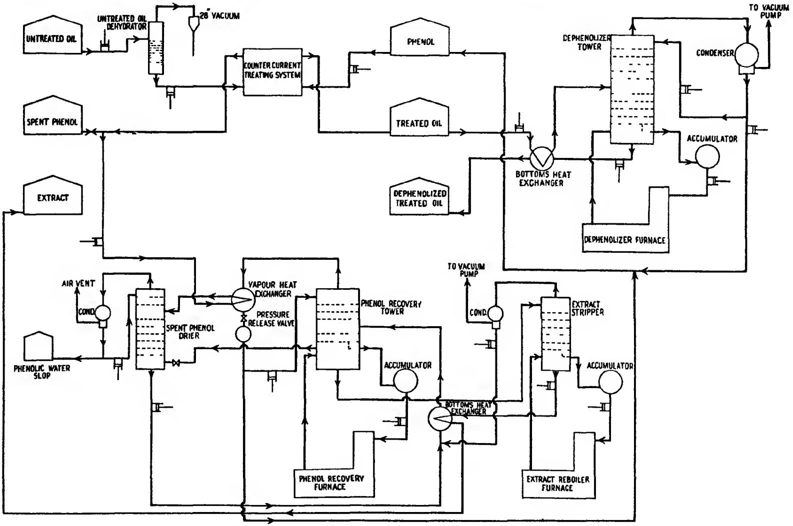
If phenol is used to treat a very wide cut which includes gas oil as well as residual oil, the phenol has a tendency to remove an excessive amount of the light ends Such difficulty does not occur if a wide lubricating oil fraction is used or if comparatively narrow-cut oils are phenol treated

Description and Operation of the Phenol Plant

The plant operates in such a manner that the distillate is continuously treated and separated into extract and raffinate portions, the phenol being continuously reclaimed and re-used The equipment consists essentially of three

FIGURE Nº 1

PHENOL TREATING PLANT-PROCESS FLOW PLAN



parts: a countercurrent treater, a dephenolizing unit, and a phenol-recovery unit.

Preheated oil (110–125° F.) and phenol pass countercurrently through a treater consisting of seven 'Leaver' mixers, seven settling drums, and the necessary pumps, &c. Treated oil is drawn from the top of the seventh settling drum and pumped to the tank from which the dephenolizing unit is charged. Spent phenol is discharged from the first settling drum through a cooler into a settling tank, which is maintained at a temperature of 95–100° F. The light oil which separates from the cooled spent phenol in this tank is recycled to the countercurrent treater. The cooled spent phenol is discharged to a tank before being pumped to the phenol-recovery unit.

The treated oil containing 8–15% phenol is pumped to a pipe still, from which the heated charge passes to a 14-plate fractionating column operating under atmospheric pressure. The phenol coming overhead is condensed and flows into a reflux drum. A portion of this phenol is refluxed down the tower, and the remainder flows to pure phenol storage. The bottoms of the bubble tower are sent to a 6-plate vacuum stripper. A portion of the condensed overhead from this stripper is refluxed and the remainder recycled to the pipe still. The bottoms from this vacuum stripper are reboiled and recycled to a point below the lowest plate in the stripping tower. The bottoms are finally pumped from this tower, through a cooler to dephenolized treated oil storage. The quantity of phenol (0.005%) in this treated oil is negligible.

The phenol-recovery unit is similar to, but larger than, the dephenolizing unit. The spent phenol containing 25–30% oil is preheated in a vapour heat exchanger before entering the pipe still. Pure phenol is taken as a side stream from the fifth plate below the top of the bubble tower, cooled, and then discharged to phenol storage. The overhead from this tower is chiefly phenolic water. The portion of this overhead not used as reflux is segregated to storage and, when sufficient accumulates, the phenol is readily recovered in a small recovery plant. The bottoms of the bubble tower are sent to a 6-plate vacuum stripper. The portion of the condensed overhead from the vacuum stripper not used as reflux is recycled with the incoming spent phenol charged to the unit. The bottoms of this tower are reboiled and finally drawn off, cooled, and the dephenolized extract oil is pumped to storage. The phenol content of this extract oil runs less than 0.07%.

The Future of the Phenol Process

There is no doubt that the use of solvents in the refining of petroleum distillates will increase very greatly during the next few years and a variety of solvents will be used for the production of oils of different qualities for a number of purposes. Phenol will undoubtedly be used by many refineries throughout the world because of its flexibility as a treating agent, in that extraction can be made without refrigeration, its remarkable stability towards heat, and the fact that it can be used in large and small installations.

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THE CHLOREX EXTRACTION PROCESS

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CHLOREX is the trade name for $\beta\beta'$-dichlorethyl ether—$ClCH_2CH_2OCH_2CH_2Cl$ It is one of the most widely used of the solvents which are employed for producing motor oils of improved viscosity index, oxidation stability, carbon residue, and other properties, from a given crude, by extraction of the undesirable constituents It owes this position in large part not only to good solvent powers, but to an unusually favourable combination of physical and chemical properties

Physical and Chemical Properties of Chlorex

Specific gravity at 68° F	1 22
Normal boiling-point, ° F	352
Freezing-point ° F	61
Flash-point (Closed Cup), ° F	168
Vapour pressure at 68° F —mm Hg	0 73
Specific heat at 77° F	0 369
Latent heat at normal boiling-point, B Th U per lb	115
Viscosity at 77° F —centipoises	2 04
„ at 352° F — „	0 38
Solubility in water—weight % at 68° F	1 01
„ at 194° F	1 71

Water is soluble in Chlorex to the extent of about 0 5 weight per cent

Chlorex shows satisfactory stability against heat and hydrolysis, as will be discussed later, and is non-corrosive to ordinary materials of construction

It will be noted that Chlorex has a high specific gravity and low viscosity, so that it tends to come to equilibrium quickly and to separate readily from the oil layer Its freezing-point is low, and its flash-point makes it about as safe to handle as kerosine Its boiling-point is low enough to make possible complete separation from light neutral oils, yet its vapour pressure at atmospheric temperatures is so low that losses from storage are negligible Its solubility in water is low enough to allow steam to be used in stripping it from the oil The Chlorex must be recovered from the condensed water, but this is very easily done in small and simple apparatus The small amount of water in the Chlorex has practically no effect on performance and it is not necessary to remove it

The proper operating temperature for Chlorex extraction is close to atmospheric temperature—mostly between 75 and 100° F Hence plants to operate on Chlorex require a minimum of heating and cooling

As a result of these factors, Chlorex is peculiarly adapted to plants in which spare equipment is available Ordinary shell stills can be used for Chlorex recovery, if desired, and other spare equipment can be used for tanks, settlers, &c This has been a factor in the wide acceptance of the process, its use is by no means confined to such conditions, however, and several of the plants now in operation have been constructed almost entirely of new equipment

Effects of Chlorex Extraction

1 **Improvement in Viscosity Index** Extraction with Chlorex improves the temperature-viscosity characteristics of lubricating fractions (increases the viscosity index and lowers the viscosity-gravity constant), this was one of the primary objects in view in developing the process Oils of Pennsylvania characteristics can be made from Mid-Continent oils, and in smaller yield from crudes containing still more naphthenes Pennsylvania oils can be further improved

2 **Improvement in Colour** A final finishing with clay is ordinarily required after Chlorex extraction The extraction renders this very much more effective, however, and the decolorizing effect of a given amount of clay is multiplied many fold by the extraction process

3 **Improvement in Stability to Oxidation** The effect of Chlorex extraction on stability to oxidation is in some cases even more important than its effect on viscosity index By the Chlorex process very stable oils are obtained, whether measured by the Indiana oxidation test, the Sligh test, or other methods

4 **Reduction in Carbon Residue** Chlorex extraction results in a lowering of the carbon residue of an oil The substances removed by Chlorex have an abnormally high carbon residue, and unless the amount of material removed is small the reduction in carbon residue is very great The carbon residue of oils from Chlorex extraction is rarely more than 50% of that of the stock charged and may be as little as 5%

5 **Reduction in Viscosity-Increase in Flash.** Normally the raffinate oil prepared by Chlorex extraction will be less viscous at the ordinary temperatures of measurement than the original stock Since the lower molecular weight oils of a given degree of paraffinicity are somewhat more soluble in Chlorex than heavier oils, it sometimes happens that long residua after extraction are more viscous at 210° F than before, but at lower temperatures the raffinate will have the lower viscosity Since the flash of a stock is not ordinarily affected by extraction, and since the viscosity falls, the use of Chlorex makes possible the production of oils having a higher flash for a given viscosity

6 **Effect on Pour-point** In the case of wax-free oils, whether they are obtained from wax-free crudes or by the thorough dewaxing of waxy oils, Chlorex extraction lowers the pour-point because it lowers the low-temperature viscosity In the case of oils containing appreciable amounts of wax, the effect of extraction is to raise the pour-point, since wax is the least soluble component of the oil and therefore concentrates in the raffinate

Ratio of Chlorex Required

The quantities of Chlorex required in the extraction operation are quite moderate In the commercial plants now in operation, all of which operate on Pennsylvania or Mid-Continent oils, the volume of Chlorex used per volume of feed oil varies from ¾ to 1½

Finishing of Chlorex-treated Oils

Generally speaking, Chlorex-extracted oils require only a moderate amount of clay, either by percolation or contacting, to produce finished oils of satisfactory colour and demulsibility The extracted oils behave much like Pennsylvania oils towards sulphuric acid and, in case it is desirable for any reason to combine acid treatment with solvent extraction, it will be found that it is easier to treat with acid before extraction Dewaxing may be done either before or after extraction If the former procedure is adopted, allowance must be made for a possible increase in pour test on extraction, but in other respects this order of the operations is more satisfactory than the reverse order, since there is no loss of extracted oil in the wax, and a dewaxed oil is easier to handle during the extraction procedure

Results obtained with Various Stocks

The plants at present in operation are all devoted to the extraction of Pennsylvania or Mid-Continent types of oils Laboratory experiments, however, have demonstrated that Chlorex can be used effectively on a wide variety of stocks, both as regards viscosity and type of crude Like practically all other single solvent processes, the Chlorex process is not well adapted to the treatment of oils containing large amounts of asphalt, such as Mid-Continent residua Such stocks are best acid treated or propane deasphalted before extraction The accompanying Table I will give an indication as to the results obtainable from representative stocks

In general, a given degree of refinement can be obtained with a better yield when the extraction temperature is lowered, but a larger amount of solvent will be required to attain the given degree of refinement, and the very highest degree of refinement can be obtained only at the highest temperature The equivalent of about five or six theoretical stages will give nearly all the improvement possible with a given solvent ratio, though on heavy, dark-coloured stocks one or two stages more may perhaps be used to advantage to effect further removal of colour The determining factor in choosing the required number of stages is sometimes the effectiveness with which clay acts on the raffinate, this is favourably affected by an increasing number of stages after their effect on viscosity index has become negligible

Recovery of Chlorex

It is quite possible to recover Chlorex by direct heat and steam distillation in batch stills, and the first Chlorex plant to be installed (at Casper, Wyo) has always been operated in this way Some decomposition of the Chlorex occurs during the latter part of the distillation, forming hydrochloric acid, and it is necessary to admit ammonia to the vapour line of the still to keep down corrosion Even under these unfavourable conditions, however, the total loss of Chlorex (including vaporization, spilling, &c) is about 0·25% per use An atmospheric pipe still and tower will reduce the loss considerably By the use of vacuum pipe still distillation followed by steam stripping in a vacuum the total losses can be brought down to 0·05% per use Chlorine in the raffinate is of the order of 0·002% before clay treatment, but is completely removed by clay treatment

TABLE I

Results of Chlorex Extraction

	Pennsylvania			Mid-Continent distillate					Gulf Coast			Mexican distillate	
Charging stock	*Neutral*	*Neutral*	*Cylinder stock*	*A*	*B*	*B*	*B*	*B*	*Mid-Cont de asphalted resid*	*Distillate*	*De asphalted resid*	*A*	*B*
Viscosity, Saybolt Univ 210° F	45·7	63·6	160	52·2	125·6	125·6	125·6	125·6	128·5	61·0	270	61·6	196·0
Viscosity index	95·5	105·5	102·5	69·9	60	60	60	60	65·5	21	45	32	28
Gravity, ° API	31·4	29·8	25·9	24·9	20·6	20·6	20·6	20·6	20·7	20·4	17·9	18·7	15·9
True colour[*]	17	68	2 530	300	800	800	800	800	2 000	85	4 000	115	525
N P A colour	3½	4½–5		9						5+		6	
Carbon residue %	0·01	0·42	2·71	0·20	2·75	2·75	2·75	2·75	3·20	0·16	5·49	0·31	3·10
Indiana oxidation—hr for 10 mg[†]	26·5	57·5		2·0	3·0	3·0	3·0	3·0		4·0		4·0	6·5
Extraction conditions													
Number of counter-current stages	7	7	4	6	5	5	5	5	7	7	3	7	7
Chlorex to charge ratio (volume)	1·5	1·5	1·5	2·5	1·0	2·0	1·0	2·0	2·0	1·5	1·85	2·5	2·5
Temperature, ° F	80	100	75	75	50	50	100	100	80	75	100	75	75
Raffinate yield—% by volume	82·4	82·6	92·1	60·4	80·7	72·3	69·1	58·2	58	50·1	61·8	28·7	43·4
Properties of raffinate—Clayed as indicated													
Yield from no 1 Attapulgus Clay—U S gal per short ton	no clay	no clay	no clay	3,350	330	540	400	980	150	5,000	250	10,000+	1,000
Viscosity, Saybolt Univ 210° F	45·0	65·3	150·8	48·1	98·5	95·3	96·3	91·6	92·2	59·2	145·2	55·5	107·9
Viscosity index	106·5	114	108·5	100	82·3	86·3	83·8	90·3	98·4	74·2	93	92·0	85·5
Gravity, ° API	33·5	31·7	27·2	31·4	25·6	26·8	26·6	28·0	27·7	26·0	24·6	28·7	25·1
True colour[*]	11	66	2 260	13	35	35	35	35	25·0	14·5	170	11·5	22
N P A colour	2½–3	4½–5		3	4–4½	4–4½	4–4½	4–4½	3½–4	3+	8	2½–3	3½–4
Carbon residue	0·02	0·25	1·79	0·02	0·50	0·26	0·33	0·19	0·3	0·01	0·80	0·01	0·25
Indiana oxidation—hr for 10 mg asphaltenes[†]	35·5	205+		44	135	185	155	225		51·5		45·5	>114
Extract properties													
Viscosity, Saybolt Univ 210 ° F	53·5	65·1	1 290							86·0		72·9	484
Viscosity index	30	42	−40							−75		−22	−70
Gravity, ° API	21·1	21·4	7·9	16·9	6·2	7·9	11·9	13·0		14·0		14·6	8·3

[*] Rogers, Grimm, and Lemmon *Ind Eng Chem* 18, 164 (1926)

[†] Rogers and Shoemaker *Ind Eng Chem* Anal Ed , 6, 419 (1934)

Chlorex is best recovered from the water in a small packed column A few per cent of steam in excess of the amount required to raise the water to the boiling-point will remove the Chlorex almost quantitatively

A flow sheet of a typical lay-out using continuous stills is shown in the accompanying figure

Plants in Operation

The first Chlorex extraction plant was started at the Casper, Wyoming, refinery of the Standard Oil Company (Indiana) in June 1932 In August 1936 there were seven plants in operation, with a total daily charging capacity of 6,150 42-gal barrels

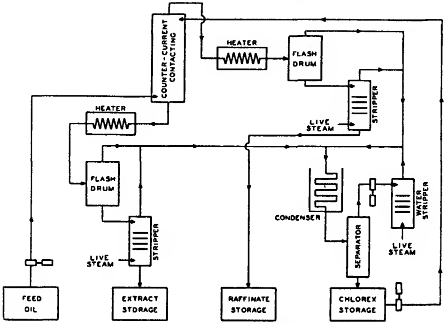

FIG 1 Flow sheet of Chlorex process

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THE APPLICATION OF FURFURAL TO THE REFINING OF LUBRICATING STOCKS

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Introduction

An ideal refining solvent should effect separation of undesired 'extract' material from the charge oil without loss of valuable 'raffinate' constituents, should be applicable to even the highest viscosity oils at temperatures high enough to obtain intimate contact and rapid separation of raffinate and extract phases in continuous counter-current application, and should be stable at the maximum stripping temperature employed In addition, the solvent must be readily available in large quantities at low cost and should be relatively non-toxic Furfural as a selective solvent closely approaches the requirements of an ideal solvent, particularly when applied to distillate lubricating stocks or residual oils of low asphalt content

The original work on the application of furfural to the selective solvent refining of lubricating oils is covered in U S Patent no 1,550,523 (1925), issued to Egon Eichwald This patent discloses broadly the use of furfural for the purification of hydrocarbon oils The development of this process and its commercial application were carried out in the laboratories of the Texas Company, and the first commercial installation was made at the Lawrenceville, Illinois, refinery of the Indian Refining Company, where operations were started in December 1933

The raw material source in the manufacture of furfural is agricultural wastes, such as oat hulls, straw, corn cobs, rice hulls, &c Its production in commercial practice is comparatively simple, and good yields of solvent are obtained from relatively inexpensive waste matter The raw material source and ease of manufacture ensures an adequate supply at a relatively low cost Furfural compares favourably in price with all the commercially available refining solvents

Physical Properties of Furfural

The physical properties of furfural are shown in Table I Pure furfural boils at 323° F at 760 mm pressure The vapour-pressure curve for furfural is shown in Fig 1 The normal grade of commercial furfural usually contains small amounts of water and the lower fatty acids Small amounts of formic and acetic acid have also been identified in the commercial product The acid content of furfural in a closed system decreases in the first recovery operations and remains at a low point due to the removal of acids with water from stripping operations

Furfural is very stable in plant solvent recovery equipment, in which temperatures have at times been maintained as high as 600° F Although furfural darkens on standing, the colour change represents only a very minute amount of actual polymerized solvent, and in a closed system in plant operation the solvent remains light yellow in colour Actual volume inventories covering several months of commercial operation of the process have shown that the furfural loss amounts to only 0 0252% of the total furfural used This amounts to only 0 0223 gal of furfural lost per barrel of oil charged when refining with a volume solvent ratio of approximately 2 00

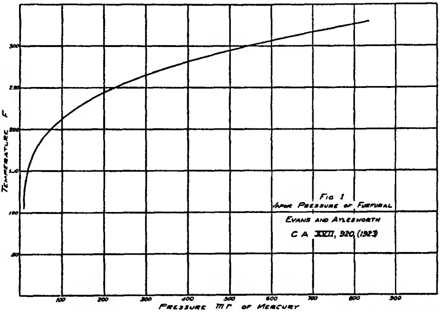
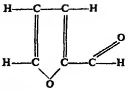


Fig 1
Vapor Pressure of Furfural
Evans and Aylesworth
C A XVII, 920 (1923)

TABLE I

Properties of Furfural

Structural formula



Boiling-point, ° F at 760 mm	323
Freezing-point, ° F	−34
Specific gravity at 60° F	1 164
Kinematic viscosity at 100° F (centistokes)	0 907
Specific heat (68–212° F)	0·416
Heat of vaporization (29 9 in Hg) B Th U per lb	193 5
Vapour pressure at 100° F	7
Tagliabue close-cup flash, ° F	138
Solubility of furfural in water at 100° F , % by weight	8·96
Critical temperature, ° F	746
Critical pressure, lb per sq in abs	798

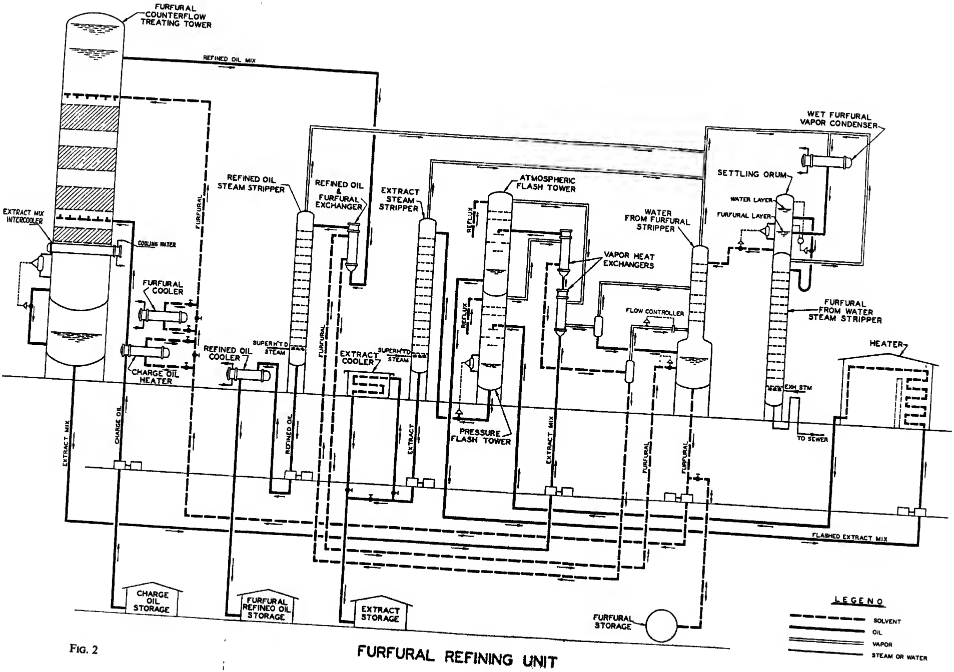


FIG. 2

FURFURAL REFINING UNIT

Furfural is relatively non-poisonous, although, in contact with the skin, it is mildly irritating and causes discoloration In rare cases men will be found who exhibit a skin sensitivity towards furfural, but this is not serious and no ill effects are encountered when the solvent is handled with reasonable care Low toxicity is an important advantage when possible solvent leakage and contact with solvent either in liquid or vapour state are considered

Application of Furfural

The temperature range of application for furfural is considerably wider than for most solvents, and the temperature of complete solution of paraffinic oil and solvent is high Furfural is employed normally in lubricating oil extraction at temperatures ranging from 90° F to 280° F In this range practically any viscous or waxy oil can be treated readily Furfural is non-viscous and has a specific gravity high enough to settle quickly through the oil

Counterflow operation is accepted as the method which gives the best fractionation of 'raffinate' and 'extract' constituents in solvent refining The high temperatures of application of furfural and the difference in specific gravity between extract and raffinate solution permit counterflow operation in either a packed tower or in a step-counterflow system This flexibility is not a characteristic of all commercially developed solvents

Settling rates of furfural in oil are not only high, but, in addition, furfural selectively wets ceramic or other packing, spreading over the surface of the tower packing in a thin film, thus offering a large surface of contact at the interface between the two phases and permitting the two layers to approach equilibrium quickly The low viscosity of the oil layer at high operating temperatures offers low resistance to the attainment of this equilibrium In step-counterflow operation the high temperature and gravity difference results in rapid settling and a minimum difficulty from emulsion formation

The analogy between fractionation by distillation and fractionation by counter-current solvent extraction was first pointed out by R N J Saal and W J D van Dyck [1, 1935]

As in fractionation by distillation, efficient fractionation by solvent extraction requires the use of a reflux Due to the high temperature of application of furfural, reflux is readily obtained by the use of a temperature gradient between the two ends of the counterflow treating system The value of this reflux in increasing the efficiency of separation has been definitely established by theoretical considerations and actual plant operations The most efficient results will be obtained by introducing the charge oil at an intermediate point in the counterflow system with a relatively large temperature gradient in the extract end This results in a high reflux ratio in the extract and where it is most needed from the standpoint of yields This type of temperature gradient can be easily obtained with furfural by introducing both oil and furfural at elevated temperatures and cooling the extract end of the counterflow system

When solvent refining paraffin base stocks furfural may be applied either to the dewaxed or to the raw undewaxed stocks The high refining temperatures ensure all wax being in solution, and consequently wax does not interfere with settling On solvent refining dewaxed stocks a slight rise in pour test will occur unless the oil is dewaxed to a low pour test, in the order of −10° F

No acid treatment is necessary after furfural refining distillate stocks, as ordinary percolation or contact filtration of the raffinate will give a product of acceptable colour Generally speaking, however, clay is not very reactive to a neutral oil, and if a pale colour (below 4 NPA) is desired it is more economical to use a light 98% acid treat of from 2 to 7 lb per barrel than to carry out all decolorizing with clay alone On residual oils, excepting the Pennsylvania type, and on some heavy distillates, acid treatment of the solvent refined oil is necessary for satisfactory colour Although acid treatment is not practical on Pennsylvania type residua, furfural treatment renders the stock much more susceptible to percolation or contact filtration

In general, it may be stated that no rigid rules regarding order of refining steps can be laid down, and the most economical procedures for different stocks can only be determined by investigation

Furfural Refining Plant

Plant facilities required for the furfural refining of lubricating stocks consist of the following main operating units

1 Vertical counterflow extraction tower with preheaters or exchangers for furfural and charge oil, together with means for charging solvent and oil at a predetermined controlled charge rate
2 Storage for refined oil solution and extract solution for supplying charge to strippers
3 Extract stripping unit for combined atmospheric and vacuum distillation of furfural from extract solution
4 Refined oil stripping unit for vacuum distillation of furfural from the refined oil solution
5 Solvent recovery system including condenser, water cooler, accumulator drum, vacuum pump, aftercooler, and receiver
6 Two vacuum steam strippers for removal of final traces of furfural from raffinate and extract
7 Separating tower and fractionator for recovering furfural from the steamings and drying of furfural prior to its return to the system
8 Slop solvent and new solvent storage tanks
9 Storage tanks for extract and refined oil

A diagrammatic flow sheet of a furfural refining unit is shown in Fig 2

A commercial plant for furfural refining Mid-Continent distillates has been in almost continuous operation for a period of 2 years This plant processes an average of 1,300 bbl per day of waxy distillates ranging in viscosity from 45 sec Saybolt at 210° F to 160 sec Saybolt at 210° F

The unique feature of this plant is the installation and successful operation of a packed counterflow extraction tower The use of a counterflow extraction tower instead of a large number of stages in step counterflow has proved advantageous from the standpoint of plant investment in equipment, simplified operation, and reduced operating and repair costs It should be emphasized, however, that furfural is equally adaptable to both continuous counterflow and step-counterflow operations Either system may be used—the choice depending upon the economics involved, the flexibility desired, and the preference of the individual refiner

Table II shows the solvent losses in plant operation as determined by actual inventories over an 8-month operating period It will be noted that the losses gradually decreased as line leaks and other defects inherent in a new plant were corrected In the Lawrenceville plant of the Indian Refining Company the solvent is circulated approximately 8 times in each 24 hours of operation

TABLE II

Average Furfural Losses

(Plant Operating Data)

Period	*Total barrels of oil treated*	*Total barrels furfural used*	*Gallons furfural loss*	*% furfural loss (basis furfural used)*	*Gallons furfural lost per barrel of oil charged*
31 3 34 to 4 6 34	79 873	152,765	3 243	0-0505	0 0406
4 6 34 to 14 8 34	84,228	159 612	2 889	0 0431	0 0343
14 8 34 to 12 11 34	100 753	212 420	2 251	0 0252	0 0223
Total for period 31 3 34 to 12 11 34	264 854	524,797	8 383	0 0380	0-0316

Investment and Operating Costs

Furfural refining-plant installation costs are dependent to a large extent on each refiner's individual problem In general, the initial investment for furfural refining is relatively low, varying from about $200 per bbl of daily charge capacity for units of 500 bbl capacity to about $70 per bbl for units having a daily charge rate of 5,000 bbl Plant design is adapted to the efficient utilization of recovered refinery equipment

In Table III are presented the labour requirements, utilities requirements, and average operating conditions of a commercial furfural refining unit having a nominal capacity of 1,350 bbl of Mid-Continent distillate (all grades) per day (2,700 bbl furfural per day)

TABLE III

Furfural Refining Unit

Labour requirements

Labour	*Hours*	*Hourly rate*	*Daily cost*
		$	$
Operating foreman	4	1 50	6 00
Shift foreman	8	1 25	10 00
Operator	24	0 90	21 60
Helper	24	0 75	18 00
Labourer	3	0 55	1 65
			$57 25

Utilities requirements

Fuel, 0 0443 bbl of fuel per bbl of charge
Steam, 151 lb per bbl of charge
Water pumping, 0 943 K.W H per bbl of charge

Average operating conditions—Wax distillate no 40 stock

Oil charged to plant, ° F	120
Temperature of oil charged to counterflow tower, °F	195
Temperature of furfural charged to counterflow tower, ° F	255
Temperature, top of tower, ° F	235
,, bottom of tower, ° F	200
Ratio of furfural to oil charged, by volume	1 97 1
Fuel distribution Extract, %	77-02
Raffinate, %	22 98
Plant charge rate (42-gal bbl), bbl per day	1,330
Furfural loss (average), % bbl of furfural used	0 0380

Labour requirements are based on actual operating conditions, where the operating foreman and shift foreman handle other operations in addition to the furfural refining unit. The labour requirements are sufficient to take care of a much larger unit, and unit labour costs on a larger plant would be reduced practically in proportion to the production

In this plant all pumps are steam driven, exhaust steam being credited for use in other parts of the refinery Due to the use of steam, electric power costs are low A circulating-water system with a cooling tower is in use which reduces the water requirements to evaporation and mechanical losses

The average operating conditions are those in actual use and do not necessarily represent the optimum conditions for a Mid-Continent distillate Production requirements, which forced operations well above rated capacity, necessitated changes in operating conditions from those normally used

In Table IV is a detailed statement of operating costs for a typical operating month Total direct operating expense amounts to only $0 1739 per 42-gal bbl of charge

TABLE IV

Operating Costs—Furfural Refining Unit

(Exclusive of Royalties)

	Unit cost per barrel of charge	
	$	
Operating labour	0 0366	
Materials, supplies, and others	0 0033	
Fuel	0 0496	
Steam power and water	0 0493	$
Total operating		0 1388
Repair labour	0 0020	
Material, supplies, and other	0 0026	
Total repairs		0 0046
Furfural loss		0 0305
Total direct expense, per bbl		$0 1739

It is felt that the low operating costs shown are quite satisfactory Due to generally improved and simplified processing operations, and to the increased value of extract over acid sludge, many installations will show a lower direct cost for a finished solvent refined oil than for the conventionally acid-treated oil without the use of solvent

In Table V are presented the tests on the raw lubricating stocks charged to the Lawrenceville plant together with the results obtained in the furfural refining-plant operations Tests are also shown on the same oils dewaxed by the Solvent Dewaxing Process using acetone-benzol mixture as the solvent

Attention is called to the fact that this plant was operating on the production of oils having viscosity indices and other characteristics which are considered to be satisfactorily high for superior performance in service Increases in solvent ratios and modifications of operating conditions would result in higher viscosity indices with proportionate decrease in charge rate for the plant The yields obtained are particularly high, due to the degree of selectivity of furfural as a refining solvent A further sacrifice in yields and increased cost of operation is not considered justified for the doubtful advantage of a few points increase in viscosity index

The finishing steps employed in the manufacture of the low pour-test solvent refined lubricants herein described consist in acid-treating the raffinate with 2–5 lb per bbl of 98% acid, contact neutralizing with 4–12 lb per bbl of fine contact clay (not acid treated), and dewaxing with acetone-benzol to a pour test below 0° F. The light acid treatment is considered more efficient and economical than straight percolation or contact filtering, although a satisfactory product can be made by the latter methods using no acid

Application of Furfural to Various Lubricating Stocks

Extensive research and development work has demonstrated the applicability of furfural to a wide variety of lubricating stocks This investigation has demonstrated that furfural is particularly adapted to the solvent refining of such widely varying stocks as Gulf Coast naphthene base distillates and Pennsylvania distillates and cylinder stocks

Table VI shows typical results that are readily obtained on Pennsylvania distillates and cylinder stocks In these examples high solvent ratios and low temperatures have been used, but equal yields and quality could be obtained by the use of lower solvent ratios and higher temperatures The action of furfural on steam-refined Pennsylvania cylinder stocks renders these stocks much more susceptible to clay filtration to a given colour specification, and materially lowers the carbon residue

In Table VII are presented data on the furfural refining of lubricating distillates from a naphthene base crude It will be noted that excellent yields of relatively high-quality refined oils are obtained With only light clay contact treatment the products have excellent demulsibility tests

Table VIII presents data on the furfural refining of distillates from various foreign crudes Here again the high degree of selectivity of furfural is of advantage in that it gives high yields of a high-quality refined oil

SUPPLEMENT

Since the preparation of the original article important improvements to the furfural refining process have been effected, and a brief description of the changes made are presented here (cf Fig 2) The effect of the changes on the economy of operation, and the further commercial application to a wide variety of lubricating stocks, are also recorded

Improvements to Furfural Refining Process

Recent changes to the design described in the original article are

1 The installation of cooling means for cooling extract mix, and maintaining controlled temperature gradients to increase yields
2 The use of two or three stages in the recovery of solvent from the extract solution The first stage being atmospheric evaporation by heat exchange against furfural vapours at about 45 lb pressure, the second stage a pressure evaporation at about 45 lb gauge pressure, and a third stage vacuum evaporation either dry or in the presence of steam or both
3 The recovery of furfural from the water in the wet solvent and the drying of the wet furfural are carried out continuously The recovered solvent is held as near extraction temperatures as possible, thus reducing the amount of cooling and reheating employed in the original process

The cooling of extract solution in the bottom of the tower extractor has been accomplished by both internal and external coolers, the choice depending on the preference of the individual refiner Both methods have been found satisfactory in commercial installations

The above changes have greatly reduced the total investment for a given size plant and have reduced the fuel requirement for the extract evaporator The fuel requirements have been reduced to about 70% of the requirements mentioned on page 1920, under comparable extraction conditions

Direct operating costs have been reduced appreciably by the changes in design, and direct costs of the larger units are approximately 75% of the costs shown in Table IV

Commercial Applications

At the present time in the United States there are four furfural units in operation with a total daily oil charge capacity of more than 14,000 bbl

In foreign countries there are two units with a total charge oil capacity of about 1,700 bbl /day, and other units are under construction, which will increase the charge oil capacity to over 4,000 bbl /day

Domestic units are processing both residual and distillate oils from Mid-Continent crudes, and Gulf Coastal type crudes, while foreign units are processing a variety of distillates from foreign crudes

TABLE V

Furfural Refining Mid-Continent Distillates

	Light Mid Continent distillate				*Heavy Mid-Continent distillate*				*Extra heavy Mid Continent distillate*			
Ratio furfural to oil charged by volume	1 91				1 90				1 91			
Temperature tower top ° F	200				235				240			
„ tower bottom ° F	170				212				220			
Yield raffinate % by vol	77 0				72 5				66 5			
„ extract % by vol	23 0				27 5				33 5			
Inspection	*Raw charge*	*Raffinate*	*Extract*	*Wax-free* product*	*Raw charge*	*Raffinate*	*Extract*	*Wax-free* product*	*Raw charge*	*Raffinate*	*Extract*	*Wax-free* product*
Gravity, ° API	25 6	30 8	11 2	28 6	23 1	28 6	10 7	26 5	20 8	27 1	10 3	26 2
Flash-point, C O C, ° F	440	450		450	500	510		505	550	550		555
Fire-point, C O C, ° F	510	510		510	80	575		580	625	625		630
Viscosity at 100° F S U				298	1,300	650		932	5,000	1,220		1,697
130° F	141	110				281						635
„ 210° F	50	48	81	52	87	72	247	82	176	102	70 Furol	112
Carbon residue, %	0 27	0·03		0 04	1 40	0 14		0 25	3 70	0 40		0 35
Colour			Black	100 (6-in cell) Lovi				40 (½-in cell) Lovi	Black			3 Tag
Pour-point (A S T M), ° F	90	100		−5	110	115		−5	+80	120		−5
Viscosity index	72 5	105		95	64	97		87	54	97		85

* Oils are finished with 3–7 lb of acid per bbl, contact filtered and dewaxed by acetone-benzol process

TABLE VI

Furfural Refining Pennsylvania Stocks

Stock	*Pennsylvania neutral*			*Pennsylvania 600 S R stock*		
Solvent ratio		1 00	1 90		1 24	2 00
Top tower temp , ° F		120	131		193	215
Bottom tower temp ° F		90	105		177	182
Raffinate yield, % by vol		95 4	91 2		95 2	93 0
	Charge	*Raffinate*	*Raffinate*	*Charge*	*Dewaxed raffinate*	*Dewaxed raffinate*
Gravity, ° API	30 1	31 5	32 3	25 9	26 7	27 3
Specific gravity at 60° F	0 8756	0 8681	0 8639	0 8990	0 8944	0 8911
Flash, ° F	430	420	420	565	560	565
Fire, ° F	495	495	495	625	630	630
Viscosity at 100° F S U	179 5	165 6	157 1	2 150	2,170	2,103
,, 210° F	45 5	44 9	44 5	147	148	146
Pour, ° F	+15	+25	+25	+25	+20	+15
Carbon residue, %	0 06	0 01	0 01	2 24	1 55	1 38
Sligh no		4 3	2 3		2	1 3
Viscosity index	104	110	113 5	103	103	104
Viscosity-gravity constant	0 822	0 813	0 808	0 813	0 803	0 803
		Extract	*Extract*		*Extract*	*Extract*
Gravity, ° API		7 2	10 0		3 5	6 8
Specific gravity at 60° F		1 0201	1 00		1 0481	1 0231
Viscosity at 210° F (sec)		100	85		3,165	1,150

TABLE VII

Furfural Refining Naphthene Base Crude Distillates

Stack	*Lubricating dist na 20 stock*			*Lubricating dist na 40 stock*			*Lubricating dist no 55 stock*		
Solvent ratio	2 00			2 06			2 04		
Top tower temp , ° F	195			195			203		
Bottom tower temp , ° F	170			175			170		
Raffinate yield, % by vol	63 5			63 3			73 8		
Extract									
Gravity, ° F	10 9			10 6			6 0		
Specific gravity	0 9937			0 9958			1 0291		
Viscosity at 210° F	67			152			901		
	Charge	*Raffinate*	*Filtered raffinate*	*Charge*	*Raffinate*	*Filtered raffinate*	*Charge*	*Raffinate*	*Filtered raffinate*
Gravity, ° API	19 6	25 1	25 1	18 8	24 0	23 8	18 9	24 1	24 1
Specific gravity	0 9365	0 9036	0 9036	0 9415	0 9100	0 9111	0 9408	0 9094	0 9094
Flash, ° F	415	410	420	480	450	475	535	500	535
Fire, ° F	465	460	470	535	525	535	620	590	610
Viscosity at 100° F S U	535		366	1,810	928	915		1,650	1,700
,, 130° F		161	163	559	345	340	465	588	616
,, 210° F	55	53	52	82	70	70	137 5	99	101 5
Pour, ° F	−10	−10	−20	−5	0	−5	+10	+10	+15
Carbon residue, %	0 04	0 03	0 01	0 15	0 04	0 04	0 96	0 13	0 13
Viscosity index	26 5		61 5	−3 5	44	46	9 5	66	67
Viscosity-gravity constant	0 886	0 843	0 843	0 881	0 842	0 844	0 870	0 836	0 834
S E. no			60			90			150
Demulsibility			1,620			1,620			1,620
Navy emulsion									
Water			40-40-0-3			40-40-0-4			40-40-0-5
Brine			40-40-0-15			40-40-0-15			40-40-0-15
Caustic			40-40-0-15			40-40-0-15			40-40-0-30

TABLE VIII

Furfural Refining Distillates from Foreign Crudes

Stock	*Long cut Haenigsen Neinhagen distillate*			*Long cut Iraq lubricating distillate*			*Mexican lubricating distillate*		
Solvent ratio	3.50			2.28			2.58		
Top tower temp., ° F	217			205			220		
Bottom tower temp., ° F	192			174			170		
Raffinate yield, % by vol	50.1			60.3			50.2		
Extract									
Gravity, ° API	11.2			11.3			10.8		
Specific gravity	0.9912			0.9910			0.9944		
Viscosity at 210° F (sec.)	158			55			75		
	Charge	*Raffinate*	*Dewaxed raffinate*	*Charge*	*Raffinate*	*Dewaxed raffinate*	*Charge*	*Raffinate*	*Filtered raffinate*
Gravity, ° API	19.4	27.7	26.0	23.6	33.3	31.2	18.9	27.9	27.9
Specific gravity	0.9377	0.8888	0.8984	0.9123	0.8586	0.8697	0.9408	0.8877	0.8877
Flash, ° F	485	490	500	375	380	380	415	435	435
Fire, ° F	555	555	565	425	425	425	480	490	490
Viscosity at 100° F S.U.	1,460	540	882	196	135	168	580	345	337
„ 130° F	228	133.5			80		232	156	157
„ 210° F	88.5	69	80	45	43	45	57	53	53
Pour, ° F	105	110	0	95	110	+5	−20	−25	−25
Carbon residue, %	2.33	0.49	0.50	0.95	0.07		0.25	0.04	0.03
Viscosity index	54	108	89	77.5	119	109	28	82	86
Viscosity-gravity constant	0.874	0.815	0.824	0.866	0.805	0.815	0.890	0.822	0.822

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THE DUO-SOL PROCESS

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THE enhanced value of crudes containing cylinder stock has long been recognized, and refiners have gone to great pains to conserve the cylinder-stock content of such crudes The additional value in crudes of this type lies in the fact that the lubricants produced from them have exceptionally good viscosity-temperature characteristics and good stability at high temperatures Such lubricants are particularly desirable for use in internal-combustion motors where ease of starting and resistance to change under the high-operating temperatures are of major importance A substantial part of these lubricants consists of very large molecules which cannot be conveniently distilled because their boiling-points, even at low pressures, are higher than the temperatures at which they decompose For this reason it has been customary to stop the distillation of cylinder-stock types of crudes at a temperature low enough to avoid all danger of cracking, or, in other words, to carry the distillation only to a 'cylinder-stock residuum' Such residua contain all the asphaltic bodies present in the crude along with their quota of other undesirable constituents common to the distillate oils These additional impurities naturally complicate the chemical refining of the residua, but, even so, the viscous lubricants present in such crudes are too valuable to be disregarded Hence the refining of residua has been considered a necessary evil because in no other way could all the lubricating value of the crude be satisfactorily preserved It is obvious, therefore, that any method of refining which will advantageously handle residuum stocks is deserving of special attention because of its economic importance

Petroleum residua may be considered as consisting of lubricants, resins, and asphalts The resins and asphalts may be considered as generally undesirable constituents The lubricants or oily portions of the crude residua, however, still contain certain types of compounds which may be loosely described as aromatic, and which experience has shown to be relatively unstable towards oxygen and other reagents, and, therefore, undesirable for most high-grade lubricating oils Hence the art of refining petroleum residua consists of the proper segregation of the desirable lubricants from all the 'other materials' present

For the purposes of this discussion, the 'other materials' may be designated as asphaltic and resinous bodies as one type, and hydrocarbons of an aromatic nature as the other type Fig 1 will serve to illustrate, in so far as two dimensions permit, the approximate distribution of these types of compounds in a raw residuum fraction from crude oil

In the above diagram the vertical axis is intended to show a progressive increase in paraffinicity of the oil from bottom to top, and, conversely, a progressive predominance towards aromatic types of compounds from top to bottom The horizontal axis shows increasing molecular weights of the constituents from left to right Values of 400 and 1,000+ are intended to be only indicative because actual values would depend upon the length of the residuum and the nature of the crude

In general, the most unstable constituents of crude oil appear to be the preponderantly aromatic types Such types of compounds are to a large extent accountable for the formation of sludge in petroleum oils, while the formation of carbon in internal-combustion motors depends to a large extent upon the presence of compounds having a very high molecular weight These have been indicated in Fig 1 by two shaded portions, representing the asphaltic and resinous bodies respectively It must be kept in mind, however, that these are not separate and distinct types of compounds as the diagram might indicate Actually, there are no definite lines of demarcation between the asphalts and resins nor between the resins and the lubricants Each tends to merge into the other by gradual and imperceptible degrees, as do the types of compounds indicated by the vertical ordinates However, it has been empirically shown by years of trial and error that for each crude there is a certain amount of material which must be removed in order to produce satisfactory lubricating oils Experience has also shown that, quite apart from the standpoint of economics and considering only the quality of the finished oil, it is unwise to overdo the elimination of certain constituents of the crude Refining may be overdone as well as underdone

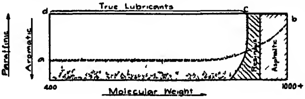

FIG 1

Referring again to Fig 1, it may be assumed that the desirable part of the residuum is bounded by the lines *a–c–d*, and the remainder is either too aromatic or too resinous and asphaltic to be acceptable for a high-grade motor oil Inclusion of the material lying outside this boundary would result in an oil prone to develop either sludge or carbon formation or both, depending upon whether the included material lay below or to the right of the *a–c* boundary

In a discussion on solvent refining it is perhaps unnecessary to dwell on the shortcomings of the older refining methods involving the use of sulphuric acid and clay It is sufficient to point out that a lubricating oil from residuum stocks, as indicated in the diagram by the *a–c–d* boundary lines, could not be produced commercially by the older methods of refining Such oils were laboratory curiosities and served only as a spur to increase the efforts of petroleum technologists to develop feasible means by which similar oils might be obtained on a commercial scale The development of solvent refining has accomplished this

Experiments with the various appropriate solvents indicated that such solvents might be roughly divided into two groups One group was particularly effective in the separation of the aromatic type of constituents, but tended to show comparatively little discrimination between compounds differing principally with respect to molecular weight Such solvents are generally strongly polar and may be said to be chemically very discriminating The phenols, certain chlor ethers, aldehydes, and ketones, and even sulphur dioxide are examples of the 'chemical' group of solvents The other group of solvents shows particular discrimination with respect to the molecular weight of the components of petroleum residua, but comparatively little selective action with respect to the paraffinicity of the compounds Propane and some of the aliphatic alcohols are examples of this group of solvents Such solvents have good solvent power for the oily part of residua, but tend to reject or precipitate the asphaltic and resinous bodies which may be present

The action of both groups may be described by reference to the residuum diagram The chemical type of solvents will selectively dissolve the lower or highly aromatic portion of the oil If, therefore, a typical residuum is subjected to the action of such solvents under suitable conditions, the oil becomes more and more paraffinic in character If the treatment is continued, a final product represented by the boundary lines *a–b–d* may readily be obtained with almost any of the better solvents belonging to this group It has also been shown that, if the treating conditions, viz temperature, solvent ratio, &c, are properly adjusted for the particular solvent used, most, if not all, of the better solvents give about the same yield and quality of finished oil from a given raw stock It will be noted, however, that the line *a–b* cuts through the resin and asphalt sections of the diagram This means that solvents of this type do not completely remove the resinous and asphaltic bodies present in a typical residuum, and, hence, the so-called raffinates produced by these solvents will contain a substantial proportion of the resin and asphalt content of the raw stock If the raw stock happens to contain only a small amount of resins and asphalts, then the amount remaining in the raffinate may be quite insignificant and easily removed by the subsequent clay filtration or other finishing operation. In such cases the chemical type of solvent may be adequate to yield a finished oil which is entirely satisfactory Some of the Pennsylvania crudes will furnish residua of this sort, but the majority of the crudes contain too great an amount of resinous and asphaltic bodies for the strictly chemical type of solvents to cope with effectively Refined oils of the *a–b–d* class may be quite stable towards oxidation, but are characterized by relatively high carbon residue values and are prone to the formation of carbon deposits when used for the lubrication of internal-combustion motors

The physical type of solvents has been described as having the ability to dissolve the lubricant portion of residua, but to reject the resinous and asphaltic portions If, therefore, a petroleum residuum were subjected to the simultaneous action of a chemical type and a physical type of solvent, an oil of the *a–c–d* description might be expected as a result Such a happy combination of solvents has been found and developed in what is known as the Duo-Sol process The solvents chosen are essentially cresylic acid for the chemical type of solvent and propane for the physical type By the suitable adjustment of these two solvents with respect to each other and the stock to be treated, a remarkable degree of flexibility is obtained and a refined oil of almost any desired character may be produced from a great variety of crudes This is readily visualized from the diagram because, regardless of the proportions of the undesirable constituents present in the raw stock, a suitable adjustment of the solvents can be made to cut at the desired point on either the vertical or horizontal ordinates Furthermore, it has been found that the counterflow action of the propane facilitates the recovery of lubricants occluded in the tar, which are ordinarily difficult to recover, so that relatively high yields of oil refined to a given quality are a characteristic of this process

In practice it has been found that cresylic acid alone is somewhat too soluble at the most convenient operating temperatures This has been corrected by the addition of phenol to the cresylic acid One of the commonly used blends of phenol and cresylic is known as No 2 Acid, and for convenience is called selecto It has the following specifications

Phenol	35 %
Cresols	65 %
Pyridin	Trace
Sulphur	0 08 maximum
Water	0 50 ,,
Unsaponifiable residue	0 05 % ,,

Distillation
5 % 181° C –50 % 186° C max –95 % 195° C max
E P 202° C max

Owing to the great flexibility of the Duo-Sol process with respect to both the stocks which may be treated and the refined oils which may be produced therefrom, it is quite impossible to give actual supporting data to cover its possibilities in such a limited space There is, however, a lower limit to the flash-point of stocks which may be successfully treated by the Duo-Sol process, because a certain difference in vapour pressure between the stock and the selecto must be maintained for efficient stripping of the selecto from the raffinate and extract The difference in vapour pressure required will depend somewhat on the design of the solvent-stripping towers, but a minimum flash-point of about 400° F is desirable for good separation of the selecto The following tables, however, will serve as examples

A Mid-Continent crude residuum (Oklahoma City) of the following characteristics is being commercially refined

Characteristics of Charging Stock

Gravity ° API	25 5
Specific gravity 60° F	0 9013
Flash, ° F	470
Viscosity 210 F S U	105
Pour, ° F	85
v g c	0 844

The above stock passing through the system as described below will produce as an end product a raffinate which, after dewaxing, yields a finished lubricating oil having the following tests

TABLE I

Characteristics of Treated Oil

	Raffinate	*Finished oil*
Gravity ° API	29 6	29 0
Specific gravity, 60° F	0 8783	0 8816
Flash ° F	460	450
Fire, ° F		515
Pour, ° F	100	0–20
Viscosity, 210° F S U	71	74
,, 100° F		658
Viscosity index		100
V G C	0 800	0 8035
Colour	8	Dark 5
% acid	0 08	
Conrad carbon		0 20

TABLE II

Oil specifications	*Penna cyl stock*	*Penna long residuum*	*Ranger Burbank residuum*	*Deep sand Reagan residuum*	*Iraq residuum*	*Coastal neutral*	*San Joaquin distillate*	*Pan-handle overhd (dewaxed)*	*Mid-Cont steum ref stk*	*Kansas long residuum*	*Hen-dricks residuum*	*Mid-Cont neutral*
Charging stock												
Gravity, ° API	25 6	28 6	23 5	22 4	14 8	18 8	16 3	22 9	21 1	18 6	16 8	25 4
Specific gravity	0 9007	0 8838	0 9129	0 9194	0 9672	0 9415	0 9574	0 9165	0 9273	0 9427	0 9541	0 9018
Visc at 210° F S U	165	70	84	205	194	51	96	95	197	154	147	48
Flash, ° F	560	435	450	555	420	350	465	520	530	485	455	430
Fire ° F	625	465	500	625	470	385	525	585	600	570	500	485
V G C	0 8135	0 8080	0 8480	0 8350	0 8990	0 8945	0 8970	0 8445	0 8465	0 8700	0 8860	0 8520
Solvent rates												
% selecto	400	400	300	325	300	125	800	225	125	400	275	300
% propane	200	300	350	250	400	250	300	200	400	300	250	150
Paraffinic oil before dewaxing												
Gravity, ° API	28 6	30 9	29 9	28 1	29 1		30 8		25 2	29 5	27 6	
Specific gravity	0 8838	0 8713	0 8767	0 8866	0 8130		0 8718		0 9030	0 8789	0 8894	
Visc at 210° F S U	122	61 5	61	121 5	53		53 6		123	66 5	67	
V G C	0 7960	0 7950	0 8030	0 8000	0 8811		0 7990		0 8210	0 8035	0 8170	
Colour N P A scale 70/30	7½	7½	5½	8	3½	3	1½	4½	7½	8+	4½	3½
Per cent yield paraffinic oil before dewaxing with relation to charge	88 1	92	78 4	76 9	55	91 3	25 4	79 5	85 8	59 5	49 3	78 3
Naphthenic fraction												
Specific gravity	1 026	1 027	1 045	1 029	1 073	1 060	0 9865	1 037	1 075	1 037	1 017	1 015
% yield tar with relation to charge	11 9	8	21 6	23 1	45	8 7	74 6	20 5	14 2	40 5	50 7	21 7
Dewaxed oil												
Gravity, ° API	27 8	30 0	29 0	27 3	27 6	20 6	30 7	28 3	24 5	29 1	27 5	31 1
Specific gravity	0 8883	0 8762	0 8816	0 8911	0 8894	0 9303	0 8724	0 8855	0 9071	0 8811	0 8899	0 8702
Visc at 100° F S U	1 625	451	509	1 930	324	316	341	667	2 700	515	580	178
Visc at 210° F	126 5	63 5	65	133 2	54 2	47 5	54 5	72 5	138 5	66	67	130°/97
Pour ° F	0	5	20	10	5	- 5	10	10	10	5	0	5
V G C	0 8010	0 8010	0 8100	0 8044	0 8220	0 8830	0 8003	0 8085	0 8250	0 8060	0 8170	0 8150
V I	106	108	100	99 5	100	15	95	97	78 5	103	94	100
Carbon residue	0 68	0 38	0 23	0 446	0 17	trace	0 02	0 20	1 0	0 20	0 15	trace

Note Colour indicated is that produced by Duo Sol processing without other treatment

For other data reference should be made to Table II and list of publications appearing at the end of this article

Fig 2 illustrates the apparatus and essential operations required for carrying out the process It is comprised of two essential parts, the extraction equipment for contacting the propane and selecto solvents with the charging stock, and the distillation equipment for the recovery of the raffinate and extract from the solvents

The extraction equipment consists of horizontal cylindrical tanks divided into a number of compartments Each compartment is provided with an individual pump to circulate and control the rate of flow of the solutions

The distillation part of the equipment is complicated by the partial miscibility of the propane and selecto in each other This necessitates that this part of the plant be designed so as not only to separate the solvents from the raffinate and extract, but to separate them from each other and return each to its individual work tank

In this flow diagram the equipment servicing the raffinate or paraffinic portion is marked *P* and that for the extract or aromatic portion *N*

In order to appreciate the actual operation of this process the following specific description of the flow diagram is given The raw material, which is a reduced crude of such character that the finished oil will have the required physical tests, and the required proportions of solvents are intimately mixed and settled in the compartments of the horizontal extractors These consist of two 8-ft diameter tanks, each 75 ft long, one divided into four compartments and the other into five, each compartment ranging from 15–25 ft in length. The propane is pumped from the work tank *P* 5 into compartment 1 of the extractor under sufficient pressure to maintain flow and keep the propane in a liquid state The selecto is introduced into compartment 9 from *N* 5, each solvent flowing counter to the other as they pass through the extractors The charging stock is mixed with the lower layer from compartment 4 and the upper layer from compartment 2 in a tank at a temperature sufficiently high to form a solution This solution is cooled to the required operating temperature by means of a vacuum-jet refrigerating unit of approximately 300 tons capacity, and enters compartment 3 of the extraction system

These horizontal extractors offer large settling areas, and as the propane solution of the charging stock moves from compartment 3 to 9 it is thoroughly scrubbed with the selecto entering compartment 9, becoming more and more paraffinic in character until it leaves the system as the upper layer from compartment 9 Conversely, the selecto in its journey through the extractors picks up more and more aromatic material until it reaches compartment 3, where it dissolves the asphaltic material precipitated by the propane and then passes on out through the system as the lower layer of compartment 1. The propane entering compartment 1 functions as a scrubbing solvent and extracts the more valuable paraffinic constituents rejected from compartment 3, allowing the process to function with maximum yields

The propane or upper layer moves through the extraction equipment by the drop in pressure between each compartment The lower layer, comprising a solution of aromatic and asphaltic materials in the selecto, is moved

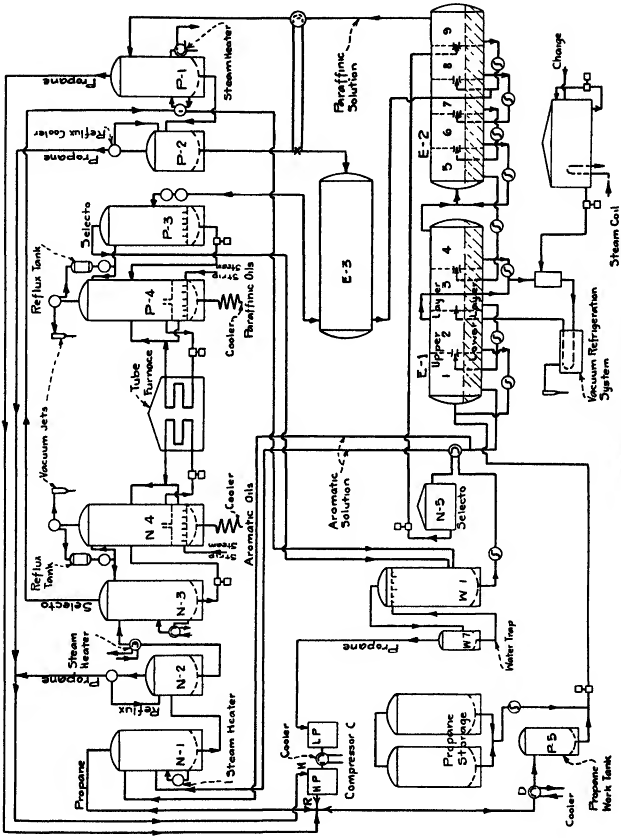

Fig 2 Flow diagram of Duo-Sol process

counterflow to the upper layer by means of individual pumps for each compartment The upper and lower layers are intimately mixed through specially designed nozzles as they enter the compartment The degree of mixing can be controlled by varying the size of the orifice in this mixing device, or adjusting the rate of circulation of the lower layer

The following table shows the progressive changes which take place in the paraffinic layer as it passes through the various compartments of the extractor, and clearly indicates the increase in paraffinicity as indicated by the increase in API gravity and reduction of the viscosity gravity constant

TABLE III

Progress of Paraffinic Solution

Compartment	*Temperature, ° F*	*Gravity, ° API*	*Viscosity 210° F S U*	*V G C*
1	85	21.2	108	0.855
2	90	24.5	94	0.832
3	90	25.8	83	0.825
4	90	25.7	89	0.824
5	86	27.1	76	0.817
6	85	28.8	74	0.805
7	83	29.3	74	0.802
8	83	29.8	72	0.799
9	78	29.7	77	0.798

The distillation systems for the separation and recovery of the solvents from the respective paraffinic and naphthenic solutions are essentially the same In following these solutions through the recovery system the aromatic layer will be considered first This solution leaves the bottom of compartment 1 of the extraction system under system pressure, and after being heated by indirect exchange with the bottoms from *W* 1 tower is flashed into tower *N* 1 which is held at about 190 lb pressure, the propane leaving the top of this tower while the bottoms are flashed into tower *N* 2 which is operated at 55 lb pressure Over 95% of the propane is removed in these two towers The bottoms from *N* 2 after passing through a steam heater are flashed in tower *N* 3 where a large portion of the selecto is removed This tower is operated at 5 lb pressure, and additional heat is added by means of circulating heat exchangers hung on the sides of the tower, 90–95% of the selecto is recovered in this tower, the balance being recovered in tower *N* 4 operating at a pressure of approximately 100 mm abs This tower operates at a maximum temperature of 600° F , heat being supplied to the system by circulating the bottoms of tower *N* 4 through an oil- or gas-fired tube heater Stripping steam is used in this tower, and the extract leaves the system containing not more than 0.03–0.05% of selecto

The paraffinic solution leaving the extraction system as the upper layer of compartment 9 passes through similar equipment *P* 1 and *P* 2 for the separation of the propane This solution then goes to *E* 3, a separating tank, which allows the selecto which was held in solution by the propane to break out This results in a further purification of the paraffinic layer, as the oil contained in the lower or selecto layer is much higher in viscosity gravity constant than that in the upper layer This lower layer is returned to the extraction system at any convenient compartment, such as 6, 7, or 8 The upper layer passes on to *P* 3 where the major portion of the selecto is recovered and then to *P* 4 for final stripping This tower is supplied with heat from a tubular heater similar to that used for the extract The paraffinic oil is substantially free from selecto

The overhead vapours from *N* 3 are used to heat the charge to *P* 1 tower These vapours are combined with the overhead from *P* 3, condensed and fractionated in *W* 1 tower for the removal of the last traces of propane and the water that may enter the system in the charging stock and that used for stripping in *N* 4 and *P* 4 towers The dehydrated selecto leaving the bottom of *W* 1 is used to heat the charge to *N* 1 and then returned to *N* 5 which is the selecto work tank

The propane recovered from *W* 1 at about 2 lb pressure and that from *N* 2 and *P* 2 at 55 lb pressure is compressed to 190 lb pressure and combined with the overhead vapours from *P* 1 and *N* 1 These vapours are condensed and returned to *P* 5, the propane work tank The steam used for stripping is generated by evaporating the water recovered from *W* 1 tower Inasmuch as this water contains a small amount of selecto, this is an effective and economical method for its salvage

The preceding description shows that the extraction part of the process is rather simple, while the oil separation and solvent recovery is very complicated If it were not for the efficient instruments available for the automatic control of flow, temperature, pressure, and liquid levels in all these various vessels, it would be next to impossible to operate the plant successfully

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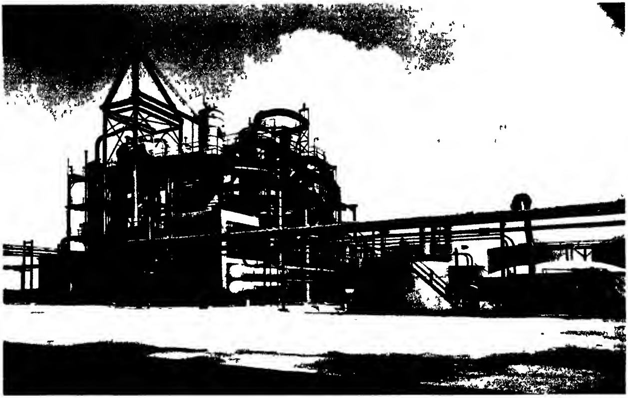

Fig 3 Front view Duo Sol plant showing solvent recovery equipment

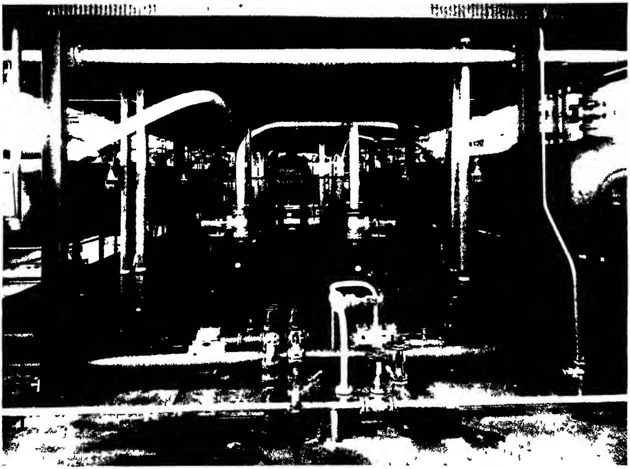

Fig 4 Interior of extractor building showing extractors, circulating pumps, and refrigeration unit at the rear centre

SECTION 29

DEWAXING

General Principles of Refrigeration	C O BROWN
The Crystallization of Petroleum Wax	F W PADGETT
Removal of Wax by Centrifuging	L D JONES
The Filter Pressing of Wax Distillate and the Sweating of Slack Wax	F W PADGETT
Dewaxing of Lubricating Oils by Benzol–Acetone Mixtures	L C STRANG
Refining with Liquid Propane	U B BRAY and W H BAHLKF
Principles of Dewaxing	T G HUNTER

GENERAL PRINCIPLES OF REFRIGERATION

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REFRIGERATION, as used in this section, refers to a lowering of the temperature of any fluid, material, or product to a temperature below that of the ordinary available cooling water or atmosphere This effect is accomplished by the use of some chemical having favourable thermal, physical, and chemical properties, such as a low specific heat and a high value for latent heat of evaporation, called the 'refrigerant', or 'refrigerating agent' The refrigerant is used in some form of compressor, together with equipment to confine and bring the refrigerant indirectly into contact with the material to be cooled Broadly, therefore, refrigeration is a problem of the economical flow or transfer of heat, having both a technical and financial side

The principles and steps by which sub-normal temperatures are produced are not complicated

Two methods can be used, one wherein any gas, such as air, is expanded from a higher pressure to a lower pressure, contacted with the material to be cooled, and is then compressed, and at the higher pressure it is cooled to the lowest temperature possible with the available cooling water, thus completing the cycle This method, although fairly efficient, has a limited application, and practically all commercial refrigerating is accomplished by the second method—evaporation of a liquid This cycle contains three parts First, any liquid when evaporating must be supplied with heat equivalent to the latent heat of evaporation This useful heat is supplied largely by transfer from the material or product to be cooled Second, the temperature at which any liquid evaporates to a vapour depends upon the pressure of the vapour over the liquid The third fact is that any vapour when compressed to a suitable pressure and cooled, can be liquefied These three physical changes control the art of mechanical refrigeration, producing a continuous economical cycle The equipment for cooling or refrigerating is also simple, consisting of three essential parts—an evaporator, a condenser, and a compressor—in which the evaporator contains sufficient surface in contact with the product to be cooled to permit the desired amount of heat to flow from product to refrigerant The condenser is equipped with a throttle-valve to confine the refrigerant and control the rate of flow to the evaporator

Definitions

Mechanical Refrigeration implies the use of heat or power as a means of extracting heat from any system, fluid, or material at a relatively low temperature, and discharging this heat into a second fluid at a higher temperature

Theoretical Horse-power is the production or absorption of 550 ft -lb per sec

Indicated Horse-power The power of a machine as calculated from pertinent data, or the power indicated by suitable instruments connected with the interior of the cylinder and capable of recording the change of pressure throughout the cycle The indicated horse-power value, in prime movers, is more than the actual output as the friction of the machine is not deducted

Brake Horse-power. The power output of a prime mover, or the power input of a secondary machine as measured at the driving pulley or the driven pulley by a suitable brake or dynamometer

Common Heat Units. The British Thermal Unit (B Th U) is the amount of heat necessary to raise one pound of water, at or near its maximum density, through 1° F The popular metric unit is the Centigrade Heat Unit, which is the amount of heat necessary to raise the temperature of one pound of water near its maximum density, 1° C The Centigrade Heat Unit is 1 8 B Th U The B Th U is the equivalent of 778 ft -lb , or 0 293 watt hr The large calorie is the amount of heat necessary to change one kg of water through one degree C , at or near the point of maximum density

Unit of Refrigeration The commercial unit of refrigeration is 2,000 lb of refrigeration per day of 24 hr , or 'the ton of refrigeration' This unit is based upon the heat absorbed by one ton of ice melting to water in 24 hr The latent heat of fusion of ice is 144 B Th U per lb , or 288,000 B Th U per ton of ice Since this heat is absorbed (or liberated) during 24 hr (1,440 min) a 'ton of refrigeration' is also equivalent to a rate of 200 B Th U per min

Refrigerant. Any fluid which can be evaporated, its vapour warmed and compressed, then cooled and liquefied without decomposition, which is not corrosive to irons and steels, copper, or brass, can be used to convey heat from one system to another and in such use is known as a Refrigerant

Quality of Refrigerant When any refrigerant passes from a system under pressure, through an expansion valve, to a lower-pressure system some part of the liquid passing the valve changes to the vapour phase, thus changing the 'quality' of the refrigerant 'Quality' is defined as the mass of vapour per unit mass of saturated mixture

Cooling Mediums. There are two places in any refrigeration system where the temperature is lowered (1) in the material or product or space where the refrigeration is desired, and (2) in the refrigerant, after compression To avoid confusion, we will call the fluid on the condenser, that cools and liquefies the refrigerant, the 'cooling medium' It may be air, water, or some other refrigerant In all cases where the heat which is removed from the product is transferred to the refrigerant by some separate fluid, this will be defined as the 'heat-transfer medium' In commercial plants for ice-making by the tank process, the tanks and ice-water actually impart their contained heat to salt brine, or to calcium chloride brine, the brine being refrigerated in a separate cooler by the evaporating refrigerant The use of a 'heat-transfer medium' enables the refrigeration to be distributed from a central plant to various scattered and distant points, and acts as a storage to supply a variable demand

Absorption System. In one commercial system the refrigerant, after evaporation, is absorbed in water, with cooling The water solution is pumped to a heater, the refrigerant boiled off, the pure vapour condensed to a liquid, and cooled again A system using this cycle is called 'the absorption system', and it is used only with ammonia as the refrigerant

Compression Systems. A system wherein the refrigerant is recovered after use, by compression in a power-driven compressor of one or more stages This name is not definitely descriptive as compression of the refrigerant also occurs in the absorption system The use of a mechanically driven compressor lends great flexibility to the system and permits of the use of a wide variety of refrigerants

Evaporation System. This system has become commercially important only recently, using water as the refrigerant In operation, water is evaporated at high vacuum, the resulting low-pressure water-vapour is withdrawn from the system and delivered to a condenser by a recently perfected steam-ject evactor or turbo-compressor The latent heat is abstracted from the remaining water, lowering the temperature This system is limited to temperatures above 39 to 40° F

Adsorption System This type of system is very little used The pressure of the refrigerant is reduced and evaporation continued, by adsorbing the gaseous refrigerant in some material, such as the common gels, or active carbon After adsorption ceases, the loaded gel is heated to recover the refrigerant

Condensers. The heat-exchange apparatus, wherein the refrigerant is cooled and liquefied by the cooling medium

Expansion Valves. The special valve which confines the refrigerant under its vapour pressure in the storage tank or receiver, and controls the amount of refrigerant passing to the lower-pressure evaporator or cooling coils, is called an expansion valve

Rating of Refrigeration Systems The rating or capacity of refrigerating machines is given in 'Tons of Refrigeration' Different makers of equipment usually specify more or less rigid conditions, all of which must prevail during a rating test For example, to meet the guaranteed rating, a machine operates between two temperature limits, over a definite pressure range, and when only liquid refrigerant at a definite temperature reaches the expansion valve and only gaseous refrigerant is delivered to the compressor In some cases pre-cooling of the liquid, and some superheat in the gas, is specified

From the rating of a machine one must subtract all the losses of the system to arrive at the useful cooling which can be realized When making water ice by means of brine circulated outside of rectangular tanks, the heat removal is analysed thus (the losses vary with the size of the plant)

Useful work done	*B Th U*
To transform 1 lb of water to 1 lb of ice	144
Cooling water to freezing-point, approx	59
Cooling ice to 16° F (0 5 = sp ht)	8
	211
Losses Cooling ice cans heat absorbed by exposed brine, cooling air used to agitate the freezing water, &c , from 58 to 64 B Th U per lb of ice	62
Total heat per lb of ice	273

To produce 1 ton of ice per day would require 2,000 lb ×273 B Th U = 546,000 B Th U

Since 1 ton of refrigeration is 288,000 B Th U per day, it requires 1 9 tons of refrigeration to produce 1 ton of water ice under the above conditions

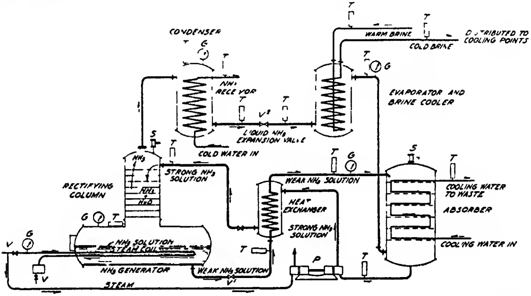

FIG 1

Description of Systems, Theory and Application

P pump for strong aqua NH_3,
S spring safety-valves,
V - shut-off valves,
V^1 - regulating valves,
V^2- expansion valves,
T thermometers,
G = pressure gauges

Fig 1 represents diagrammatically the equipment and flow of materials in a continuous absorption system, where brine is used as the heat-transfer agent, ammonia as the refrigerant, and water as the cooling medium

The absorber, continuously cooled with water, contacts gas with weak ammonia solution, absorbing the ammonia and thus reducing the pressure in the absorber below that in the evaporator, a condition that permits the liquid ammonia in the evaporator to evaporate continuously, cooling the system brine. Pure ammonia gas is recovered from the strong ammonia solution leaving the bottom of the absorber, by pumping it through a heat exchanger to the rectifying column of the generator Here the solution is heated by direct heat or by steam, pure ammonia gas leaving the solution until equilibrium corresponding to the higher temperature is obtained, the ammonia gas passing continuously to the condenser, and the weak solution passing through the heat exchanger to the absorber to complete the cycle The condenser cools and liquefies ammonia gas which collects in a suitable storage, ready to enter the evaporator, as regulated by the expansion valve

It is most difficult to predict the performance of an absorption system by calculations, but by means of numerous gauges and thermometers, the best operating practice can be determined Heat enters the system in the steam from the generator H_1, in the brine from the evaporator coil H_2, and in the energy used for the pump, converted to its heat equivalent, H_3 Heat leaves the system in the water from the condenser H_4, water from the absorber H_5, in the condensate from the generator heating coils H_6, and by a net radiation loss H_7 That is, heat flows into the system in those parts below atmospheric temperature, but a larger amount is radiated to the atmosphere by the equipment at temperatures above atmospheric The system heat balance may be expressed by

$$H_1+H_2+H_3 = H_4 + H_5+H_6+ H_7,$$

and the approximate overall efficiency by

$$\frac{H_2}{(H_1-H_6)+H_3}$$

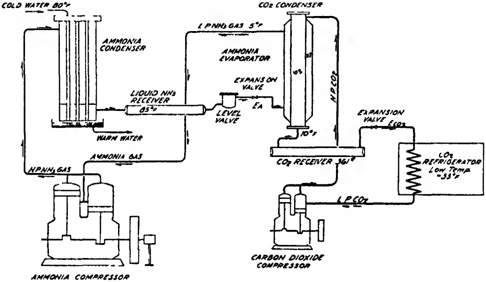

FIG 2

The industrial use of the absorption system is decreasing because of the lower cost and greater flexibility of the other systems available

The absorption system requires more apparatus, more space, and higher first costs than the various compression systems, but has the advantage that steam and fuel heat can be used directly, and the only moving machinery consists of small liquor pumps Absorption systems are operated intermittently or continuously

Compression Systems.

Fig 2 represents the schematic layout of two simple compression systems The system on the left uses ammonia as the refrigerant, water as the cooling medium, and a single-stage compressor The system on the right uses carbon dioxide as the refrigerant, ammonia as the cooling medium, and a single-stage compressor

By using ammonia as the cooling medium of the carbon dioxide condenser, making part of this condenser the ammonia evaporator, a compound or split-stage cooling system results The split-stage principle, applied to ammonia and carbon dioxide, has advantages and disadvantages, which may be summarized as follows

Advantages

- Lower first cost of equipment for a given capacity,
- Lower temperatures attainable,
- Very high vacuum on the NH_3 compressor intake is not required, and high positive pressure on the CO_2 condenser is unnecessary

Disadvantages

- Requires more power to operate than a two-stage ammonia system,
- Great care must be used to keep the systems separate as CO_2 and NH_3 under pressure react most violently

A brief description will explain the operation of this system

Ammonia in liquid form (from cylinders) is charged into the liquid ammonia receiver in sufficient quantity to provide liquid in the evaporator, to fill the system with gaseous ammonia, to allow for some liquid ammonia to hang up in the condenser, and still leave enough liquid in the storage receiver to fill and operate the level valve As soon as the compressor is started, the ammonia pressure in the suction line becomes less and the condenser pressure increases to a value higher than corresponds to the pressure of saturated ammonia gas at the temperature of the condenser, and then gas passes to the liquid phase and the pressure remains constant The heat of compression and the latent heat of evaporation are transferred through the metal of the condenser to the cooling water in the tubes It is apparent that the work of the compressor decreases, the lower the temperature of the cooling water As liquid ammonia forms, it flows by gravity (in most cases) to the receiver, which serves as a storage of liquid, feeding the automatic level valve, or hand-controlled expansion valve The apparatus just described comprises the 'condensing' or high-pressure side of the system, the pressure is developed by the compressor and retained by the expansion valve After passing the expansion valve the liquid ammonia flows readily to the evaporator, the automatic float valve, or expansion valve, maintaining a supply of liquid NH_3 in the body of the evaporator As long as the compressor is operating, ammonia gas is withdrawn from the evaporator reducing the pressure below that corresponding to the pressure of ammonia at the temperature desired in the evaporator, and the ammonia boils, the required latent heat being supplied by both the ammonia (liquid) lowering its temperature, and by the product which it is desired to cool In Fig 2 this product is carbon dioxide The part of the system just described is called the 'low pressure' or evaporator side of the ammonia system

Considering the above system, it is quite apparent that the principal heat flows are, as in the absorption system, the heat extracted in the condenser from the refrigerant and to a lesser amount in the compressor cooling water, and the heat entering the system in the ammonia evaporator, to vaporize the refrigerant It is obvious that the theories of refrigeration are those of heat transfer and are based upon the Laws of Thermodynamics In the systems described the refrigerant circulates around the plant in continuous cycles, heat entering the refrigerant from the product and leaving by the condenser water This may be expressed by

H_2 — heat absorbed by refrigerant in evaporator,
H_3 = heat equivalent of power to drive compressor,
H_4 - heat removed in condenser water,

and equated by

$$H_4 = H_2 + H_3$$

The efficiency of any system can be expressed as

$$\frac{\text{the refrigeration produced}}{\text{the power, as heat, to drive the compressor}} \qquad \frac{H_2}{H_3} \qquad \frac{H_2}{H_4 - H_2}$$

To design a refrigeration system, or to analyse one in performance, it is necessary to have complete data on the Thermodynamic properties of the refrigerant This information is used in three ways

1 If a process occurs at constant pressure, the change in heat content is equal to the heat added, or taken away
2 When a fluid is compressed adiabatically, the difference in its heat content between compressor suction and discharge is equal to the heat equivalent of the work of compression
3 When a fluid is expanded, as in the expansion valve, there is no change in heat content except by the heat added or subtracted

Tables of thermodynamic properties of the refrigerant [3, 1916] furnish a means of calculating the various heat quantities and work required in an 'ideal' refrigerating system, i e one in which losses due to friction, inefficiency of certain mechanical parts, radiation, and heat leakage are not considered After obtaining the characteristics of the ideal system, the necessary modifications can be made to give actual performance data, based upon good chemical engineering practice

The use of the tables can be made clear by giving an example based upon the compression system shown in Fig 2, for which the following conditions apply The water available for the ammonia condenser has a maximum temperature of 80° F The condenser can be designed to produce a temperature of 85° F in the saturated ammonia vapour The carbon dioxide is condensed at 10° F and, here again, a reasonable heat head is 5° F, so that the ammonia boiling in the evaporator must have a temperature of 5° F Given these conditions, the following design data can be obtained from the tables given in Bureau of Standards Circular, no 142 [1, 1923], to which the page numbers given here apply

1 *The refrigerating effect per lb of ammonia*—which is the heat transferred *from* carbon dioxide to ammonia By No 3 above, this quantity is the difference between the heat content of saturated vapour at 85° F, or 137 8 B Th U per lb (Table I, p 20), and the heat content of saturated vapour at 5° F, or 613 3 B Th U per lb This difference is 475 5 B Th U taken out of the CO_2 per lb of ammonia evaporated

2 *Pressure on ammonia gas in evaporator* (or omitting the friction of the piping in this ideal system, this value is also the suction pressure of the compressor) From the above conditions the temperature of this refrigerant is 5° F and in Table I, p 19, the pressure is read directly as 34 27 lb per sq in abs To specify the compressor capacity one must know the volume of ammonia under 34 27 lb per sq in pressure, which is also read from the table as 8 15 cu ft per lb

3 Disregarding pipe friction *what must be the compressor discharge pressure* to deliver ammonia gas into the condenser at 85° F ? On p 20, Table I, the pressure of saturated vapour is found to be 166 4 lb per sq in abs, at a temperature of 85° F

4 *What is the temperature of the superheated gas* at the *compressor outlet? What is its volume per lb ?* This is based upon the temperature of the gas at the compressor inlet, 5° F The entropy of saturated vapour at 5° F = 1 3253 The condenser pressure is 166 4 lb per sq in abs The temperature of the vapour at this value of entropy and 166 4 lb per sq in is found on p 44 Only values for 160 lb per sq in and 170 lb per sq in abs are given, and the desired values, 206 7° F and 2 393 cu ft per lb, are obtained by interpolation

5 *What is the work done by the compressor?* This value is found from the tables, being the increase in heat content in the gas between compressor inlet, 613 3 B Th U per lb, and compressor discharge (interpolated value from p 44), 711 1 B Th U per lb, i e 97 8 B Th U per lb of ammonia

6 *What quantity of heat is removed by the condenser per lb of ammonia?* This value is the difference between the heat content of superheated vapour at 206 7° F, or 711 1 B Th U per lb, and the heat content of saturated liquid at 85° F, or 137 8 B Th U

7 What is the *quality* of the liquid after passing the expansion valve, under the above conditions? This value is found from the equation

$$\text{Quality} \quad \frac{\begin{Bmatrix}\text{heat content } h \text{ of} \\ \text{sat liquid at cond} \\ \text{temp}\end{Bmatrix} - \begin{Bmatrix}\text{heat content of sat} \\ \text{liquid at evap temp}\end{Bmatrix}}{\begin{Bmatrix}\text{heat content } H \text{ of} \\ \text{sat vapour at evap} \\ \text{temp}\end{Bmatrix} - \begin{Bmatrix}\text{heat content of sat} \\ \text{liquid at evap temp}\end{Bmatrix}}$$

Using the conditions set above, the equation is

$$\frac{h_{85} - h_5}{H_5 - h_5} = \text{quality}$$

$$\frac{137\ 8 - 48\ 3}{613\ 3 - 48\ 3} = \frac{89\ 5}{565\ 0} = 0\ 1584$$

0 1584 lb of gas is mixed with 0 8416 lb of liquid in the saturated mixture

8 How many lb of NH_3 per min must be circulated per ton of refrigeration ?

A ton of refrigeration is a continuous flow of 200 B Th U per min From No 1, it was shown that the refrigeration effect of 1 lb of ammonia in the system conditions herewith is 475 5 B Th U per lb

$$\frac{200}{475\ 5} = 0\ 4206 \text{ lb } NH_3 \text{ per min per ton of refrigeration}$$

9 The Horse-power required per ton of refrigeration, under the above conditions

The heat equivalent of the work of compression was found to be 97 8 B Th U per lb of ammonia 1 B Th U is equivalent to 777 46 ft -lb of work, and 0 4206 lb of ammonia are to be circulated per min

$$\text{H P} = \frac{97\ 8 \times 0\ 4206 \times 777\ 46}{33{,}000} \quad 0\ 97 \text{ H P per ton of refrigeration}$$

10 The ratio of the heat transferred to the refrigerant evaporating and the heat equivalent of the work of compression is called the 'performance coefficient' For the ideal refrigerant, between 5° F and 86° F the coefficient is given as 5 74 [2, 1923] Under the conditions described here, the coefficient of performance for the ammonia system is

$$\frac{475\ 5 \text{ B Th U}}{97\ 8 \text{ B Th U}} \quad 4\ 86$$

The numerical values of the properties of a fluid can be expressed graphically as well as in the form of tables Such charts were introduced by Mollier, who plotted pressures as the ordinates and heat content as abscissa. Since any two properties may be used to develop such a chart, some preference has been shown for a chart based upon 'total heat' as ordinates and 'entropy' as parallel segments at a proper angle to the ordinates It is not necessary to go into the construction of such a chart as well designed copies are readily available for a variety of fluids [4, 1927]

The use of such charts makes the analysis of the variation in the heat content rapid, convenient, and simple The amount of information quickly available on such a chart may be seen by a chart analysis of the carbon dioxide system shown in Fig 2, using the Total Heat Chart Fig 3 In that split-stage system, there is one fixed condition in the CO_2 condenser, which has a temperature of 5° F Allowing for a reasonable resistance to heat flow, the working temperature on the CO_2 side could be 10° F This is used as the starting-point in laying out the 'diagram' on the chart, located at point (1), 10° F (−12° C) and 362 lb per sq in abs The liquid CO_2 passes to refrigerator coil through expansion valve E_{CO_2}, no heat is lost or added, only the quality of the refrigerant is changed, so the line 1–2 is drawn at constant heat—parallel to constant heat line −5 Assume that it is required to keep the refrigerator coils at −33° F (−36° C), a temperature not economically reached by ammonia refrigerant in one stage of compression Point 2 is fixed by the evaporator condition −33° F (−36° C) On the right-hand side of the chart above the saturation line the −36° C temperature line intersects the saturation line at the 170 lb constant pressure line Therefore, the line 1–2 is drawn at constant heat content from the saturation boundary line at point (1) to the 170 lb pressure line, locating point 2 Evaporation is one process taking place isothermally, and the line 2–3 is drawn at constant pressure to the saturation line, locating point 3 Next, compression of the vapour occurs at constant entropy—adiabatically, represented by the line 3–4, along a line of constant entropy The point 4 is located by the condenser temperature, controlled by the ammonia evaporator temperature of 10° F (−12° C), and the corresponding pressure of 362 lb per sq in Condensation takes place at constant pressure along the line 4–1, and the diagram representing the cycle for CO_2 is complete From this diagram the following data are easily obtained

1 The refrigerating effect per lb of carbon dioxide evaporated is read directly from the difference in heat content at point (2) −5 6 and point (3) 56 8, a total of 62 4 B Th U per lb of CO_2

2 The pressure on the CO_2 in the refrigerator is read directly from the intersection of the −36° C temperature line with the saturation curve, approximately 170 lb per sq in

3 Disregarding system friction, the discharge of the compressor is read from the chart at point (4) which is 362 lb per sq in abs

4 The temperature of the gas at the compressor outlet is read from the intersection of the temperature lines at the right of the chart and the pressure line 362° F The value is about 72° F (22° C)

5 To find the work done by the compressor per lb of refrigerant, it is only necessary to subtract the heat content at point (3) 56 8 B Th U per lb, from the heat content at (4) 64 9 B Th U per lb, a difference of 8 1 B Th U per lb This is converted to H P by the calculation shown in the use of the ammonia tables under No 9

6 The heat removed by the condenser is read directly from the chart as the difference in heat content at point (4) 64 9 B Th U and at point (1) 5 7 B Th U, totalling 70 6 B Th U per lb of refrigerant

7 The 'quality' of the liquid is also read directly from the chart Point (2), representing the refrigerant about to enter the evaporator after passing the expansion valve, is located between lines of constant dryness 0 1 and 0 2 and point (2) has a value of 0 13 13% of the liquid has been vaporized by throttling passing the expansion valve

8 The weight of refrigerant which must be circulated per ton of refrigeration is the heat absorbed by 1 lb of CO_2 evaporating under the specific conditions 62 4 B Th U per lb divided into 200 B Th U per min

$$\frac{200}{62\ 4} = 3\ 21 \text{ lb per min}$$

9 The energy required to compress the gas (not including friction and inefficiency of compressor) is found by a calculation similar to the expression for power for ammonia compression. Paragraph 5 gives the heat equivalent of the work of compression as 8 1 B Th U per lb of CO_2, 3 21 lb are to be circulated per min, and 1 B Th U = 777 46 ft -lb

$$\text{H P} = \frac{8\ 1 \times 3\ 21 \times 777\ 46}{33{,}000} = 0\ 613 \text{ h p per ton of refrigerant}$$

It will be noticed that the use of thermodynamic tables will perhaps give more exact values than the average chart The size of the chart and quality of printing will contribute a great deal to the accuracy of results

Multiple-stage Compression Systems.

In mechanical refrigeration it is the weight of the refrigerant, which passes through the cycle in unit time, which fixes the amount of cooling done, and not the volume

of refrigerant But, in any compressor, the volume of the cylinders is a characteristic permanently fixed by design, size, and speed of rotation The quantity of vapour handled by the machine is, therefore, nearly a function of the volume The volume of unit weight of any gaseous refrigerant varies inversely as the pressure, and directly as the temperature These factors, therefore, vary the weight of refrigerant handled, or the capacity of the machine over wide limits At +5° F, ammonia vapour has a specific volume of 8 15 cu ft per lb If a compressor has a delivered volume of 8 15 cu ft per min at normal speed, it will handle 1 lb. of ammonia per min, having a temperature of 5° F If, however, the required temperature in the refrigerator is −40° F, at which temperature the specific volume of ammonia is 24 86 cu. ft per lb, to deliver the same amount of refrigeration would require a compressor 3 05 times as large, with increases in the first cost of the machine, and in cost of operation because of increased friction losses in the larger mechanism Since the cost of refrigeration is largely the cost of transferring heat or power, any modification of the mode of compression to a more efficient cycle will reduce this major cost The most direct method for the reduction of the power of compression is to reduce the 'compression ratio', that is, to compress in stages, removing the superheat from the gas between each stage This is universally used when compressing gases to high pressures, and it is used in refrigeration with refrigerants which superheat highly on compression, such as ammonia and carbon dioxide Rotary boosters are much lighter and less expensive than reciprocating compressors Further, the

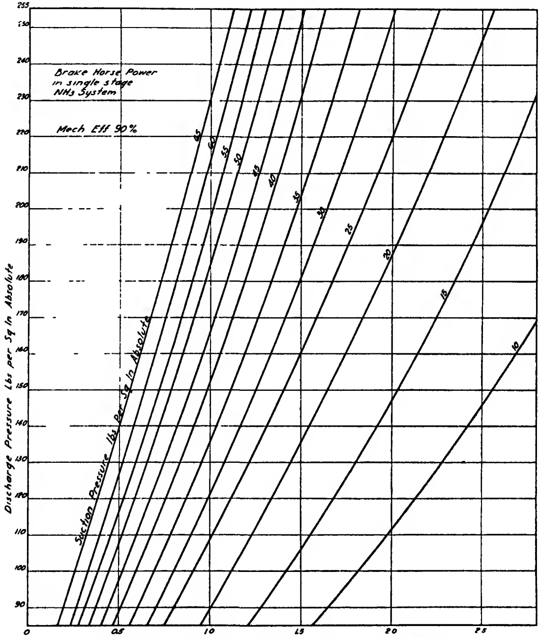

FIG 4 Brake horse-power per ton of refrigeration Mechanical efficiency 90%

first, or low-pressure stage of a multi-stage compressor, contains much more than its proportional part of the weight and friction load of the machine For this reason, in some ammonia systems, a rotary compressor is substituted for the first stage to draw the low pressure gas from the evaporator, compress it to a moderate pressure, cool the gas and then deliver it to a second-stage reciprocating compressor In refrigeration work the number of stages seldom exceeds two It is seen that any two-stage system also offers the possibility of developing cooling at two different levels of temperature It is not necessary that each compressor handle equal amounts of refrigerant

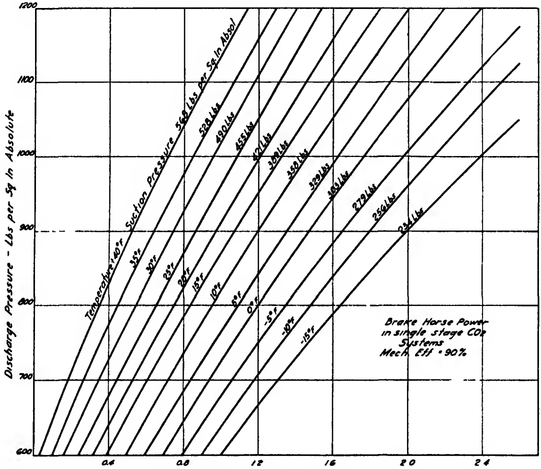

Fig 5 Brake horse power per ton of refrigeration (1 115×I H P)

Evaporation Systems.

Evaporation systems are so called because the refrigerant evaporates, but is not recovered or returned to the system For this reason the refrigerant used is the lowest cost material available, water, or some saline solution, from which it is desired to recover the salt

First, a brief description of the apparatus as represented in Fig 6 will clarify the operation on which the theory is based Assume that water at 40° F is desired for the cooling of an oil product This water after circulating as a heat-transfer medium through the cooling coils, absorbing heat from the product, enters the evaporator in which a high vacuum is maintained by the rapid removal of water vapour from the boiling water in the body of the evaporator Steam at high velocity picks up the water vapour, compresses it to a pressure at which it will condense by direct contact with water in the condenser at prevailing temperatures The remaining water vapour and non-condensable gases are pulled out of the system by a second steam-jet vacuum pump The condensed water, mixed with cooling water, is removed from the condenser by a pump

Several modifications of this system are possible If the coils containing the oil product to be cooled are not too bulky, or do not have to be cleaned too frequently, these coils may be placed within the evaporator, saving piping, heat losses, and the circulating water pump If it is desired to recover salt from a warm saturated brine, the brine may be run into the evaporator directly, and concentrated and cooled One should note that the heat-transfer medium becomes the refrigerant, and later becomes the cooling medium

Since water is the refrigerant, this system is limited to cold temperatures above the freezing-point of water In operation the system works as follows The steam-jet compressor is put into operation, maintaining an absolute pressure of ¼ in of Hg in the evaporator When water at ordinary temperatures of 70° F is admitted to the evaporator, it immediately flashes to vapour and is removed The latent heat of evaporation of water at ¼ in Hg absolute is 1069 3 B Th U This heat is all supplied by the remaining water in the evaporator (omitting heat leakage)

It is desired to lower the temperature of this water 30° F (70° F −40° F) and the weight of water required is

$$\frac{1069\ 3}{30} = 35\ 6 \text{ lb}$$

By this direct method the evaporation of 1 lb (2 8%) of the water has lowered the remaining 35 6 lb of water 30° F, or less than 1% of the total water is evaporated for each 10° F cooling obtained

The volume of 1 lb of water vapour at 0 25 in Hg pressure absolute is 2,400 cu ft In the example above to obtain 1 ton of refrigeration

$$\frac{200}{1069\ 3} \text{ lb of water must be evaporated}$$

$$= 0\ 187 \text{ lb per min}$$

This vapour has a volume of 450 cu ft which indicates that the size of any displacement compressor to handle this vapour would be unreasonably large, and when only displacement compressors were available, this evactor system was not used

With the development of efficient steam-jet compressors, wherein at 150 lb pressure steam velocities of 4,000 ft per sec are reached, this type of system becomes an efficient one with many advantages There is no risk from explosions, as high gaseous pressures are impossible There are no poisonous chemicals used The only moving parts are the rotors of small pumps

Refrigerants.

When selecting a refrigerant, the combustibility of the suitable chemicals must often be considered before their thermal properties The following division of the more common refrigerants can be made, into Group 1, which are non-inflammable, but which have toxic properties, and Group II, refrigerants which are to some extent inflammable and toxic Only water and air are free from both of these objections

Group I

Carbon dioxide
Sulphur dioxide
Nitrous Oxide
Carbon tetrachloride
Dichlorodifloromethane
Dichlormethane
Trichlorethylene

Group II

Ammonia
Butane
Carbon bisulphide
Methyl chloride
Ethyl chloride
Propane
Chloroform

The comparative vapour pressure of the common refrigerant is given in Fig 7

Carrier and Waterfill have given a comparison of some of the common refrigerants as follows, based upon 1 ton of refrigeration at 5° F to 86° F

TABLE I

Name	*Boiling point ° F*	*Wt lb per min*	*Vol in cu ft per min*	*Compression ratio*	*Coeff of performance*	*H P*	*Relative Eff*
Ideal cycle					5 74	0 821	100·0
Ammonia	−28	0 4214	3 44	4 93	4 85	0 973	84 5
Propane	−48 6	1 396	3 35	3 64	4 88	0 9668	85 0
Carbon dioxide	−110 0*	3 74	0 999	3 11	2 56	1 843	44 6
Sulphur	+14	1 388	9 24	5 63	4 735	0 995	82 5
Dichloroethylene	98 6	1 768	108 4	8 23	5 14	0 918	89 4
Water	212	0 1996	1972 0	21·9	4 1	1 15	71 5

* Sublimed

The selection of the proper refrigerant from the list of those available, or the development of better refrigerants, has occupied research investigators for years The requirements, however, are so varied that no one chemical can be picked, excluding all others

The ideal refrigerant should have a boiling-point high enough so that the system is under a slight pressure to avoid air leakage into the apparatus This refrigerant should not decompose under any operating condition and must not be corrosive to iron or non-ferrous metals, and when mixed with air it must not be explosive or toxic These broad requirements have limited the field to the several chemicals listed in this chapter, and many of the characteristics mentioned in this paragraph are given more weight than the thermal properties and performance coefficient of a refrigerant

Considering the efficiency of a refrigerant, three factors are important Its vapour pressure over the temperature range of the available cooling water should be a small positive pressure Its volume, per pound of refrigerant, should be as small as possible The latent heat of vaporization, which is approximately the measure of available cooling capacity of a refrigerant per unit weight, should be as high as possible, and its specific heat as low as possible The advantage of low specific heat is at once apparent from the

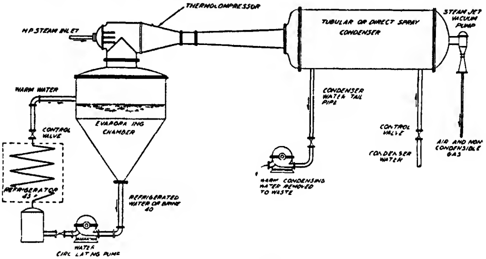

FIG 6 Evactor cooling system

process taking place in the expansion valve On reducing the pressure from condenser pressure to evaporator pressure, some liquid must evaporate to cool the refrigerant to temperature corresponding to the lower pressure The amount of liquid lost is a function of the specific heat, and when this property is a low value, less refrigerant is vaporized and more of the liquid refrigerant is available for evaporation and cooling

Ammonia

The cost of charging a system with refrigerant is always an item, especially in isolated plants During the last few years synthetic ammonia of the highest purity has been available everywhere at a constantly decreasing price, and taken with all other favourable factors, ammonia heads the list of refrigerants, especially in large commercial uses. It will burn, if heated, and mixtures of ammonia vapour and air in concentrations from 13% to 27% are explosive Its characteristic odour reveals leaks promptly, and very little danger from poisoning need be feared unless a person is trapped or unconscious and thus exposed a long time

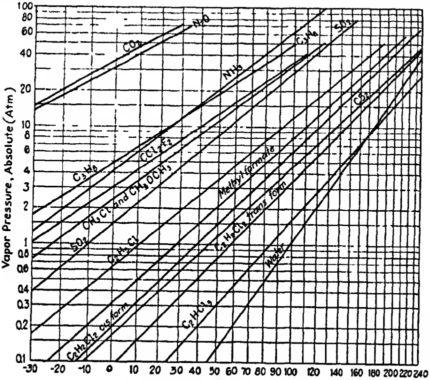

Fig 7 Vapour pressure of refrigerants

Dry ammonia is non-corrosive, but it is usually used only in all iron systems, as traces of moisture, forming hydroxide, causes it to react with copper and brass alloys Wet ammonia also forms emulsions with some grades of lubricating oils, seriously lowering the usefulness of the oil

Propane.

The vapour pressure-temperature curve for propane is near and similar to that for ammonia Very little is known about its toxic properties, but real exposure to the concentrated vapour for 1 or 2 hours will produce anaesthesia The propane-air mixtures are, of course, quite explosive. Its chemical activity is very low, and in cases where ammonia has been found objectionable because of the presence in the same equipment of acid or chlorine, propane has been substituted in the same compressor and equipment

Carbon Dioxide.

A very important refrigerant It is non-corrosive, non-toxic, and not only inflammable, but a combustion inhibitor It is odourless and harmless in contact with foodstuffs Persons subjected to the pure gas suffer from lack of oxygen When used as a refrigerant at temperatures below −60° F some troubles may be encountered from needle crystals of water ice, and perhaps also solid CO_2 snow Although carbon dioxide has no effect on, or reaction with, lubricating oil, it must be remembered that it is usually used for very low temperature work and the lubricating oil must be suitable for such low temperatures

Sulphur Dioxide.

Best known as a refrigerant in small household machines although fast losing this position to complicated, high molecular weight compounds, such as dichlorodifluoromethane It is a very stable, colourless gas, but with a most objectionable suffocating odour, it is non-corrosive, when dry, to iron, copper, or the brasses It has no effect upon the proper lubricating oil, but since liquid sulphur dioxide is itself used in the purification of some oils, the lubricating oil used in sulphur dioxide machines must be highly refined and as free from moisture as possible It should be noted from Table I that the compressor in any sulphur dioxide system must have a displacement capacity three times that of ammonia machines and ten times CO_2 machines, for unit refrigeration effect

Dichloroethylene.

This fluid is the symmetrically chlorinated compound of ethylene CHCl CHCl Its boiling-point of 98 6° F and freezing-point of −70° F give it advantageous properties as a refrigerant It is used to a great extent in rotary displacement compressors Its use as a refrigerant has some complications While it is non-corrosive to metals when dry, it is toxic to humans, and inflammable It is stable at temperatures up to 600° F, but must not contact alkalies or decomposition results It has solvent properties and disintegrates or dissolves rubber, cellulose, oils, fats, waxes and resins, and shellac

The high solubility of oils in this refrigerant tends to keep heat-transfer surfaces clean and materially decreases the heat head necessary for the required heat transfer by the constant removal of any film of oil on the walls or tubes of the condenser or evaporator The explosion risks are serious at concentrations as low as 3 5% The large volume of vapour per unit of weight almost preclude its use in displacement machines.

Water.

But little need be recorded about the properties of water, it is so well known However, the significant point about water is that its application is limited to thermo-compressors, in which enormous volumes can be moved and handled economically A small amount of equipment is required, having a low first cost and practically no moving parts In certain applications, many in the oil industry, the total cost of large-scale refrigeration using water, with all charges included, will be lower per ton than with other chemical refrigerants and displacement machines

Machine Types.

The Compressor The compressor, in most refrigerating plants, has the greatest influence on the capital cost of the plant, and the operating cost of a ton of refrigeration Even where the cycle used and the refrigerant are normal and standard, there are still many important details about the compressor which may differ widely and still perform the required work

Compressors have been used which are single acting and double acting, vertical and horizontal in design, high speed and slow-moving heavy machines The tendency at the present time is toward vertical, high speed, single acting compressors up to medium-sized units of 100 tons capacity Modern technique has been successful in producing machines almost free from vibration For capacities larger than 100 tons, the tendency is to use a double acting, horizontal machine of moderate speeds, for the advantages of the large-area foundations for the big machines predominate For the largest capacities, the turbo-compressor has been used This machine theoretically cannot be as efficient as a reciprocating compressor, because it operates without valves, against the maximum back pressure at all times Actually, the efficiency of a large turbo-compressor is relatively high due to high speeds, simplicity, and extraordinarily low friction losses The turbo-compressor is a high-speed machine, and the smallest impellers it is possible to construct will handle enormous volumes of gas It is, therefore, difficult to specify the capacity of refrigeration at which one should use the turbo-compressor, and since the specific volumes of refrigerants vary, the smallest economical size of turbo-compressor depends upon the refrigerant used The smallest turbo-compressor for carbon dioxide is about 1,000 tons capacity, while the limiting capacity decreases for ammonia, methyl chloride, sulphur dioxide, butane, &c, while for water, as the refrigerant, a plant of 30 tons capacity might use a turbo-compressor

The small-sized vertical compressor may be designed for high speeds, limited only by the rise in temperature of the fluid being compressed, and the effect of this temperature upon lubrication The temperature of the refrigerant at the compressor outlet can be read directly from the total heat chart as previously explained, or it can be calculated from temperature-pressure relations

$$T_f = T_i\left(\frac{P_f}{P_i}\right)\frac{k-1}{k},$$

T_f = final temperature,
T_i = intake temperature,
P_f = final pressure,
P_i = intake pressure,
k = ratio of specific heats of the gas being compressed (usually about 1 4) assuming that this ratio does not change within the temperatures T_f and T_i

The work absorbed in adiabatic compression can be calculated from the pressure, volume, and specific heat data of any gas by the formula

$$W = \frac{knp_1v_1}{k-1}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{kn}} - 1\right],$$

in which

	Metric system (kg, metres)	English system (ft, lb)
W = work,		
k = ratio of specific heats,		
n - number of stages in which compression takes place, with intercooling between each stage		
p_1 = initial pressure,	kg per sq metre	lb per sq ft abs
v_1 - initial volume,	in cu metres	cu ft
p_2 = final pressure,	kg per sq metre	lb per sq ft abs

Since compression cannot be effected in an ideal machine in true adiabatic manner, some efficiency factor must be used to compensate for the total losses This factor is evaluated usually by the manufacturer for each type of machine by actual test The mechanical efficiency of compressors improves each year with better design, workmanship, and anti-friction bearings W, in the above formula, is converted into total H P required to compress v_1 volumes of gas per min in a compressor of ordinary efficiency by the expression

$$\text{H P} = \frac{W\text{(ft lb per min)}}{33{,}000\times 0\ 83}$$

It is not necessary here to go extensively into the details of design of compressors The popular machine is the high speed, single acting vertical, which is not radically different from any gas compressor except that it must be built heavier and stronger It is not only because of the pressure that greater strength is required, but because of the loss of ductility, and the strains set up in the metal due to the chilling effect of the cold refrigerant Further, there is a possibility that some quantities of liquid will get into the cylinder, while operating at full speed, and while the design of the compressor has provided for this possibility, yet the strains caused by expelling this liquid are more than the normal gas-compression load For this reason it is customary to use a safety factor of 5 to 10, where a factor of 3 to 5 would be conservative in the ordinary air-compressor

All refrigerating compressors, like any large power-using unit, should be connected direct to the prime mover or motor In the larger machines it is necessary and in the small machines desirable If a compressor must be belt-driven, a three or four 'V' belt drive should be selected

Condensers.

This apparatus, used to desuperheat, liquefy, and cool the refrigerant, is essentially a device for efficient heat transfer In general, all condensers are much the same as they were years ago, but in the details of design, and the engineering of the dimensions of the equipment, great strides have taken place, made possible by a better knowledge of the laws of fluid flow and heat flow It is not necessary to develop the various formulae for flow of heat, or the concept of film resistance, as these data have been amply given in various texts and publications [5]

While the performance of any condenser or evaporator should be calculated with the use of the excellent heat-flow data and formulae now available, it is convenient to use rough approximations for rapid estimating and checking work

In the ordinary small unit used to cool the air in a room where the evaporator consists of runs of 1¼-in pipe, from 4 to 6 B Th U per sq ft per hr per ° F of mean temperature difference, can be obtained

For cooling coils immersed in brine, properly designed to operate one-quarter flooded with liquid and with moderate lengths of pipe carrying gas at high velocity, use from 16 to 130 B Th U per sq ft per hr per ° F mean temperature difference, with an average figure of 25 B Th U The rewards of good design can be measured in the great increase of 130 B Th U over the average figure of 25 B Th U

For atmospheric type condensers, where the liquid is cooled to about 5° F above the water temperature at the bottom pipe, an over-all coefficient of 170 B Th U per hr per ° F per sq ft can be realized, or about 8 sq ft for each 15,000 B Th U per hr to be removed

The double-pipe and multi-pass condensers, properly designed, can give an over-all transfer rate of 150 to 275 B Th U per hr per sq ft per ° F mean temperature difference, but the higher rate requires increased water-pressure to impart great velocity to the water

The shell and tube condenser cannot well exceed the above very high heat-transfer rates, but a rate of 200 B Th U per hr per sq ft per ° F of mean temperature difference can be realized in this type of condenser or evaporator, which at the same time possesses advantages of low first cost, low operating cost, and small floor space required This condenser has a very favourable shape factor for the complete removal of all non-condensable gases, and very large capacities can be built in one unit Non-condensed gases must be regularly removed from any refrigerating system, and this is best accomplished by special appliances designed for the purpose, sold by most equipment manufacturers

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THE CRYSTALLIZATION OF PETROLEUM WAX

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As early as 1888 Zaloziecki [32, 1888] advanced a theory that the crystalline waxes are composed of normal paraffins and that an amorphous variety, consisting of branched chain or isoparaffins, exists in petroleum and ceresine. When the amorphous wax (protoparaffin) is distilled, pyrolysis may occur with the formation of crystalline wax (pyroparaffin). That Zaloziecki may have been correct in some respects will appear later, but the impression existing in the practical refining art for a long time that a mild cracking distillation is necessary to produce 'pressable' and 'sweatable' products has been exploded for several years.

Zaloziecki drew his conclusions from solvent extraction experiments with ceresine, the residues being hard and crystalline, the extracts soft and amorphous. Marcusson [18, 1914] compared petroleum wax with ceresine by solvent extraction methods and arrived at essentially the same conclusion as Zaloziecki. Gurwitsch [12, 1913] did not agree entirely with Zaloziecki. He distilled a petrolatum under conditions in which decomposition was eliminated and secured a distillate which contained quite large crystals. After the distillate was dissolved back in the residue, and the mixture cooled, the appearance and physical properties were the same as before the distillation. Gurwitsch decided that the amorphous nature of the products was influenced largely by the oily components of high viscosity, and by resinous and asphaltic bodies, all of which exerted an inhibiting action on crystal growth.

A paper on wax crystallization by Padgett, Hefley, and Henriksen [22, 1926] pointed out that the actual nature (i.e. inherent characteristics) of the waxes is important, although asphaltic matter and oil, the latter through its viscosity, have an influence on the crystallization. One type of crystallization is that characteristic of residual oils and petrolatum, being indicated by small crystals which grow in size only slightly under the influence of slow cooling. Another is the needle crystal, found especially in slack wax and in some of the waxes of commerce. In the growth of needle crystals, small plates of various forms—triangular, rounded, pentagonal, &c.—appear first, followed by the sprouting of needles from the plates. The plate crystal is a form which predominates in distillates comparatively low in wax concentration. Both the plate and needle crystals grow to surprising size under slow, controlled cooling. The effect of the viscosity of the medium was studied and it was shown that while viscosity of medium has an influence on crystal size the mode of crystallization peculiar, or inherent, to the wax was maintained throughout a series of mixtures in which a constant percentage of wax was dissolved in oils varying in viscosity from 60 to 1,500 sec. Saybolt at 100° F.

While the petroleum waxes may be divided, in a broad way, into crystalline and amorphous, the former, then, may include plate and needle crystals. It will be shown there is another form, the mal-crystalline wax, which might be described as approaching the amorphous condition—the substance seems to be making a desperate effort to assume a definite crystalline form—and even may be the material which has the greatest influence in inducing the amorphous condition in wax-containing products like petrolatum. The presence of amorphous (non-crystalline) wax has not been demonstrated positively by any one although its existence has been indicated by a number of workers.

The crystallization of slack wax (wax from filter presses) has been studied under the microscope by Rhodes, Mason, and Sutton [27, 1927]. Slack wax often contains about 50% oil, the remainder consisting mainly of wax. A sample of slack wax was sweated on a small scale and the fractions studied under the microscope. By cooling the samples slowly on a warm stage it was observed that the plates which were formed initially curled on the edges, followed by the growth of needles tangentially from the rolled sections. The plates were very thin, existing in various forms, sometimes rounded. A cross-section of needle crystals showed light and dark crosses, a phenomenon peculiar to spiral and radiating growths. When the sample was cooled through a period of several hours the entire mass consisted of plates. Rhodes, Mason, and Sutton state that the two types of crystals must be considered as two separate crystalline habits of the same solid phase and 'the transition from plates to needles is certainly more than a simple alteration of habits or a change in the relative development of the various crystallographic faces, such as is exhibited by many substances.' They suggest that a difference in surface tension between the crystal and melt on the two sides of the plates may cause them to curl.

Next in order probably should be a consideration of the work of Buchler and Graves and that of Ferris, Cowles, and Henderson. Buchler and Graves [2, 1927] used slack wax, slop wax (unpressable cut from coking operations) and rod wax (wax from pumping rods in oilfields) as raw material for their experiments. The oil was removed by crystallization from ethylene dichloride at a low temperature and the finished waxes were distilled at 1 mm. pressure absolute. When the melting-points were plotted against indices of refraction the lower fractions fell on a straight line, but the higher fractions fell sharply above. Upon hot extraction of the fractions by solvent an 'impurity' was removed and the residues then adjusted themselves to a straight line. This impurity is the 'soft wax' which it was thought had the property of changing plate to needle crystals when in small percentage and of inducing the amorphous condition when present in larger quantities. In order to be effective the 'soft wax' impurity must separate at the crystallizing temperature; in dilute solutions this does not occur, hence plate crystals appear.

Ferris, Cowles, and Henderson [7, 1931] worked with slack wax from Mid-Continent petroleum. They extracted with ethylene dichloride at -12 to $-14°$ C. to remove oil, following up with distillation of the wax at 1 to 3 mm. pressure, collecting 10% fractions and leaving a residue of 10%. Certain of the cuts were subjected to refractionation and then fractional crystallization from ethylene dichloride. As a result several 'series' which were homologous at least in regard to physical properties and crystal form were separated. The three series showed individual crystal forms, namely, plate, needle, and mal-crystalline The needle crystals and the mal-crystalline variety could impress their forms upon the plate crystals if the solubility relations permitted separation of the modifying wax simultaneously with the plates The plate did not impress its form on the needle and mal-crystalline wax The needle wax was found to be much more soluble than the plate wax for the same molecular weight, the mal-crystalline wax being intermediate in solubility between the needle and the plate wax However, waxes of the same melting-point, regardless of type, showed the same degree of solubility in a given solvent Davis and Campbell [6, 1933] studied the crystallization of vacuum fractions from wax distillate and their results tended to confirm the findings of Ferris, Cowles, and Henderson

Applied to the practical problem of the filter-pressing of wax distillate and the sweating of slack wax, the facts and theories so far collected from the literature can be stated briefly as follows If the distillate is properly fractionated so that mal-crystalline wax is essentially excluded from the distillate then effective pressing and sweating can be expected When the wax distillate is chilled, plate crystals, which are favourable for the pressing operations, will predominate, when the resulting slack wax is solidified on the sweating pans, needle crystals, which are favourable for sweating, will predominate Should the oil in the distillate be so high in viscosity as to interfere with the filtration, the difficulty might be remedied by dilution of the distillate with gas oil or kerosine

Other researches on wax crystallization which should be considered are as follows Carpenter [3, 1926] suggested that there was a transition temperature above which needles formed and below which plates were produced Katz [16, 1930] has indicated that plates may be changed to needles but that the transformation is irreversible, also, while the crystal form is influenced by the concentration, needles always develop from plates Tanaka [28, 1929] concluded that the viscosity of the medium and rate of cooling are the factors which control the formation of plates and needles Bergel [1, 1918] finds that the viscosity of the medium affects crystal size and that substances like asphalt influence the crystallization, but their effects can be overcome by cooling in stages Gascard [11, 1921], in the course of preparation of synthetic paraffins, remarked that when the hydrocarbons were pure they crystallized as plates, when impure as needles Pyhala [24, 1908] studied the solidification of wax before sweating and observed that slow cooling gave plates, more rapid cooling needles, and when plates were formed the sweating was hindered Rakusin [25, 1914] has advanced a theory of composition of petroleum waxes based on consistency they may consist of hard, medium, and soft paraffins, all of which, however, are crystalline

An interesting discussion of the properties of amorphous as compared with crystalline wax is presented by Jones and Blachly [15, 1929] These authors state that 'since the centrifugal process is primarily adapted to those stocks containing wax that is precipitated in the amorphous form, a study of the conditions affecting the occurrence of amorphous wax and of theories as to its nature become desirable' The property of this 'amorphous wax' is that of softness or salve-like consistency, although the products generally show crystals of the plate or mal-crystalline form Petrolatum sometimes is called amorphous wax It should be noted, however, that often quite a hard crystalline wax can be separated from petrolatum by solvents

Jones and Blachly point out that when a glass rod is dipped into a solution containing a precipitate of amorphous wax and then withdrawn, the solution will drain away leaving only a thin layer of oil solution on the rod If the solution contains a precipitate of crystalline wax, crystals will remain on the rod The above differences in properties are explained by surface tension relationships crystalline wax has appreciable surface tension in the presence of oil solution, but is less than that of the oil solution On the other hand, the surface tension of the amorphous wax is greater than that of the oil solution in which it is suspended Another way of explaining the difference in behaviour might be to consider that the amorphous wax has greater wetting power for the solution than the crystalline wax—it is known that the mal-crystalline and amorphous waxes have the property of occluding oil when they solidify, while the crystalline wax tends to exclude it Furthermore, according to Jones and Blachly, the amorphousness of the wax is related to some substance which is adsorbed from the solution, or occluded with the wax when it is precipitated, imparting or increasing the amorphousness This substance is more effective at low than high temperatures and more readily absorbed from naphtha solution than, for example, ethylene dichloride solution In support of this theory of Jones and Blachly are the known facts that when an amorphous wax is percolated in melted condition through fuller's earth the filtrate nearly always will show better crystallization than before percolation, however, petrolatums are known which are nearly water white in colour but which are highly amorphous Another illustration is the influence of petrolatum upon stocks which do not centrifuge readily—an amount as small as 10% may cause the refractory product to respond to the centrifugal operation Very often, too, overhead 'semi-amorphous' stocks, which will not centrifuge, are blended back with residual oils before being subjected to the series of refining operations which include centrifuging

The researches of a large number of investigators indicate that petroleum wax is composed of paraffin hydrocarbons, but there is no such consensus of opinion in regard to whether the hydrocarbons are normal, iso, or a mixture of the two Piper, Brown, and Dyment [23, 1925] in an X-ray study of solid paraffins secured from shale oil by Francis and co-workers [10, 1922] found them to be normal paraffins Fischer and Schneider [9, 1920] report that wax from lignite tar contained no branched chain hydrocarbons but the oil secured by low temperature retorting contained solid isoparaffins Carpenter [3, 1926] identified a number of normal paraffins in wax from Burma crude and suspected the existence of isoparaffins Buchler and Graves leaned toward the supposition that the waxes are composed of normal paraffins Ferris, Cowles, and Henderson [8, 1929] brought forth evidence in support of the presence of isoparaffins in petroleum wax Clark and Smith [4, 1931] made careful X-ray studies of waxes from Mid-Continent crude and identified isoparaffins—they concluded that at least 20% of the wax from Mid-Continent petroleum consists of branched chain paraffins From the work of the various investigators it is safe to state that petroleum waxes contain at least small percentages of isoparaffins, that the percentage may vary considerably with the source, and that the proportion is greater in the higher than in the lower distillates Later work indicates the presence of cyclic hydrocarbons, besides paraffins, see Mair and Schichtanz [17, 1936], Muller and Pilat [20, 1935]

The question of the crystal system (or systems) of paraffin wax possibly merits some attention in this discussion Wahl [30, 1912] studied the lower members of the paraffins and found the following methane crystallizes in the isotropic system, ethane in the hexagonal, normal pentane probably orthorhombic, normal hexane, heptane, and octane in the monoclinic or triclinic He also noted transformations from one system to another In regard to paraffin wax, Hefley [13, 1927] states that the crystals, whether plates or needles, exist in the orthorhombic system as indicated by parallel extinction and biaxial interference figures This conclusion has been verified by Rhodes, Mason, and Sutton, by Tanaka and co-workers, and by Reistle and Blade [26, 1932] Hefley attempted to locate a transition-point by varying the temperature but was not successful, although Muller and Saville [21, 1925] found indications of a change in an eicosane Considering the variation in crystal system that occurs among the lower paraffins according to Wall, and remembering that petroleum wax contains from 6 to 12 or 14 different molecules, it is surprising, to say the least, to find no variations in the crystals of paraffin wax Further reference to crystal transition points is made in papers by Carpenter [3, 1926], Jackson [14, 1934] and Yannaquis [31, 1933]

The solidification or pour-point of an oil often is affected by the temperature to which the product has been heated before cooling When the Amarillo field of the Texas Panhandle developed, it was noted that the oil possessed an unusually high pour-point (about 60° F normally) and that this solidification-point was reduced by heating the oil above 100° F prior to cooling, upon standing, however, the original pour-point was attained again This crude oil was high not only in percentage of wax but in asphalt also Reistle indicates that oils essentially free from asphaltic matter are less susceptible to this phenomenon than those higher in asphalt content Moore and Beard [19, 1932] have studied this problem in connexion with residual lubricating oils They noted that if the oil was heated above 200° F the wax separated in clusters on cooling—while if heated to some lower temperature which gave the highest pour-point the wax separated in crystals uniformly distributed through the oil On heating the oils from which wax had crystallized it was observed that the crystals went into solution completely at about the temperature at which the highest pour-point was established, hence it was indicated that in order to establish the highest pour-point it is necessary to heat the oil to the temperature at which the wax just goes into solution Moore and Beard also found one sample which did not display the large and small aggregates but formed crystals on cooling which resembled those in paraffin distillate This phenomenon of variation of pour-point with temperature of heating also has been investigated by Tychinin [29, 1924]

Substances in solution or dispersion in oils also are known to affect the pour-point directly Among these are asphaltic and resinous bodies, soaps, and, in fact many finely divided solid or colloidal substances Recently a synthetic hydrocarbon called paraflow [5, 1931] composed of a long paraffinic side-chain attached to a closed chain nucleus has been placed on the market for commercial use in reducing pour-points of oils The effect of the substance appears to be to cause the formation of smaller crystals and to lubricate the crystal surfaces so that the aggregates do not adhere or interlock Paraflow is a viscous oil

When an oil solidifies due to separation of wax, small crystals first appear, which continue to increase in size until they adhere or interlock, when solidification is attained If the oils are stirred during cooling, or undergo only slight movement, it is obvious that the pour-point will be effected and will be lower than when the liquid is entirely at rest, or, if, after solidification, the mass is stirred the crystal structure will be disrupted and the oil can be poured again The 'solidified' oil then, in the case of lubricating oils containing wax, is not a true solid but a finely drawn system of wax crystals in which oil is entrapped or adsorbed A few tenths per cent of crystalline wax in a lubricating oil often is sufficient to bring about this phenomenon of solidification or setting The viscosity of the associated oil also has an influence on the setting temperature

Conclusions

It is evident that the crystal forms occurring in petroleum wax are plate crystals, needle crystals, a mal-crystalline form, sometimes called foliatious, and possibly an amorphous variety When needle crystals are formed in petroleum products they grow generally, though not always, from small plates first appearing Whether needle crystals, plate crystals, the mal-crystalline variety, or mixtures of these result when wax is precipitated from a petroleum product depends upon the inherent characteristics of the wax present, the influence of one type upon another, the concentration of the wax, and to some extent to the rate of cooling

Petroleum wax contains normal and branched paraffins, also possibly hydrocarbons from other series which are solid, semi-solid, or soft The lower molecular weight waxes are largely normal paraffins, as the molecular weight increases the iso-paraffins and hydrocarbons from other series enter the picture

The action of 'impurities' or extraneous matter plays a part in wax crystallization The needle, mal-crystalline, and amorphous varieties have the power of impressing their forms on the plate crystals, particularly if the concentration of the wax is sufficiently high for the impurity to separate simultaneously with the plates The associated oil has an influence through its viscosity, the higher the viscosity the smaller the crystals and the greater the tendency to needle formation Asphaltenes, resins, and colouring matter in heavy distillates, residues, and petrolatum appear to increase the degree of amorphousness, probably as a result of the power to decrease crystal size In connexion with the effect of impurities reference should be made to the possibility of the influence of substances like paraflow which are not waxes but oils of the same nature as waxes, hence possessing high wetting and adsorbing power for the waxes

Rapid cooling of oils containing wax has the effect of decreasing the crystal size and promoting needle formation Plate crystals of surprising size can be secured by slowly cooling the lower lubricating oil distillates from paraffinaceous petroleum, but the same does not hold true generally for the higher distillates and residues such as raw cylinder stocks and petrolatum Slack wax, when cooled rapidly to a temperature slightly below the solidification-point, then held at this point or cooled very slowly thereafter, will display large needles

The temperature to which the product has been heated before cooling may have a pronounced effect on the crystallization, particularly of residual oils such as cylinder oils and stocks If heated to a temperature well above that at which all of the wax goes into solution, crystal clusters may form on cooling

The degree of fractionation and elimination of entrainment during distillation has a pronounced effect on the crystallization of distillates Well-fractionated products are characterized by larger and better-formed crystals and a suppression of mal-crystalline growth

The crystals of wax found in petroleum distillates, slack wax, and waxes of commerce are in the orthorhombic system

When plate and needle crystals are formed in an oil solution the tendency is for the crystals to exclude oil On the other hand, it is the property of the mal-crystalline and amorphous wax (if such exists) to occlude oil during the formation of the new phase This may be stated in another way by saying that when the crystallization is good, and the solution not too concentrated, oil is excluded from the crystals

The amorphous condition of heavy distillates and residues, and the waxes separated from them, is not well understood, but may be due to the presence of mal-crystalline and amorphous waxes which not only are salve-like in consistency but have the property of imparting this amorphousness to crystalline, harder waxes, or at least of inhibiting crystal growth Asphaltenes, resins, colouring matter, and viscous oils tend to increase the degree of amorphousness

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REMOVAL OF WAX BY CENTRIFUGING

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THE removal of wax from petroleum products depends upon the solidification of the wax on temperature reduction with the subsequent separation of the solid wax from the liquid oil When lubricating oils containing wax are cooled the character of the precipitated wax does not admit of its easy separation from the oil, because of the viscosity of the oil, the limited space available for the formation of the wax crystals, and the presence of colloids The wax is either precipitated in a highly dispersed form, or the entire mass solidifies in a form resembling a gel

Effect of Diluents

In order to overcome these unfavourable conditions of wax precipitation diluents are added to the oil before precipitating the wax The diluents have several rather obvious effects First, they reduce the viscosity of the oil, thereby providing more favourable conditions for the formation of the wax crystals, and also subsequently assisting in the separation of the solid wax phase from the liquid oil phase Second, they increase the bulk of the liquid phase This provides more room for the formation of the wax crystals In all separations of solids from liquids a portion of the liquid remains adhering to the surface of the solid and in the interstices between the solid particles Diluting the oil will therefore leave less oil on the wax after separation

In addition to those mentioned above, the diluent has other less obvious effects which are not characteristics of the diluent *per se*, but are specific to the particular diluent chosen The diluent effects the solubility of the wax in the resultant liquid phase The diluent may have selective solvent characteristics for various constituents of the oil, as for instance the asphaltic material and colouring bodies. By its effect on the solubility of these constituents, the diluent affects the character of the wax precipitation, the completeness of the wax precipitation, and, therefore, the ease and completeness of the subsequent separation of the wax

Centrifugal Separation

The separation of wax by centrifugals depends upon a difference in density between the precipitated wax and the liquid phase from which the wax has been precipitated Normally, in petroleum products, the wax is lighter in density than the liquid constituents with which it occurs The difference is small and is increased by the density of the diluent used which changes the density of the liquid phase, but has little or no effect upon the density of the precipitated wax When a diluent lighter than the wax is used the resultant oil solution is lighter than the precipitated wax, and in centrifugal separation the oil solution separates nearer to the axis of rotation than the wax When a diluent heavier than the wax is used the precipitated wax is lighter than the oil solution, and in centrifugal separation the wax separates nearer to the axis of rotation than the oil solution

Centrifugal dewaxing processes have been developed using both lighter and heavier diluents In view of the many practical differences between these processes each will be fully described separately

Sharples Process [9, 1920]

In the Sharples process the diluent is petroleum naphtha or benzine

A flow diagram of the process in its most modern form is shown in Fig 1 The stock to be dewaxed and the diluent are pumped in predetermined correct proportion through an orifice mixer, and a heater where the temperature is raised to the point at which the wax is in complete solution, and then into a blending tank From the blending tank the dilute stock is pumped through a series of chilling towers in which the temperature of the dilute stock is reduced to the separating temperature The chilled dilute stock passes then to the centrifuges, the rate of feed to which is maintained uniform by the constant level tank

In the centrifuges the wax is separated and there is continuously discharged from the centrifuges dilute wax-free oil

A carrier liquid, which is water at a high enough temperature to melt the wax, is continuously supplied to the centrifuges, where it assists in the discharge of the wax from the bowl and melts the wax so that it may flow in ordinary piping The wax and the carrier liquid flow to the separator tank where the mixture separates by gravity, the carrier liquid flowing to the carrier liquid tank and the wax to the wax tank, from which it is pumped to storage and subsequently topped for recovery of diluent

The most complete economical refrigeration recovery is accomplished by passing the cold dilute wax-free oil from the centrifuges through the coils in the chilling towers countercurrently to the dilute stock being chilled

The remaining chilling is accomplished by direct ammonia expansion coils in chilling towers, each at a successively lower temperature The temperature in each tower is controlled by the ammonia pressure Accurate control of the temperature difference between the last wax-free oil chilling tower and the first ammonia chilling tower is further accomplished by an ammonia chiller on the wax-free oil passing to the last wax-free oil chilling tower

Sharples Solid Discharge Super-Centrifuge [8, 1917].

A cross-section of the solid discharge centrifuge and bowl with its material content when in operation is shown in Fig 2 The carrier liquid forms a thin layer on the wall of the bowl from end to end Chilled, dilute oil is fed into the bowl through the feed nozzle against a plate which deflects it into the wings, not shown, which bring it up to the speed of the bowl There is a separation under centrifugal force of the dilute oil into an inner layer of dilute wax-free oil floating on an outer layer of wax which in turn floats upon the carrier liquid The dilute wax-free oil continuously discharges over the circular weir, *L*, and flows out through the holes in the end of the bowl into the dilute wax-free oil cover Wax continually escapes around the edge of the disk at *X* floating up through the carrier liquid and continually discharges over the weir at *H* to the wax cover

The carrier liquid serves two purposes One of these is the provision of a frictionless surface on which the wax floats and readily flows from one end of the bowl to the other The other is the provision of a uniform and non-resistant liquid for maintaining the hydrostatic balance of substances within the bowl The layer of carrier liquid in the space *T* is in hydrostatic balance with the layer of dilute wax-free oil and wax within the main body of the bowl Any tendency for an increase in the thickness of the wax layer within the bowl produces an excess of pressure over that produced by the column *T*, of carrier liquid, and wax escapes around *X*, discharging from the bowl The relative thickness of the dilute wax-free oil layer and the wax layer within the bowl and the position of the dividing line *O* between these two layers are dependent upon the height of the column *T*, and in turn on the dimension of the weir *H* The position of the dividing line *O* may therefore be changed by changing the dimension of *H* The relationships are also affected by the relative density of the wax layer and the wax-free oil layer, and for different stocks and different dilutions the value of *H* is changed to give the most favourable condition for the dividing line *O*

In the original development of the solid discharge bowl, carrier liquid was continuously fed into the bowl along with the liquid to be separated This required a carrier liquid chilled to the temperature of the chilled dilute oil

Better results can be obtained by feeding the carrier liquid to the place at which the wax discharges from the bowl This arrangement is shown in Fig 2 where the carrier liquid is fed through the nozzle *S* into the channel within the weir *H* Operating in this way when sufficient carrier liquid has entered the bowl to form a layer as shown in the figure, no further carrier liquid enters the bowl Any excess continuously discharges along with the discharging wax As the carrier liquid does not come in contact with the chilled dilute oil, it need not be chilled and, in fact, is actually heated to such a temperature as will melt the discharging wax and carry it away as a liquid

In the complete Sharples super-centrifuge, the bowl and covers described above are enclosed in a vapour-tight frame The bowl rotates at 15,000 r p m The most efficient separation is obtained with a throughput of dilute waxy oil of between 150 and 200 U S gal per hour At higher rates, separation becomes less effective with rise in the pour test of the finished oil and reduction in yield of oil

It is a necessary condition for operation that the wax separated in the centrifuge be sufficiently fluid under the forces existing in the centrifuge bowl for the wax to flow around the edge of the disk at *X* Precipitated crystalline wax and precipitated hard asphalt both form structures which will not flow, and cannot, therefore, be continuously discharged This failure of the solid discharge principle to handle other than amorphous wax is the most important limitation of the process Methods for controlling the character of the wax precipitate to facilitate its discharge are discussed later

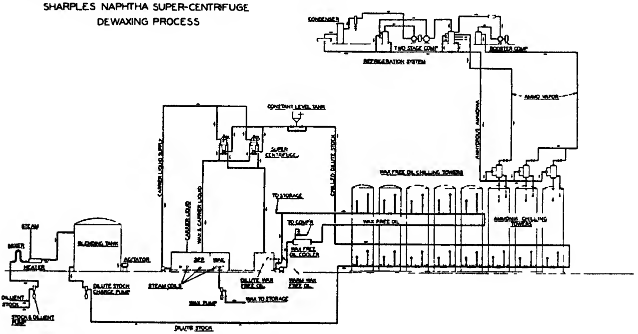


FIG 1

Much study has been given to methods for overcoming the inability to discharge crystalline wax, none of which have met with commercial success The most notable of these are schemes involving melting of the wax within the centrifugal bowl Failure occurred because when the wax was heated to a sufficient temperature to permit it to flow, the density of the wax was less than that of the surrounding solid wax and less even than that of the dilute wax-free oil from which it had been separated, with the result that the melted wax floated through the wax layer and the dilute wax-free oil layer and discharged with the latter Under average conditions the wax layer contains about 40% naphtha, 20% oil, and 40% wax, and the wax in melting dissolves in this associated oil and naphtha which accounts for the low density of the melted wax

Diluent.

The diluent commonly used in the Sharples process is straight run petroleum naphtha In order to reduce evaporation losses the I B P should not be lower than 150°F In order that too high a temperature may be avoided in recovering the diluent from the dewaxed oil, it is desirable that the E P be lower than 400° F A much lower E P is commonly used, and it is now common practice to use a naphtha with a boiling range of 150° F to 300° F

There has been much discussion on the effect of the solubility of wax in the diluent on the final pour-point of the oil obtained Data published by Bahlke, Giles, and Adams [1, 1933] show that naphtha with an average molecular weight of 85 has the highest solubility for wax and that the solubility falls off with increasing and decreasing molecular weight In commercial operation there is ample evidence that lower pour tests are obtained with naphtha of 50° F boiling range, and consisting mostly of hexane, than have been obtained with naphtha of a higher boiling range and higher molecular weight

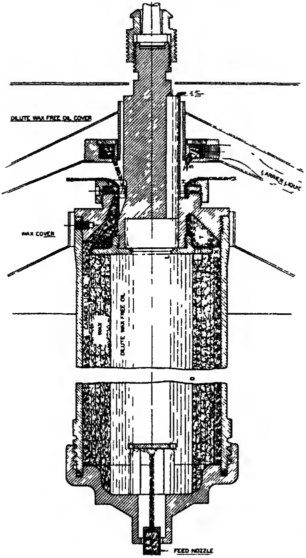


FIG 2

So many other factors affect the precipitation of wax in commercial dewaxing aside from the solubility of the wax in the diluent that this discrepancy is not surprising In the dewaxing operation there is no difficulty in separating the higher melting-point waxes, but in order to obtain a low pour test it is necessary to separate waxes which have melting-points so low that they can hardly be considered waxes Furthermore, the effect of the particular diluent on the asphaltic and colouring matter present must be considered, as the condition of the impurities affects the solubility of the wax and its crystal formation

While narrow boiling-range naphthas have been found especially good in obtaining low pour tests, naphthas blended from light and heavy naphthas give unexpectedly high pour tests in consideration of the separating temperature The presence of petroleum distillates of the gas oil range has a bad effect on pour tests and should be eliminated from the diluent or the stock to be dewaxed

The quantity of diluent in relation to waxy stock required depends upon the character of the stock For high fire test cylinder stocks containing very amorphous wax the dilute mixture may contain as little as 55% diluent with 45% oil when a finished pour test of +15° F is required Higher proportion of diluent is required if the stock is of lower flash-point, if the wax contained in the stock is less amorphous, and if the pour test required is lower For an extreme case of a 450° F flash distillate to be dewaxed to a 0° F pour test, the dilute mixture should contain 75% of diluent and 25% oil

'Non-Shock Chilling'.

In 1920 the writer [3, 1925] discovered that in order to obtain a precipitate of amorphous wax favourable for centrifugal separation from naphtha oil solution, it was necessary not only to chill slowly but also to use chilling surfaces or media not greatly different in temperature from the oil solution This principle in chilling has been designated 'Non-Shock Chilling'

In commercial practice the temperature of the chilling medium is maintained between 10° and 15° F below that of the oil solution being chilled and sufficient chilling surface is provided to chill through the complete range in about 48 hours Many efforts have been made to avoid the limitation of 'Non-Shock Chilling' None of them appeared to be economically justifiable The differential between the chilling medium and the oil solution being chilled may be increased and the rate of chilling increased and centrifugal separation of wax obtained However, with such departures from the best chilling conditions, there will be a sacrifice in pour test of the dewaxed oil and a loss of oil to the wax side, due to oil entrainment in the colloidal wax precipitate

For satisfactory results it is essential that waxy stock and diluent be brought to a sufficient temperature to completely dissolve all of the wax before chilling is started Failure to completely dissolve the wax will result in an unsatisfactory precipitate which will again give a reduced yield of higher pour test oil

Under favourable conditions of chilling as outlined above the pour test of the dewaxed oil will be approximately 25° higher than the temperature of wax separation down to a pour test of 15° F In other words 'the dewaxing spread' is 25° F For pour tests of lower than 15° F the spread increases so that it is necessary to chill to −40° F to obtain 0° F pour-test oil

There have been important improvements in the Sharples process from time to time in the application of refrigeration to the oil In early installations chilling was accomplished by circulation of brine through pipe coils in batch chilling tanks The brine was chilled by ammonia expansion and the temperature of the circulating brine was carefully controlled to provide 'Non-Shock Chilling' I C Carpenter

[2, 1934] introduced the Carpenter Chilling Tower which made it possible to continuously 'Non-Shock Chill' directly from ammonia to dilute oil This was accomplished by providing flooded ammonia chilling coils with vaporizing chambers at the highest point in the circuit, and with circulation of the liquid ammonia induced by thermo-syphon action The temperature of the circulating liquid ammonia is controlled by the control of the pressure on the vaporizing chamber

The development of the Carpenter Chilling Tower made possible economic refrigeration to −40° F and commercial manufacture of 0° F pour-test bright stocks

Recovery of refrigeration was first accomplished by exchanging heat from dilute wax-free oil with brine Later, the dilute wax-free oil was exchanged against dilute waxy oil, followed by brine and then ammonia for the lower temperatures Finally the brine has been entirely eliminated with the development of the system as shown in the flow diagram in this article

Suitable Charging Stocks for the Sharples Process

As has already been stated in discussing the solid discharge super-centrifuge, it is essential that the wax precipitated from the dilute oil be sufficiently fluid to flow in the centrifuge bowl Such wax naturally occurs in cylinder stocks, long residues, and properly prepared heavy distillates

Cylinder stocks and long residues directly from the still contain impurities which interfere with wax precipitation and centrifugal separation The hard asphalt content is precipitated on dilution and chilling and interferes with the wax discharge The asphalt and colouring matter as well interfere with or inhibit wax precipitation so that satisfactory pour tests are not possible in finished filtered stocks It is therefore necessary in the case of cylinder stock and long residues to either acid treat and clay treat or to only clay treat in the case of Pennsylvania type oils to approximately final colour before the stock is charged

As the length of the residue is increased by allowing lighter fractions to remain in the residue, the amorphousness of the wax is reduced until finally a point is reached at which satisfactory wax separation is not possible The flash-point of the stock has been found to be a good criterion of the suitability of a residue stock for the Sharples process The stock should not have a flash below 450° F With sharp fractionations between the overhead and the residues this figure may be somewhat reduced

Overhead stocks tend to be crystalline rather than amorphous, because the constituents of the petroleum contributing to the amorphousness of the wax remain in the residues Efforts to drive these amorphizing constituents out of the residue into the overhead lead to cracking, which increases the crystalline character of the wax in the overhead rather than reducing it Despite this difficulty overhead stocks can be produced by vacuum and steam distillation which can be readily handled by the Sharples process The overhead stock should have a flash of 450° F or higher and a viscosity of 70 sec S U at 210° F or higher The most favourable conditions are obtained if the still is so operated that there is no priming of residue into the overhead which will then be asphalt-free and may be dewaxed before acid treating and clay treating

In practice, refiners have preferred less critical operation of their distillation Some have operated their stills at a rate at which priming of residue into the overhead occurs, thereby carrying some of the amorphizing agencies from the residue into the overhead and then acid treating and clay treating before dewaxing A more common practice and a more rational one has been to blend residue cylinder stocks with distillate cylinder stocks, acid treating and clay treating either before or after blending, and dewaxing the blend Blends consisting of 75% overhead cylinder stock with 25% of residue cylinder stock have been found to dewax very satisfactorily in practice This procedure has the advantages in the final product of a good cast, due to the residue, and a low carbon residue, due to the distillate

Amorphizing Agents.

In addition to selecting stocks, the wax content of which is inherently amorphous, various expedients are available for modifying the natural wax characteristics so that it may be separated Materials which when added to oils increase the amorphous character of this wax content have been named amorphizing agents

Natural impurities occurring in petroleum are effective amorphizing agents and controlling the amount of these impurities will control the character of the wax [5, 1930] Colour may be used as a measure of the content of the natural impurities Too high a content of impurities inhibits the wax precipitation, whereas too low a content has no effect on the wax precipitation When the colour is darker than 80 Lovibond Series D, using a 10% solution of the oil in a ½-in cell, wax precipitation will be inhibited to an undesirable degree Using the same conditions of testing colour, when the colour is less than 80, amount of wax precipitation will not be affected but character will be Colour ranging from 80 down to 30 will show successively decreasing effect of the impurities upon the character of the wax precipitate, and with colours below 30 the effect of the remaining impurities will be found to be negligible These figures may not be used with great exactness and vary with different types of stocks, but may be considered as a rough guide

Discharge of Crystalline Wax

Many proposals have been made to effect the continuous discharge of crystalline wax from a centrifugal rotor, using naphtha as a solvent and separating the wax as the heavier phase Schemes for melting the wax within the bowl or rotor have been discussed above Other schemes proposed have been mechanical, involving the use of conveyors or similar devices within the centrifugal rotor for carrying the wax out of the rotor Such schemes have met with no commercial success It now appears that other developments have accomplished the desired results in another way so that further developments along the line of mechanical discharge of crystalline wax in naphtha solution is not to be expected

Wax Anti-solvents

Wax anti-solvents have a much lower solvent power for wax than naphtha, and yield a pour test in the finished oil much closer to the temperature at which the wax is separated than when naphtha is used In other words the dewaxing differential is less

Among others, C R Wagner has proposed the use of butyl-alcohol and naphtha [10, 1928], and methyl ethyl ketone [11, 1928]

The difficulty with such proposals has been due to the effect of the anti-solvent on the character of the wax. When wax anti-solvents are used as diluents the wax precipitates in a more crystalline form than from naphtha solution, and even distinctly amorphous wax such as occurs in cylinder stocks develops such crystalline characteristics that it may not be continuously discharged from the solid discharge centrifuge

Heavy Solvents

At the beginning of this article it was pointed out that in contrast to the use of naphtha as a diluent lighter than the wax, diluents heavier than the wax might be used where the precipitated wax was to be centrifugally separated When a diluent heavier than the wax is used the separated wax floats upon the heavy wax-free oil solution in the centrifugal rotor This wax-free oil solution may then be considered as a carrier liquid in the rotor, assisting in the discharge of the wax Solvents heavy enough to effect this purpose are found among the chlorinnated hydrocarbons which are noted for their high density

In cases where the precipitated wax is sufficiently amorphous, it may be continuously discharged as if it were a liquid as in the case of the dilute wax-free oil discharge from the bowl shown in Fig 2, and the dilute wax-free oil is discharged where the wax and carrier liquid discharge in Fig 2 When the precipitated wax is crystalline it will not discharge over a weir, such as *L*

De Laval Separator-Nobel Process

De Laval Separator-Nobel have developed a process for dewaxing, using trichlor ethylene as the preferred heavy solvent

Trichlor ethylene as a solvent in dewaxing has characteristics very similar to naphtha The dewaxing differential is even higher than for naphtha Data reported by the user of the process and tests made by the writer give pour tests from 32° to 60° F higher than the separating temperatures

The wax precipitated from a solution of oil and trichlor ethylene tends to be amorphous, as when naphtha is used as a diluent and the wax is readily discharged over weirs in the centrifuge, especially designed for the process by the Separator-Nobel

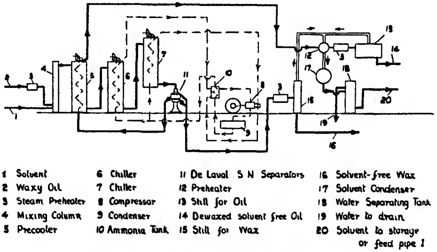
Fig 3 shows a complete dewaxing plant for continuous operation with direct ammonia chilling The oil or solvent (or both) is heated to an appropriate blending temperature, e g 120° F, depending on the pour-point of the oil, the blending being effected in a mixing column From here the solution passes through a heat exchanger, where it is precooled by the cold solution discharged from the separators It then passes through two chillers which are equipped with agitators in the top and work with direct expansion of ammonia from the refrigerating plant From the second chiller the solution flows into the separators at the desired separating temperature, which is normally about −20° F The dewaxed solution, after being used to precool the ingoing solution, is preheated by means of the vapours arising from the solvent-recovery still and then passed through a steam preheater into the still where it is heated to about 230° F by indirect exhaust steam, the last traces of solvent being removed by means of live steam

When treating oils containing only a small percentage of wax, the wax discharged from the separators may be stored and run into the oil-phase solvent-removal still, when the separator plant is shut down For oils containing a large percentage of wax, however, a separator solution-removal still for the wax is employed

The overhead solvent and water vapours from the still are condensed and separated in a static tank, from which the recovered solvent is returned to the blending column

The Separator-Nobel Centrifuge.

The design of bowl and covers is somewhat different from the usual type of centrifuge The solid wax is automatically and continuously discharged from the central part of the bowl into one upper and one lower wax receptacle, both of which are provided with closed steam coils in order to render the wax sufficiently fluid to be easily discharged from the receptacles On the other hand, the receptacle into which the dewaxed cold oil is discharged from the bowl is carefully heat insulated, as this oil is used to precool the ingoing solvent-oil blend



FLOW DIAGRAM OF DE LAVAL S-N DEWAXING PLANT WITH CONTINUOUS COOLING AND SOLVENT DISTILLING

FIG 3

The separator is belt driven by an electric motor Its capacity is dependent on wax content, viscosity, and desired pour-point required

Imp gallons of oil-solvent blend per hour	220–440
Imp gallons of dewaxed solvent-free oil per hour	74–176
r p m of bowl	9,000
r p m of pulley	900
Power consumption	4 5–5 5 h p
Suitable motor	6 5 h p

The best average chilling rate has been found to be 10–15° F per hour, so that chilling from 110° F down to −20° F takes about 12 hours With exceptionally difficult stocks a lower chilling rate of about 8° F per hour is necessary

Charging Stocks for the Separator-Nobel Process.

The following table illustrates some of the results obtained by the De Laval Separator-Nobel method

Stock	Viscosity sec R	Oil-solvent by volume	Chilling temp F	Yield %	Pour-point, °F
1 Press oil concentrate (unrefined)	230 at 122 F	60 40	4		10 5
2 From Boryslaw crude (refined)	190 at 122° F	„	−4		18
3 Cylinder oil distillate from Columbian crude	100 at 212° F	50 50	26	96 5–97 3	7
4			0	98	12 14
5		55-45	−6	98	18
6			0	98 2	19
7 Cylinder oil stock	110 at 212° F	40 60	24	86 6	12 14
8 Ditto—treated with fuller's earth			−24	87 5	17–21

Barisol Process

In the Barisol process there have been co-ordinated successful means for the continuous discharge of crystalline wax from a centrifugal rotor and the use of a heavy anti-solvent as a diluent A flow diagram of the Barisol process is shown as Fig 4

BARISOL PROCESS

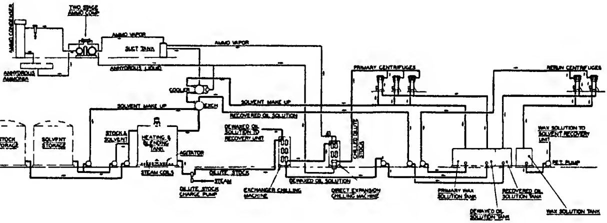


FIG 4

Stock and solvent from storage are picked up by pumps and transferred to the heating and blending tank There is also introduced into this heating and blending tank a mixture of solvent and oil recovered from the secondary separation, to be described later

In the heating and blending tank the solvent, stock, and recovered oil are heated to a temperature to completely dissolve the wax, that is approximately 100° F , and agitated to produce a uniform mixture

From the heating and blending tank the dilute stock passes to the dilute stock charge pump which forces it through chilling machines In the chilling machines the dilute stock is first chilled by exchange with dewaxed oil solution coming from the wax separation, and then by direct ammonia expansion From the last chiller, at a temperature from 0° to −20° F , depending upon the stock, the diluent and the pour test required, the mixture passes to the primary centrifuges

In the primary centrifuges the mixture is separated into a dewaxed oil solution and a wax solution containing some recoverable oil

The dewaxed oil solution passes to the dewaxed oil solution tank, from which it is pumped to the first exchanger chilling machines for the recovery of its refrigeration and then on to the solvent recovery unit

Another portion of solvent from storage, referred to as solvent make-up, is pumped to a heat exchanger and ammonia cooler and then mixes with the wax solution from the primary centrifuges and flows into the primary wax solution tank

The mixture of solvent make-up and wax solution from the primary centrifuges is pumped to the re-run centrifuges

The re-run centrifuges discharge a wax solution substantially free of oil, which flows to the wax solution tank, from which it is pumped to the solvent recovery unit

The oil solution from the re-run centrifuges, which is very low in concentration of wax, flows to the recovered oil solution tank and is then pumped through the heat exchanger to recover its refrigeration and returned to the heating and blending tank

Ammonia refrigeration is applied to the direct expansion chilling machine and to the cooler for the solvent make-up

The recovery of the solvent or diluent from the dewaxed oil solution and the wax solution is accomplished by distillation followed by steam stripping, both at atmospheric pressure

The Barisol Dewaxing Centrifuge.

A new type of centrifuge has been developed for use in the Barisol process The rotor or bowl of the centrifuge is comparatively short and large in diameter This shape of bowl facilitates the flow of crystalline wax within the bowl A nozzle extending into the bowl takes up the wax as it is separated by the centrifugal force, utilizing the inertia in the rapidly rotating wax to assist in this operation and the discharge of the wax through the nozzle and tube to which it is attached This method of wax discharge has been found successful for the continuous discharge of even the most crystalline wax met with in petroleum oils

Commercial sizes of the Barisol centrifuge operate at a rate of 600 U S gal per hour of waxy oil solution

Solvents.

Various solvents may be used in the Barisol process as diluents, and, because of the ability of the centrifuge to discharge the most crystalline wax, full advantage may be taken of the wax anti-solvents The writer [7, 1933] has found ethylene dichloride to be an excellent heavy antisolvent. An oil solvent such as benzene must be added to the ethylene dichloride to prevent the precipitation of highly paraffinic oil with the wax. This mixture of ethylene dichloride and benzene has a dewaxing differential of from 10° to 15° F.

By reason of the high solvent effect of this diluent for asphaltic material, such constituents of the stock to be dewaxed have no inhibiting effect upon the wax precipitation, and the most asphaltic residues may be completely dewaxed and the dewaxed oil subsequently purified by acid treating or solvent extracting, with satisfactory pour tests in the finished oil.

Chilling.

Because of the crystalline character of the wax precipitated from the solvent described above there is some tendency for the coating of the chilling surfaces. Chilling machines are therefore preferred and, because of the higher transfer rate obtained through the scraped surfaces, are economically justifiable.

Chilling conditions are not critical either with regard to rate of temperature reduction or temperature differential.

Suitable Charging Stocks for the Barisol Process

Because of the ability of the solvent mixture used as a diluent in the Barisol process to overcome the inhibiting effect of asphaltic material on wax precipitating and because of the ability of the centrifuge to discharge crystalline wax as well as amorphous wax, any type of raw lubricating stock may be dewaxed by the Barisol process. Because of this flexibility the decision as to what stock should be dewaxed involves a relationship between the dewaxing process and the other steps in the refinery, such as distillation, acid treating, and solvent extraction. Economy of operation and increased yield of finished lubricating oil are obtained by dewaxing first and acid treating or solvent extracting afterward. This is especially true in the case of residual stocks.

Examples of dewaxing of typical American Lubricating Stocks are tabulated below.

Re-running Primary Wax

When the Barisol process is operated on stocks which can be handled by the Sharples process, the yield and character of the primary wax is substantially the same as that obtained from the Sharples process. In the Barisol process the primary wax is discharged cold and in such a condition that it may be re-suspended in additional diluents. This makes possible the recovery of additional oil by centrifuging the mixture so obtained. By this procedure the yield of wax is reduced to about two-thirds of that obtained by the Sharples process, with corresponding increase in oil yield. This re-running operation requires no additional refrigeration and no additional distillation for the recovery of diluents, since the oil solution recovered in the re-run is returned to the first run operation. Additional separating capacity is of course required.

Examples of Barisol Dewaxing

Type of raw stock	*Mid-Cont wax distillate*	*Mid-Cont wax distillate*	*Mid-Cont slop oil filtered*	*Mid-Cont slop oil dark*	*Mid-Cont lube distillate*
Tests on raw stock					
Gr. API	28.0	23.8	27.5	26.2	23.7
Fl., ° F	400	430	455	460	465
Fr., ° F	455	495	535	545	545
Visc. at 100° F	139	304			
Visc. at 210° F		50	57	58	68.5
V.G.C.		0.859			
Solid-point, ° F	94	60	102	98	74
Colour	dark	1¾ T.R.	10 T.R.	½ T.R.	green
Dewaxing conditions					
Vol. of sol. for dilution	3.0	2.5	3.0	3.0	3.0
Vol. of sol. for wash	2.0	1.5	2.0	1.75	1.5
Centrifuging temp., ° F	−20	−16	8	−8	−9
Yield					
Dewaxed oil	74.0	91.3	82.6	85.5	85.2
Wax	26.0	8.7	17.4	14.5	14.8
After treatment of dewaxed oil	Treated and filtered	Treated and filtered	None	Treated and filtered	Treated and filtered
Tests on finished oil					
Gr. API	25.3	23.7	25.8	25.4	24.0
Fl., ° F	390	425	455	460	475
Fr., ° F	455	495	535	545	545
Visc. at 100° F	209.5	339	536	550	854
Visc. at 210° F	46	50.25	61	61.5	72
V.I.	80	53.5	75.3	74.6	66
Solid-point, ° F	−4	−4	−6	−2	−18
Cloud, ° F	−4	−4	−6	−2	−30
Colour T.R.	10	9¾	9	9	4½
Tests on wax					
Gr. API					
Melting-point, ° F	121	110	134	135	124

Examples of Barisol Dewaxing

Type of raw stock	Mid-Cont vac O H cyl st	Mid-Cont cyl st	Mid-Cont cyl st	Mid-Cont residue	East Texas dark residue
Tests on raw stock					
Gr API	21 6	21 6	21 1	24 6	19 0
Fl, ° F	560	510	530	420	475
Fr, ° F	655	600	610	475	555
Visc at 100° F					
Visc at 210° F	171	134	182	78 5	170
V G C					0 865
Solid-point, ° F	66	60	70	86	
Colour	green	dark green	dark green	dark green	black
Dewaxing conditions					
Vol of sol for dilution	3 0	3 25	3 5	3 0	4 0
Vol of sol for wash	1 5	1 5	1 5	1 5	2 0
Centrifuging temp ° F	−5	+1	−2	18	+3
Yield					
Dewaxed oil	86 0	83 8	85 2	83 0	69 1
Wax	14 0	16 2	14 8	17 0	30 9
After treatment of dewaxed oil	Treated and filtered	Treated and filtered	Treated and filtered	Treated and filtered	Treated and filtered
Tests on finished oil					
Gr API	23 2	23 5	23 5	25 2	21 6
Fl, ° F	555	505	525	415	460
Fr, ° F	660	580	615	475	530
Visc at 100° F	3 261	1,892	2 673	725	1,973
Visc at 210° F	154	109	140	70 5	108
V I	78 2	71 2	81 2	81 2	64 6
Solid-point, ° F	−6	−10	−2	6	−8
Cloud ° F	−16	−20	−30		
Colour T R	$4\frac{1}{2}$	5	$\frac{3}{4}$	$2\frac{1}{2}$	$\frac{3}{8}$
Tests on wax					
Gr API				33 1	
Melting-point, ° F	152	137	137 5	130	140

Examples of Barisol Dewaxing

Type of raw stock	Pa cyl st dark	Pa l res dark	Pa l res duo-solled	M C cyl st filtered
Tests on raw stock				
Gr API	26 2	27 6	31 0	24 0
Fl, ° F	530	460	400	535
Fr, ° F	620	510	470	615
Visc at 100° F				
Visc at 210° F	146	76	61 5	137
V G C				
Solid-point, ° F	36	16	88	100
Colour	green	green	$\frac{3}{4}$ T R	$\frac{3}{4}$
Dewaxing conditions				
Vol of sol for dilution	3 0	3 0	3 5	3 0
Vol of sol for wash	1 5	1 0	2 0	1 5
Centrifuging temp ° F	-7	-8	−13	+1
Yield				
Dewaxed oil	83 8	90 3	80 8	87 0
Wax	16 2	9 7	19 2	13 0
After treatment of dewaxed oil	Filtered	Filtered	None	None
Tests on finished oil				
Gr API	24 8	27 5	29 9	22 3
Fl, ° F	520	445	410	525
Fr, ° F	625	510	470	615
Visc at 100° F		683	452	3,294
Visc at 210° F	157	74	63 5	153
V I		99 4	108 2	76 5
Solid-point, ° F	−4	−6	−4	− 2
Cloud, F	−14	−14		
Colour T R	$\frac{1}{2}$	$1\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{2}$
Tests on wax				
Gr API	32 6	33 0		
Melting-point, ° F	124	121	117	134

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THE FILTER PRESSING OF WAX DISTILLATE AND THE SWEATING OF SLACK WAX

By **FRED W PADGETT, M S**

Moore and Murger Company

AN understanding of the fundamentals applying to the filter-pressing operation results from a consideration of Poiseuille's law of viscous flow and its application, qualitatively, to the particular process According to this law the linear velocity of flow of a viscous liquid through a capillary is

$$V = K\frac{Pr^2}{L\eta},$$

where V equals linear velocity of the liquid, K is a constant, P is pressure drop through the tube, r is radius of the tube, L is length of the tube, and η is the absolute viscosity of the liquid The filter cake is a porous wall of wax crystals, the capillary openings between the crystals permitting passage of oil in a manner which is assumed to follow the equation given above The linear rate of flow through a filter cake is approximately proportional to the volume throughput for a given area and thickness of cake, since for a fairly uniform size of particle in the cake the per cent voids in the cake is approximately independent of the actual size of the particle The volume rate of flow through a cake as influenced by the crystal size and therefore by the size of the capillary passages between the crystals hence is seen by Poiseuille's law to be directly proportional to the pressure drop through the cake and to the average of the square of the radii of the capillary openings, and inversely proportional to the thickness of the cake and the absolute viscosity of the oil at the pressing temperatures The size of the capillary openings in the cake will depend upon the character of the wax in the distillate, the rate of chilling of the distillate, and the viscosity of the medium (influence on crystal size) As the cake becomes thicker and the pressure drop through the cake greater, it is reasonable to expect that the capillary openings will become smaller to some extent, due to compressibility of the cake While the viscosity of the oil associated with the wax is not great at 100° F, where the chilling starts, it is considerable at the temperature where the pressing occurs and hence is an important factor in filter rates A Mid-Continent oil having a viscosity of 60 Saybolt at 100° F will have a viscosity of 200 to 250 at 40° F and between 900 and 1,500 at 0° F, one having a viscosity of 80 Saybolt at 100° F will have a viscosity of 300 to 500 at 40° F and more than 1,800 sec at 0° F

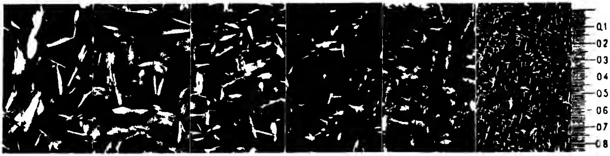
The conventional picture of the filter-pressing operation as presented in the above paragraph is extended by considering that the filter cloth may become clogged with wax crystals and that in the extreme case the fine crystals and mal-crystalline wax may be forced through the filter cloth

In view of the factors which limit the direct pressing of wax distillate, it is evident that the preparation of the distillate prior to the chilling and pressing is extremely important In truth, this problem is the one which concerns the refiner more than any other in connexion with the technology under consideration, for the simple reason that when the distillate is suitable, the difficulties in the subsequent operations disappear

Until recent years wax distillate generally was prepared in two ways One was to separate a 'pressable' product in the course of distilling paraffinaceous, residual crude oil to coke in coking stills The vapours went up into air-cooled towers where a number of fractions were separated, one or more of these fractions being in the category of 'pressable' wax distillate The towers acted as partial condensers and separators, and generally no effort was made to introduce efficient fractionation Another method of preparing wax distillate was to separate a 'raw wax distillate' when distilling a residual oil down to 'cylinder stock', 'tar', or 'flux' with fire and steam in batch, semi-continuous, but usually in continuous, batteries of shell stills The raw wax distillate, which might have a viscosity of 90 to 150 sec Saybolt at 100° F, was then redistilled, generally in batch stills, with fire and steam, permitting mild cracking, and leaving a residue of 5 to 15% This 'cracked wax distillate' had a viscosity of 50 to 80 sec Saybolt at 100° F, and usually contained from 8 to 15% wax, it would afford a satisfactory filter rate if it had been properly fractionated and entrainment eliminated The cracking served to produce diluent and possibly to eliminate by pyrolysis the higher, mal-crystalline waxes

In recent years there has come the realization that cracking is not necessary in the preparation of distillates for pressing, the requirements being good fractionation and elimination of entrainment of heavy residues and distilates If dilution is necessary to reduce viscosity of the medium this can be accomplished by adding a low-boiling product to the wax distillate This advance appears to have been coincident with the application of principles of fractionation to petroleum refining during the past 10 years It is reported that pressable distillates having viscosities as high as 100 sec Saybolt have been prepared by careful fractionation, but in this connexion it should be remembered that the important consideration is the viscosity at the pressing temperature and depends upon the slope of the viscosity-temperature curve Naturally, the refiner desires to obtain the maximum yield of, say, 200 viscosity neutral oil, and hence he is going to work with the highest end-point and viscosity of medium possible, all of which indicates that precise and practical control methods are desirable

The control of wax distillate for filter-pressing is accomplished through laboratory filtration tests on a small scale, routine distillation tests under vacuum, and photomicrographs Refineries which process wax distillate generally have available small batch chillers and filter presses which are used for working up wax distillates experimentally This equipment can be operated to parallel the large-scale process, but is time-consuming More often a small scale, quick test, which includes chilling and pressing, is used for control work For example, the 'squeeze test' used by the Atlantic Refining Company consisted in placing some of the chilled distillate in a cloth, folding and then twisting to determine whether the oil comes through rapidly, and whether there is wax appearing at the same time



End-point 648 End point 632 End point 637 End point 643 End point 625 End point 652

Characteristic commercial paraffin distillates End-points in °F under 40 mm absolute pressure

FIG. 1 Photomicrographs of wax crystals in chilled distillates (Davis and Campbell A P I, 1933)

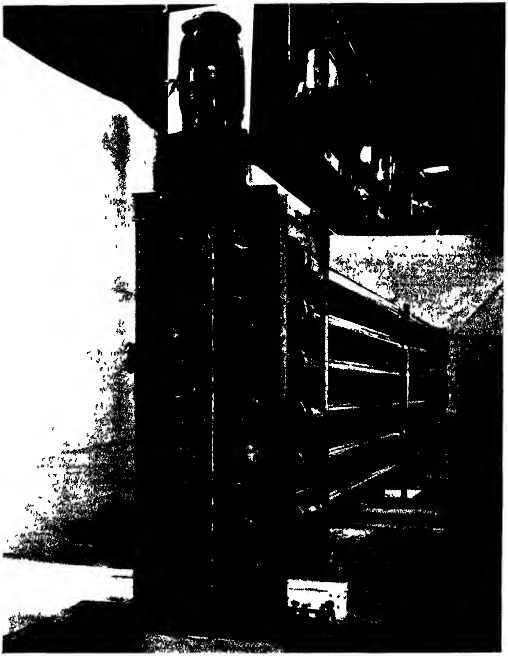


FIG. 3 Vogt worm-and gear drive, direct expansion, double-pipe chiller

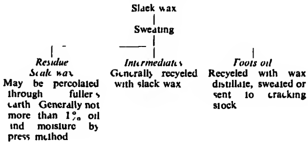
In regard to distillation tests for control of wax distillate for pressing, Peterkin [6, 1928], writes the following 'Experiments show that first a gradual increase in pressing rate and finally a sudden decrease may be expected as the 95% point of a vacuum assay increases and this in spite of the fact that sufficient gas oil may be added to the lower end of the boiling-range to make the viscosities in each case the same Coincident with sudden change in pressing rate the wax becomes either difficult or impossible to sweat' Scheumann [7, 1933] states that a vacuum assay at 2 mm pressure absolute and then correcting the boiling-points by means of the Ashworth vapour-pressure chart indicates that a maximum boiling-point of 850 to 900° F provides a wax distillate which gives a desirable crystal structure Commenting in regard to wax distillates in general, it canbe said, however, that a rigid designation of end or maximum point cannot be applied universally because the nature of the original crude oil has an influence, this fact, nevertheless, does not destroy the practical value of the distillation test

Hefley [5, 1927] expressed the opinion that pressing and sweating properties could be determined by microscopic study, and the method has been applied widely to commercial practice Very useful information on this method has been given by Davis and Campbell [3, 1933] The apparatus consists of camera, microscope equipped with nicol prisms, and warm stage The warm stage is fitted internally with a hanging-drop microscope slide, and a thermometer is inserted in the air space above the slide The water-jacket of the warm stage is connected to the hot and cold water supply with needle-valves The procedure in microscopic study is as follows a drop of the sample (after filtering through filter-paper) is placed in the slide depression and distributed by tilting the slide The instrument is adjusted so that the sample is between crossed nicols and the microscope is focused on the sample Cold water is first passed through the stage until crystals begin to appear, this is designated the 'saturation' temperature Hot water is then passed through until a temperature 40 F above the saturation-point is reached Thereafter cold water is added so that the stage temperature decreases at the rate of 1 7° F per min until a point 10° F below the saturation temperature is attained The photograph is then taken, or the crystallization is compared with a series of standard photographs and indicated by number Fig 1 shows photomicrographs, by Davis and Campbell, of a number of wax distillates with end-points at 40 mm pressure The last two products at the right give low-pressing rates and poor oil yields

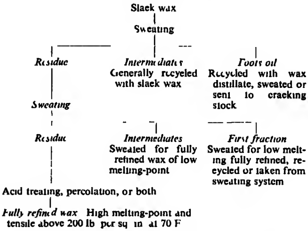
As stated previously, the effect of viscosity of medium may be counteracted by dilution of the distillate with a low viscosity product such as kerosine, gas oil, or naphtha distillate, but, generally, this will not correct a poor pressing distillate which has been improperly fractionated It is worth while mentioning, in this connexion, that the solvent power of the diluent may have an effect through its tendency to dissolve the mal-crystalline wax, but, on the other hand, it may cause a higher pour-point for a given pressing temperature due to solubility of wax

The question of rate of chilling of wax distillate is one that cannot be discussed positively The chilling rates vary considerably and various refiners do not agree as to the proper rate Some believe that a correlation of chilling rate and viscosity for the plant in question is necessary, while others indicate that no advantages are to be gained by a slow rate of chilling and that the only limit, when a properly fractionated distillate is being processed, is that imposed by the heat-transfer rate However, border-line products might be rendered pressable by slowing down the chilling rate The overall rate of chilling of wax distillates in commercial operation may be as high as 2° F per min, but generally is considerably less

In most refineries the wax distillate is chilled and pressed in two stages, one at some temperature between 30 to 60 F, and the other down to 0° F or below The two slack waxes so secured may be combined and sweated, that obtained at the higher temperature only may be sweated, or the two sweated separately The reason for the pressing at two temperatures is mainly a mechanical one direct chilling down to 0° F or below results in a distillate so hard in consistency that the resistance set up to the movement of conveyors and chillers may cause damage to the chilling equipment


(1) *Sweating to Scale Wax*

Slack wax
Sweating
Residue
Scale wax
May be percolated through fuller's earth Generally not more than 1% oil and moisture by press method
Intermediates
Generally recycled with slack wax
Foots oil
Recycled with wax distillate, sweated or sent to cracking stock


(2) *Sweating to Fully Refined Wax*

Slack wax
Sweating
Residue
Sweating
Residue
Acid treating, percolation, or both
Fully refined wax High melting-point and tensile above 200 lb per sq in at 70 F
Intermediates
Generally recycled with slack wax
Intermediates
Sweated for fully refined wax of low melting-point
Foots oil
Recycled with wax distillate, sweated or sent to cracking stock
First fraction
Sweated for low melting fully refined, recycled or taken from sweating system

FIG 2 Outline for sweating to scale wax and fully refined wax

According to Campbell and Wilson [2, 1919], one of the first methods used for chilling wax distillate was the internally cooled drum chiller, the distillate being chilled on the outside surface However, the 'shock chilling' which occurred resulted in poor crystallization, and consequently there was trouble in pressing Another apparatus was a cylinder externally cooled by brine and equipped with scrapers on the inside In the United States double-pipe chillers with screw conveyors in the inner space were introduced into the refining industry early in its history At the present time most of the refineries employ the double-pipe chiller, operated continuously with helical conveyors or other surface-scraping and stirring devices located in the inner space where the oil is moving The conveyor or scraper is an important part of the equipment, not as a means of moving the oil forward, but serving to remove solidified distillate from the heat-exchange surface and to stir up the mass of oil and wax crystals, thus aiding heat transfer from the sides of the body of the distillate, and promoting favourable crystal growth Cold brine is circulated counter-currently through the outside jacket, or ammonia is expanded directly through the same space as cooling agent

Illustrations of double-pipe chillers for wax distillates are shown in Fig 3 The rate of heat exchange is necessarily low, the maximum reported being about 20, but the average 4 to 8 B Th U per hr , per sq ft of exchange surface, per degree mean temperature difference Another type of chiller used rather extensively for chilling wax distillate is the Gray Chiller shown in Fig 4 It is vertical and resembles a large ice-cream freezer, and the scraper blades are forced positively against the heat-exchange surface, resulting in effective removal of solidified distillate from the walls The York Chiller resembles the usual horizontal double-pipe chiller, but scraper blades are forced against the heat-exchange surface The Carbondale Chiller utilizes long pitch, helical ribbon scrapers

In addition to the brine and ammonia, water and sometimes cold distillates from the presses are used as cooling media in the early stages of the chilling Absorption refrigerating machines are used widely for cooling the brine for the chilling machines, the use of ammonia by direct expansion into the jackets of the chillers being a rather new development resulting from the demand for lower temperatures However, increased capacity and lower temperatures also are secured by adding a booster unit to the absorption machines One ton of refrigeration will provide a throughput of about 8 to 10 bbl of wax distillate when double pressing from a temperature of 100° F down to a final temperature of 0° F , the first-stage temperature being 40° F

The Moore-Burmah chiller, Fig 5, is a type radically different from those discussed previously, and consists of a number of vertical, shallow cells, superimposed one above the other The oil and cooling medium pass countercurrent through alternate cells, those for the oil being equipped with scraper blades

In plant practice wax distillate is chilled continuously The oil, at a temperature in the region of 100° F , is pumped through the chillers, going thence to the filter presses In double pressing the distillate comes from the first-stage chillers, proceeds to the first-stage presses, and the oil which emerges is sent through the second-stage chillers, appearing at a temperature of 0° F or below

The press used for filtering chilled wax distillate is a long, horizontal, segmented cylinder, divided into as many as 500 cells, each ½ in in thickness and 46 in in diameter A circular opening runs horizontally through the centre of the press A more detailed consideration of the apparatus reveals an outside frame consisting of two heads, one stationary and the other movable, the rods connecting the heads, and a hydraulic cylinder for operating the movable head Filter plates alternate with spacing rings within the frame, and both are suspended by lugs on the side rods The filter plate is covered on both sides with cloth and has an opening in the centre Underneath the filter cloth on the two sides of the filter plate is located either a perforated plate or a screen, which will permit the oil, as it comes through the filter cloth, to flow down and away The faces of the filter plates are equipped with knobs, called bungs, which serve to maintain the cells at a constant thickness

The chilled wax distillate is forced into the press through the centre opening, where it distributes into the cells, the wax cake gradually building up therein, the oil finding its way out through the wax cake and the filter cloth, dripping down into the oil trough, and proceeding finally to the receiving tank for pressed distillate The operation is complete when the pressure indicates that a safe limit is reached If the distillate has been properly prepared and the pressing operation continued long enough, the press will be filled with a compact cake In order to remove the slack wax from the press the oil trough is moved aside, the tie rods unbolted, and the loose head moved back Next the cells are forced open one by one and the slack wax prised loose and dropped into the wax trough, where the screw conveyor takes it to the receiving tank for slack wax Clamping back the movable head by means of the hydraulic cylinder and bolting up the tie rods serves to assemble the press for another filtration

The various filter presses used for wax distillate are of similar design, but may differ somewhat in detail In one type the filter cloth is backed by wire screen, in another by a perforated plate The filter cloth used often is 12 oz canvas duck The pressures which filter presses will withstand vary up to 500 lb , but often the safe limit is 350 to 400 lb to the square inch

The filter rates secured in pressing wax distillate vary considerably, but an average of 0 02 to 0 06 gal pressed distillate per hr per sq ft of filter area gives a good idea of the performance

The wax from the filter presses is known as 'slack wax' and often contains about 50% oil If the distillate has been properly prepared, this slack wax will sweat satisfactorily, otherwise not Wax distillates of the ideal variety show good pressing rates, and the slack wax sweats with facility, giving yields of 30 to 45% of scale wax Sometimes a distillate can be filter-pressed, but the wax will not sweat The extreme case is the distillate so poorly prepared that it will not press, hence there is no slack wax to sweat All of this, of course, goes back to the preparation of the distillate, which in composition should include all of the waxes up to the mal-crystalline wax, but essentially excluding the last mentioned

The process of sweating is one of drainage, fractional fusion, and solution The wax first is chilled to a temperature below the solidification point, the result being a matrix in which needle crystals predominate if the sweating is to proceed in a satisfactory manner As the temperature is raised slowly, the oil, softer and lower-melting waxes flow away, leaving a porous cake having a distinctly fibrous structure resembling that of cotton batting As the heating continues the oil drains away from the fibres and capillary openings accompanied by a partial melting

Recycling is an important part of the sweating process In sweating slack wax two fractions are separated, leaving a residue which is the product sought after The first fraction is foots oil, and may have a solidification point of 90° F It may be resweated, separating another foots oil which may be recycled with the wax distillate or be taken from the system and sent to cracking stock The residue left from the sweating of foots oil is a low-melting wax which may be marketed, for example, as match wax, or recycled with the slack wax Generally, however, foots oil is not resweated, but either is recycled with the wax distillate or taken from the system The second fraction secured in sweating slack wax, known as intermediate wax, may have a melting-point of 100 to 115° F , and is recycled with the next batch of slack wax

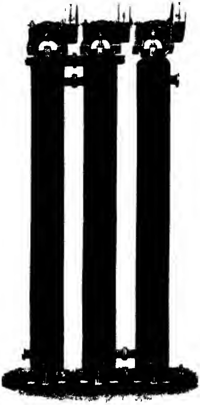


Photo by courtesy of Bethlehem Steel Company

FIG. 4. Three Bethlehem sectional unit type distillate chilling machines connected to form a single machine

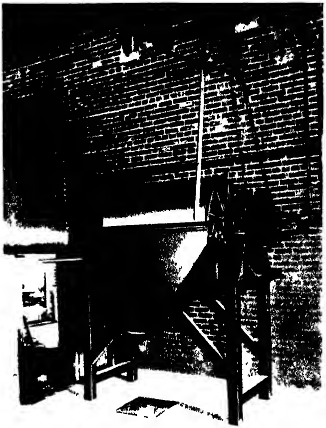


FIG. 8. Wax barrelling machine

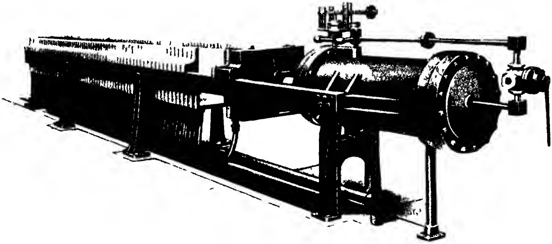
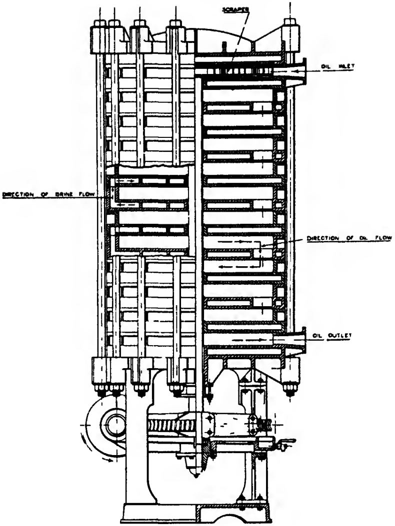
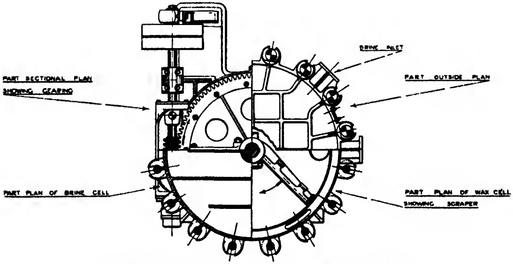


Photo by courtesy of Bethlehem Steel Company

FIG. 9. Bethlehem 10½ lb. cake wax moulding press fitted with pipe for carrying away discharge water



ELEVATION SECTION



MOORE-BURMAH PATENT OIL COOLER

Fig 5

The waxes of commerce made by sweating may be divided broadly into the 'scale' and 'fully refined' varieties The scale wax is crumbly and contains 1% or less of oil and moisture by the press method of test (A S T M Method D 308–29 T), while the fully refined waxes are non-crumbly and contain much less oil The scale waxes will sweat oil in packages while the fully refined products do not The melting-points of the waxes secured by sweating usually are below 135° F by the A S T M Method (138° F American melting-point) and generally above 120° F, although match wax has a melting-point about 110° F The tensile strengths of the scale waxes at 70° F, unless specially treated, generally are below 60 lb to the square inch, while those of the fully refined waxes vary between 200 and 400 lb per square inch at 70° F

It is usually not possible to prepare a fully refined wax from slack in one sweating In resweating to secure fully refined wax the product secured first is melted down, recrystallized, and sweated again Fig 2 shows outlines for sweating slack wax down to scale wax and full refined wax The methods shown are not to be accepted as standard because the methods and equipment vary in different refineries

A survey of the technical and patent literature shows that a great variety of methods and equipment have been proposed for sweating wax, only some of the more interesting ones will be mentioned here An early method of partially separating wax and oil was to place the solidified wax or distillate in bags in a special room and permit some of the oil to drain away Early patents proposed placing moulded blocks of the wax in cells or cages and to pass them slowly through a heated zone Another method was to force the chilled mass into a press consisting of a perforated tube lined with filter cloth and heated indirectly with steam Still another was a sweating apparatus consisting of an annular space for the slack wax and a vertical, cylindrical sweating surface on the inside the slack wax is cooled from the outside inwardly and the sweating consummated by heating from the inside outwardly Pressing and sweating are combined in another method which specifies the removal of oil laterally through perforated surfaces, the pressure being applied in a direction at right angles to the flow of oil A different method is to mix the wax at a temperature a little above the melting-point with water at a temperature of a little below the melting-point of the wax and then working, kneading, or sweating to produce separation A recent patent specifies sweating in a solution of sodium silicate Cooling and heating surfaces with fins attached also are specified, while somewhat along the same line are small rods located vertically to produce drainage channels

The apparatus most generally used, however, for sweating wax in refineries of the United States is the 'sweating pan' which is a shallow tray with sloping bottom The pan may be 8 to 12 in in height at the sides and 14 to 16 in at the centre where the sloping bottom converges to the outlet line A screen or a perforated plate is located at the junction of the sloping bottom with the sides of the pan, and a continuous coil of pipe is laid above the screen or perforated plate If a screen is used, it is supported by angle or T-iron, and is of 40 or 50 mesh laid over a heavier screen having openings about 1 in square The perforated plate may have openings $\frac{1}{16}$ to $\frac{1}{8}$ in in diameter The coil in the pans consists of 1-in pipes connected by return bends Sweating pans are assembled in stacks of 6 to 8 in well-insulated rooms with steam coils arranged around the sides of the room. The pans are connected to piping for admission of water and charging stock, circulation of cold and hot water through the coils on the screen, and sometimes connexions are provided for direct steam to aid in melting down the final product It is desirable that the coil in each pan have a visible overflow or other means to ensure uniform flow of water through each pan during the sweating The sweating room has large doors or shutters located at the ends which are opened to assist in the cooling of the wax and to provide ventilation, these doors are closed tightly during the sweating The pans vary in size up to 12 ft wide by 60 ft in length

The operation of the sweating pan is as follows the sloping bottom is filled with water to a point slightly above the screen and the melted slack wax is introduced above the water, filling up the pan In order to chill the wax before sweating, cold water is circulated through the coils, and air permitted or forced to circulate over and around the pans After the wax has solidified, the water is withdrawn and the sweating started by circulating water at a gradually increasing temperature through the coils in the pans, also bringing up the temperature of the room simultaneously by admitting steam to the coils on the side walls If the slack wax is of good sweating quality, the oil will drain away rapidly, and thereafter the temperature may be increased rather quickly to the necessary temperature and held at that point until the residue comes to grade Finally, the cycle is completed by heating the oven to a higher temperature to melt down the wax The overall rate of heating, during sweating, is 1 to 2 F per hr

The complete sweating cycle varies from 25 to 75 hr, depending upon the equipment used, the product being sweated and upon the final product desired This cycle includes charging the pan, cooling the wax, sweating, and melting down The actual sweating operation requires 50 to 65% of the total cycle time

The completion of the sweating is ascertained by test of the residue, such as melting-point oil content, or tensile strength When running to scale wax, operators can gauge rather closely when the sweating is completed by the taste of the sweat residue The press method (A S T M D 308–29 T) for oil content consists in pressing a small sample of wax, located between disks of cloth, for 5 min at a pressure of 1,000 lb to the square inch and temperature of 60° F The expressible oil and moisture is calculated from the loss in weight of the cloth-wax sandwich This method can be applied to routine testing and has been useful, although the results show in no way the actual oil content of the wax Various methods of determining the oil content of wax by use of a solvent have been proposed, but often they are not sufficiently accurate for waxes containing only a small percentage of oil, or are too involved for routine work One method is the solvent index of refraction method of Wilson and Wilkin [8, 1924] A direct refractometric method of estimating oil content is that proposed by Diggs and Buchler [4, 1927] It includes taking the index of refraction before and after percolation through an equal weight of Attapulgus or Floridin clay and using a graphical method, established experimentally, to find the oil content It is claimed that the method is more accurate than the press method, gives more consistent results, and is more rapid The tensile strength method is applicable to fully refined waxes and has the advantage that the results not only give a rough indication of the oil content, but have a relation to the performance of the wax in service The disadvantages of the test are the time required and rather poor checks secured The latter disadvantage can be overcome to some extent by testing at least 6 briquettes from each sample Despite the disadvantages, the test is valuable, particularly for fully refined waxes The procedure of the test is as follows the wax is melted in a glass beaker and heated to 130° C The moulds located on metal plates, are then poured as full of melted wax as possible and permitted to stand 1 or 2 hr After this time the surface of the wax is scraped away at the constricted portion, or shank, of the briquette, leaving a square section ½ in on the sides The briquettes are taken from the moulds and placed in water at a definite temperature (70° F is often used) for ¼ to ½ hr , then broken on the tensile machine, bringing up the indicator on the gauge at a slow, uniform rate Since the sides of the shank are of ½-in dimension, the reading on the gauge must be multiplied by 4 in order to secure tensile strength in pounds per square inch

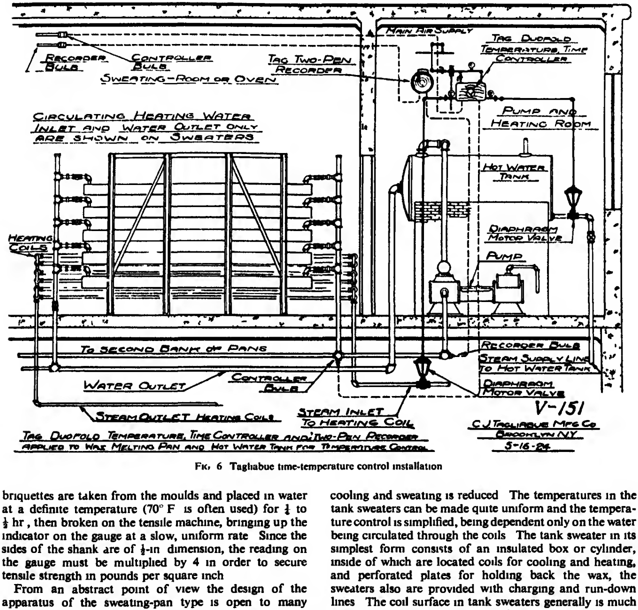
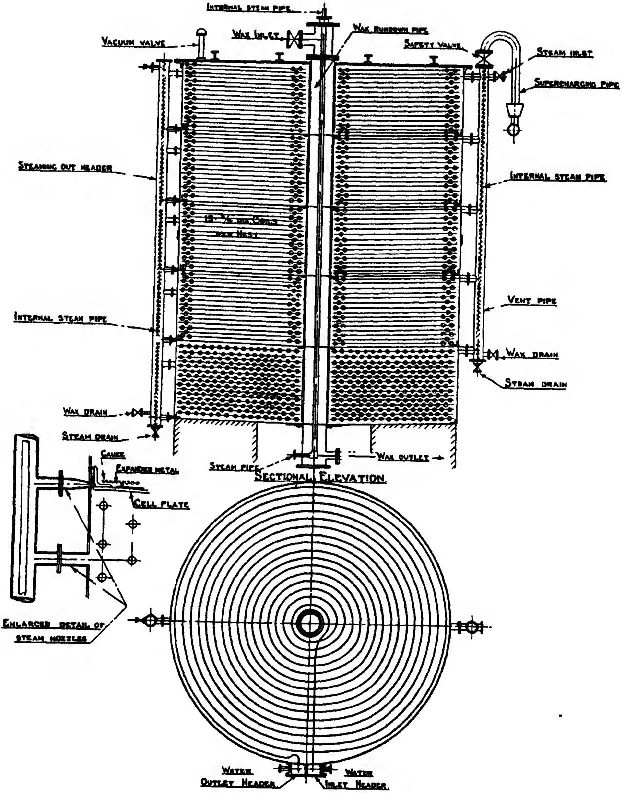


Fig 6 Tagliabue time-temperature control installation

From an abstract point of view the design of the apparatus of the sweating-pan type is open to many objections But the operating and maintenance costs are low, and satisfactory results are secured in operation, despite the fact that everything seems to be wrong It has been difficult to introduce new forms of apparatus or to make improvements in existing installations However, in some cases, temperatures have been made more uniform by improved circulation of air and by more coils placed in the pans to hasten cooling and facilitate sweating Automatic control of temperatures of the water circulating through the coils, and of room temperatures, has been found useful Fig 6 shows the Tagliabue time-temperature control mechanism, which consists of two cams, operated by clock mechanism, one of the cams controlling the water temperature and the other the room during the sweating

Tank-type sweaters have been installed in a number of refineries and have been found satisfactory, particularly for sweating foots oil and slack wax This type of equipment occupies less space than the pan system, and the time of cooling and sweating is reduced The temperatures in the tank sweaters can be made quite uniform and the temperature control is simplified, being dependent only on the water being circulated through the coils The tank sweater in its simplest form consists of an insulated box or cylinder, inside of which are located coils for cooling and heating, and perforated plates for holding back the wax, the sweaters also are provided with charging and run-down lines The coil surface in tank sweaters generally is much greater than in the pan system The Allan Moore sweater, Fig 7, is divided into 7 sections by horizontal deck plates, each slightly coned at the centre and covered with sheets of expanded metal and wire screen to permit drainage towards the centre pipe, which pipe is the run-down line for the apparatus Spiral, horizontal coils are located in each section of the sweater and connected to manifolds outside the shell Cold water circulated through the coils serves to chill the slack wax, while water of gradually increasing temperature does the sweating



'Alanmor" patent wax sweating stove.
Coil type.

Fig 7.

Buildings of substantial construction are required for wax-plant equipment The refrigeration machinery and brine coolers are often located in the same building with the chillers and filter-presses but in separate rooms, while the sweating ovens are in separate buildings Chillers are insulated by placing jackets around them and filling with material such as cork Filter presses are in rooms which are well insulated, sometimes special vaults are provided Buildings for sweating pans are of heavy brick construction where the pan system is used, but shelter for tank sweaters may be of less substantial build Sweating ovens and filter presses may be located at sufficient height so that the products will move to receiving tanks above ground or at lower levels where the flow is into tanks with bottoms below ground-level For details of wax-plant buildings and equipment reference is here made to the work of Bell [1, 1930]

Pressed distillate from the filter presses is subjected to fractionation under vacuum or with fire and steam, separating gas oil, one or more lubricating oil distillates, and leaving a residue These are the low viscosity neutral stocks which are refined further by treating with acid contact with clay, percolation through filter clay, or combinations

The waxes secured by sweating are generally refined further before marketing The sweating process not only reduces the oil content but improves the colour also, though not sufficiently to provide a white wax for the market Therefore the wax is refined by treatment with sulphuric acid followed with sodium carbonate solution or dilute sodium hydroxide solution, percolation through fuller's earth, or by combinations of the above treatments Wax gives yields by percolation varying from 100 to 400 bbl to the ton of clay

The wax is marketed in various ways in cakes, barrels, bags, slabs, and in tank-cars A machine for packing wax in barrels is shown in Fig 8 The drum is cooled internally by water, and as the drum revolves it picks up a layer of wax from the pan underneath, which pan contains molten wax The layer of wax is removed by scrapers, falls off into chutes and then into barrels where it is tamped by hand or by mechanical devices In preparing slabs of wax, pans arranged in stacks are filled with the molten wax and allowed to cool, after the wax has solidified the slabs are dumped from the pans Considerable wax is transported throughout the United States in tank-cars equipped with heating coils, and this constitutes an economical method of shipment The Gray machine for moulding wax cakes is shown in Fig 9 The operation of this machine depends upon the arrangement of cooling plates on the sides of the moulds and a flow of molten wax into the moulds as the cooling takes place The arrangement of the machine suggests that of a filter press with chilling plates (cooled by water) taking the place of filter plates, and moulds that of the spacing rings

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DEWAXING OF LUBRICATING OILS BY BENZOL-ACETONE MIXTURES

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LUBRICATING oils must not only possess the property of forming coherent and adherent films, but must also possess 'body' enough for the required duty They must at all times remain homogeneous, and not become cloudy or opaque at low temperatures In order to fulfil these conditions the crude oil must be subjected, amongst other treatment, to the process of dewaxing, that is, the removal of solid hydrocarbons which separate out at low temperatures

In the past two quite separate and distinct dewaxing processes had to be used for high viscosity and low viscosity wax stocks Pressing and sweating processes were used for removing and producing wax from wax distillate, while cold-settling and centrifuging were used for dewaxing cylinder stock

The lubricants as dewaxed in this manner were not entirely satisfactory, those manufactured from naphthene base oils being suitable at low temperatures, but not possessing the necessary degree of oiliness at elevated temperatures On the other hand, those lubricants manufactured from paraffin base crudes became cloudy at low temperatures due to the separation of wax

The use of two separate processes for the dewaxing of various types of lubricating stocks has been a source of great expense to refiners, and methods have recently been devised whereby the entire range of wax-bearing stocks can be dewaxed by a single operation requiring the use of a special solvent The use of a single process for dewaxing any wax-bearing stock has many advantages The cuts that must be produced in a vacuum tower are reduced to gas oil, lubricating-oil stock, and tar, only one type of dewaxing equipment is required, and the production of several blending stocks are unnecessary

The general requirements of the solvent are as follows

1 At approximately 100° F the lubricating-oil stock must be completely miscible with the solvent
2 At −5° F or below the solvent must have substantially complete solvent action upon the liquid hydrocarbons present, but substantially no solvent action on the solid hydrocarbons present
3 On cooling a solution of the lubricating-oil stock in the solvent to 0° F , removing the solid hydrocarbons so precipitated, and distilling off the solvent, the resulting lubricating oil must have a cold test of substantially 0° F .
4 The solvent must be cheap and non-corrosive
5 The wax must be precipitated in a form in which it is easily separated
6 It is desirable that the solvent be one which can be used both for dewaxing and solvent extraction

Benzol-acetone Mixture as a Dewaxing Solvent

It has been found that a mixture of acetone and benzol is a very satisfactory solvent Methyl-ethyl ketone can be used in place of acetone, while the addition of toluol to replace some of the benzol is sometimes advocated The use of acetone alone results in the formation of two layers with the oil The use of benzol alone results in the production of lubricating fractions which, after removal of the benzol, possess a high pour-point A further disadvantage in the use of benzol alone is that it crystallizes out at low temperatures By combining these two solvents in the proper proportion, however, there is no separation of the liquid hydrocarbons as a second liquid phase, and on chilling, the solid hydrocarbons are entirely separated in such a state as to permit easy filtration or centrifuging After removal of the solvent by distillation the resulting lubricating oils retain their oiliness at all temperatures and remain homogeneous at low temperatures The function of the benzol is to retain the oil in complete solution at the dewaxing temperature, while that of the acetone is to eliminate effectually any tendency of the wax to remain in solution at the dewaxing temperature The mixed solvent is also a material aid to filtration by reducing the viscosity of the oil solution

This process has been proved commercially and is now widely used The first plant was constructed at the Lawrenceville refinery of the Indian Refinery Company in 1927 and is still in successful operation, dealing with 1,000–1,500 bbl per day By March 1936 a daily total of 6,000 bbl was being dealt with at the refineries of the Atlantic Refinery Company, Gulf Refinery Company, Herbert Green & Company Ltd , and the Texas Company, while several other plants were being constructed

The reason for the commercial success of the above process was that it fulfilled the following requirements

1 Produced from waxy stocks the maximum yield of wax-free oil consistent with normal stock fluidity and having the desired pour-point
2 Was suitable for dewaxing any lubricating stock
3 Permitted changing from one stock to another with minimum loss of time
4 Was economical to operate and low in initial cost
5 Was sound in fundamental theory, thereby enabling processing improvements to be incorporated without completely altering the plant

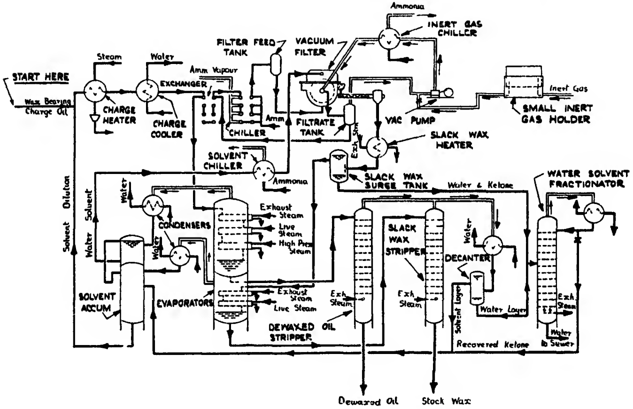
The Benzol-acetone Dewaxing Process

The method of operation and plant at present used for the dewaxing of lubricating-oil stocks by solvents of the acetone-benzol type are as follows

The solvent mixture, which, as seen in the tables given later, varies in composition with the type of stock used, but which usually consists of 35% acetone and 65% industrial benzol, is contained in gas-tight storage tanks The solvent and oil streams flow continuously into a mixer, the rate of these streams being controlled by means of a ratio-flow controller so as to ensure a continuously uniform solution

A solution temperature of the order of 100–120° F is all that is usually required With some oils, however, filter rates and yields can be improved by the previous heat treatment of the solution In these cases the solution is heated about 50–60° F above the complete solution temperature and then immediately cooled again by the insertion of a steam heater and water cooler in the charge line from the mixing tank to the chilling equipment

The mixture of solvent and oil stock is pumped from the mixing tank through continuous chilling equipment—the first part of which consists of heat exchangers—exchanging heat with the cold-pressed distillate mix from the presses, thereby cooling the solution down to about 25° F The solution is then chilled by direct ammonia-expansion chilling, the ammonia being supplied by either absorption or compression machines The final double-pipe chiller is automatically controlled to give the desired dewaxing temperature The pump must be installed in the line prior to the chilling, so that the wax crystals are disturbed as little as possible between chilling and filtering



Two types of filters have been applied to the process, viz continuous drum-type vacuum filters and rotating-leaf pressure filters Both these types permit the use of insulated filter shells Pressure filters now in use have a filtering surface of 800 sq ft, while vacuum filters in use have a filtering area up to 500 sq ft The filters are emptied without opening by means of inert gas pressure First gas pressure is applied to displace all the unfiltered stock from the filter back into the filter tank Gas pressure is then maintained on the filter, thereby displacing liquid remaining on the slack wax cake, which is about ¾ in to 1½ in thick This pressure is maintained until all the liquid has been driven from the cake, as indicated by a rapid falling in pressure on the filter, which occurs in 7–10 minutes This pressure is then released and the cake falls off into the bottom of the filter and is carried away by a screw conveyor, the action of which renders the slack wax cake easily pumpable The cycle of filtering operations is as follows

Filtering time	25 min
Displacing unfiltered solution	2-4
Applying gas pressure on the cake	7–10 ,
Dumping	10 ,

The filter rates used average from 0 3 bbl of oil per square foot per day for the heavier distillates to 0 5 bbl of oil per square foot per day for the lighter distillates These rates include blowing and dumping times

Provision is made for washing the cake on the filter, as it is sometimes desirable to wash it with chilled solvent before blowing it off the leaf

The wax cake, on emerging from the conveyor, is mixed up by a rotary pump and pumped through a heat exchanger where its temperature is raised to about 200° F, into a settling tank Here any water which may have inadvertently entered the system is withdrawn Any acetone dissolved in this water is recovered in a small fractionating column The wax is then pumped to the solvent-recovery equipment

The pressed distillate, on emerging from the filter, exchanges heat with the charging solution as previously mentioned and then passes to the solvent-recovery equipment

Several designs may be employed with equal success for the solvent-recovery equipment By using steam-heated evaporators 80–90% of the solvent can be removed by means of exhaust steam furnished by steam-driven pumps and other machinery These evaporators consist of a horizontal cylindrical shell containing three flat shallow pans placed one above the other. In each pan there are steam pipes. The liquid flows into the top pan across the steam pipes there, then by means of suitable downtake pipes the remaining liquid passes to the second tray and across the steam pipes there. In this way a small head of boiling liquid is maintained, which combined with a high cross-flow velocity results in high heat transfer rates. Exhaust steam is charged to the top tray pipes where most of the solvent is removed. Higher pressure steam is charged to the pipes in the other two trays. The heated oil from the lowest tray contains approximately 0.5% of solvent which is easily removed in a conventional steam-stripping column. Solvent is removed from the slack wax in the same manner.

In cases where exhaust steam is not available multiple-effect evaporators are used. Steam is used to vaporize solvent from the filtrate solution, and these vapours used to vaporize more solvent at reduced pressure. The process therefore affords the designer wide latitude in selecting an economical basis for design.

Solvent Losses

For economical operation the solvents used must be stable at the temperatures required in the recovery process, easily removed from the oil and not chemically reactive with it. Acetone, methyl-ethyl-ketone, benzol, and toluol all have excellent qualities in these respects as substantiated by records of solvent loss attending commercial operation of the process over long periods of time. The total overall loss of solvent due to all causes amounts to only 0.05% of the solvent turnover. Precautions taken to keep this loss to a minimum include the use of welded lines and vessels, blanketing of solvent tanks with inert gas, and grease-sealed lantern glands on pump rods, chiller shafts, filter trunnions, and similar glands through which the solvent might leak. The inert gas, which is used for pressing and blowing the wax cake off the filter leaf, passes through an oil seal before escaping to the atmosphere. In this way any solvent present in the inert gas is trapped.

Composition of the Solvent

The solvent usually used is a mixture of benzol, toluol, and acetone. Benzol and toluol are solvents for the oil, acetone a precipitant for the wax, and acetone and toluol act as anti-freezes for the benzol. These factors must be borne in mind in adjusting the composition of the solvent to suit the particular conditions. In actual practice the acetone fraction varies from 25% to 35%, the toluol 12% to 25%, with benzol making up the remainder. The more paraffinic stocks require lower acetone concentrations; lower operating temperatures require higher combined acetone and toluol concentrations. Naphtha is sometimes used instead of toluol.

The ratio of solvent to charge stock varies from two parts of solvent per one part of stock to four parts of

TABLE I

Stock	*Raw distillate*		*Raw distillate*		*Raw distillate*		*Raw distillate*		*Raw Oklahoma residuum*	
Source	*Mid-Continent*		*East Texas*		*Mid-Continent*		*Mid-Continent*		*Mid-Continent*	
Solvent composition										
Acetone	25–35		25–35		35		35			
Methyl-ethyl ketone									55	
Benzol	40–63		40–63		65		65		45	
Toluol	12–25		12–25							
Yield of wax-free oil					70		60		88	
Dewaxing temperature, ° F	−20		−10		−10		−50		−12	
Solvent ratio	2½:1		4:1		3:1		3:1			
Tests	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*
Gravity API	23.9	23.3	26.6	22.3	24.0	23.0	30.1	28.0	23.6	22.4
Viscosity S.U. at 100° F	320	350					72	82	1,200	1,644
" " 210° F	50	50	58	58	70	74			90	102
Pour-point, ° F	+30	−10	+110	−5	+110	5	+65	40	+85	−5

Stock	*Raw long residuum*		*Raw distillate*		*Solvent-refined distillate*		*Solvent-refined Huenigsen residuum*		*Solvent-refined distillate*	
Source	*Pennsylvania*		*Pennsylvania*		*Mid-Continent*		*Germany*		*Iraq-Iran*	
Solvent composition										
Acetone					35		30		35	
Methyl-ethyl ketone	40		40							
Benzol	60		60		52		65		65	
Toluol					13		5			
Yield of wax-free oil	85		82		84		82		78	
Dewaxing temperature, ° F	−10		−10		−11		−12		−15	
Solvent ratio										
Tests	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*	*Charge oil*	*Dewaxed oil*
Gravity API	28.3	27.3	34	31.2	28.1	27.3	27.4	25.9	31.1	29.3
Viscosity S.U. at 100° F	590	730	80	107	625	755	630	804		176
" " 210° F	74	76	38	40	67	72	72	77	44	45
Pour-point, ° F	+45	−5	+70	0	+110	−5	+110	0	+110	−5

solvent per one part of stock, depending on the wax concentration and viscosity of the stock

Stocks Dewaxed

In general this type of plant has been used for dewaxing distillate oils, normally ranging in viscosity from 40 Saybolt sec at 110° F to 160 Saybolt sec at 210° F from Mid-Continent, Kentucky, and Illinois crudes to produce oils with pour-points varying from 0° F to 35° F Oils outside this range have also been successfully dewaxed by this method, and Table I illustrates typical results

For dewaxing heavy oils at low temperatures it is necessary to add toluol or naphtha to the acetone-benzol mixture to prevent the acetone forming two layers with the oil and the benzol from freezing Table II indicates the amount of naphtha to be added for various oils

TABLE II

			Composition of solvent		
Source	*Viscosity S U at 210 F*	*Dewaxing temp*	*% acetone*	*% benzol*	*% naphtha*
Mid-Continent	70–120	10 F	32	65	3
	120–180	,,	30	65	5
Pennsylvania	45–60		30	65	5
,,	60–100		27	65	8
,,	100–140		25	65	10

Two-stage Dewaxing

It is claimed that dewaxing can best be carried out in two or more stages Most of the wax is removed at a relatively high temperature where the viscosity is much lower and hence filtering rates higher On further cooling, the small amount of residual wax is able to crystallize out unencumbered by the larger portion of wax and therefore more complete dewaxing is ultimately obtained During the second-stage low-temperature filtration a finer cloth is used The advantages of this system are

1. Less clogging of the chilling equipment
2. The wax removed at high temperatures has a higher melting-point and hence greater value
3. Any wax passing through the first-stage filtration cloth is removed in the second-stage filtration

To carry out this procedure relatively more acetone is used in the high-temperature dewaxing stage since at this temperature there is less tendency to form two layers

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REFINING WITH LIQUID PROPANE

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DURING recent years liquid propane has been developed into a valuable refining agent in the production of high quality lubricating oil Although propane is a gas under atmospheric conditions of temperature and pressure (normal boiling-point, −42° F), it is maintained in the liquid state under moderate pressures at ordinary temperatures In the liquid state, propane may be used effectively in lubricating oil refining over a wide range of temperatures, for a number of purposes The uses of liquid propane in lubricating oil refining are principally for (1) deasphalting, (2) dewaxing, and (3) improving the efficiency of other refining processes

These different uses of propane in lubricating oil refining were developed almost simultaneously for the purpose of completely refining high grade lubricants from mixed base residua containing both asphalt and wax, but the applications have since been extended to include refining of all types of lubricating fractions of petroleum For the sake of clarity it is best to discuss separately these several uses of propane Since asphalt separation occurs immediately upon mixing the stock with propane at atmospheric or elevated temperatures, attention will be given first to deasphalting, then to dewaxing, and finally to treating in the presence of propane, keeping in mind that a complete procedure is to mix the stock with propane under pressure at atmospheric or higher temperatures to obtain precipitation of asphalt in a form suitable for separation by decantation, then to release the pressure to obtain automatic or internal refrigeration and precipitate wax in a form readily removable by mechanical means, such as filtering, centrifuging, or settling, and finally treat the deasphalted and dewaxed oil for the removal of undesirable constituents while the oil is still dissolved in propane The order of the last two steps may be reversed

Deasphalting

Of the various low molecular weight hydrocarbons of the methane series, propane is peculiarly effective in precipitating asphalt In comparing the action of the various homologues of methane on a residuum containing asphalt, it is found that at ordinary temperatures hexane precipitates only a small amount of bituminous material with a relatively high melting-point, about 325° F , pentane gives a somewhat larger precipitation of bituminous material, having a slightly lower melting-point, butane precipitates appreciably more asphalt than the higher molecular weight homologues, but the asphalt precipitation is only about 50% complete as compared with the amount of hard asphalt obtainable by distillation The asphalt precipitated by propane is practically identical in yield and melting-point with that obtained by distillation Ethane, on the other hand, not only precipitates all of the asphalt, but also a major portion of the intermediate and heavy grade lubricating oils Table I illustrates the variation in yield and properties of the extracted oil and asphalt obtained with the various hydrocarbon solvents on an asphaltic residuum

TABLE I

Properties and Yields of Oil and Asphalt produced from Poso Creek Residuum (topped to 66 sec Saybolt Universal Viscosity at 100° F on Overhead Stream) by Extraction with Low Molecular Weight Hydrocarbon Solvents

(10 volumes of solvent at 80° F)

Solvent	Yld of oil (% by vol res)	Yld of Asph (% by vol res)	Properties of extracted oils: Grav API at 60 F	Viscosity Say Univ sec at 210 F	Car res %
Ethane	11 0	89 0	24 2		0 077
Propane (boiling point 42 to 40° F)	75 0	25 0	17 5	94	2 35
Propane 50 % butane 50% (boiling point 42 to + 36° F)	87 3	12 7	15 8	119	4 2
Butane 50% isobutane 50% normal butane (boiling point 14° to 31° F)	89 2	10 8	15 7	139	5 3
Butane (boiling point 30 to 36° F)	88 8	11 2	15 2	139	5 12
Pentane (boiling point 82° to 100 F)	95 2	4 8	14 5	192	6 23
Hexane (boiling point 140 to 156 F)	98 0	2 0	13 8	208	7 09

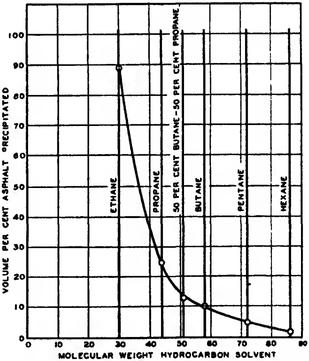

FIG 1 Effect of molecular weight of saturated hydrocarbon solvent on volume per cent asphalt precipitated from Poso Creek residuum 10 volumes solvent at 80° F

Fig 1 shows the yield of asphalt as a function of the molecular weight of the hydrocarbon solvent

For the sake of consistency in description it is desirable to classify as asphalt the non-waxy propane-insoluble product obtained under any given set of conditions. Generally, the asphalt obtained at ordinary temperature has the usual black appearance of ordinary asphalt, but in the case of stocks containing little or no high melting-point bitumen, the propane-precipitated material has the character of a brown, resinous material. This should, however, still be classified as asphalt, both for the sake of consistency and on account of the fact that this material is always a component of the propane-insoluble phase regardless of the proportion of high melting, black bitumen.

The ratio of propane to stock has a very marked effect on the efficiency of separation of asphalt and oil at a given temperature. Additions of small amounts of propane to the residuum up to a certain proportion serve only to reduce the viscosity in a manner analogous to the addition of any light solvent. Further addition of propane beyond a critical ratio for the particular stock in question causes separation into two phases, with the asphalt-bearing phase appearing as a heavy viscous liquid in comparison to the extremely light and fluid propane phase. The asphalt phase recovered at this point shows, after removing dissolved propane, a low melting-point due to the presence of oils, and the oil phase recovered may contain several per cent of asphalt. If the propane ratio is increased, the efficiency of the separation or fractionation is improved so that oil and asphalt are less and less contaminated with each other until eventually a point is reached where further additions of propane produce no further improvement in fractionation of oil and asphalt.

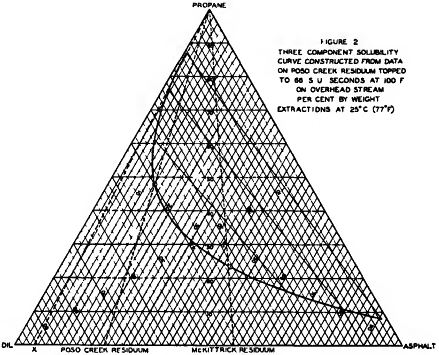

FIGURE 2
THREE COMPONENT SOLUBILITY CURVE CONSTRUCTED FROM DATA ON POSO CREEK RESIDUUM TOPPED TO 66 S U SECONDS AT 100 F ON OVERHEAD STREAM
PER CENT BY WEIGHT
EXTRACTIONS AT 25°C (77°F)

Considering a lubricating stock to be composed of propane-insoluble asphalt and lubricating oil which is soluble in propane, a three-component phase diagram for equilibrium conditions in propane deasphalting may be constructed for any one temperature from a series of experiments on a given stock with various propane ratios. Such a diagram will permit a prediction of the results to be obtained with any propane ratio at that temperature. While some variation occurs with different types of stock on account of variations in the nature of both the oil and asphalt, the diagram for a typical asphaltic stock is helpful in predicting, roughly at least, the results with any stock of known propane-insoluble asphalt content. Fig 2 shows the phase diagram obtained with the same residuum as that used for the experiments shown in Table I and Fig 1. Strictly speaking, this diagram is applicable only to stocks in which the oil component has the same solvent properties (as related to both viscosity-gravity constant and molecular weight), and the bitumen is also of essentially the same character as these respective components of the stock used in constructing the diagram. The solvent property of the oil is probably more important than the character of the bitumen, since the former influences to such a marked extent the solvent power of the propane phase, particularly at low-propane ratios, and as far as is known at present, there is not so great a variation in bitumens from different crudes of the low-sulphur type.

Temperature is equally as important as propane ratio in determining the results to be obtained in propane deasphalting on account of the fact that over the range of temperatures employed, propane is sufficiently close to its critical temperature to show marked variations in physical properties, such as density and solvent power, with changes in temperature. As the critical temperature is approached, the properties of the liquid begin to resemble more nearly those of a compressed gas, so that the solvent power of propane for heavy, high molecular weight hydrocarbons becomes less and less, until at the critical temperature of propane it is capable of carrying in solution only a few per cent by volume of the lower molecular weight components of an ordinary lubricating stock. At temperatures below about 110° to 120° F., propane behaves more like a normal liquid, since it is found that the decrease in solvent power with increase in temperature is insufficient to counteract the usual tendency of a solvent to dissolve more of a solute with increase in temperature, and the overall effect is to obtain more complete removal of asphaltic constituents at, say, −30° F than at room temperature. Above about 100° to 120 F., however, the sign of the temperature coefficient of solubility of high molecular weight hydrocarbons in liquid propane is apparently reversed.

In the high temperature region pressure has a marked influence on the solubility of oil in propane. As the pressure is increased at a given temperature the solubility increases. This effect is no doubt due to the fact that the increased density resulting from the high pressure changes the solvent characteristics of the propane so that they more nearly resemble those of the low temperature region.

The situation, however, is not quite as simple as indicated above, because the rejection of heavy hydrocarbons by propane at any given temperature is apparently based on both molecular weight and chemical composition For any given hydrocarbon series (designated hypothetically at least as consisting of compounds having the same viscosity-gravity constant), there is apparently a point of cutting or rejection in the molecular weight scale (analogous to a cut point in distillation) which is fixed by the temperature of extraction, but the exact position of the point of cutting on the molecular weight scale at a given temperature will be dependent upon the constitution, and hence viscosity-gravity constant, of the series The greater the paraffinicity (or lower the viscosity-gravity constant), the higher will be the molecular weight at the cutting-point for that series, and conversely the lower the degree of paraffinicity (or higher the viscosity-gravity constant), the lower will be the molecular weight corresponding to the point of rejection Recognizing an indicated point of cutting at some molecular weight value for each series of hydrocarbons present, it should be kept in mind that the efficiency of the fractionation, or the amount of overlap obtained, is dependent up to a certain point on the propane ratio

With this behaviour of propane in mind it is instructive to compare the action of propane with that of an ordinary selective solvent, such as aniline, phenol, or chlorex In performing extractions with selective solvents of the latter type, the object is to dissolve into the solvent layer the less paraffinic constituents having a high viscosity-gravity constant, and leave the more paraffinic materials undissolved as the raffinate On account of the fact that for any given series the higher the molecular weight, the higher the temperature required to obtain solution in the solvent, it follows that in simple solvent extraction with one of the usual selective solvents, efficiency of removal of the less paraffinic constituents at a given temperature is greatest in the lower molecular weight portions of the stock with the result that it is difficult to obtain complete removal of the undesirable constituents from the highest boiling fractions without undue loss of the low viscosity components of high paraffinicity Comparing this characteristic behaviour of ordinary selective solvents with the action of propane, it is apparent that at a fixed temperature propane shows a similar greater solvent power for the low molecular weight members than for the high molecular weight members of any series There are two striking dissimilarities between the behaviour of propane and an ordinary selective solvent which are very significant First, the temperature coefficient of solvent power for propane is reversed over the range 110 to 200° F, with propane exhibiting less solvent power as the temperature is increased, whereas with phenol for example, the solvent power increases with temperature Second, at a fixed temperature propane has less solvent power for the less paraffinic components whereas the reverse is true for a solvent like phenol These peculiar characteristics of propane make it a valuable adjunct in selective solvent refining as will be discussed in a later section

The effects of both propane ratio and temperature are shown in Figs 3 and 4 for a reduced California mixed base residuum and a vacuum overhead cylinder stock obtained from the same crude

In Table II are given similar data for a Mid-Continent residuum The unusual behaviour with propane is again evident, note, for example, that at the lower temperatures the yield of deasphalted oil decreases with increasing propane ratio while at higher temperatures the opposite holds true This behaviour is represented graphically in Figs 5 and 6 which give solubility diagrams for the isotherms at 136° F and 165° F The method of representation used is similar to the usual method of representation for three-component systems, except that properties of the propane-free material in the coexisting phases are used as dimensions of the base line rather than the usual percentage composition

Referring to Fig 5, as propane is added to the 298 viscosity residuum no separation occurs until the propane concentration is 66%, or a propane ratio of 1 94 The first tie line is shown at 71% propane, the two phases which separate at this point are represented at *C* and *D* It will be noted that the quantity of the heavier phase of composi-

TABLE II

Propane Deasphalting of Mid-Continent Residuum Viscosity 298 sec (S U) at 210° F

Temperature, ° F	103	106	102	102	135	136	138	136	151	157	157	161
Volume ratio, propane/ stock	2 3	4 0	5 7	10 1	2 4	2 3	4 0	11 5	2 3	2 3	3 0	2 3
Deasphalted oil												
Viscosity—sec (S U) at 210° F	233	182	168	153	215	232	153	139	238	192	139	166
Gravity, ° API	19 7	20 8	22 0	22 0	20 3	20 2	22 1	22 2	19 6	20 3	22 6	21 4
Viscosity-gravity constant	0 854	0 849	0 840	0 842	0 851	0 851	0 842	0 843	0 855	0 852	0 839	0 845
Carbon residue	4 38		2 85									
Volume % yield	93	86	84 2	81 6	88 5	93	76 4	78	93	47 5	47 2	26
Temperature, ° F	167	164	166	166	165	193	191	192	192			
Volume ratio, propane/ stock	2 4	3 0	4 0	5 7	11 5	2 4	5 7	11 5	11 5			
Deasphalted oil												
Viscosity—sec (S U) at 210° F	115	104	107	107	109	82	81	82	82			
Gravity, ° API	23 3	23 6	23 5	23 7	23 4	25 2	25 2	24 8	24 8			
Viscosity-gravity constant	0 838	0 836	0 835	0 835	0 837	0 830	0 830	0 832	0 832			
Carbon residue	2 4				1 9							
Volume % yield	12 2	25 1	37 7	51 5	59 6	6 3	25 5	34 4	39 4			

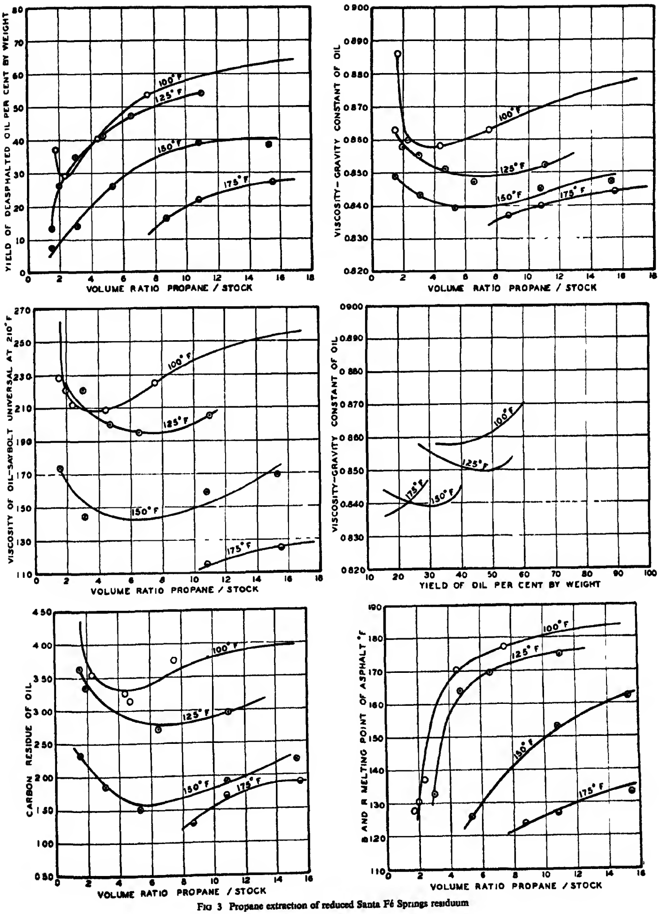

Fig 3 Propane extraction of reduced Santa Fé Springs residuum

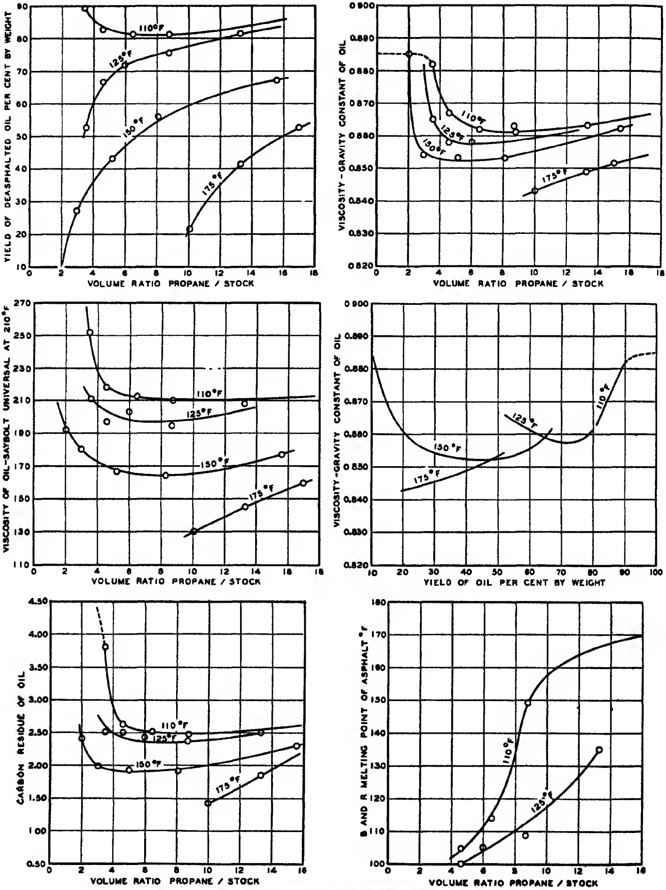

FIG 4 Propane extraction of S.A.E. 70 vacuum overhead distillate stock from Santa Fé Springs crude.

tion *D* (represented by the relative length of the line *BC* to that of *CD*) is very small The characteristics of the propane-free material in either phase are obtained by drawing a line through the *P* and tie-line extremity for that phase, the point of intersection of this line with the base gives the characteristics sought The relative amounts of propane-free material in the two phases are obtained by measurement of the relative distances of these intersections along the base line, from the point *A*

It will be noted that after separation begins the relative amount of the lighter, oil-bearing phase increases as the percentage of propane is increased Note also that the melting-point of the asphalt also increases and that the percentage of asphalt increases with increasing propane ratio

On the other hand, at 165° F, as shown in Fig 6, while the amount of the lighter phase increases with increasing propane ratio, the relative amount of propane-free material in the lighter phase also increases The difference between the two isotherms lies in the fact that at 136° F the plait point is on the right of the composition line (*AP*) while at 165° F it lies to the left of the composition line Such systems are indeed rare and the present example represents an interesting contribution to the physical chemistry of solubility

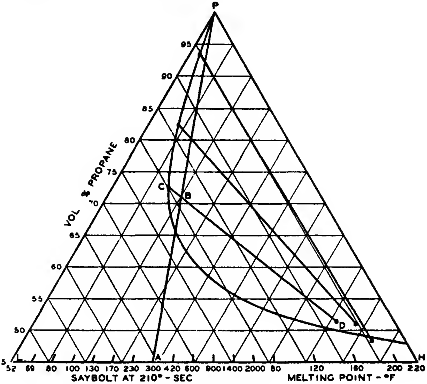

Fig 5 Isotherm at 136° F

The foregoing data and figures for propane deasphalting correspond to batch extraction or a single-stage continuous extraction In commercial practice, however, it is desirable to perform the extraction in two or more stages with countercurrent flow of asphalt and propane in order to reduce the propane required to give the desired degree of separation

An interesting development in continuous deasphalting is the use of temperature to fractionate the stock into a lower viscosity oil and two or more heavy, asphaltic fractions For instance, instead of deasphalting directly at 150° F, a primary deasphalting operation is carried out at 110° F with countercurrent washing of the asphalt to take into solution as much of the oily fractions as possible The propane phase is then heated to 150° F with the separation of a heavy, tarry, or resinous phase which is also washed with propane The secondary propane precipitated phase rejected at the higher temperature is predominantly naphthenic, and appears to be on the border line between asphalt and oil Fig 7 illustrates diagrammatically the flow of materials in such a deasphalting operation

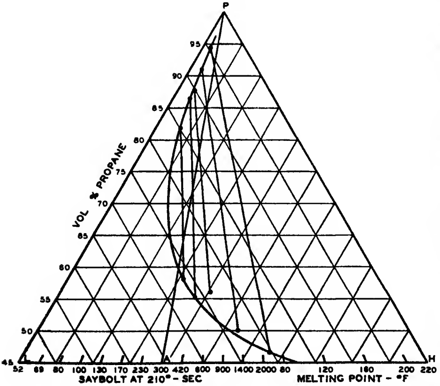

Fig 6 Isotherm at 165° F Mid-Continent residuum

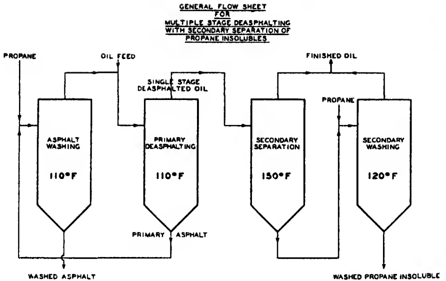

Fig 7

Dewaxing

The propane dewaxing process consists essentially in mixing the oil to be dewaxed, at atmospheric or slightly higher temperatures, with liquid propane under pressure, chilling the mixture by permitting part of the solvent to evaporate (with or without the addition of more solvent during the chilling), and filtering the chilled mix, with subsequent removal of the solvent and its recovery for re-use by evaporation and/or compression followed by condensation Part or all of the self-evaporation may be replaced by heat exchange with some cold liquid The separation of the wax can also be made by settling, but this procedure is so far not of commercial importance because of the ease of removal by filtration

Other low molecular weight hydrocarbons might be used, but of these ethane and ethylene have inconveniently low critical temperatures (90° F and 50° F respectively) and the solubility of oils in the liquids is limited The butanes and butylenes require, in general, rather low pressures if low temperatures are to be attained by their use as internal refrigerants, moreover, they are generally valuable as constituents of gasoline or as liquid fuel gas Propane (which includes propylene if the gases come from cracking operations) exhibits the most desirable combination of qualities and is the solvent in all existing and projected plants, butane might prove to be the best solution for particular cases A high degree of purity in the propane is not required for dewaxing, a few per cent of ethane and/or (say) 10% by weight of butanes will generally not appreciably affect the operation of a plant designed for pure propane Little is known of the relative advantages of pure propane and propane containing propylene but it appears that there is little difference in their suitability for dewaxing operations

Propane has two distinct functions in the dewaxing process here considered—it is at one and the same time the solvent which reduces the viscosity, and the medium employed in the refrigerating cycle Considered as the solvent in the dewaxing operation propane is characterized by an outstandingly low viscosity and an unexpectedly low solvent power for wax

Fig. 8 shows the viscosity of solutions of varying concentrations of a few typical oils in pure propane at −40°. The enormous reduction in viscosity produced by the addition of relatively small proportions of propane is very striking Similar solutions of higher-boiling solvents do not approach these values—as indicated in the figure This low viscosity, other things being equal, makes for high filter rates even at low temperatures, or permits the more economical use of low solvent ratios for the same filter rate

It is interesting to point out that from the standpoint of dewaxed oil production there is a certain dilution beyond which the effect of decreased viscosity does not compensate for the increased volume to be filtered Fig 9 shows the relative rates of viscous oil filtration for various dilutions, on the supposition (which is, of course, never exactly realized) that the wax is exactly the same in amount and character regardless of the dilution

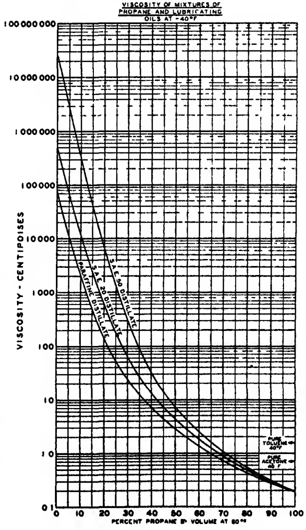

Fig 8.

and that the rate of filtration is inversely proportional to the viscosity of the mother liquor In the ordinary range of dilutions (from 35 to 75 vol per cent propane) increased dilution is accompanied by increased viscous oil production for a given filtering time An economic balance will generally result in the choice of a ratio giving less than the maximum rate

Previous data had indicated that the solubility of wax in petroleum cuts, on a weight or volume basis, increased as the molecular weight of the cut decreased This was in accordance with theory, since it can be shown that the solubility of a wax in a solvent for which the solution obeys Raoult's law (which can usually be assumed to hold for petroleum fractions) would be the same for equal *molal* quantities of the various solvents This rule breaks down, however, for the very light solvents, as is shown by Fig 10, which gives the solubility of a 122° F melting-point wax in solvents of varying molecular weight It will be seen that the solubility in propane is much less than might have been expected

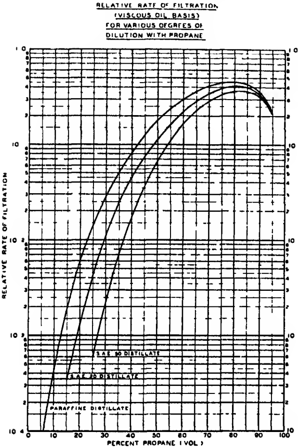

Fig 9

Considered from a refrigeration point of view, the process is of the compression type employing propane as the refrigerating medium, since the propane which is evaporated during the chilling is recompressed Propane in itself is essentially as efficient a refrigerating medium as ammonia Fig. 11 shows the theoretical adiabatic horse-power for 1 ton of refrigeration, using ammonia or propane, with 90° F. condenser temperature and various temperatures of the refrigerating medium There is a slight advantage for ammonia when the same suction temperatures are compared However, (1) ammonia must do its cooling indirectly, and therefore its temperature must be lower than that of the solution to be chilled, whereas the propane used as refrigerant is always at the same temperature as the solution to be chilled, (2) if the minimum temperature difference between ammonia and solution is to be maintained, a very complicated step system of evaporating and recompressing the ammonia is required, whereas in the case of propane this is taken care of automatically, (3) in the case of propane no expensive heat exchange surface is required

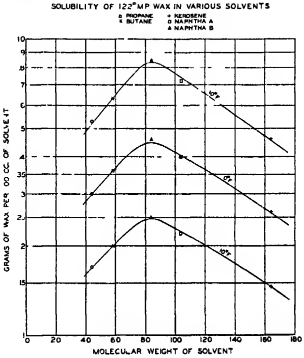

Fig 10

Since propane is undesirable as a constituent of gasoline, and has as a rule no other than a fuel value, it is often the cheapest liquid available in a refinery except water It is available in almost every modern refinery, and the supply is not dependent on conditions outside the petroleum industry

Propane is relatively non-toxic Because of its volatility propane can be readily removed from the solution without heating the oil to injuriously high temperatures The wax slurry produced in the process can be readily pumped The fact that other processes of lubricating oil refining utilize propane often makes possible attractive combinations of these processes with dewaxing in propane The necessity for handling a volatile inflammable liquid under pressures of the order of 200 lb per sq in is, of course, no more than is done as a routine matter in other processes of the petroleum industry At the low temperatures involved ordinary steel becomes relatively brittle, so that safest practice requires the use of some special material of construction for such parts as are to be chilled Existing plants are of 2½% nickel steel, but cheaper steels are now available, and are being used in a plant now under construction Of course, other chilling processes using temperatures below 0° F also require special materials for maximum safety

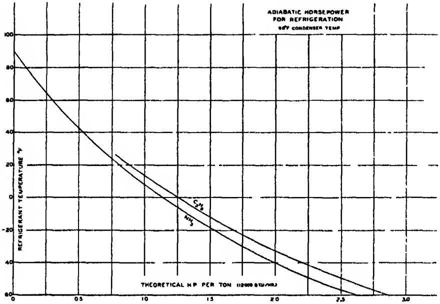

FIG 11

Fig 12 gives a simplified flow diagram of a large recently constructed plant using continuous filters, and embodying also a two-stage deasphalting unit The plant is designed to handle about 135,000 U S gallons of mid-Continent long residuum per day Residuum is mixed first with the main portion of clean propane and with the small fraction of propane which has been used in the second stage The mixture enters the horizontal settler *A* whence the clean oil-propane layer is drawn off to be dewaxed, while the asphalt is mixed with a small portion of clean propane from *F* and resettled in the second settler *B*, whence the washed asphalt is drawn off to the heater *C* and flash drum *D*, the propane vapours going to the condenser *E* and thence back to storage

The deasphalted oil enters the chillers *G* in rotation When enough mix has entered a given chiller, the stream is diverted to another, and chilling is conducted by venting the chiller to the suction of the compressor *N* To maintain the concentration of the mix, propane which has been chilled by heat exchange with the filtrate in exchanger *I* is added during the chilling

When a batch in one of the chillers has reached about −45° F it is ready to pump to the filters *H*, of which there are actually six These filters are of the drum type especially designed for this work They are enclosed in a tight shell which also serves as a filter bowl The operations of filtering, washing, and removing the cake from the drum with blow-back and a scraper are conducted exactly as in ordinary filters of this type The differential pressure required for filtration, however, is produced by introducing propane gas into the shell, and not as in the usual type by applying a vacuum to the receiver The cake is removed by a screw conveyor and pumped through heater *K* to flash drum *L*, the propane returning to storage through *E* and the wax being drawn off (with further stripping if necessary)

The dewaxed oil is solvent extracted in the presence of propane

Other existing propane dewaxing plants differ from the one just described mainly in the filters These are operated batchwise, and consist of pressure vessels containing a number of vertical filter leaves The mix is pumped in to fill the shell, and filtrate then passes through the canvas into the space between the leaves and thence to a receiver After about 40 minutes a sufficient cake is built up, the mix is drained from the shell, and the cake is discharged by blowing back and is pumped to the wax still

The rate of filtration and character of the cake produced in these plants is affected by numerous factors As has already been indicated, more dilute solutions at the time of filtration lead to a greater throughput, based on dewaxed oil produced Economical operation, however, requires that the propane concentration be kept as low as possible From the standpoint of operating costs the optimum ratio of propane to oil in the cold mix appears to lie, in the case of motor-oil distillates, in the vicinity of 2 to 1, by volume (measured at 60° F) For lighter oils such as paraffin distillate the most economical ratio of propane to oil will be lower—between 0 5 and 1 0 to 1 However, if yields of dewaxed oil are of predominating importance higher propane ratios may be justified

Small-scale experiments indicate that slightly better results can be obtained when the whole of the propane required for the chilling is added to the warm mix so that the initial warm mix is considerably more dilute than the mix as filtered However, important heat economies can

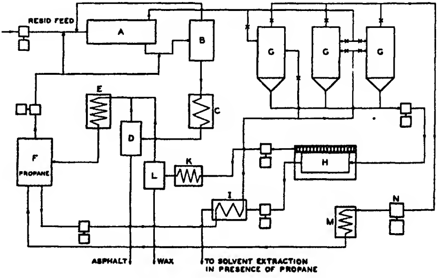

FIG 12

be effected by adding the chilling propane during the chilling operation, and precooling the propane added during chilling by heat exchange with the cold filtrate This economic consideration is much more important than the minor change in rate, because of dilution during mixing and is, therefore, the preferred method of operation

With some stocks (for example, deasphalted residuum) it appears to be important to start with an oil-propane solution in which there are no wax crystals If this is not done, very erratic results are obtained, possibly because the crystals formed in the oil before dilution with propane are not of a type suitable for filtration In the case of distillates this condition does not seem to be so important The temperature to which the mix must be heated varies greatly with the stock to be dewaxed—at least from 70° F for paraffin distillate to 130° F for certain stocks containing unusually high-melting wax

So long as the operation is conducted batchwise by self-evaporation, the rate of chilling appears to have little effect on the filterability of the mix Commercial plants employ chilling rates of about three degrees per minute Chilling at twelve degrees per minute has been tried experimentally and found to produce results which are as satisfactory as much lower rates

The temperature of filtration will generally be determined by the pour-point desired on the dewaxed oil Generally speaking, with the lighter motor oils a differential of 25 to 30° F may be expected between filtration temperature and pour-point of oil produced The heavier oils may show a larger differential, because the viscosity of the oil at the low temperatures affects the pour-point, even an entirely wax-free oil will become solid by the standard test when a sufficiently low temperature has been reached Hence it is not uncommon to observe a fall in pour-point when propane dewaxed oils are subsequently solvent extracted

With paraffin distillate, a smaller differential, amounting to a difference of only 15 to 25° F between temperature of filtration and pour-point, can be obtained, because the percentage of diluent can be smaller

The cost of dewaxing, of course, increases as the temperature of filtration goes down, so that it is desirable to employ as high a temperature as possible There is no limitation on the batch or continuous filtration process that would prevent filtering at 0° F or higher

On the batch leaf-type filters, the pressure differential at the start of the filtration is about 10–15 lb , this is increased gradually to about 50 lb as the cake builds up If the full 50 lb pressure were put on at the start, the filtrate would be cloudy

On the continuous drum-type filter much lower differentials are employed—2 to 6 lb being typical There are several reasons for this The full pressure is applied from the start of the filtration, hence low pressures should be used Also experience on pilot-plant apparatus indicates that an increase in pressure is not accompanied by a corresponding increase in throughput—apparently the throughput is proportional to something like the fourth root of the pressure Further, a high-pressure differential would result in the condensation of a large amount of propane into the chilled mix being filtered, which would cause an objectionable warming of the mix In spite of the low pressure, the cycle times with the continuous drum-type filter are so short that the capacity per square foot of filtering surface is considerably greater than that of leaf-type batch filters

The general behaviour of the various classes of stocks on propane dewaxing may be described as follows

Deasphalted or moderately acid-treated residual stocks are characterized by high filter rates and compact cakes of high wax content—typically about 30 to 40% oil without washing Filter rates on a small continuous drum-type filter, operating at 25% submergence and 3 lb per sq in differential on a solution of two volumes of propane to one of oil at −45° F , are from 2 to 6 U S gal of viscous oil per sq ft per hour With this type of stock, however, mixing and chilling conditions must be controlled more closely than for distillates in order to produce uniform rates of filtering When this is done, the cake produced at the rates noted above is sufficiently thick to discharge readily without plugging of the filter cloth In the batch-type filter under the same conditions, and using a 40-min filtering period with 50 lb pressure differential at the end of the period, the rates are from 2 to 5 gal of viscous oil per sq ft per hour

Heavy motor-oil distillates (such as are intended for S A E 50 or 60 oils) show slightly lower filter rates than residual stocks (at the same propane concentration) and give cakes having (say) 50% wax without washing On Mid-Continent stocks this means a yield of from 80 to 85% of dewaxed oil—somewhat higher yields can be obtained by washing However, the cakes are easy to discharge from the continuous filter drum

Light motor-oil distillates intended for S A E 10 or 20 oil give still lower filter rates and they yield cakes containing typically 65 to 75% of oil before washing However, the rates and wax contents can be greatly increased by the addition of very small amounts of modifying agents such as those which produce a depression of the pour-point in light lubricating oils A great variety of such agents are effective—not only Paraflow and similar synthetic products, but also various crude or cracked tar residuums or products remaining when such residuums are extracted with light solvents Besides, the addition of a few per cent of an S A E 50 or heavier distillate to an S A E 20 distillate will aid the filtration and the addition of waxes from residual stocks is even more effective As might be expected from these results, the degree of fractionation employed in the preparation of the distillate will affect its filterability—better fractionation leading to more difficult filtration

Results with S A E 30 and 40 distillates are intermediate between those obtained with the light and the heavy motor oils

With propane as a diluent, without the presence of a wax-crystallization modifier, the filter rate on paraffin distillate is materially better than is obtained in conventional cold-pressing operations, but is less than for the heavier motor-oil stocks However, the response to the modifying agents referred to above is very marked With 0 1% of a synthetic pour-point depressor, the oil content of the slack wax can be reduced to 20 to 45% by volume, depending on the propane ratio, and the filter rate made to approximate that obtained with heavier motor oils Experiments indicate that the inhibitor is recovered in the drips from the sweating of the slack wax, and can be recycled by returning the drips directly to the stock tank or by distilling the drips to concentrate the inhibitor in a small amount of bottoms, and then admixing these bottoms with the stock before dewaxing

On the continuous filter, paraffin distillate forms a very desirable type of cake which is hard and easily discharged This stock also seems to be relatively insensitive to chilling conditions

Treatment in the Presence of Propane

The uses of propane as an aid in treating embrace acid treating, clay percolation, and selective solvent treating of the stock in propane solution

Acid Treatment.

Acid treatment in propane solution gives a marked improvement over the results obtained by treating the stock with acid or while the stock is dissolved in a heavier solvent, such as naphtha One of the advantages is that any stock, regardless of source or previous history, can apparently be acid treated successfully if the stock is dissolved in three or more volumes of propane Sludge separation is quick and positive, and, in fact, the agglomeration and settling of the acid sludge is often so rapid as to necessitate caution to make certain that efficient contact between acid and oil is obtained Because of the inherent tendency of propane to reject the coloured, asphaltic, low-gravity components, better reductions in colour, carbon residue, and viscosity-gravity constant for the same amount of acid are obtained when the treatment is conducted in the presence of propane On account of freedom from emulsification and occlusion of good oil in sludge or alkali washes, as well as the selective action of propane, the yields of treated oil are higher than for direct treatment to the same gravity

There is a marked similarity between acid treating in propane solution and solvent treating in propane solution In fact, it appears that when the acid is employed in the presence of propane, the action of the acid is more like that of a solvent than when the acid is applied to the stock directly While acid treating in the presence of propane was first developed with mixed base residua which had been propane deasphalted, this method of treating has been found to be very effective on Pennsylvania oils and on solvent raffinates, both of which are known to be extremely difficult to acid treat on account of failure of the sludge to gather and settle In fact, acid treating in the presence of propane has been found to be one of the most effective methods of improving the carbon residue of Pennsylvania residual oils, while producing specification colours without the use of clay Improvements in other properties, such as gravity, viscosity index, oxidation resistance, and a decrease in viscosity, are also obtained

In nearly all cases the sludge separates so completely from the propane solution that the latter contains no inorganic acidity, as shown by the propane solution being neutral to methyl orange However, if the stock is one which requires caustic treatment to remove organic acidity, emulsification difficulties are practically absent when the neutralization is performed in the presence of propane

Table III shows typical data for the acid treatment of a deasphalted California long residuum, a Mid-Continent cylinder stock, and a Pennsylvania cylinder stock

TABLE III

Acid Treatment of Residual Stocks, with and without Propane Present

Crude	Sample	Vol % of propane	Acid treated		Yld vol %	Flash and fire ° F	Pour-pt ° F	Car res %	Colour N P A	Grav ° API at 60° F	Viscosity Say Univ sec at		Visc gravity constant	Vis index
			Strength of acid	lb per bbl							100° F	210° F		
Kettleman Hills long residuum	Deasphalted dewaxed				100	450/525	0	2 35	green	18 3	2 350	107	0 878	44
	Neutral oil	none	98	15	72 1	450/525	0	2 17	opaque	19 8	2,130	102	0 866	42
	„	300	98	15	82 0	450/525	5	1 28	7½	20 8	1,665	92 5	0 861	47
Pennsylvania S R	Deasphalted dewaxed				100	610/675	0	1 70	green	25 4	2 380	153	0 816	101
	„	none	Sludge failed to separate											
	„	300	103	15	91 2	610/675	0	1 09	7	26 8	2,025	144	0 807	106
									*		130° F			
Mid-Continent residuum	Raw stock	none			100	530/605	70	7 9	12,000	18 1	4,400	352	0 861	53
		none†	93	63	57	530/605	80	3 2	800	21 9	1 320	176	0 840	78
		350	93	18 5	72	525,600	80	2 4	500	22 4	1 160	162	0 838	80

* True colour (ROGERS, GRIMM, and LEMMON, *Ind Eng Chem* 18, 164 (1926))

† Will not separate by gravity, separated in centrifuge

Clay Treatment.

Clay treatment by percolation is more efficient when the stock is dissolved in propane than when dissolved in naphtha The yield of oil of specification colour per ton of clay is noticeably greater and percolation rates are very high when propane is used After acid treatment in the presence of propane, the propane solution decanted from the sludge is conveniently percolated through fuller's earth at 80° to 130° F to safeguard against possibility of acid entrainment, to obtain further reduction in colour, and to correct acidity Under these conditions the yield of treated oil per ton of clay is very large

Solvent Extraction in the Presence of Propane.

One of the properties of propane is its complementary action in treating a stock with ordinary selective solvents Through the use of propane, solvent extraction of residual stocks to give oils of lower carbon residue is greatly facilitated, although the advantages of solvent treating in combination with propane are not limited to residual oils

It will be recalled that, in the above discussion of the role of propane in asphalt separation, it was pointed out that both propane and selective solvents have a greater solvent power for the lower than the higher molecular weight members of any given hydrocarbon series, but that while the reagents commonly called selective solvents have a greater solvent power for the aromatics and naphthenes than for the paraffins of a given molecular weight, propane has greater solvent power for the paraffins Thus both propane and selective solvents compete for the low molecular weight members, but on account of the difference in preference as regards type or structure, the propane phase retains most of the low molecular weight compounds of a paraffinic nature, while the selective solvent acquires only the low-gravity components in the low molecular weight range Without propane being present, an appreciable proportion of low molecular weight compounds of a paraffinic nature would be lost to the solvent phase

Considering next the behaviour of the propane selective solvent combination in comparison to the action of a selective solvent alone in the high molecular weight range of the stock, it is apparent that neither propane nor the selective solvent has a high-solvent power for the highest molecular weight fractions However, the relative incompatibility of propane and the high molecular weight aromatics and naphthenes operates to make it possible for the highest boiling low-grade components to be efficiently extracted from the stock by the selective solvent when applied in the presence of propane The removal of the highest molecular weight naphthenic compounds is difficult to accomplish on a wide boiling-range oil without excessive loss of light components with a selective solvent operating alone So great, in fact, is the rejecting effect of propane on the highest molecular weight components of residual stocks that even a large portion of the highest boiling paraffinic components may be removed into the selective solvent phase when certain very active selective solvents, such as nitrobenzene, chloroanilines, phenol, and the cresols are used in conjunction with propane

It is apparent from the foregoing that on account of the solvent properties of propane, the lower boiling paraffinic components of the lubricating stock are conserved more efficiently, and the highest boiling components, regardless of paraffinicity, are eliminated from the raffinate The result is that the yield of raffinate of a specified viscosity-gravity constant is exceptionally good, the viscosity is lower than when the selective solvent is used alone, and the carbon residue is very materially improved over that obtained by simple solvent extraction to the same viscosity-gravity constant The data in Table IV show the course of the results obtained in multiple-batch extractions on the same stock, with and without the presence of propane It will be noted that the extracts obtained in the presence of propane are lower in A P I gravity and more viscous than those obtained without propane being present If one wishes to do so, an instructive set of graphs is obtained by plotting the properties of the various extracts and raffinates against the volume per cent stock or raffinate remaining after each batch extraction

TABLE IV

Multiple Batch Extractions of Propane Deasphalted and Dewaxed Kettleman Hills Long Residuum, using Nitrobenzene, with and without Propane being Present during the Extractions

Sample	*Temp of extraction °F*	$C_6H_5NO_2$ *vol %**	*Yld vol %**	*Grav °API at 60 F*	*Car res %*	*Colour N P A*	*Viscosity Say Univ sec at 100° F*	*210° F*	*Visc index*	*Visc-gravity constant*
Stock			100	18 6	2 08	opaque	2,030	97		0 876
Extraction without propane being present										
Extract no 1	37	100	42 4	14 1		opaque		162		0 906
„ no 2	37	100	22 7	15 7		„		141		0 895
„ no 3	38	100	11 0	20 9		„		91 0		0 861
Raffinate A after 3rd extraction		300	23 3	27 4	0 38	nearly opaque	770	75 5	92	0 815
Extract no 4	38	100	5 9	23 9	0 86		980	79 0	76	0 840
„ no 5	68	100	6 9	25 3	1 19		775	75 0	89	0 831
Raffinate B after 5th extraction		500	10 4	28 4	0 21		820	82 0	101	0 806
Extraction with 300 volume per cent * propane present										
Extract no 1	37	100	23 9	8 8	6 28			422		0 942
„ no 2	37	100	15 0	12 2	3 69			211		0 920
„ no 3	37	100	7 7	14 3	2 53			174		0 904
Raffinate A after 3rd extraction		300	51 8	26 0	0 21	nearly opaque	662	68 5	83	0 828
Extract no 4	65	100	7 9	19 2	1 34	opaque		110		0 871
„ no 5	68	100	7 1	21 5	0 92	„	2,000	95	32	0 858
„ no 6	72	100	7 2	23 9	0 45	„	940	74	62	0 842
Raffinate B after 6th extraction		600	29 4	29 3	0 11			62	102	0 806

* Volume percentage based on volume of dewaxed stock at beginning of experiment

To illustrate the effect of propane on miscibility temperatures, data from a phase study of oil-solvent-propane systems are shown in Table V On the general principle that solvent selectivity is better the farther the treating temperature is from the miscibility temperature, the data for phenol-propane shown in Table III indicate the desirability of using 400 or more volume per cent propane It is obvious that the propane to oil ratio is higher at the raffinate end of the treating system than at the feed or extract end

In performing selective solvent extraction in the presence of propane, many combinations of solvents and methods of operation are possible For instance, the stock may be treated with propane to effect deasphalting as a separate step, and the deasphalted oil treated with the selective solvents in a counter-current treater while still dissolved in propane, or the stock, with or without premixing with propane, may be injected at an intermediate point into the solvent-treating system while part or all of the propane is injected at one end, and the selective solvent at the other end The former method produces asphalt as one product and the aromatic-naphthenic factions of the oil as another product, while the latter method combines both asphalt

Table V

Miscibility Temperatures of Oil-Phenol-Propane

Systems Propane deasphalted Kettleman Hills long residuum, and propane-phenol raffinate therefrom

Volume ratios Oil-Phenol-Propane	*Miscibility Temperatures ° F* New stock*	Raffinate†
1-1 0	157 0	233 0
1-1-1	104 0	179 5
1 1-2	117 5	158 5
1-1-3	138 5	161 75
1-1-4	164 4	>181 0
1-1-5	> 182 0	>185 0
1-2-0	175 5	238 0
1-2-1	125 75	185 0
1-2-2	120 25	>185 0
1-2-3	141 0	>185 0
1-2-4	174 0	>185 0
1-2-5	>182 0	>185 0
1-3-0	185 5	241 0
1-3-1	137 0	185 0
1-3-2	132 75	185 0
1-3-3	158 5	>185 0
1-3-4	185 0	185 0

* Propane deasphalted, but undewaxed Kettleman Hills long residuum Gravity, ° API at 60° F 19 5, Flash, COC, ° F, 440, Viscosity, Say Univ sec at 210° F, 103 v g c 0 870

† Propane-phenol raffinate produced from (*a*) Gravity, ° API at 60° F, 29 4, Viscosity, Say Univ sec at 210° F, 68, v g c, 0 803, Carbon residue, 0 15

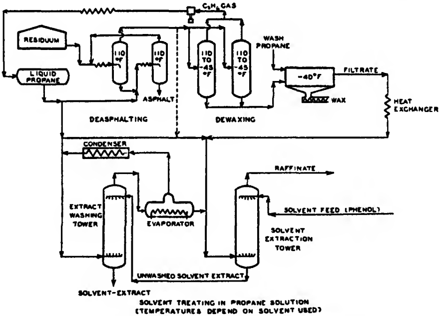

Fig 13 Deasphalting-dewaxing-solvent treating in propane solution

and aromatic-naphthenic oils into one extract product which is dissolved in the selective solvent This latter variation of the propane-solvent method of treating when all of the propane is introduced at one end of the system, is commonly known as the Duo-Sol method of treatment, but on account of limitations is not as flexible in scope as the more general design which is also capable of producing asphalt as a separate product The yields and the characteristics of the high-quality oil can be made essentially the same for either of the methods of operation, indicating that the results are the inherent consequences of the principles discussed above and not due primarily to a particular variation in the flow of the streams in the treating system

Fig 13 represents diagrammatically the operation of a lubricating oil plant employing propane for deasphalting, dewaxing, and solvent treating Either deasphalting or dewaxing, or both, can be omitted before sending the stock to the propane solvent-treating system Also, the use of propane for washing the extract phase may be omitted if this additional expense cannot be justified on the basis of economics However, the entire operations shown in Fig 13 permit the refiner to produce oils of excellent qualities and represent efficient utilization of propane in each of the major refining steps

Commercial Plants

In June 1936 there were in operation in the United States seven plants using liquid propane as a refining agent These plants, in all, embody countercurrent deasphalting, dewaxing, and treating in the presence of propane Of the most recently constructed plants, one employs countercurrent deasphalting and dewaxing by means of continuous filtration, followed by solvent treating in the presence of propane Another plant embodies deasphalting and acid treating in the presence of propane The first commercial plant was constructed in 1931-2 at the Wood River Refinery of the Standard Oil Company (Indiana) The remaining plants are located in the refineries of the Union Oil Company of California, Standard Oil Company (Indiana), Socony-Vacuum Company, Gulf Company, and the Shell Petroleum Corporation Another plant is under construction for the Kendall Refining Company.

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PRINCIPLES OF DEWAXING

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DURING the last five years the principles of solvent extraction have been investigated extensively [3, 1934, 4, 1934, 6, 1936, 7, 1936] These investigations have led, among other things, to a graphical method of representing equilibrium data for complex oil-solvent systems [5, 1935, 7, 1936] Computation methods based on such equilibrium diagrams have also been presented and are now in use by many workers [14, 1936] These principles and methods are by no means confined to solvent-extraction problems and processes, however, and may be applied with success to other physical refining processes

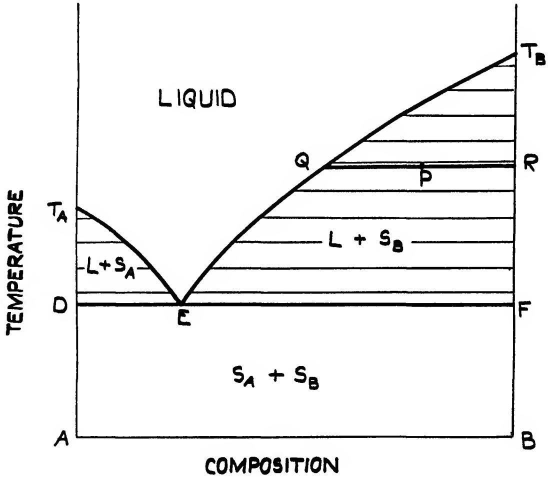

FIG 1

The equilibria involved in dewaxing operations are equilibria between a solid phase or solid phases, paraffin wax, and a complex liquid mixture of hydrocarbons, oil, together with a second liquid, solvent or diluent Before considering equilibria in such a system, the simplest system involving a single solid component and two liquid components will be described

Equilibrium in a Simple Three-component Solid-liquid System

A system consisting of three components *A*, *B*, and *C* may be regarded as a combination of the three binary systems *AB*, *BC*, and *CA* Fig 1 represents the equilibrium data for the separation of solid from the binary system *AB*, where temperature is plotted against composition. T_A and T_B are the melting-points of the two pure components *A* and *B* It will be seen from this diagram that the addition of a small amount of one component to the pure melt of the other component lowers the temperature of equilibrium between solid and liquid Curve T_AE represents liquid mixtures of *A* and *B*, of steadily increasing concentration in *B*, which are in equilibrium with solid *A* Similarly, curve T_BE represents liquid mixtures of steadily increasing concentration in *A* which are in equilibrium with solid *B* Any mixture of components corresponding to a point such as P will resolve itself into pure solid B (point R) and a liquid mixture of A and B represented by point Q on $T_B E$. The horizontal straight line QPR is a tie-line indicating equilibrium between pure solid B and the liquid mixture of A and B of composition Q.

At point E identity of composition is reached in the two liquid mixtures so that at this point, called the eutectic-point, solid A and solid B must exist in equilibrium with a single solution of composition E. The horizontal line DEF is the lower boundary of the liquid-solid areas $T_A DE$ and $T_B FE$, and below it only solid can exist.

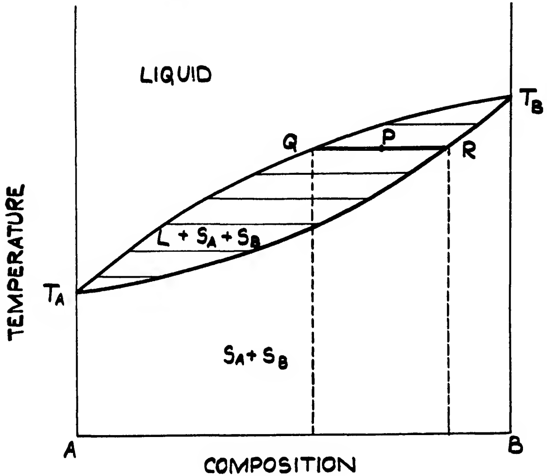

FIG 2

Another type of equilibrium between A and B is shown in Fig 2. In this case the addition of B to the melt of pure A raises the temperature of equilibrium between solid and liquid.

Further, a liquid mixture of A and B is in equilibrium with a single solid phase which is a solid solution of A and B. The composition represented by a point P now separates into liquid of composition Q and a single solid phase of composition R. The curves $T_A Q T_B$ and $T_A R T_B$ are the freezing-point and melting-point curves respectively for the system AB.

Each of the three binary mixtures AB, BC, and CA making up the ternary system ABC may be one or other of the two equilibrium types described above. The three binary equilibrium systems may then be attached to the sides of an equilateral triangle as in Fig 3 and the equilibrium of the ternary system at any given temperature represented within the triangle ABC.

By folding along AB, BC, and CA in Fig 3 a solid prismatic figure would be obtained with ABC remaining in the horizontal plane and the temperature axes situated vertically above A, B, and C. The equilibrium at any temperature for the ternary system would then be represented by a surface within the prism.

In Fig 4 equilibrium in the ternary system ABC is represented in the triangle ABC at temperature T_1. Attached to the two sides AB and CB of the triangle are representations of equilibrium in the two binary systems AB and CB. These two binary systems are of the type shown in Fig 1, but the temperature range has been restricted to such limits that only component B appears in the solid phase. On the side CB of the triangle point E represents the composition of the liquid phase (a mixture of B and C) in equilibrium with solid B at temperature T_1. Similarly, point D on the side AB represents the composition of the liquid phase (a mixture of A and B) in equilibrium with solid B. Point F represents the composition of a liquid phase, which is a mixture of A, B, and C in equilibrium with solid B. The lines BD, BF, and BE are tie-lines. Any mixture of A, B, and C at temperature T_1 whose composition can be represented by a point within the area $BDFE$ must exist as two phases, a solid phase B in equilibrium with a liquid phase which has a composition represented by a point on the

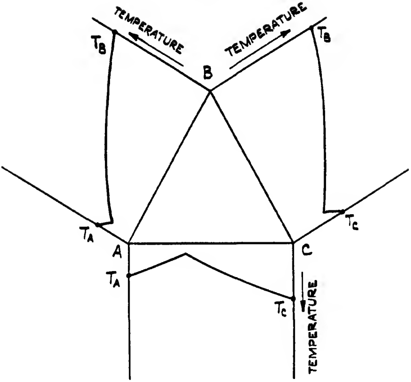
TEMPERATURE
TEMPERATURE
T_B
T_B
B
T_A
A
C
T_C
T_A
T_C
TEMPERATURE

Fig 3

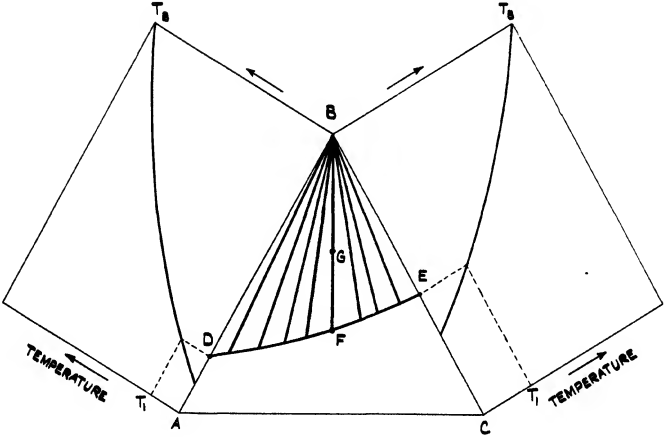
T_B
T_B
B
G
E
D
F
TEMPERATURE
T_1
A
C
T_1
TEMPERATURE

Fig 4

curve *DFE* For example, a mixture of composition *G* at temperature T_1 will exist as a solid-liquid system consisting of solid *B* in equilibrium with a liquid of composition *F* The ratio of solid phase *B* to liquid phase of composition *F* will be the ratio of the length *GF* to the length *GB* All mixtures whose compositions can be represented by a point within the area *ADFEC* will exist at temperature T_1 as a single liquid phase The equilibrium in the ternary system *ABC* at temperature T_1, where one component, *B*, is a solid and two components, *A* and *C*, are liquids, is represented by the equilibrium or solubility curve *DFE* and the tie-lines on the triangular diagram Since all the tie-lines pass through an apex of the triangle they are usually omitted on the triangular equilibrium diagram

Oil-wax-solvent Equilibria

An approximate representation of equilibrium in an oil-wax-solvent system may be obtained by assuming the oil and the wax each to be a single pure component Since oil and wax are complicated liquid and solid solutions of hydrocarbons, this assumption introduces certain quantitative inaccuracies into any equilibrium representation based upon it Exact quantitative representation of equilibrium in an oil-wax-solvent system can be obtained by the use of solid geometrical figures Such methods are, however, rather complicated, and clumsy in use The employment of graphical representation on a single plane made available by the above assumption has many advantages which more than offset any slight loss of accuracy, and the actual quantitative error involved is small and of little importance in technical calculations and interpretations

A necessary condition of the dewaxing process is that the diluent or solvent and the oil be completely miscible and liquid at the operating temperature The lowest temperature to be considered, therefore, must be higher than both the freezing-point of the oil and the freezing-point of the solvent These temperature considerations restrict the ternary equilibrium isotherm to the simpler case already discussed and illustrated in Fig 4 The three components *A*, *B*, and *C* of this figure may now be replaced by the three components, oil, wax, and solvent or diluent The resulting equilibrium diagram for this system is shown in Fig. 5 Since the oil-solvent mixtures are totally liquid over the temperature range in question, there is no solid-liquid equilibrium curve attached to the oil-solvent composition side of the triangle Only these portions of the oil-wax and solvent-wax equilibrium curves embracing the cooling range of temperatures are required, and these portions are, again, above the freezing-points of pure oil and pure solvent, and hence also above the eutectic points of the oil-wax and solvent-wax mixtures, if such exist The rectangular coordinate portions of Fig 5, therefore, show the solubility curves of wax in pure oil and pure solvent over the required temperature range From these two curves the terminal points of the equilibrium curves on the ternary diagram are obtained Intermediate points in the triangle can be obtained from the solubility curves of wax in different oil-solvent mixtures In the case, for example, of a 1 1 solvent-oil mixture the rectangular coordinate graph containing the solubility curve of wax in this mixture would be attached to the line joining the apex representing pure wax to the mid-point of the oil-solvent composition line In this way the isothermal equilibrium line at any required temperature may be constructed Two isothermal lines are shown in Fig 5 at temperatures T_1 and T_2

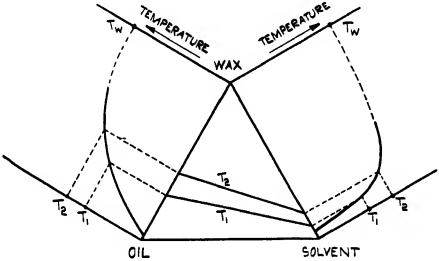

Fig 5

Fig 6 is a representation of equilibrium data for an oil-wax-solvent system giving the temperature variable This takes the form of a solid prismatic figure with the temperature variable along the vertical axis The shaded portion of the prism represents the solid-liquid region of the system, and the unshaded portion the completely liquid region Projection of the solid surface at any temperature plane on to the triangular base produces the isothermal solubility curve on the triangular diagram Fig 6 is a reproduction of actual equilibrium data for the system lubricating oil–paraffin wax–light naphtha over the temperature range 40–60° F

Fig 7 shows the complete representation of an oil-wax-solvent system On to the ternary diagram, in which is drawn the equilibrium curve *XY* for the system at a given temperature *t*° F, are attached rectangular coordinates, linked to the oil-wax composition line of the triangle The oil-wax composition side of the triangle is also the abscissa of the rectangular coordinates, of which the ordinate represents temperature The two scales of the attached rectangular co-ordinates are therefore oil-wax composition and temperature On these scales are plotted the pour-point of varying oil-wax mixtures, shown in Fig 7 as the oil-wax pour-point curve, and also the melting-point of varying oil-wax mixtures, shown in the figure as the oil-wax melting-point curve In this particular form the diagram is most useful for dewaxing calculations

As mentioned above, this method of representation is not completely quantitative Over the temperature range used in dewaxing only two phases exist, liquid and solid Under these conditions the liquid phase must vary between wax-free oil+solvent and wax+oil+solvent Therefore, as long as temperature conditions are such that only one liquid phase is present, the oil may be treated as if it were a single pure component, since the total oil present in the system will always be in the liquid phase The original assumption then introduces no error in this connexion Over the specified temperature range, the solid phase will be wax varying in amount with varying temperature and solvent conditions The total wax present in the system will thus be divided between the two phases, with varying amounts in the solid phase and in the liquid phase, depending on conditions Since wax is a complex solid solution or solid mixture of hydrocarbons, the composition of the solid wax phase and the composition of the wax dissolved in the liquid phase must vary with varying conditions This variation in composition of the wax could be represented quantitatively by some characteristic physical property such as melting-point If on Fig 7 the melting-point of the pure solid phase could be shown, then the equilibrium representation would be quantitatively exact In order to do this Fig 7 would have to be replaced by a solid figure

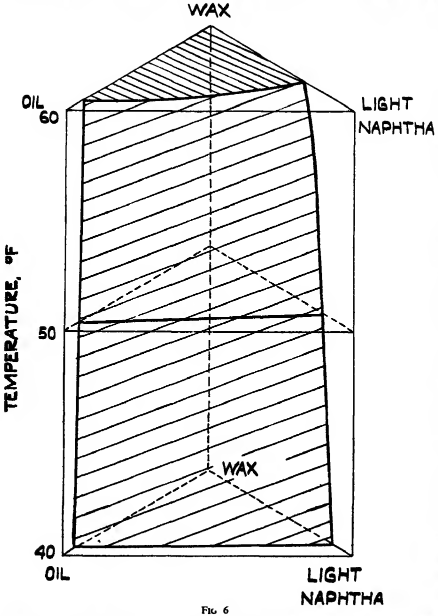

FIG 6

Dewaxing Computations

Fig 7 may be used for graphical computations on dewaxing operations For example, suppose a lubricating-oil stock with a pour-point of 73° F is to be dewaxed with the addition of a solvent or diluent by chilling to, and filtering at, t° F The ratio of solvent to stock to be used in the process is R Suppose, also, that the filtering process gives a cake of melting-point 104° F consisting of wax and mechanically entrained oil What is the yield of solvent-free cake and dewaxed oil? What is the percentage of oil in the solvent-free cake, and what is the pour-point of the solvent-free dewaxed oil? What percentage of solvent is present in the cake and filtrate obtained from the process? If the curve XY of Fig 7 represents the equilibrium between wax-free oil, paraffin wax, and solvent at the dewaxing temperature t° F, then this figure can be used as a basis for computing the answers to these questions

In Fig 7 D' represents the pour-point of the oil stock to be dewaxed, namely 73° F From D' by means of the wax-oil pour-point curve the point D, representing the percentage wax in the stock, is obtained To the stock solvent is added in amount such that the ratio of solvent to stock is R The composition of the mixture of solvent and stock so obtained must be on the line joining point D, representing the composition of the stock, to the point S, representing the composition of the solvent If the composition of this stock and solvent mixture is represented by point E, then E must be located on DS so that DE/ES equals the required solvent/oil ratio R The solvent and stock mixture, of composition represented by point E, is now cooled to the dewaxing temperature t° F Since E lies within the two-phase solid-liquid area of the isothermal ternary diagram, the stock and solvent mixture must exist as two phases, a solid phase and a liquid phase The composition of these two phases must be located by the tie-line passing through the point E, that is by the line FEB The point B then represents the composition of the solid phase, namely wax, while F represents the composition of the liquid phase, a solution consisting of wax, oil, and solvent. The ratio of the solid to the liquid phase will be equal to the ratio FE/EB.

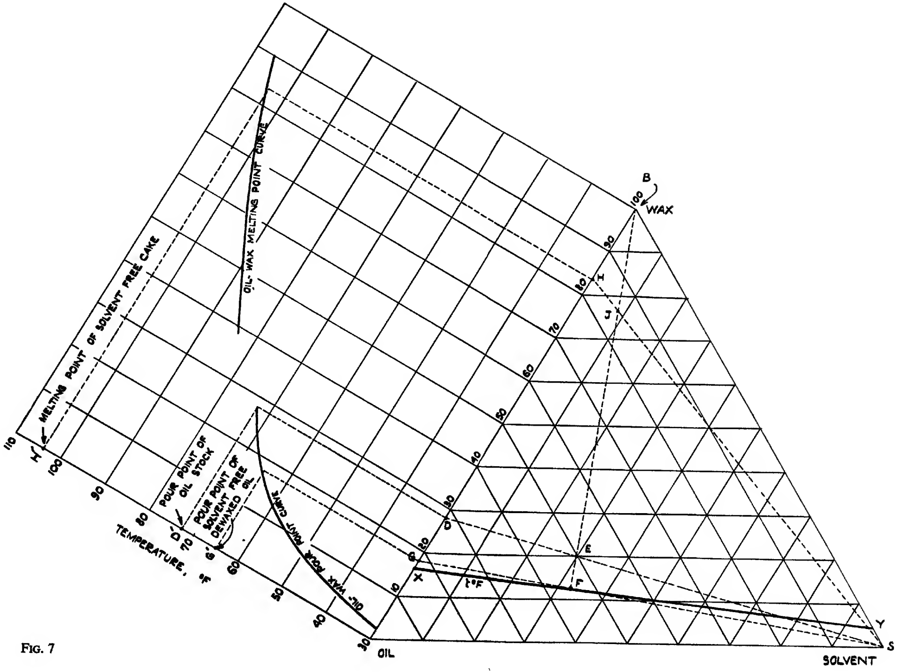
B
100
WAX
90
80
70
60
50
40
30
20
10
H
J
E
F
D
G
X
t°F
Y
S
OIL
SOLVENT
OIL- WAX MELTING POINT CURVE
MELTING POINT OF SOLVENT FREE CAKE
H'
110
100
90
80
70
60
50
40
30
POUR POINT OF OIL STOCK
D'
POUR POINT OF SOLVENT FREE DEWAXED OIL
G'
OIL- WAX POUR POINT CURVE
TEMPERATURE, °F

FIG. 7

The cake obtained on filtration consists of the solid phase, wax, together with mechanically held liquid This liquid must have the composition indicated by *F* Therefore the composition of the cake, a mixture of the solid phase and mechanically held liquid phase, obtained on filtration before solvent is removed from it must be somewhere on the line *FB* The melting-point of the solvent-free cake is 104° F and the composition of the solvent-free cake can be taken as the composition of the wax-oil mixture having this melting-point From the melting-point, *H'*, of the solvent-free cake and from the wax-oil melting-point curve the composition of the solvent-free cake in terms of oil and wax is located as point *H* The composition of the cake obtained on filtration before the solvent is removed must therefore also lie on the line joining the point representing the composition of the solvent-free cake *H*, and the point representing the composition of the solvent *S* The intersection of *HS* and *FB* at *J* must represent the composition of the cake obtained on filtration before solvent removal The yields of actual cake and filtrate can then be obtained from the ratio *EF*/*EJ* which is the ratio of cake to filtrate The percentage of solvent in both the cake and the filtrate can be read directly from points *J* and *F* respectively

The composition of the dewaxed oil after freeing from solvent must lie on the straight line passing through *F* and *S*, and must be the point on this line where the solvent concentration is zero, that is, where it cuts the left-hand side of the triangle, namely, point *G* The pour-point of the dewaxed oil is then easily read from the oil-wax pour-point curve as *G'* equal to 65° F in Fig 7 The final yields of solvent-free cake of melting-point 104° F and dewaxed oil of pour-point 65° F are obtained from the relationship *DG*/*DH* equal to the ratio of solvent-free cake to dewaxed oil

The equilibrium diagram can be used in the above way for computing the results to be obtained from a dewaxing operation, provided that either the melting-point of the solvent-free cake or the amount of oil in the solvent-free cake is known Since the oil present in the solvent-free cake is purely oil mechanically retained during the filtering operation, the cake melting-point must be entirely determined by the filtration method and equipment employed, and its value and variation could easily be determined for a given piece of equipment as a function of operating conditions It is possible that some of the oil present in the cake may be actually dissolved in the solid wax If this was so, the solid phase at equilibrium would be, not wax, but a solid solution of oil or oil and solvent in wax In such a case the equilibrium diagram would differ somewhat from that shown in Fig 7, but computations would still be possible In all the instances so far examined experimentally [1, 1937] no evidence for the existence of a solid solution of oil, solvent, or oil and solvent in wax was obtained, and it is believed that the possible occurrence of such solid solutions is remote

Experimental Determination of the Equilibrium Diagram

Experimental data for the construction of the equilibrium diagrams may be obtained by either a direct or an indirect method Since the yield and character of the dewaxed oil, obtained in the dewaxing process, sometimes depend to some extent on the rate of chilling and on the length of time the chilled mixture is held at the dewaxing temperature, a direct method is usually more satisfactory In a direct method the data used for constructing the equilibrium diagram must be obtained by small-scale dewaxing experiments These experiments most conveniently consist of filtration experiments carried out, at chilling rates and time at dewaxing temperature, identical with the rates and time employed under the proposed working conditions The equilibrium line at any one particular temperature, *t*° F, can then be plotted from the results of three, or more accurately from four, determinations These experiments are, first, filtration of the wax-bearing stock at *t*° F, second and third, filtrations at *t*° F, of wax-bearing stock with known suitable amounts of solvent added, and fourth, filtration of a suitable mixture of solvent and wax at *t*° F Analyses of the filtrates obtained gives sufficient information to construct the equilibrium diagram at *t*° F for the particular wax-bearing stock and solvent used Since the equilibrium curve represents the composition of the liquid phase in equilibrium with the solid phase, wax, only analysis of the liquid phase, filtrate, is required The pour-point of the filtrate from the first filtration, the per cent solvent in the filtrate and the pour-point of the solvent-free oil from the second and third filtrations, and the per cent wax in the fourth filtrate are the only analytical data required By the use of an oil-wax pour-point curve, attached to the side of the triangular diagram as in Fig 7, these data can be plotted on the triangular diagram to produce the required equilibrium curve The oil-wax pour-point and the wax-oil melting-point curves are best constructed from synthetic mixtures of previously separated oil and wax Care has to be taken that the previously separated wax used is representative of the bulk of the wax present in the oil The pour-point and the melting-point curves are used of course, for all equilibrium diagrams pertaining to one wax-bearing stock at all dewaxing temperatures In all the cases so far examined [1, 1937] the oil-wax pour-point curve has been found to be a straight line when pour-point is plotted against log oil-wax composition If this relationship is general, it is obvious that this curve could be constructed from two or three points only, provided the extrapolated range was not too extensive In carrying out pour-point determination it must be emphasized that the standard method of determination where the pour tube is inverted every 5° F is not sufficiently accurate for this type of work Using the standard method the error varies from +1 to +4° F In the construction of, and in computations based on the equilibrium diagram, the pour-point curve is used as a measure of wax content, and since an error of +4° F in the pour-point represents an error in wax content of about +20%, pour-points should therefore be determined correct to within 1° F

In Fig 8 the equilibrium diagram for a wax-free Iranian lubricating-oil fraction and a paraffin wax, melting-point 108° F, with methyl ethyl ketone as a solvent, at 50° F, is illustrated This diagram was constructed from the data obtained from four filtration experiments as described above In Fig 9 the equilibrium curves at temperatures of 40°, 50°, and 60° F for the same oil and wax, but with amyl alcohol as a solvent, are shown As in Fig 8 these were obtained by direct filtration experiments Carlisle and Levine [2, 1932] describe the dewaxing of a wax distillate with methylene chloride From their dewaxing data at a chilling temperature of −13° F, using a chilling rate of 18° F per hour, with a standing time of 1 hour, Fig 10 has been constructed.

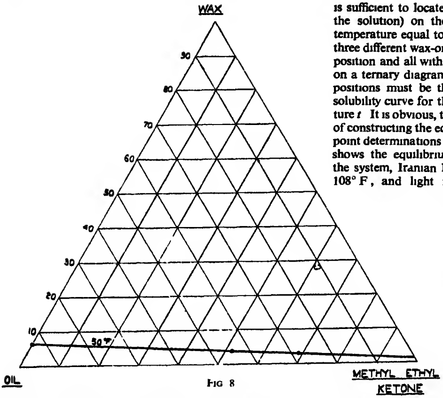

Fig 8

These investigators tabulate data for dewaxing with four different solvent/oil ratios This data gave the four points on Fig 10 joined to the apex by the broken constructional lines Of the remaining two points in the figure one was obtained from data given in the paper on the solubility of wax in methylene chloride at −13° F, while the other was obtained by extrapolation The equilibrium curves for all the above three solvents are straight lines at the prevailing temperatures

The equilibrium curve in the ternary diagram is actually a solubility curve representing the solubility of wax in oil, in oil-solvent mixtures, and in pure solvent at the prevailing temperature A point on this solubility curve represents the composition of the binary or ternary mixture which at the equilibrium temperature is saturated with wax An unsaturated ternary solution at a temperature t_1 if cooled to a temperature, say t, at which it is saturated, still remains a homogeneous solution If it is further cooled a fraction of a degree below t, the solution becomes supersaturated and tends to attain equilibrium by depositing wax as a solid phase Cooling a solution of wax, oil, and solvent of known composition down to a temperature t where the solution becomes cloudy due to appearance of solid wax means that at temperature t the solution of original known composition is in equilibrium with the solid wax phase That is, the original known composition of the solution must represent a point on the isothermal solubility curve for the ternary system wax, oil, solvent at temperature t Therefore determining the cloud-point of a solution of oil, wax, and solvent of known composition is sufficient to locate a point (the known composition of the solution) on the solubility curve at an equilibrium temperature equal to the cloud-point temperature Given three different wax-oil-solvent mixtures all of known composition and all with a cloud-point t, then the three points on a ternary diagram representing the three known compositions must be three points lying on the isothermal solubility curve for the wax-oil-solvent system at temperature t It is obvious, therefore, that an easy indirect method of constructing the equilibrium curve is by ordinary cloud-point determinations on known synthetic mixtures Fig 11 shows the equilibrium curves at three temperatures for the system, Iranian lubricating oil, wax of melting-point 108° F, and light naphtha boiling range 100–120° C These curves were constructed entirely from ordinary cloud-point determinations

The cloud-point method of obtaining the equilibrium diagram is obviously a convenient and easy method It possesses, however, one grave disadvantage in that when employed with certain solvents it is inaccurate For a system of three pure components, data obtained from cloud-point or, more usually termed for this case, freezing-point determinations are, of course, entirely reliable For a system where the solid phase consists of a large number of components, like paraffin wax, unavoidable errors are introduced by the use of cloud-points, particularly for certain solvents For example, on cooling a single homogeneous solution of composition, say, 10, 50, and 40% wax, oil, and solvent respectively, in a cloud-point determination, the solid phase would appear, say, at

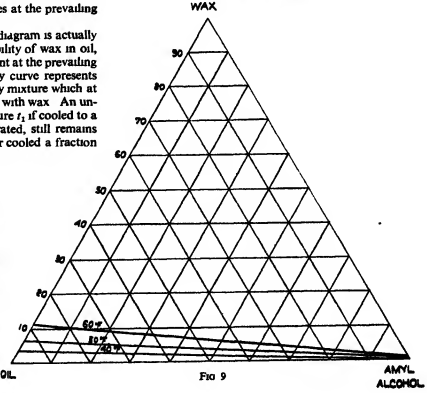

Fig 9

50° F This result, in the usual way, would be taken to mean that a liquid of composition 10, 50, and 40% wax, oil, and solvent was in equilibrium with solid wax at 50° F When checked by the direct filtration method, however, equilibrium between a liquid of this composition and solid wax would be found to occur at a lower temperature, say 45° F By filtration the liquid phase in equilibrium with solid wax at 50° F would be found to be not 10, 50, and 40% wax, oil, solvent, but, say, 15, 45, and 40% wax, oil, solvent That is, at 50° F the cloud-point method gives an apparent wax solubility of 10%, whereas 15% is obtained by the filtration method Wax is, of course, a mixture of a large number of components all of different solubility in the solvent, some being more and others less soluble Since wax is being considered as a single substance, the average solubility of the wax as a whole is the solubility desired and is the solubility obtained by the filtration method In the cloud-point determination the first solid phase to appear consists mainly of the least soluble components of the wax, and hence this method gives not the average solubility of the wax as a whole, but the solubility of the less soluble constituents The less soluble components of the wax possess higher melting-points than the more soluble components A solvent from which the wax crystallizes as a first fraction with a much higher melting-point than the original wax therefore tends to give erroneous solubility data when the equilibrium is determined by the cloud-point method Such a solvent is amyl alcohol from which, for example, wax of original melting-point 108° F was found to crystallize in the first fraction as wax of melting-point 126° F The two different solubility curves obtained from such a solvent at temperature t° F using the filtration and cloud-point methods are shown in Fig 12 For the purposes of illustration the difference between the two curves has been exaggerated in the figure It will be seen that when no solvent is present the data obtained from both the cloud-point and the filtration methods agree With increasing amounts of solvent the cloud-point solubilities are increasingly lower than the filtration solubilities up to a point where, on still further increasing the amount of solvent in the mixture the two lines begin to approach each other When the wax-solvent binary mixture is reached the error in the solubility measured by the cloud-point is large compared to the actual bulk or average solubility which is small here The data obtained from filtration experiments fall on a straight line, while those from cloud-point determinations fall on a slight curve Sullivan, McGill, and French [13, 1932] have found that difference of solubility due to difference of melting-point decreases with decreasing temperature, so that it is highly probable that at low temperatures both methods would give identical results In the case of a solvent in which the difference in solubility between the high and low melting-point waxes is not pronounced, the cloud-point method may be used with success for determining average solubility data The light naphtha used for the equilibrium data of Fig 11 is such a solvent

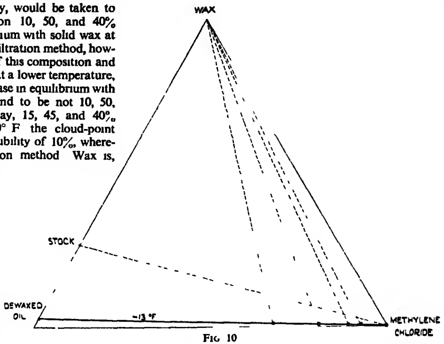

FIG 10

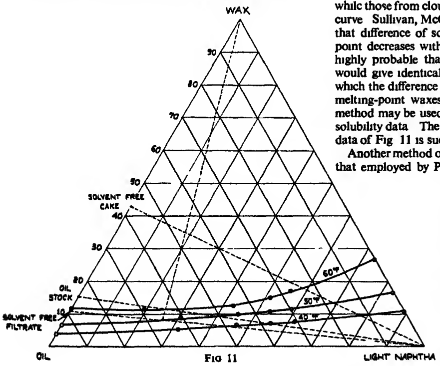

FIG 11

Another method of determining average solubility data is that employed by Poole [10, 1929] This method is very convenient and is free from the error sometimes introduced by certain solvents into the cloud-point method. In this method a known mixture of oil and solvent is placed in a test-tube and excess wax added. The whole is kept at the desired temperature for a period of about 12 hours At the end of this time both liquid and solid phases must be present, the solid phase in fair amount Some of the liquid phase is then removed and its composition ascertained by analysis. Various liquid-phase compositions at constant temperature give the isothermal solubility curve on the ternary diagram This method is accurate, provided sufficient wax is present in the solid phase to be representative of the wax as a whole

Poole [10, 1929, 11, 1931, 12, 1932] in three papers has published solubility data determined by the above method for paraffin wax melting-point 50° C, in various solvents and solvent-oil mixtures at different temperatures, using as the oil two Pennsylvanian paraffin-base lubricating oils Poole's data for four solvents, butyl acetate, butyl formate, pentasol, and diethyl carbinol, have been recalculated and plotted on ternary diagrams in Fig 13 The equilibrium lines obtained from Poole's experiments are incomplete owing to the fact that he did not determine the solubility of the wax in the oils used

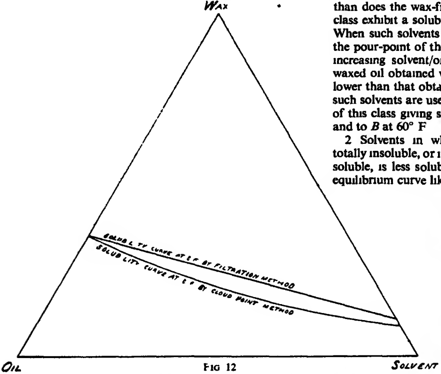

FIG 12

For all solvents so far examined [1, 1937] the solubility curves when plotted on the triangular diagram are straight lines The one exception is light naphtha used as a solvent at temperatures higher than 60° F, and the deviation from a straight line in this instance would appear to be due to the high equilibrium temperature, which is much higher than any likely to be employed in actual dewaxing practice. If all such equilibrium curves at low temperatures proved to be straight lines or curves deviating very slightly from a straight line, then the following very easy method of constructing the ternary equilibrium solubility diagram could be used One terminal point of the solubility curve at a given temperature could be easily obtained from cloud-point determinations on oil-wax mixtures or from one solubility determination of wax in oil at the required temperature using Poole's method The other terminal point could be determined from one solubility measurement of wax in solvent at the required temperature also by Poole's method Merely connecting these two points in the ternary diagram by a straight line would then complete the data

Classification of Solvents

The ternary equilibrium diagrams form a sound basis for the classification and comparison of dewaxing solvents The first essential feature of a solvent is that it must be completely miscible with the oil at the dewaxing temperature All known solvents of this type fall into four classes

1 Solvents which possess a greater solvent power for wax than does the wax-free hydrocarbon oil Solvents in this class exhibit a solubility curve, such as *A* or *B* in Fig 14 When such solvents are employed in a dewaxing process the pour-point of the dewaxed oil obtained increases with increasing solvent/oil ratio The pour-point of the dewaxed oil obtained without the use of a solvent is always lower than that obtained at any similar temperature when such solvents are used Light naphtha is a typical solvent of this class giving solubility curves similar to *A* at 40° F and to *B* at 60° F

2 Solvents in which the wax is negligibly soluble, totally insoluble, or in which the wax, although appreciably soluble, is less soluble than it is in the wax-free oil An equilibrium curve like *C* in Fig 14 is characteristic of this class of solvents Alteration of the solvent oil ratio when dewaxing with solvents in which the wax is negligibly soluble or totally insoluble has either very little or no effect on the pour-point of the dewaxed oil For such solvents the equilibrium curve differs from curve *C*, Fig 14, in that it passes through or nearly through the solvent apex, and the pour-point of the dewaxed oil obtained without the use of a solvent is either the same or lower than that obtained with any similar temperature, when such solvents are used For solvents of this class in which the wax is appreciably soluble, but still of course less soluble than in the wax-free oil, then the pour-point of the dewaxed oil increases with increasing solvent/oil ratio, while the pour-point of the dewaxed oil obtained without the use of a solvent is lower than that obtained at any similar temperature when such solvents are used A typical solvent in this class is amyl alcohol

3 Solvents which, when added to an oil-wax mixture, at a given temperature, first precipitate wax and then on the addition of more solvent redissolve part or all of the precipitated wax These solvents give an equilibrium curve like *D* When used for dewaxing, an increase in the solvent/oil ratio up to a certain point decreases the pour-point of the dewaxed oil Any increase in the solvent/oil ratio above this point increases the pour-point of the dewaxed oil The pour-point of the dewaxed oil obtained without the use of a solvent would always be higher than the pour-point obtained using such solvents up to the critical solvent/oil ratio, while at a ratio above the critical ratio the pour-point of the dewaxed oil is always higher than that obtained when no solvent is used

4 With solvents of this class the amount of wax precipitated increases and the pour-point of the dewaxed oil decreases with increasing solvent/oil ratio up to a critical ratio A typical solubility curve for such solvents is shown by *E* in Fig 14 The pour-point of the dewaxed oil obtained by the use of such solvents up to the critical ratio is

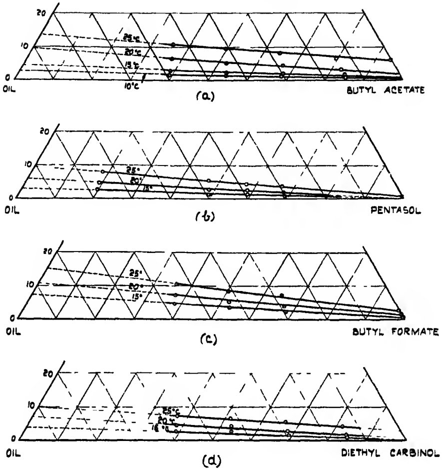
20
10
0
25°C
20°C
15°C
10°C
OIL
BUTYL ACETATE
(a)
25°
20°
15°
OIL
PENTASOL
(b)
25°
20°
15°
OIL
BUTYL FORMATE
(c)
25°C
20°C
15°C
OIL
DIETHYL CARBINOL
(d)

Fig 13

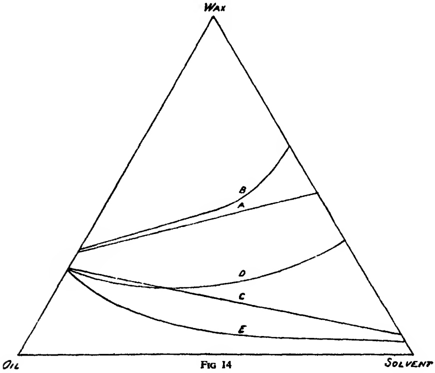
Wax
B
A
D
C
E
Oil
Solvent

Fig 14

always lower than the pour-point of the dewaxed oil obtained when no solvent is used

For dewaxing processes solvents of class 1 are obviously the least efficient and those of class 4, at solvent ratios below the critical ratio, the most efficient A large majority of the solvents usually used approximate to class 2, solvents in which the wax is negligibly soluble or nearly insoluble For this special type of class 2 solvents the best solvent-oil ratio to be employed is determined entirely by the viscosity and ease of filtration or centrifuging of the oil-wax-solvent mixture at the dewaxing temperature

It is doubtful whether solvents of the third and fourth classes really exist Maksorov [9, 1924] gives a list of solvents which he claims belong to classes 3 and 4 Most of these solvents, however, fail to fulfil the essential condition of solvents, viz to be completely miscible with the oil at the dewaxing temperature

Poole [10, 1929, 11, 1931, 12, 1932] has examined the solubility of wax and oil in a large number of organic solvents Many of these solvents were only slightly miscible with oil at the usual dewaxing temperatures and hence no further research on their possible uses in dewaxing was carried out The most promising were examined in detail by Poole, and their equilibrium curves at several temperatures calculated from Poole's data are plotted in Fig 13 It will be seen from this figure that all these solvents give straight lines on the ternary diagram, and at the lowest temperature examined are approaching class 2 solvents Of other solvents examined by Poole butanol, and to a slight extent chlorobenzene, appear to belong to class 3 solvents at certain temperatures With chlorobenzene deviation from a class 2 type towards a class 3 type solubility curve is only very slight and probably is due to experimental error Below 30° C butanol shows a limited miscibility with oil Kalichevsky and Stagner [8, 1933], discussing Poole's results, state that these 'solvents are especially promising because when added in small proportions to the oils they greatly decrease the capacity of the oils to retain their dissolved wax

As seen from Fig 14, this statement is incorrect The evidence, that any solvent when added to an oil-wax mixture actually precipitates wax, is extremely slight, and any tendency to do so is small and apparently within the limits of experimental error for all oil-miscible solvents so far investigated

The classification of all solvents so far examined and which are completely miscible with the oil at the dewaxing temperature is given in Table I As the solubility of the wax, not only in the solvent but also in the oil at the particular temperature used, determines the behaviour of a solvent in dewaxing, this classification of these solvents pertains only to the particular temperature conditions and for the particular oil stocks mentioned in this article

Table I

Classification of Oil-soluble Dewaxing Solvents

Class 1	*Class 2*	*Class 3*	*Class 4*
Naphtha	Amyl alcohol	Chlorobenzene	
	Diethyl carbinol	Butanol	
	Methy ethyl ketone		
	Methylene chloride		
	Butyl acetate		
	Butyl formate		

Comparison of Calculated and Experimental Data

Computations to forecast the results to be expected by a dewaxing process at any given temperature and using any given solvent have already been described Small-scale dewaxing operations have been carried out, using light naphtha as a diluent, in order to check the accuracy of the computation method [1, 1937]

These experimental and calculated results are compared in Table II In columns 2 and 3 the wax content and pour-point of the oil stock used are given This stock was obtained by dissolving paraffin wax, melting-point 108° F, in Iranian lubricating oil The solvent/oil ratio and dewaxing temperatures employed are detailed in columns 3 and 4 In column 5 the melting-point of the cake obtained in the experiments is tabulated The calculated yield of cake, and dewaxed oil, and the pour-point of the dewaxed oil shown in columns 7, 11, and 9 respectively, was computed graphically from a ternary equilibrium diagram assuming the melting-point of the cake was that shown in column 5 The actual yields and pour-point are given in columns 6, 8, and 10

It will be seen from the table that agreement between the actual and calculated data is really excellent, considering the complicated nature of the materials handled The equilibrium data used for the calculations were those for the naphtha-wax-oil system illustrated in Fig 11, and the dotted lines appearing in this figure are those actually used for calculating yields, &c, for run 3 The equilibrium data in Fig 11 were constructed entirely from cloud-point determinations, which makes the agreement between the actual and calculated values still more remarkable

Table II

Solvent Light Naphtha (b p 100–120° C)

	Oil stock used					*Cake*		*Dewaxed Oil*			
Run no	*Content wax, %*	*Pour-point, ° F*	*Solvent/ oil ratio*	*Dewaxing temp ° F*	*Melting-point, ° F*	*yield %*		*Pour-point, ° F*		*yield %*	
						Actual	*Calculated*	*Actual*	*Calculated*	*Actual*	*Calculated*
1	54	91*	1 0	60	106	26 4	26 6	82 3*	83 5	73 6	73 4
2	20	67	0 25	60	90	11 6	16 0	62	61	88 4	84
3	15	62	0 33	50	90	6 4	9 8	58	57	93 6	90 2
4	15	62	0 25	50	85	16 1	15 5	55	55	83 9	84 5
5	15	62	0 25	50	89 5	9 4	12 3	56	55	90 6	87 7
6	15	62	0 11	50	72†	38 1	38 1	50	51	61 9	61 9
7	10	55	0 25	40	82	12 4	18 4	46	45	87 6	81 6

* Melting-point † Pour-point

Experimental and calculated results, using methyl ethyl ketone and amyl alcohol as solvents, are compared in

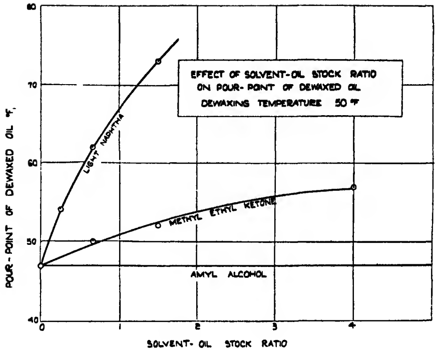
EFFECT OF SOLVENT-OIL STOCK RATIO
ON POUR-POINT OF DEWAXED OIL
DEWAXING TEMPERATURE 50 °F
POUR-POINT OF DEWAXED OIL °F
80
70
60
50
40
0
1
2
3
4
LIGHT NAPHTHA
METHYL ETHYL KETONE
AMYL ALCOHOL
SOLVENT-OIL STOCK RATIO

Fig 15

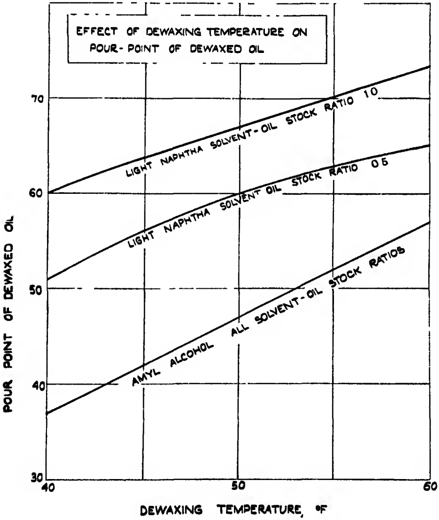
EFFECT OF DEWAXING TEMPERATURE ON
POUR-POINT OF DEWAXED OIL
POUR POINT OF DEWAXED OIL
70
60
50
40
30
40
50
60
LIGHT NAPHTHA SOLVENT-OIL STOCK RATIO 1 0
LIGHT NAPHTHA SOLVENT OIL STOCK RATIO 0 5
AMYL ALCOHOL ALL SOLVENT-OIL STOCK RATIOS
DEWAXING TEMPERATURE, °F

Fig 16

Table III in the same way as before [1, 1937] Once again agreement is excellent In this case the equilibrium solubility diagrams for both solvents were constructed from equilibrium data obtained by the direct method The wax and lubricating oil were the same as those used for the light naphtha experiments The actual equilibrium data on which the calculations were based is shown in Figs 8 and 9

Comparison of Dewaxing Solvents

One of the most useful applications of the ternary diagram to dewaxing computations is for the comparison of different solvents The effect of dewaxing temperature and solvent/oil ratio for any solvent with a given oil in yield of cake, dewaxed oil, and on the pour-point of the dewaxed oil are easily calculated The efficiency of various solvents apart from ease of filtration and mechanical operation for a given oil is then readily compared on the above basis

In Fig 15 the pour-point of the dewaxed oil obtained by using naphtha, methyl ethyl ketone, and amyl alcohol for dewaxing a given stock oil at 50° F is compared at different solvent/oil ratios Fig 16 shows the effect of varying the dewaxing temperature with amyl alcohol and naphtha as solvents for the same stock oil at constant solvent/oil ratio. Comparison of solvents on these lines allows the best solvent and the most favourable conditions to be chosen without the necessity for carrying out a large number of dewaxing experiments

TABLE III

Solvent Amyl Alcohol

	Oil stock used				*Cake,*			*Dewaxed oil*			
								Pour-point, ° F			
Run no	*Content wax, %*	*Pour-point, ° F*	*Solvent-oil ratio*	*Dewaxing temp ° F*	*Melting-point, ° F*	*Actual*	*Calculated*	*Actual*	*Calculated*	*Actual*	*Calculated*
8	14.6	61.5	0.83	50	74†	35.8	33.8	47	47	64.2	66.2
9	15.6	63	0.84	40	83	32.2	33.7	37	37	67.8	66.3
10	11.4	57	1.65	40	95	12.1	14.4	37	37	87.9	85.6

Solvent Methyl Ethyl Ketone

11	17.9	65	0.98	50	104.25	8.6	11.4	51	51	91.4	88.6
12	25.9	72	1.79	50	100.1	26.2	25.1	52.3	52	73.8	74.9

* Melting-point † Pour-point

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SECTION 30

GAS PYROLYSIS AND POLYMERIZATION

THERMAL REACTIONS OF GASEOUS HYDROCARBONS

By F. E FREY, M S , and H. J. HEPP

Phillip's Petroleum Company

THE pyrolysis or 'cracking' of gaseous hydrocarbons has received much attention from both the scientific and the applied standpoints [73, 1932–5] On the scientific side, the thermal decomposition of the simpler hydrocarbons affords perhaps the best opportunity for learning something of the fundamental nature of the chemical reactions involved in pyrolysis, and the best prospects for unravelling the more complex reactions taking place in the cracking of petroleum and destructive distillation of coal On the applied side, pyrolysis affords a means of converting the vast volumes of available natural gas and gas produced by the cracking of petroleum into gasoline, benzol, carbon black, and other products Pyrolysis may also constitute a step in the manufacture of chemical derivatives, such as solvents and resins and many other products having a variety of special applications At the present time active development in many directions is taking place, and both the chemistry and applications of pyrolysis deserve a detailed consideration

Chemistry of Pyrolysis

Thermal treatment of even the simpler hydrocarbons in the absence of a catalyst yields a variety of products, but with aid of improved experimental methods, particularly analytical methods employing precise fractional distillation, it has been possible to obtain fairly exact information about many pyrolysis reactions The normally gaseous hydrocarbons are limited in number, and pyrolysis studies of nearly all of them have been made The paraffins are methane, ethane, propane, *n*-butane, iso-butane, and the rarely occurring neo-pentane The olefines are ethylenes, propylene, and the four isomeric butylenes More highly unsaturated gaseous hydrocarbons have been investigated, but of these acetylene and 1,3-butadiene, which are commonly formed in pyrolytic reactions, have received most attention

The paraffins, perhaps with the exception of methane, pyrolyse in a less complex manner than do the unsaturated hydrocarbons, the molecule splitting to produce simpler complementary molecules of olefine and paraffin and sometimes hydrogen This decomposition requires hours at 400° C (752° F), but the decomposition velocity increases rapidly with temperature and is a matter of seconds at 800° C (1,472° F) As exposure to a pyrolysis temperature is prolonged and reaction becomes extensive, secondary decomposition occurs The products first formed in turn may undergo splitting reactions The olefines, however, have also a tendency to unite with each other to produce polymer molecules of higher molecular weight Complex reactions take place as the heating time is further prolonged, the more reactive hydrocarbons being progressively destroyed, until only the most heat-stable hydrocarbons (methane and aromatics) survive, and even the aromatics are degraded to carbon in the end At very high temperatures acetylene is stable and is produced in significant amount, while at low-temperature levels non-aromatic oils result from extended reaction

Among these complex reactions, one class, namely, the uncatalysed primary decomposition of ethane and higher paraffins, has yielded on investigation fairly exact information amenable to correlation and is first presented Pyrolysis of olefines and secondary reactions are next discussed, and methane is considered last because, due to its high stability, the decomposition is largely a matter of secondary reactions

Primary Decomposition of Paraffins

Ethane propane, the butanes, and higher paraffins can be decomposed in glass, silica and copper vessels with little interference from catalytic action Both flow through a heated tube and a timed exposure in a heated bulb have been commonly used to effect decomposition experimentally, after which the pyrolysed hydrocarbon is analysed and reactions taking place may be deduced This rather elementary procedure has been used almost exclusively for studying pyrolysis If the fraction of the paraffin decomposed is small, the products are those formed by the decomposition of the paraffin itself

Many investigations have established for the paraffins the course of primary decomposition Ethane decomposes into equivalent amounts of ethylene and hydrogen Propane decomposes similarly into propylene and hydrogen, but an equal amount decomposes by fracture of the carbon–carbon bond to produce equivalent amounts of ethylene and methane Iso-butane decomposes in the same way as propane, somewhat more of the decomposition following the dehydrogenation route *n*-Butane decomposes mainly through fracture of the carbon chain to produce ethylene plus ethane by fracture of the middle carbon–carbon bond, and propylene plus methane, by fracture of the terminal bond Neo-pentane gives iso-butylene plus methane The mode of decomposition is expressed by the rule of Hague and Wheeler [21, 1929] 'The primary decomposition can be represented by a series of equations indicating the rupture of the chain at any position with the production of an olefine and the complementary lower paraffin, or, at the limit, hydrogen '

The decomposition is represented by the following equations The numerical values give the percentage of the total decomposition which follows the route indicated, and are averages of values obtained by different investigators

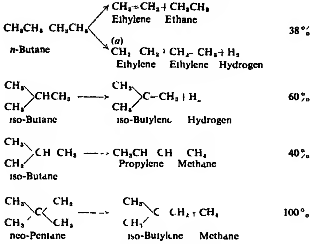
$$\underset{\text{Ethane}}{\mathrm{CH_3CH_3}} \longrightarrow \underset{\text{Ethylene}}{\mathrm{CH_2{=}CH_2}} + \underset{\text{Hydrogen}}{\mathrm{H_2}} \qquad 100\%$$

$$\underset{\text{Propane}}{\mathrm{CH_3CH_2CH_3}} \longrightarrow \underset{\text{Propylene}}{\mathrm{CH_3CH{=}CH_2}} + \underset{\text{Hydrogen}}{\mathrm{H_2}} \qquad 45\%$$

$$\underset{\text{Propane}}{\mathrm{CH_3CH_2\ CH_3}} \longrightarrow \underset{\text{Ethylene}}{\mathrm{CH_2{=}CH_2}} + \underset{\text{Methane}}{\mathrm{CH_4}} \qquad 55\%$$

$$\underset{n\text{-Butane}}{\mathrm{CH_3CH_2CH_2CH_3}} \begin{array}{l} \nearrow \underset{\text{1-Butene}}{\mathrm{CH_3CH_2CH{=}CH_2}} + \underset{\text{Hydrogen}}{\mathrm{H_2}} \\ \searrow \underset{\text{2-Butene}}{\mathrm{CH_3CH{=}CHCH_3}} + \underset{\text{Hydrogen}}{\mathrm{H_2}} \end{array} \qquad 12\%$$

$$\underset{n\text{-Butane}}{\mathrm{CH_3CH_2CH_2\ CH_3}} \longrightarrow \underset{\text{Propylene}}{\mathrm{CH_3CH{=}CH_2}} + \underset{\text{Methane}}{\mathrm{CH_4}} \qquad 50\%$$



Note (*a*) At high temperatures

While the velocity of decomposition increases rapidly with temperature the relative proportions of the products initially formed vary only a little with temperature over a wide range, 400–800° C, and likewise are affected little by pressure

Kinetics

The decomposition rates for all the gaseous paraffins have been determined by maintaining the hydrocarbon at a known temperature for a known time and determining the extent of decomposition analytically The decomposition is extremely slow below 400 C, but above this temperature the decomposition rates for all gaseous paraffins have been determined [21, 1929, 27, 1929, 34, 1932, 36, 1931, 37, 1934, 44, 1928, 64, 1934] The rate is virtually independent of pressure, but increases rapidly with increase in temperature for a given hydrocarbon, while at a given temperature the rate increases as the molecular weight of the hydrocarbon increases Methane, the lowest member, is by far the most stable paraffin In Fig 1 is shown decomposition rate data for the gaseous paraffins The decomposition rate increases 2 5- to 3 0-fold for an increase in temperature of 25° C in the neighbourhood of 600° C This coefficient corresponds to a heat of activation of 60,000 to 70,000 calories per mol

Thermodynamics

Thermodynamic calculations show that the paraffins decrease in stability with rise in temperature The elevated temperatures necessary to induce pyrolysis as a rule are well within the range of thermodynamic instability The composition of products depends upon the relative velocity of the competing reactions, and these velocities, in general, do not reflect the thermodynamic driving force This is generally the case with pyrolysis reactions, though in a number of cases thermodynamic reaction limits are encountered Ethane decomposition proceeds readily only to 15% at 600° C and atmospheric pressure, since at this point the recombination of the ethylene and hydrogen formed takes place at an equal rate Decomposition continues slowly as ethylene is destroyed by other reactions

Thermodynamic data for the two typical cracking reactions of propane, computed from recent data, are given below.

$$C_3H_8 \rightarrow C_2H_4 + CH_4,$$
$$\Delta H_{600^\circ C} = 18{,}800 \text{ cal}, \ \Delta F_{600^\circ C} = -17{,}090$$
$$C_3H_8 \rightarrow C_3H_6 + H_2,$$
$$\Delta H_{600^\circ C} = 29{,}410 \text{ cal}, \ \Delta F_{600^\circ C} = 2\,090$$

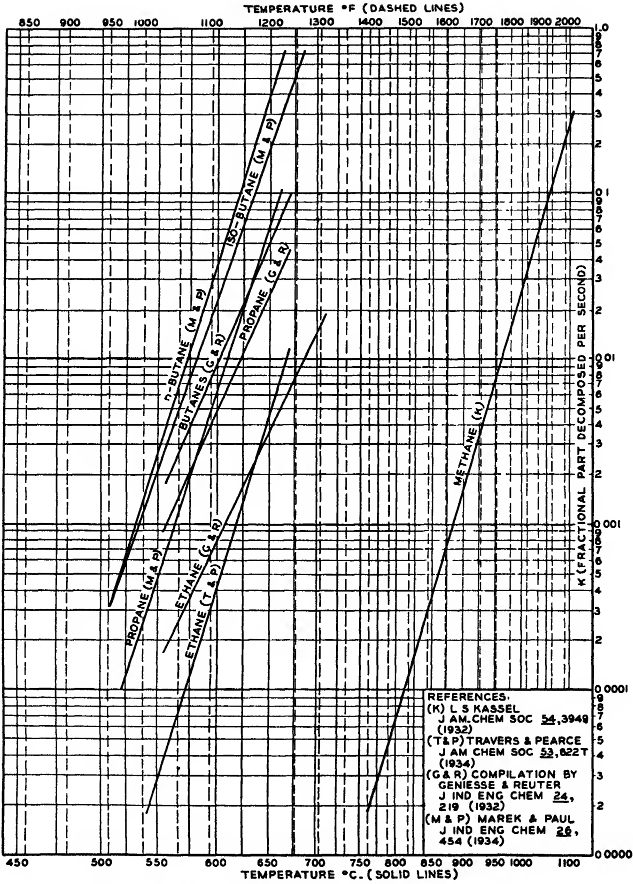
The primary decomposition of propane absorbs heat to the extent of about 24,000 calories per mol decomposed at 600° C The molar heat of decomposition is slightly lower for the butanes, and higher for ethane

Mechanism of Primary Decomposition.

In attempting to visualize how the decomposition takes place, a chief difficulty has been the transfer of a hydrogen atom from the carbon atom one removed from the point of fracture to the other fragment formed Dissociation into alkyl radicals, one of which takes a hydrogen atom from the other, has been suggested by Hurd [23, 1929] It has been thought that a prohibitively high activation energy may be required to effect dissociation into free alkyl radicals To avoid this difficulty, Burk [2, 1931] has suggested that the one radical may transfer its allegiance to the hydrogen atom of the other radical by a semi-ionization process Kassel [31, 1932] has suggested that the decomposition may proceed through the formation of a paraffin and alkylidene, this alkylidene then rearranging to olefine More recently Kassel [32, 1933] proposed a theory, based on fundamental valence considerations, which accounts for the formation of more than two product molecules ((*a*) preceding tabulation) without the formation of free alkyl radicals In the case of *n*-butane, for example, two hydrogen atoms at opposite ends of the carbon chain are assumed to come into proximity and unite with each other to form a molecule of free hydrogen The carbon chain breaks in the middle to yield two ethylene molecules Similarly, *n*-pentane may yield methane and two ethylene molecules, in agreement with experiment

Rice [50 1931] has proposed a theory for the decomposition of paraffins based on the formation of free alkyl radicals A few molecules are assumed to dissociate into free alkyl radicals, each of which may then initiate a reaction chain by extracting a hydrogen atom from another paraffin molecule which thus becomes in turn an alkyl radical, and may then decompose by fracture of the carbon chain at that point which will allow of the formation of a molecule of olefine and a simpler complementary alkyl radical without migration of hydrogen The simpler radical may in turn extract hydrogen from a paraffin molecule, and thus the chain continues That alkyl radicals actually undergo fracture reactions is indicated by the data of Frey and Hepp [12, 1933] who decomposed di-*n*-butyl mercury and di-sec-butyl mercury, and found *n*-hexane among the reaction products in the former case and iso-pentane in the latter These products can be accounted for by assuming fracture of butyl radicals to produce free ethyl and methyl which unite with butyl

Rice [51, 1933–4, 52, 1934, 53, 1933–4, 54, 1932] detected free methyl radicals in hydrocarbons decomposed by the Paneth method Simple paraffins were passed through a tube heated to about 1,000° C at very low pressure and high velocity, and the products were allowed to impinge upon and react with lead, mercury, and tellurium Alkyl compounds containing the methyl group were produced That the decomposition of butane may proceed by a chain mechanism is suggested by experiments (unpublished data) in which butane was heated to 525° C for too short a time to effect decomposition The addition of very small amounts



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(T & P) TRAVERS & PEARCE J AM CHEM SOC 53, 622T (1934)
(G & R) COMPILATION BY GENIESSE & REUTER J IND ENG CHEM 24, 219 (1932)
(M & P) MAREK & PAUL J IND ENG CHEM 26, 454 (1934)

FIG I–CHANGE OF PRIMARY CRACKING RATE WITH TEMPERATURE

F E F 8-12-35.

of dimethylmercury, however, induced the decomposition of many equivalents of butane to the usual products A critical discussion of the Rice mechanism has been given by Kassel [33, 1935]

The experimental evidence at present available cannot be considered to furnish decisive tests for theory

Pyrolysis of Olefines

The reactions taking place when olefines are pyrolysed non-catalytically are more complex than in the case of paraffins The primary reactions are not well understood and experimental results available have in fewer cases lent themselves to theoretical treatment Nevertheless, much useful information has been amassed

Olefines exhibit three types of reaction on pyrolysis

1 Splitting reactions analogous to the splitting of paraffins
2 Structural rearrangement
3 Polymerization to larger molecules

Ethylene is converted at atmospheric pressure and 400–600° C into products of higher molecular weight, mostly olefinic in structure, and so little methane is formed initially that a splitting reaction analogous to that of the paraffins can be considered negligible The reaction velocity has been shown by Pease [43, 1930] to increase as the square of the pressure An attempt to determine the primary products was made by Storch [60, 1932] who heated pure ethylene to 377° C under 141 5 cm Hg pressure in a glass bulb and interrupted the reaction when exceedingly small conversions had taken place With 0 6% conversion the chief product was butylene, which suggests a simple dimerization

$$C_2H_4 + C_2H_4 \rightarrow C_4H_8$$

As the reaction was prolonged the velocity accelerated greatly and propylene, butylene, pentenes, and higher hydrocarbons were formed, even with a small extent of reaction (5%) The peculiarities of the reaction have not been satisfactorily accounted for Schneider and Frolich [56, 1931] studied the initial stages of ethylene pyrolysis at a higher temperature, 725° C, and a low pressure, 0 2 atm (Fig 2), with a different result The chief products formed in the early stages of the reaction (5% conversion) were butadiene and hydrogen

$$C_2H_4 + C_2H_4 \rightarrow CH_2{=}CH{-}CH{-}CH_2 + H_2$$

Under those conditions the formation of butylene as an initial product was considered questionable

At high pressures polymerization of ethylene proceeds so rapidly that reaction can be brought about at temperatures well below the pyrolysis range for the paraffins Ipatiev [28, 1911] heated ethylene at 380° C and 70 atm pressure and produced polymers boiling all the way to 280° C and above The polymers contained chiefly olefines, paraffins, and naphthenes Ethylene, propylene, and the butylenes have been polymerized at high pressures in more recent investigations with a similar result Under an extremely high pressure, 9,000 atm, polymerization of the unsaturateds in cracked gasoline has been induced at 60° C [59, 1934].

Propylene, like ethylene, is polymerized under high pressure and undergoes complex reactions involving polymerization at lower pressures Propylene, however, also undergoes a splitting reaction analogous to that of propane Pyrolysis at 600–900° C and atmospheric pressure [25, 1930] yielded, in addition to products of higher molecular weight, ethylene and methane, indicating the reaction

$$C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4,$$

and in the presence of hydrogen this reaction may predominate [14, 1928] The hydrogen may be acquired either from molecular hydrogen present or from hydrocarbons

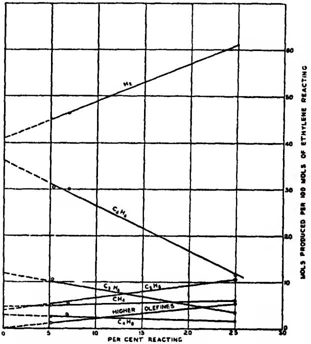

FIG 2 —PYROLYSIS OF ETHYLENE (IN SILICA) AT 725 °C AND 0 2 ATMOSPHERE (SCHNEIDER & FROLICH)

In a study of the initial stages of the pyrolysis of propylene at a high temperature, 725° C, and low pressure, 0 2 atm, Schneider and Frolich [56, 1931] found that 48% of the propylene was converted into ethylene and butylene and suggested the reaction

$$C_3H_6 + C_3H_6 \rightarrow C_4H_8 + C_2H_4,$$

which Wheeler and Wood [70, 1930] previously proposed, in connexion with their study of propylene pyrolysis Other reactions apparently taking place were

$$2C_3H_6 \rightarrow C_2H_6 + CH_2{=}CH{-}CH{-}CH_2,$$
$$2C_3H_6 \rightarrow C_5H_8 + CH_4,$$
$$2C_3H_6 \rightarrow C_6H_{10} + H_2$$

Highly unsaturated products of molecular weight higher than propylene were formed

The butylenes likewise have been found to exhibit both splitting and polymerization reactions The pyrolysis of 1-butene and 2-butene at 600° C and atmospheric pressure was studied by Wheeler and Wood [70, 1930] who obtained equivalent amounts of methane and propylene and suggested that the terminal carbon bond was ruptured in primary decomposition, the radicals being then hydrogenated Liquid products were also formed in large amount

In Table I are shown results obtained when 1-butene and 2-butene were pyrolysed in the presence of about 5 vol of hydrogen (unpublished data) Polymerization occurred, but the predominant reaction was decomposition in which hydrogen was consumed to yield the dissociation products of *n*-butane Butene-2 was somewhat more stable than butene-1, and exhibited less scission of the middle carbon-carbon bond which in the case of butene-2 is a double bond In the case of the butenes direct rearrangement of one isomer to form others is possible, but in the absence of a catalyst is probably slow

TABLE I

Pyrolysis of Butenes at 575° C (1,067° F) and Atmospheric Pressure

	Butene-1	*Butene-2*
Composition of gas cracked (volume per cent)		
H_2	81.4	83.4
C_4H_8	18.6	16.6
	100.0	100.0
Time of heating (sec)	30	29
Volume expansion on cracking	1.035	1.018
Composition of products (gas volume per cent)		
H_2	76.58	82.97
CH_4	4.59	1.35
C_2H_4	0.89	0.20
C_2H_6	0.80	0.02
C_3H_6	3.03	0.95
C_3H_8	0.13	0.04
C_4H_6	12.20	0.29
C_4H_8		13.92
C_4H_{10}		0.01
C_5H_{10}	1.08	0.25
C_5H_{12}	0.13	
Heavier	0.57	
	100.00	100.00

The pyrolysis of iso-butylene at 600–800° C and atmospheric pressure was studied by Hurd and Spence [27, 1929] and Hurd and Eilers [24, 1934] Iso-butylene was found to react more slowly than iso-butane A large fraction of the iso-butylene converted formed polymers, whose subsequent decomposition even with small conversions, obscured the splitting reactions However, the principal decomposition reaction was the splitting of iso-butylene to give methane and propylene

The diolefines and acetylenes pyrolyse somewhat more readily at atmospheric pressure than the olefines to produce more polymers and less of scission products Rearrangement of methyl- and ethyl-acetylene to 1,2 dienes takes place readily [26, 1931, 38, 1930]

To summarize the pyrolysis of the olefines, propylene and the butylenes have been shown to undergo a splitting reaction analogous to that of the paraffins, and C–C bonds are present in the molecule The ethylenic linkages are less subject to fracture This reaction may be overshadowed by polymerization when the pressure is high, but is important at atmospheric pressure or less and above 550° C The reaction may be represented for propylene as follows

$$C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4$$

The hydrogen may come from molecular hydrogen present or from hydrocarbons Ethylene alone does not decompose extensively in this way

At temperatures above 550° C and pressures of the order of one atmosphere polymerizing reactions take place which differ from simple polymerization into higher olefines in that elision of hydrogen and splitting of the molecules formed by association take place and diolefines and olefines of higher and lower molecular weight are chiefly formed

The rate of pyrolysis under such conditions is on the average lower than that of the corresponding paraffins Ethylene pyrolyses more slowly than ethane, iso-butylene more slowly than iso-butane, but propylene and the butenes correspond more nearly with propane and butane Butene-1 pyrolyses more rapidly than butene-2

At high pressure polymerization is the dominant reaction of the olefines and proceeds rapidly at comparatively low temperatures to produce higher mono-olefines and other polymeric hydrocarbons more rich in hydrogen than diolefines The reaction evolves heat and may proceed explosively with rise in temperature The polymers formed boil for the most part in the gasoline range, and this reaction is made use of for the conversion of olefinic gases into gasoline

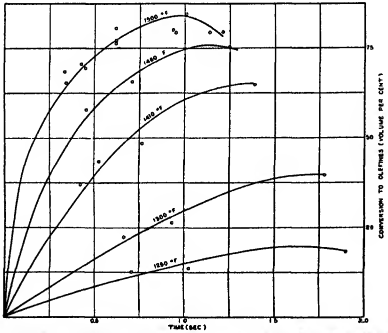

FIG 3-PROPANE PYROLYSIS-EFFECT OF TEMPERATURE ON YIELD OF OLEFINES (SULLIVAN, RUTHRUFF & KUENTZEL)

The many peculiarities of olefine pyrolysis reactions have stood in the way of determining reaction mechanism The olefinic double bond is activated by heat, and the union of two olefine molecules after such activation accounts for simple polymerization Theories involving the intermediate formation of free alkyl and alkylidene radicals have been applied to olefine pyrolysis to account for reactions other than simple polymerization

Secondary Reactions

When pyrolysis of ethane, propane, or butane is allowed to proceed until decomposition of the original paraffin is extensive, the olefines and paraffins first formed (excepting methane) in turn undergo pyrolysis, and if the pressure is not high, a maximum conversion into gaseous olefines is effected before the formation of oils becomes marked Propylene and the butylenes formed undergo splitting reactions and decrease in amount, while ethylene increases, and a decrease in average molecular weight takes place The higher the temperature level, the greater the percentage of olefines developed This is due chiefly to the tendency of ethylene once formed to rehydrogenate to ethane at the lower temperatures The production of olefines by such extensive decomposition is of practical interest because the olefines so formed can be polymerized to gasoline, or used for the synthesis of chemical derivatives

Sullivan *et al* [63, 1935] decomposed ethane and propane at several temperatures, with varying times of reaction The case of propane is typical and the results are shown in Fig 3 The maximum conversion into olefines was 80 vol % of the propane at 816° C (1,500° F) and 65 vol % at 766° C (1,410° F) Ethane gives somewhat lower conversion and the butanes somewhat higher under the same conditions

The changes in composition taking place during protracted pyrolysis of this kind have been investigated in several instances Propane was subjected to extensive pyrolysis by Schneider and Frolich [56, 1931] (Figs 4 and 5)

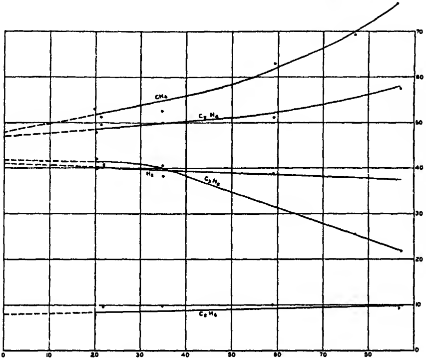

FIG 4—PYROLYSIS OF PROPANE AT 725 °C AND 1 ATMOSPHERE (SCHNEIDER & FROLICH)

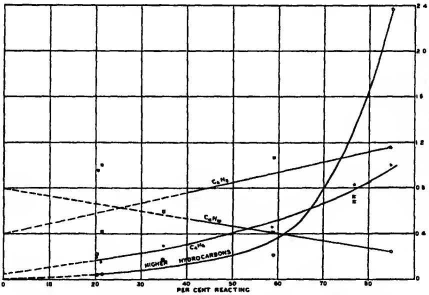

FIG 5—PYROLYSIS OF PROPANE AT 725 °C AND 1 ATMOSPHERE (SCHNEIDER & FROLICH)

The extent of cracking was varied in order to allow of distinguishing between primary and secondary products As cracking proceeded propylene formed as an initial product was destroyed Methane and ethylene were formed in increasing amount chiefly from the propylene, and higher hydrocarbons were formed in increasing amounts through reactions involving polymerization Similarly, *n*-butane and iso-butane were subjected to extensive decomposition by Neuhaus and Marek [40, 1932, 41, 1933] and analogous results were obtained (Figs 6 and 7) The decomposition of iso-butane was made 75% complete. At this point the iso-butylene and propylene formed by primary decomposition were largely destroyed, iso-butylene yielding propylene and methane, and propylene yielding ethylene and methane The propylene formed was approximately equal to the propylene destroyed

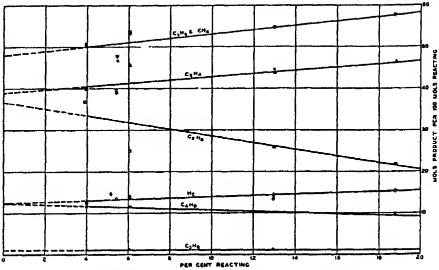

FIG 6—PYROLYSIS OF *n*-BUTANE AT 650 °C AND 1 ATMOSPHERE (NEUHAUS AND MAREK)

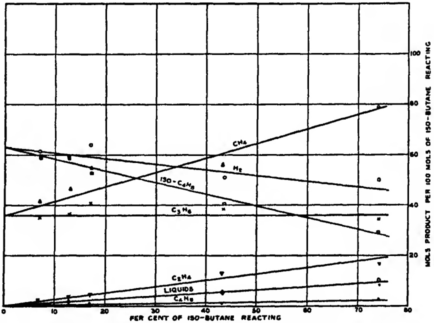

FIG 7—PYROLYSIS OF ISO-BUTANE AT 650 °C AND 1 ATMOSPHERE (MAREK AND NEUHAUS)

Carbon formation is slight in virtually all pyrolyses unless reaction is sufficiently protracted to develop oils and tar which degrade into carbon, and decomposition of the type described is accordingly accompanied by very little carbon formation

Drastic Pyrolysis—Acetylene, Diolefines, Aromatics, and Carbon

While the initial stage of pyrolysis yields products characteristic of the hydrocarbon pyrolysed, it becomes more difficult to distinguish between the behaviour of the various paraffins and olefines under more drastic conditions.

After the initial stages the pyrolysis is essentially the pyrolysis of olefines and other unsaturated hydrocarbons, and the multiplicity of products obtained—olefinic and naphthenic oils, diolefines, acetylene, aromatic light oils, tar, and carbon—do not in most instances reflect the composition of the original paraffins and olefines pyrolysed, but are determined by the temperature, pressure, and time factors Each of these variables has an independent effect on the products obtained Many combinations of these variables are possible, and several regions have been investigated experimentally A description of each will cover the range of published work The temperature level of the pyrolysis is most important and largely determines the products The various products may be arranged in order of increasing stability to heat under reaction conditions as follows

Olefine and naphthene polymers
Diolefines and triolefines
Benzene and toluene
Aromatic tars
Methane
Acetylene
Carbon

The production of olefine and naphthene polymers takes place at moderate temperatures The pyrolysis at higher temperatures produces diolefines and aromatics and, at still higher temperatures, acetylene Fig 8 depicts in a general way the course of pyrolysis over a wide range of temperature, pressure, and time

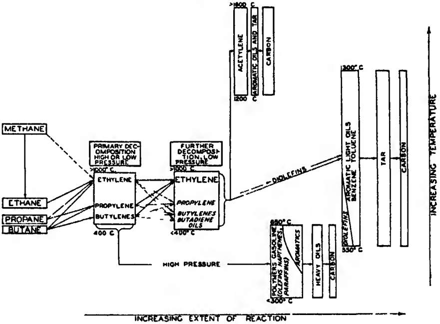

FIG 8-PROLYSIS OF GASEOUS HYDROCARBONS (WITHOUT CATALYST)

Acetylene.

Acetylene is the only hydrocarbon thermodynamically stable at very high temperatures Its formation in small amounts has been detected in the pyrolysis of various hydrocarbons around 800° C, but at temperatures in excess of 1,200° C it is produced in large amounts Rapid cooling of the products is essential for preserving the acetylene, since protracted reaction converts acetylene into aromatic oils and carbon The formation of acetylene has been accounted for in two ways

(1) Free radicals are formed which unite Thus CH may be formed and two molecules unite to produce acetylene

$$CH + CH \rightarrow CH \equiv CH$$

(2) Ethylene may lose hydrogen at a high temperature

$$CH_2{-}CH_2 \rightarrow CH{-}CH + H_2$$

Many investigators have studied the formation of acetylene in the pyrolysis of methane at 950 to 1,200° C and higher Typical results will be mentioned Smith [57, 1931] passed methane through a heated tube and found at 1,200° C and a time of reaction of 0 1 sec a conversion into acetylene of 2 1 vol % in the gas, or 3 9 wt % Aromatic oils, ethylene, and hydrogen were also formed By prolonging the reaction the formation of oils increased, but the acetylene yield remained virtually constant Peters and Meyer [45, 1929] obtained higher yields of acetylene from methane by heating to 1,600 to 3,000° C for extremely short periods of time in the presence of tungsten carbon-heating elements As high as 65% conversion into acetylene was obtained without the formation of other hydrocarbon products Reduced pressure favours acetylene formation De Rudder and Biederman [55, 1930] explored a range of pressures and temperatures and obtained at the highest temperature used, 1,500° C (reaction time 0 013 sec), and a low pressure (44 mm of mercury) the highest conversion into acetylene of 14 85 vol % of the effluent gas or 52 5% of theoretical Reduced pressure, dilution with hydrogen and carbon dioxide favour high acetylene yields

Higher concentrations of acetylene have been obtained from other gaseous hydrocarbons usually because they decompose more readily than methane to form ethylene in high yield which then dehydrogenates efficiently to acetylene Ethylene heated for a very short time at 1,300 to 1,400° C at reduced pressure has been converted to the extent of 90% into acetylene [6, 1932] and propane and the butanes at 1,400° C and atmospheric pressure likewise gives high yields of acetylene [65, 1935]

Many patents directed to the manufacture of acetylene have been issued They are concerned chiefly with means for providing high temperatures, short reaction times, and quick cooling The electric arc, electrically heated elements in the gas stream, flames in the gas stream, addition of oxygen to the gas, as well as the external heating of a tube through which the gas flows rapidly have been described.

Aromatic Oils and Diolefines.

At temperatures of 600-1,200° C or more and at atmospheric or somewhat higher pressures, pyrolysis of any of the gaseous hydrocarbons produces benzene, toluene, and aromatic tar, provided the reaction is prolonged considerably beyond the time required for primary decomposition

Frey and Hepp [10, 1932] studied the pyrolysis of propane, butane, and other gaseous hydrocarbons with special attention to the time factor Butane (89% *n*-butane, 11% iso-butane) was pyrolysed at 850° C and atmospheric pressure. In 0.09 sec. nearly all the butane was destroyed. Olefines of lower molecular weight, ethane, methane, and hydrogen, were produced. At this moderate pressure the velocity of polymerization is comparatively low and a maximum concentration of simple olefines was obtained. On prolonging the reaction to 3.9 sec.—over 40 times the reaction time required for decomposition to a maximum content of gaseous olefines—the maximum conversion into benzene and toluene was obtained. During the early part of the oil-forming stage of the pyrolysis propylene and butylene were destroyed while ethylene disappeared gradually as oils were formed. Ethylene is consequently the olefine chiefly responsible for oil formation under these conditions.

Diolefines were formed in low concentration during the oil-forming stage of the reaction, but decreased as the aromatics approached a maximum. The diolefines are generated from the olefines in the gas, and in turn are polymerized into aromatics. The pyrolysis was carried far enough to degrade the aromatics. Tar increased in amount with protracted heating, and diolefines and toluene were destroyed, leaving the more stable benzene. Carbon formation became rapid when tar of high molecular weight had been formed in large amount. Carbon formation in pyrolysis is nearly always due to decomposition of high molecular weight polymers of aromatic structure. Table II illustrates the course of the pyrolysis.

TABLE II

Composition of Volatile Oils from Butane at 850° C

Heating time, sec.	0.09	0.9	2.4	3.9	7.2
Vol. ratio exit gaseous products to inlet gas	2.0	1.9	2.1	2.3	2.4
Yields, weight per cent					
Volatile oils	3.0	10.5	15.5	16.0	17.0
Tar	0.0	5.0	9.5	11.0	17.0
C				0.2	1.7
Analyses of gaseous products, per cent by volume					
CO_2	0.0	0.0	No analysis	0.7	0.1
CO	0.0	0.5		2.1	0.5
H_2	10.0	16.7		16.6	28.1
CH_4	23.1	48.4		57.4	60.0
C_2H_6	4.2				
C_2H_4	25.5				
C_3H_6	16.9				
C_3H_8	0.0				
C_4H_8	4.4				
C_4H_{10}	15.9				
Unsaturateds		34.4		23.2	11.3
Total	100.0	100.0		100.0	100.0
Analyses of volatile oils, weight per cent					
Propylene		3	0.9	0.7	1.9
Butenes		5	5	3	
Butadiene		4			
Pentenes		1	4	2.5	
Cyclopentadiene		6			
Hexadienes		1	0.3	0.5	
Benzene		61.1	74.8	82.8	92·0
Intermediate		0.9	1.0	1.0	0.3
Toluene		9.85	12.0	9.5	5.8
Intermediate		0.15	0.0	0.0	0.0
Xylenes plus styrene		8	(2)		
Total		100.00	100.0	100.0	100.0

The complexity of the reactions is brought out by the variety of diolefines formed, nearly all of which were of the 1,3 type. Butadiene, 1,3-pentadiene, isoprene, 1,4-pentadiene, cyclopentadiene, methylcyclopentadiene, and fulvenes were isolated. Of the mono-olefines, only isobutylene and trimethylethylene were present in significant amount. All these have in common the absence of the —C—C—C— structure, except 1,4-pentadiene, and to this their thermal stability can be ascribed.

The sequence of reactions can be represented as follows:

$$\text{Butane} \rightarrow \text{olefines} \rightarrow \text{diolefines}$$
$$\rightarrow \text{benzene and toluene} \rightarrow \text{tar}$$

The formation of benzene has been ascribed to the union of butadiene with ethylene $C_2H_4 + C_4H_6 \rightarrow C_6H_6 + H_2$, but the identity of intermediate molecules formed in the synthesis of aromatics is obscure. The experiments of Frolich [56, 1931] support such an explanation. A mixture of butadiene and ethylene was pyrolysed and benzene produced. A hydrocarbon with the formula C_8H_8 was identified which may have been an intermediate in the formation of benzene.

The heat of reaction throughout the pyrolysis was computed from the analyses of the products and their known heats of formation. The decomposition to olefines is strongly endothermic, but the subsequent oil-forming stage of the reaction is somewhat exothermic. In large-scale experiments butane was cracked in a tube coil to a maximum olefine content and passed into an insulated reaction chamber wherein the oil-forming reactions took place with a temperature rise of as much as 100° C.

While the temperature level of pyrolysis influences the products obtained, the pyrolysis may often be made to yield a given result over a rather wide temperature range if the same extent of reaction is obtained by decreasing the time to compensate an increase in temperature. The range is particularly wide for the production of aromatics. Butane and propane were converted into aromatic oils in virtually constant yield at from 700 to 1,500° C. with appropriate reaction times ranging from 240 to 0.012 sec. At acetylene-forming temperatures of 1,200° C. and higher, aromatics are produced by prolonging the reaction to allow acetylene and ethylene polymerization to take place, and, at the other extreme, a protracted polymerization of olefines will yield aromatics at 500° C.

Pyrolysis of Methane

While methane is the simplest and most abundant of the gaseous hydrocarbons, its thermal stability is so great that its pyrolysis largely involves the secondary reactions which have been discussed. Decomposition is extremely slow below 900° C. Early investigators found only carbon and hydrogen to result from methane pyrolysis, but recent investigations show carbon to be the end product of a series of rapid reactions which follow closely the primary decomposition. By heating methane to 1,700° C. by a carbon filament in a glass bulb surrounded by liquid oxygen to condense the products, Storch [60, 1932] has found ethane and hydrogen to be formed almost exclusively. Kassel [34, 1932] suggested the reaction mechanism

$$CH_4 \rightarrow CH_2 + H_2$$
$$CH_4 + CH_2 \rightarrow C_2H_6$$

The formation of CH_3 radicals which unite to form ethane has also been suggested.

By passing methane rapidly through a heated tube at 950–1,250° C. ethylene predominates when decomposition is limited, but is accompanied by increasing amounts of acetylene when heating is more protracted, indicating a sequence of reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + 2H_2$$

As reaction is further prolonged, light aromatic oils and tar are formed as rapidly as ethylene and acetylene are generated, the concentration of ethylene plus acetylene reaching only 3 8% by volume at atmospheric pressure and 1,200° C [57, 1931] Carbon began to form rapidly, presumably from the tar, by the time 27% of the methane was decomposed with a reaction time of 0 2 sec, and a maximum of 6% by weight of light oils was developed

Both higher temperatures and lower pressures favour the development of higher concentrations of acetylene while increased pressure decreases the formation of hydrocarbon products Dilution with hydrogen or carbon dioxide as well as reduced pressure increase acetylene formation and, to preserve the acetylene formed, rapid cooling from the reaction temperature is necessary

Pyrolysis under Pressure

Pyrolysis of gaseous hydrocarbons at low pressures and temperatures much below 600° C has received a limited amount of attention because of the inconveniently long reaction times required to carry pyrolysis past the primary stages At high pressures, however, the polymerization of olefines is accelerated and rapid reaction even below 400 C may be obtained Ethylene, propylene, and the butylenes polymerize, ethylene somewhat more readily than the others, to form polymers which, in the initial stages may be largely normally liquid mono-olefines of low molecular weight As the reaction continues, polymers of higher molecular weight make their appearance, and finally tar The liquid products of an extensive conversion contain paraffins, olefines, naphthenes, and also aromatics

The pyrolysis of gaseous paraffins, particularly propane and the butanes, under pressure leads to the formation of hydrocarbons of higher molecular weight resembling the polymers from olefines The primary dissociation into simpler paraffins and olefines proceeds in much the same way as at low pressures However, the olefines are generated at a high partial pressure before primary decomposition is very extensive and their polymerization begins, the cracking and polymerizing then proceeding concurrently As reaction proceeds, tar formation sets in and finally carbon is produced, while the decomposition of the original paraffin may be far from complete Butane and propane may be converted into volatile normally liquid hydrocarbons, largely non-aromatic, by pyrolysing under pressures of 100 atm or more, lower hydrocarbons, chiefly methane and ethane, being produced at the same time

Catalytic Conversion

The use of catalytic materials for effecting pyrolytic reactions has been extensively investigated, but in many cases the part played by the catalyst is difficult to distinguish, though it has been shown that many metals, non-metals, oxides, and salts exert catalytic action A few cases may be singled out in which the course taken by the pyrolysis is definitely due to the catalyst

The gaseous paraffins and olefines in the presence of nickel, cobalt, and iron are converted into carbon and hydrogen, and when the reaction temperature is not too high methane is also formed from any of the higher hydrocarbons Hydrocarbons formed intermediately in the course of the reaction are rapidly degraded to these end products Finely divided nickel is the most active of these catalysts and has been found to convert propane into carbon and methane at 200° C [14, 1928]

Paraffins (except methane) can be dehydrogenated to the corresponding olefines and hydrogen according to the reaction

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$$

by chromium oxide gel, activated charcoal, zinc chromium alloy, and certain other catalysts By means of chromium oxide catalyst, ethane, propane, *n*-butane, and iso-butane have been dehydrogenated at atmospheric pressure and 350° C and above to produce the corresponding olefines plus hydrogen with little interference from side reaction, *n*-butane producing all three of the isomeric butenes [13, 1928] Below this temperature little dissociation is thermodynamically possible, but equilibrium for the hydrogenation-dehydrogenation reaction may be attained at 350–450° C At 400° C and atmospheric pressure ethane, propane, *n*-butane, and iso-butane are dehydrogenated at equilibrium to the extent of 1 2, 4 5, 8 5, and 9 5 % respectively The dissociation increases with temperature

The catalytic decomposition of paraffins with fracture of the carbon chain to produce olefines and paraffins of lower molecular weight appears to be brought about by many substances, notably aluminium oxide and aluminium chloride, but concurrent homogeneous reaction has usually made it difficult to determine what role to ascribe to the catalyst Aluminium oxide also effects rearrangement of olefines

Olefines can be induced to polymerize by means of catalysts at very low temperatures Aluminium chloride, boron fluoride, and fuller's earth bring about polymerization of propylene and the butylenes at ordinary temperatures and below Polymers of high molecular weight are formed and synthetic lubricating oils may be produced Under suitable conditions low molecular weight polymers of gasoline boiling-range may be the chief products At 250–300° C phosphoric acid catalyst [29, 1935] and anhydrous silica impregnated with alumina [17, 1933] produce polymers boiling in the gasoline range The simple union of 2, 3, and more olefine molecules has been shown to predominate in some cases, but this is not always the only reaction taking place Polymer molecules of intermediate molecular weight may also result In the polymerization of propylene by silica impregnated with alumina, Gayer [17,1933] has reported the formation of 5, 7, and 8 carbon-atom molecules as well as those of 6 and 9, which represent the dimer and trimer of propylene

Dissociation of olefines into olefines of lower molecular weight has been effected catalytically Di-iso-butylene was dissociated into iso-butylene by fuller's earth at 300° C [35, 1930], and with a catalyst of this type the equilibrium for the reaction iso-butylene ⇌ di-iso-butylene can be approached from both sides

At the present time the use of catalysts in pyrolytic reactions is under active investigation, and a clearer understanding of the catalytic conversion of hydrocarbons can be expected to result

Paraffin-Olefine Union

The direct union of olefines with paraffins to produce paraffins of higher molecular weight has been effected catalytically as well as thermally The union of iso-butane and iso-butylene, for example, has been effected by a catalyst consisting of boron fluoride and nickel, water being present.

Aluminium chloride is also an effective catalyst The reaction takes place at elevated pressures in the absence of a catalyst and occurs extensively in the thermal conversion under pressure of propane and butane into higher boiling hydrocarbons, the olefines formed by pyrolysis uniting with unreacted paraffin

Applications of Pyrolysis

Up to the time of the World War there was little incentive for applying industrially the pyrolysis of gaseous hydrocarbons The war created a demand for benzene and toluene which brought about a study of their production by pyrolysis of oils as well as hydrocarbon gases Interest in benzene and toluene declined with the termination of the War, but the manufacture of chemical derivatives from hydrocarbon gases received an impetus from chemical warfare activities and has developed into an important and diversified industry Alcohols, ethers, acids, esters, resins, rubber-like materials, and many other products are made from light unsaturated hydrocarbons, sometimes produced by gas pyrolysis Carbon black, hydrogen, and benzol are produced directly by pyrolysis

During the past decade gas pyrolysis has engaged the interest of the petroleum industry, and developments within the industry have stimulated research of a fundamental type, improved experimental technique has been brought to bear, and as a result a more intimate understanding of the chemistry of pyrolysis has developed Of chief interest to the industry is the conversion of gases into gasoline and lubricating oils Refinery gases have been produced in increasing amount with a more extensive use of oil cracking, and cracking-still gases together with natural gas constitute a raw material for conversion into gasoline

Gasoline

Methane is the most abundant of the gaseous hydrocarbons, but it is difficult to pyrolyse, and the higher paraffins and olefines have received most attention in the United States as a potential source of gasoline The conversion of methane has been studied extensively in Europe By pyrolysis a conversion into acetylene and ethylene can be effected which may be subsequently polymerized into gasoline with the aid of a catalyst By interaction with steam, methane may be converted into oxides of carbon and hydrogen which can be converted catalytically by the method of Fischer and Tropsch into liquid and solid hydrocarbons [7, 1926]

The olefines lend themselves most readily to conversion into gasoline because they polymerize directly under heat and pressure into normally liquid hydrocarbons boiling in the gasoline range Pressures in excess of 500 lb per sq in are usually recommended Wagner [66, 1935] converts olefine-containing gases resulting from oil cracking by passing the gases under pressure through a tube coil in which the temperature is raised, then passing the gases through a reaction chamber in which polymerization takes place Heat is evolved and the reaction is controlled by extracting heat within the reaction chamber housing After the reaction the gasoline is separated from the effluents by fractionation and unconverted olefines may be returned to the tube coil Gasoline yields of 2 9 and 8 1 g p m (gallons per thousand cubic feet) are reported for gases containing 45 and 69 vol % olefines Many other process modifications have been described for conducting the polymerization The reaction may be conducted in two or more steps with intermediate separation of polymers [8, 1932, 46, 1933–5], the reaction heat may be extracted by indirect heat exchange [46, 1933–5, 68, 1934], or heat extraction may be avoided by a suitably low inlet temperature of the hydrocarbons entering the reaction zone [8, 1932]

With the aid of catalysts polymerization may be brought about at a lower temperature and pressure Ipatieff and Egloff [29, 1935] use a solid phosphoric acid catalyst for producing gasoline from cracking-still gases A temperature of 245° C (473° F) and a pressure of 160 lb per sq in are used Polymer yields of 3 8 and 8 4 g p m were obtained from two gases whose propylene plus butylene content was 27 and 37 5 vol % respectively 80–90 % of the polymer boiled in the gasoline range Many catalysts for the reaction have been mentioned in patent literature

Yields of gasoline from the polymerization of olefines are high The gasoline formed, after treating, is satisfactory with respect to gum formation and colour and has a high-blending octane number when incorporated in an average refinery gasoline

The paraffin hydrocarbons, ethane, propane, and the butanes, have been converted into gasoline by pyrolysing to produce simple olefines which may then be polymerized to gasoline

The conversion may be effected in a single reaction step by heating to a cracking temperature at an elevated pressure Youker [72, 1931] employs a pressure above 500 lb per sq in The effluents from the reaction are subjected to fractional distillation Gasoline is separated from the products, light gases are released, and normally gaseous hydrocarbons of intermediate molecular weight are returned to the reaction step Gasoline yields of 50% by weight may be obtained from butane with such recycling

The decomposing and polymerizing steps may be conducted separately under conditions appropriate for each and a catalyst may be used in either step Many modifications of a process of this type have been described

To obtain high yields of simple olefines, the decomposing step is preferably conducted at a high temperature and low pressure Sullivan *et al* [62, 1934] crack hydrocarbon gases, other than methane, at temperatures of 760–870° C (1,400–1,598° F) and pressures under 200 lb per sq in Wagner [68, 1934] prefers to crack natural gas at 1,250–1,350° F and 30 lb per sq in, separating therefrom aromatic oils formed, and then polymerizing in a tube coil at 500–950° F and 1,000 lb per sq in pressure Gasoline yields of 50% or more of the propane-butane fraction of natural gas are obtained

Hydrogen is produced in the cracking step, and may cause a reduction in gasoline yield in subsequent pressure polymerizing Frolich removes the hydrogen by causing it to reduce copper oxide [15, 1932] A gasoline yield of 4 26 g p m was obtained from propane by cracking at 800° C, adding 15% oxygen and passing over copper at 400° C to remove hydrogen, and polymerizing at 525° C. and 600 lb per sq in The yield of gasoline can be increased by using for the decomposition step a catalyst which effects dehydrogenation for converting paraffins into olefines, thereby decreasing the amount of hydrocarbon which is lost in the form of methane and ethane in simple uncatalysed cracking [16, 1934]. By separating the products of cracking and polymerizing into several fractions, those rich in olefines and in paraffins can be led to the polymerizing and cracking operations respectively [46, 1933–5].

Olefines produced by cracking paraffins may be concentrated prior to the polymerizing step Reid [49, 1933] eliminates hydrogen, methane, and undesirable high-boiling compounds by fractional distillation Plummer [46, 1933–5] prepares a high olefine charging stock by selectively extracting the olefines at 500–3,000 lb per sq in with the polymer liquid formed in the process

Since the conversion of gaseous hydrocarbons into gasoline involves synthesis reactions and the hydrocarbons which may form the starting-point are limited in number, it is possible to synthesize or build up a variety of motor fuels of special characteristics Iso-octane is an interesting example It is particularly suitable for use under the conditions existing in an aviation engine and gives a high power output in an engine of suitable design [71, 1935] It can be prepared by polymerizing iso-butylene, which occurs in cracking-still gases, to di-iso-butylene and hydrogenating the latter to the corresponding paraffin, 2,2,4-trimethylpentane or iso-octane Iso-octane is being manufactured for aviation use at the present time By hydrogenating polymer gasoline motor fuels of paraffinic characteristics and high anti-knock rating can be produced

Olefines and Diolefines

As a starting-point for the preparation of chemical derivatives the olefines, particularly ethylene, have been of first importance Cracking-still gases constitute a source of olefines, and ethane, propane, and the butanes can be pyrolysed to produce olefines under conditions which have been described Brooks [1, 1928] has stated that 'The cracking of butane is carried out industrially for the production of ethylene and propylene, which are used for the manufacture of somewhat more than 30 tons per day of the corresponding glycols and related compounds' Both the use of catalysts to produce olefines from paraffins and the use of favourable conditions for the non-catalytic pyrolysis have been considered Propane and butane yield chiefly ethylene when cracking is sufficiently drastic to decompose most of the higher olefines initially formed Baffles which improve turbulence in the heating tube increase the conversion [3, 1933–4] For the surfaces in contact with the gas, silicon, chromium, high chromium alloy, tin, copper, and other materials have been recommended to minimize carbon formation due to catalytic action

Olefines can be produced in a concentrated state from the products of cracking by selective absorption, fractional distillation, or through the formation of dissociable chemical complexes Chemical methods of purification can be used Ethylene has been concentrated by selective removal of the higher olefines with sulphuric acid of suitable strength, and sulphuric acid has been used to remove iso-butylene from a butylene mixture Diolefines can be removed by reaction with cuprous chloride, sulphur dioxide, and other reagents

Diolefines can be converted into rubber-like or resinous polymers Their production by hydrocarbon pyrolysis calls for the use of conditions somewhat less drastic than those necessary for the optimum conversion into aromatics, and low pressures which discourage their polymerization have been recommended Both chemical and physical methods of concentrating and purifying diolefines have been described

Benzene and Toluene.

The simple pyrolysis of gases at atmospheric and somewhat higher pressures to produce benzene and toluene represents the most direct type of conversion, and nearly all processes proposed are essentially various ways of conducting this pyrolysis which has been previously described The yield of benzene and toluene increases with molecular weight of the paraffin converted, methane yielding about 0 30 gal per thousand cubic feet, and butane about 3 0 by a once-through pyrolytic treatment Methane requires temperature somewhat above 950° C, and the higher paraffins and the olefines 700 to 950° C, for optimum conversion The weight per cent yields obtainable from the olefines are somewhat greater than those from butane Aromatic tar is always produced at the same time, usually in quantity of 50% or more of the light oils Toluene accompanied by low molecular weight polymers may be produced by pressure polymerization at 700° C [66, 1935]

The pyrolysis applied to gaseous hydrocarbons not predominantly methane may be carried out in a tube coil [47, 1930] The gas may be heated and subsequently pyrolysed in externally heated tubes [4, 1927, 1931–2, 1934] Preheated gases or products of combustion may be mixed with the gas prior to conversion to supply heat [19, 1932, 20, 1932] Steam may be added [30, 1934] The gas may be decomposed to a maximum unsaturateds content and passed into an unheated reaction chamber wherein the oil-forming reactions take place [9, 1932] The pyrolysis may be conducted intermittently by alternately heating a refractory-filled chamber by products of combustion and passing through the chamber the gas to be pyrolysed [48, 1930] The flow rate of the gas may be reduced as the temperature falls during the cracking cycle

Hydrogen decreases the yield of oils and may be removed from pyrolysed gases prior to further thermal treatment [69, 1928] The yield may also be increased by pyrolysing in two or more stages, separating oils after each stage [42, 1932] Gaseous olefines produced with the aromatic oils may be recycled The use of many catalytic materials has been proposed Their effectiveness is necessarily limited when carbon deposition takes place

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PYROLYSIS OF GASEOUS HYDROCARBONS

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As a preliminary to the detailed consideration of the various pyrolysis and polymerization processes now in operation or in a stage of advanced development, it is necessary to consider the chemistry of the reactions involved Comprehensive reviews on this subject are available, such as those prepared by Lomax, Dunstan, and Thole [42, 1917]—which covers the work published between 1809 and 1915, and by Egloff, Schaad, and Lowry [13, 1930–1], which deals with information made available over the same period and up to 1930 Further more recent reviews have been presented by Egloff and Wilson [14, 1935], Dunstan [9, 1936], Lawrence [38, 1935], Hague and Wheeler [24, 1929], and Travers [72, 1935]

The earlier investigations were very incomplete, whereas recently considerable work has been carried out in much detail There were many early investigators [49, 1792–1915] who were hampered by the lack of equipment which is at the disposal of the chemist of to-day, particularly analytical fractionating columns, improved analytical apparatus, and new materials for apparatus, by means of which it is now possible to obtain more complete data In considering the reported results, more consideration must be given to those completed in the last few years, because of the more accurate nature of the work involved

Much confusion has been caused in this field of scientific investigation by the publication of many apparently contradictory results, the error in which lay in a lack of complete understanding of the interdependence of the large number of variables involved One of the most difficult features in making a critical study is the correlation of data under different reaction temperatures and different contact times The effect of time of reaction is largely responsible not only for the observed extent of decomposition, but also for the character of the products obtained Unfortunately, this fact was not realized as being of more than minor importance until a few years ago In the thermal reactions of gaseous hydrocarbons it appears to be a fact that they are all unstable with respect to their elements Although the ultimate products of decomposition are in each case carbon and hydrogen, it is the mechanism of the reactions involved which is of theoretical interest, whereby, as the reaction progresses, many more stable products are continuously being formed from less stable ones Since each investigator has been interested in, at most, only a few of the particular stages of this process, contradictory results have been obtained because of the large number of variables involved It is therefore necessary, in correlating the results of various investigators, to pay full attention to the effects of such variables

The Thermal Reactions of the Gaseous Paraffins

The differences in behaviour of the individual paraffin hydrocarbons towards heat have been studied to some degree, but not intensively. Hague and Wheeler [24, 1929] found that among the normal members of the series, from methane to hexane, the stability decreased with increasing molecular weight, and gave the following decomposition temperatures as obtained in static experiments in electrically heated silica bulbs at atmospheric pressure, and as indicated by the first evidence of pressure increase

Methane	683° C
Ethane	485° C
Propane	460° C
n-Butane	435° C

Bone and Coward [4, 1908] also found that methane is more stable than ethane, while Francis [17, 1928] concluded, on thermodynamic grounds, that 'only the paraffins and the higher olefines have any thermodynamic stability whatever, and above 260° C, methane is the only stable hydrocarbon' Similarly it has been calculated, on the basis of the Nernst heat theorem, that methane should be the most stable of the paraffin series [76, 1907]

Methane.

Since methane is the simplest of the paraffin hydrocarbons and the one which is available commercially in largest amount, it is not surprising that the thermal reactions of this hydrocarbon have been the subject of more thorough study than has the breakdown of any other member of the paraffin series On the other hand, due to the relative stability of methane and the high temperatures necessary for its degradation, very little advance has been made commercially in the production of liquid hydrocarbons from methane by pyrolysis processes

The temperature at which methane starts to decompose on heating varies with the experimental conditions In contact with substances possessing little or no catalytic action, methane has been reported to undergo change at between 650 and 700° C Catalysts markedly reduce this temperature In the presence of palladium, decomposition occurs at 250° C, with nickel at 320° C, and with iron at 350° C

The decomposition of methane into carbon and hydrogen is an equilibrium reaction, 90% conversion being realized at 750° C and 50% conversion at 525° C Except in the presence of catalysts which favour this decomposition to the elements, however, breakdown is accompanied by the formation of hydrocarbons of higher molecular weight These products include ethane and the olefines propylene and ethylene, along with butadiene and acetylene By careful regulation of the conditions of pyrolysis—i e temperature, catalysts, time of heating, &c —small amounts of aromatic hydrocarbons are also produced, such as benzene, toluene, xylene, naphthalene, and anthracene

The present considerations of the thermal reactions of methane may be divided into two points

(*a*) Studies of the methane-carbon-hydrogen equilibrium, and investigations carried out on the production of carbon and hydrogen

(*b*) Work done on the production of higher hydrocarbons —both gaseous and liquid.

The Methane Equilibrium. The decomposition of methane into its elements according to the equation

$$CH_4 \rightleftharpoons C+2H_2$$

is a reversible, true equilibrium reaction This was first demonstrated by Mayer and Altmayer [46, 1907, 1909], who investigated the equilibrium from both directions at atmospheric pressure and at varying temperatures, with nickel, cobalt, and iron as catalysts. Their equilibrium values were as follows.

TABLE I

Methane Equilibrium (Mayer and Altmayer)

Temp, ° *C*	CH_4 %	H_2 %
300	96.90	3.10
400	86.16	13.84
500	62.53	37.47
600	31.68	68.32
650	19.03	80.97
700	11.07	88.93
750	6.08	93.92
800	4.41	95.59
850	1.59	98.41

This reaction, being endothermic, is favoured by the use of high temperatures.

During 1910–12 Pring and Fairlie [56] investigated the synthesis of methane from its elements and found that the velocity of formation of methane increased at elevated pressures when carbon was used in a compact state, either with or without a catalyst, and that equilibrium conditions were reached in about 2 hours at 1,200–1,300° C under 30–50 atm pressure. All experiments at 10–200 atm gave the same values for the equilibrium constant at the same temperature, when the same modification of carbon was used. At atmospheric pressure the amount of methane in equilibrium with hydrogen and graphite was 0.24% at 1,200° C and 0.07% at 1,500° C. For amorphous carbon 'metastable equilibrium' values of 0.36% methane at 1,200° C and 0.21% at 1,500° C were obtained, but these were less definite than those for graphite due to the gradual change of amorphous carbon to graphite at the temperatures employed.

Cantelo [5, 1924] investigated the methane equilibrium in 1924–6 along lines previously employed by Mayer and Altmayer. Using the Nernst approximation formula, Cantelo calculated the equilibrium constant, K_p, and the equilibrium concentrations of hydrogen and methane, and obtained the following figures.

TABLE II

Methane Equilibrium. Calculated Values of Equilibrium Constant and Equilibrium Concentrations (Cantelo)

Temp ° *C*	$K_p = \frac{p_{CH_4}}{p^2_{H_2}}$	*Methane* %	*Hydrogen* %
600	0.077	6.9	93.1
650	0.039	3.5	96.5
700	0.021	2.0	98.0
750	0.012	1.0	99.0
800	0.007	0.5	99.5
850	0·003	0·4	99.6
900	0.003	0.4	99.6
1,000	0.0015	0.2	99.8

Cantelo failed to realize these values experimentally. About the same time (1924), Saunders [61] developed the following equations for the methane equilibrium from the Nernst heat theorem, and demonstrated that the results calculated from these equations agreed with the experimental data of Mayer and Altmayer, and of Pring and Fairlie.

1. $\log K_p = \frac{4{,}538}{T} - 1.75 \log T + 0.000630T - 0.7$ (For amorphous carbon.)

2. $\log K_p = \frac{4{,}008}{T} - 1.75 \log T + 0.000630T - 0.7$. (For graphite.)

The dissociation equilibrium of methane at atmospheric pressure and at temperatures between 480 and 680° C was examined by Scheffer, Dokkum, and Al [63, 1926], by circulating methane and hydrogen separately through a heated porcelain tube containing a layer of asbestos impregnated with nickel and covered with active carbon by a preliminary decomposition of methane or ethylene. The results obtained, when plotted, did not conform to the equation developed by Scheffer [62, 1913, 1916], and indicated, not only the expected dissociation, but also a second equilibrium previously unknown. The Scheffer equation is

$$\log K_p = -\frac{A'}{T} + B',$$

in which A' represents heat of reaction and B' is a constant nearly equal to the entropy at unit partial pressure. Scheffer postulated that the second equilibrium involved the formation of a nickel carbide capable of combining with hydrogen to produce methane. They thus assumed two simultaneous reactions

$$C + 2H_2 = CH_4 + 18.8 \text{ cal (constant pressure)}$$

and $$Ni_xC + 2H_2 = xNi + CH_4 + 11.4 \text{ cal (constant pressure)}$$

Experimental data supporting these equations were summarized by the equations

1. *Methane equilibrium* $\log K_p = \frac{4108}{T} - 4.924$

2. *Carbide equilibrium* $\log K_p = \frac{2492}{T} - 2.589$

Nickel carbide was found to be stable up to 420° C. On the basis of these equations, calculation of the degree of dissociation of methane at atmospheric pressure in the presence of nickel gave the values reproduced in Table III. Methane decomposition in the presence of iron was studied by Schenck, Krageloh, Eisenstecken, and Klas [64, 1926–7] at temperatures ranging from 300 to 900° C, and the following reactions investigated:

(1) $CH_4 = C + 2H_2$

(2) $CH_4 + 3Fe = Fe_3C + 2H_2$

TABLE III

Methane Equilibrium in the Presence of Nickel (Scheffer, Dokkum, and Al)

$C + 2H_4 \rightleftharpoons CH_4$

Concentrations calculated from equations for K_p

Temp ° *C*	H_2%	CH_4%	*Temp* ° *C*	H_4%	CH_4%
350*	13.6	86.4	700	85.5	14.5
400*	22.6	77.4	800*	93.0	7.0
450	34.0	66.0	900*	96.5	3.5
500	46.6	53.4	1,000*	98.1	1.9
550	59.2	40.8	1,100*	89.9	1.1
600	70.2	29.8	1,200*	99.3	0.7
650	79.0	21·0			

* Extrapolated value

$Ni_xC + 2H_2 \rightleftharpoons xNi + CH_4$

Temp ° *C*	H_4%	CH_4%	*Temp* ° *C*	H_4%	CH_4%
350	17.9	82.1	550	44.8	55.2
400	24.2	75.8	600	51.3	48.7
450	30.9	69.1	650	57·4	42.6
500	37.9	62.1			

To facilitate reaction the iron was deposited on porous pieces of pumice. The iron carbide was prepared by the action of methane on iron at 700° C The progress of the reactions was followed by measurement of pressure difference developed in the reaction tube at different temperatures In the presence of iron at 302° C no methane was decomposed At 350° C about 1% by volume of methane was decomposed, and iron carbide could be detected, at 445° C the decomposition amounted to about 4 4% by volume The fact that the same proportions of hydrogen and methane were obtained by passing pure hydrogen over iron carbide, as were formed when methane was passed over iron, proved the existence of a true equilibrium in the second reaction The percentages of methane decomposed, according to these two reactions, are included in the data given in Fig 1 Schenck, Krageloh, and Eisenstecken [65, 1927] investigated the methane-hydrogen equilibrium in the presence of cobalt over the temperature range 310 to 740° C At low temperatures a secondary equilibrium involving cobalt carbide was found, but above 680° C this reaction was no longer encountered The data obtained are plotted in Fig 1

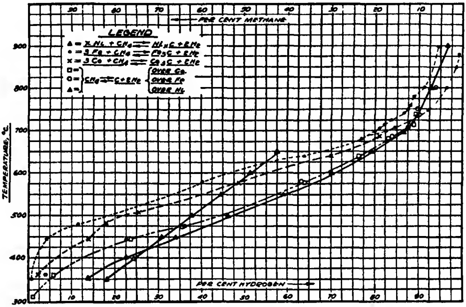


FIG 1 Methane equilibria in the presence of cobalt, iron, and nickel

In the absence of catalysts some investigators have found the methane equilibrium difficult, if not impossible, to obtain Hollıday and Exell [25, 1929] observed that the decomposition of methane in silica and porcelain bulbs at temperatures between 900 and 1,200° C is at first rapid, but later becomes so strongly retarded that, for all practical purposes, a condition of false equilibrium, far removed from the theoretical, is set up These workers suggested that the retardation of the decomposition of methane 'is almost certainly due to the preferential absorption of methane by silica, which finally protects the surface so efficiently that further decomposition of methane is practically prevented' At 900° C, in the presence of a nickel catalyst, no retardation took place Only 3% of methane remained after 18 minutes' heating, showing that under these conditions equilibrium was rapidly approached

In Fig 2 are summarized the values for the methane equilibrium obtained by the various workers mentioned above The agreement is seen to be good

Investigations carried out with the Prime Object of producing Carbon and Hydrogen from Methane. Because of the small yields of carbon black, usually not over 2 lb per 1,000 cu ft, obtained in the usual method of manufacture by the incomplete combustion of natural gas, investigators have studied the thermal decomposition of this gas, and of pure methane, in the hopes of getting increased yields of carbon At the same time the great increase in recent years in the demand for hydrogen, due to the success achieved in the high-pressure synthesis of ammonia and methanol and in the destructive hydrogenation of coal and oils, has been a further incentive to study the decomposition of methane into its elements

With regard to carbon production, it is theoretically possible to produce from methane 75% by weight of carbon or 31 6 lb per 1,000 cu ft (measured at N T P), but these yields are not obtained in practice, due to side reactions leading to the production of higher hydrocarbons Yields as high as 13 5 lb per 1,000 cu ft of natural gas have been reported, while a commercial process (Thermatomic) produces 7 lb per 1,000 ft when handling a natural gas containing 94% methane Yield is not the only consideration in this type of process, however, as carbon blacks vary greatly in quality High temperatures, in general, cause the production of hard, graphitic carbon of low value, while that produced at low temperatures is far superior To lower the temperature of decomposition, as well as to direct the reaction towards carbon and hydrogen, instead of towards the production of higher hydrocarbons, catalysts have been employed in most of the experimental studies made, a detailed account of which is given by Egloff and his associates [13, 1930–2]

The Thermatomic Process Undoubtedly, the most important of the methods developed for making carbon black by thermal decomposition is the so-called Thermatomic process [60, 1935], the basic ideas of which have been described by Brownlee and Uhlinger in a series of patents [74] The process consists in heating a furnace, lined with refractory brick and filled with chequer brick, to incandescence by an upward blast of natural gas and air, shutting off the air and allowing the natural gas (admitted from the top at this stage) to decompose The heating and cracking processes are carried out alternately Approximately two-thirds of the total quantity of carbon black produced is formed by impingement against the refractory material, or comes into contact with it after formation Such carbon is valueless commercially and is left in the furnace to be consumed in the next air blow It has been stated [75] that the most desirable operating temperature for the decomposition reaction is 1,200–1,400° C , and the mixture of hydrocarbon and resulting gases, together with the carbon produced, is subjected to these temperatures for a period of 3–4 sec only

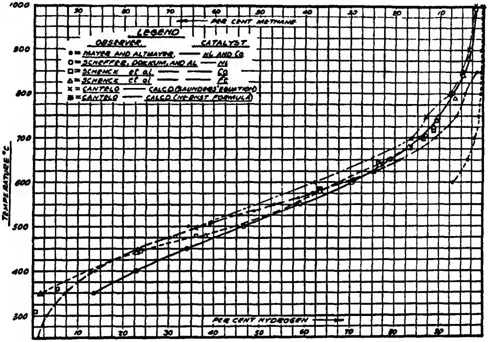


FIG 2 The methane equilibrium $CH_4 \rightleftharpoons C + 2H_2$ (comparison of observed and calculated values)

On issuing rapidly from the furnace, the mixture of gases and carbon is passed through a cooling chamber, where just enough water is sprayed counter-current to the gas stream to cool it to a safe temperature for filtering through cloth bags without leaving an excess to wet either the bags or the carbon Analyses of the natural gas treated and the resultant gas have been given as follows [60, 1935]

	Natural gas	*Resultant gas*
Carbon dioxide	0 4	0 9
Illuminants	0 7	1 3
Hydrogen		85 4
Carbon monoxide		1 1
Methane	93 8	5 0
Nitrogen	5 1	6 3

The process has been producing the carbon called 'Thermax' since 1922 Another brand, called 'P 33', which is blacker and finer than 'Thermax' and was put on the market later, is made in the same way as 'Thermax', except that a portion of the resulting gas is recirculated and acts as a diluent for the decomposing natural gas This dilution principle is so effective that it reduces the average particle size to about one-fifth that of 'Thermax' Typical properties of these two carbons are as follows [60, 1935]

	'Thermax'	*'P 33'*
Specific gravity	1 80	1 80
Apparent gravity (kg /m ³)	481 5	356 1
Tinting strength*	14%	50%
Average particle size	1 0 micron	0 23 micron
Moisture	0 25%	0 25%
Ash	0 05%	0 15%
Benzene extract	0 60%	1 25%

* As compared with Cabot s channel black

The Production of Higher Hydrocarbons from Methane. It has already been mentioned that, by appropriate choice of temperature and reaction time conditions, it is possible to convert methane partly into higher hydrocarbons ranging from ethane to naphthalene and anthracene Among the gaseous hydrocarbons formed are the olefines ethylene and propylene, and also butadiene Acetylene is also an important reaction product, but this is formed mainly at high temperatures—such as those existing in the electric arc

In a number of publications which appeared during the period 1862–9 Berthelot [2] reported that decomposition of methane in sealed glass tubes yielded propylene, benzene, and naphthalene, although most of the methane remained undecomposed In 1892 Lewes [41] observed the formation of acetylene, some benzene, and other unsaturated hydrocarbons from methane by heating in a platinum tube at 1,000° C., and concluded, with Berthelot (loc cit), that benzene was formed by the polymerization of acetylene.

During the last few years the investigation of the conversion of methane into higher hydrocarbons, particularly aromatic hydrocarbons, has been particularly active Studies have been made independently in England, United States, and Germany

In 1927 Williamson [83, 1928] mentioned that valuable liquid hydrocarbons, particularly benzene, were being produced in a semi-commercial plant of the Anglo-Iranian Oil Company, and mentioned yields of 0 22 imp gal of benzene per 1,000 cu ft of gas containing 80% methane At the same time Fischer [16, 1928] was also investigating the production of higher hydrocarbons from methane in an endeavour to increase the small yields reported by previous workers Experiments in 16-mm diameter porcelain tubes at temperatures between 900 and 1,150° C on a gas containing 93% methane and 1 8% higher hydrocarbons showed that, under these conditions, heavier gaseous hydrocarbons and oils could be produced in small yield if the time of reaction was sufficiently low to prevent the formation of carbon and hydrogen Fischer also used quartz capillary heating tubes of 3 mm I D, and he proved that at 1,130° C quartz does not accelerate the decomposition of methane into its elements With these tubes the yield of light oil and tar reached 12% by weight of the methane treated

With the intention of keeping the reaction temperature as low as possible and so reduce carbon production, Fischer also investigated the influence of different catalysts Thin iron and molybdenum wires within small porcelain tubes had no effect Caustic soda in an iron boat in the reaction tube at 1,000° C produced a gas containing 56% hydrogen, and large quantities of carbon were found, but no oil or tar If the methane was diluted with carbon monoxide, carbon dioxide, or nitrogen, the temperature required for the same degree of decomposition was higher than that necessary when the undiluted methane was used Fischer examined the oils formed from methane in some detail and found that the fraction of the light oil boiling up to 55° C (7 8%) consisted mainly of unsaturated hydrocarbons A second fraction, b p 55–85° C, was largely benzene, while toluene, xylenes, naphthalene, and anthracene were identified in the higher boiling fractions The treated gas contained acetylene besides hydrogen and unreacted methane

According to Fischer, his experiments 'confirmed the supposition that for the production of higher hydrocarbons by the thermal decomposition of methane, the duration of the heating is of just as great importance as the temperature If the duration of heating exceeds 60 seconds, there is usually time enough to separate all the hydrogen from the methane molecule' Fischer also found that the use of catalysts is not desirable if carbon deposition is to be prevented

Wheeler [79, 1928] claimed priority over Fischer in the production of higher hydrocarbons, particularly aromatics, by the thermal treatment of methane

Static experiments in which methane initially at 400 mm pressure was heated at various temperatures in a small quartz bulb showed that the initial decomposition point of the gas was between 650 and 685° C Pressure changes in the reaction bulb at 700°, 800°, and 900°, indicated an abnormally rapid rate of decomposition during the first 10 minutes, followed by a period of nearly constant speed

Experiments in which methane was circulated in a closed system through a glass tube at 900 and 950° C, and the course of decomposition followed by pressure changes, gave time-pressure curves similar to those during the static experiments At 950° C liquid products were formed during the first few minutes of heating, and later, crystals of napthalene were deposited in the cooled condensers

Liquid hydrocarbons were formed during the passage of methane at rates of 2 to 60 litres per hour through a quartz tube 130 cm × 3 cm held at temperatures higher than 875° C Benzene was an important product of pyrolysis between 875 and 1,100° C By bromination the gaseous products of combustion at 950° C were shown to contain ethylene and butadiene The liquids of higher boiling-point contained naphthalene and anthracene The optimum temperature for the production of benzene was 1,050° C under the conditions employed Dilution of the methane with nitrogen had only a slight effect on the yield of aromatic hydrocarbons at 1,000° C, but the yields were decreased by the presence of hydrogen in the gas entering the reaction tube

Stanley and Nash [68, 1929] have also published valuable data on the production of higher hydrocarbons from methane These investigators found that at any given temperature the proportion of methane converted into higher hydrocarbons increased rapidly to a maximum with increasing gas rate As the gas rate was further increased there was a decrease in the production of higher hydrocarbons, at first rapid and later more gradual An increase in the temperature caused an increase in the gas velocity at which the maximum production of hydrocarbons occurred The ratio of the acetylene/ethylene content of the exit gas increased with increase in gas velocity for a given reaction temperature, reached a maximum (which appeared to coincide with the conditions for the maximum yield of light oil and tar), and then decreased rapidly Accumulation of carbon in the reaction tube caused a decrease in the yield of higher hydrocarbons The best yields of higher hydrocarbons were obtained at 1,150° C, with a heating period of 0 6 sec Under these conditions the yield of light oil and tar was 11% calculated on the methane used, whilst the quantities of acetylene and ethylene in the reaction gas corresponded with a total conversion of methane into these gases of 8 8% Thus the total conversion of methane into higher hydrocarbons was nearly 20% of the theoretical, while only about 6% of the methane was decomposed into its elements The yield of light oil was 4 8% or 0 2 gal per 1,000 cu ft of methane treated

Similar results have been obtained by Hague and Wheeler [24, 1929], Vysoky [77, 1929], and Chamberlin and Bloom [6, 1929]

A detailed account of work carried out by the United States Bureau of Mines on the production of motor fuels by the pyrolysis of methane has been published by Smith, Grandone, and Rall [67, 1931]

Mechanism of Higher Hydrocarbon Production from Methane by Pyrolysis. Considerable doubt is involved in definitely establishing whether, in the decomposition of methane, a hydrogen atom or a hydrogen molecule splits off in the primary step, and a decision on the exact mechanism of breakdown must await further evidence Kassel [35, 1932] has suggested that a molecule of hydrogen splits off, and the methylene radical formed unites with a methane molecule to give ethane The whole kinetics of the methane decomposition was accounted for by the further decomposition into ethylene, acetylene, carbon, and hydrogen

Kassel

$$CH_4 \rightarrow CH_2 + H_2$$
$$CH_2 + CH_4 \rightarrow C_2H_6$$
$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_2H_4 \rightarrow C_2H_2 + H_2$$
$$C_2H_2 \rightarrow 2C + H_2$$

Rice

$$CH_4 \rightarrow CH_3 + H$$
$$H + CH_4 \rightarrow CH_3 + H_2$$

On the other hand, Rice and Dooley [59, 1934] obtained only di-methyl-tellurium in the Paneth experiments with methane at 1,150–1,200° C, and therefore favoured the primary decomposition into a hydrogen atom and a methyl radical In these experiments atomic hydrogen was not identified, and Rice concluded therefore that the atomic hydrogen united with another hydrogen atom on the walls of the reaction bulb, or with a methane molecule to give molecular hydrogen and a methyl radical Assuming a chain mechanism due to methyl radicals, Kassel [36, 1935] has shown by calculation that, with the assumptions made by Rice, the concentration of the hydrogen atom must be greater than 10^4 times the concentration of methyl radicals, and it does not seem possible that such a factor could be overcome by a wall recombination of atomic hydrogen This calculation is further negative evidence against the primary decomposition of methane into a methyl radical and atomic hydrogen Furthermore, since the methylene radical was not identified over the same temperature range in the decomposition of diazomethane where the concentration of methane must be lower than in the decomposition of methane, and therefore the concentration of methylene radicals higher, it does not follow that the methylene should be identified in the decomposition of methane At these high temperatures the rate of reaction of methylene radicals and methane may be so much greater than the rate of reaction for methylene radicals and tellurium that the latter does not occur Whatever the primary mechanism of the decomposition of methane may be, ethane, ethylene, and acetylene are important secondary products

The mechanism suggested by Kassel accounts satisfactorily for the results obtained by Storch [69, 1932] on the decomposition of methane by carbon filaments The latter observed ethane to be the earliest product of the decomposition From the decomposition in a carbon filament lamp immersed in liquid nitrogen as much as 95% of the theoretical yield of ethane was obtained

Ethane.

As already stated, ethane occupies a position between methane and propane with regard to ease of thermal breakdown, and in the absence of catalysts it starts to decompose at about 485° C, although the reaction is not appreciable below 650° C Until temperatures several hundred degrees above the initial decomposition temperature are reached, the major reaction involved is dehydrogenation to ethylene and hydrogen—although reactions resulting in the production of carbon, methane, acetylene, and aromatic hydrocarbons take place to small extents

Berthelot [2, 1862–1901] considered that ethane on decomposition gave either ethylene and hydrogen, or acetylene, methane, and hydrogen as follows

$$C_2H_6 \rightarrow C_2H_4+H_2$$
$$2C_2H_6 \rightarrow 2CH_4+C_2H_2+H_2$$

The first comprehensive work was that of Bone and Coward [4, 1908] who obtained evidence of the reactions—

$$C_2H_6 \rightarrow C_2H_4+H_2 \rightarrow C+CH_4+H_2$$

On continued heating large proportions of methane were produced, and to explain this Bone and Coward assumed the existence of labile residues, $\equiv CH$, $=CH_2$, and $-CH_3$ 'These residues, which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C{=}CH_2$ and $HC{\equiv}CH$, as the result of encounters with similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly hydrogenised to methane in an atmosphere already rich in hydrogen'

It must be noted, however, that the accumulation of methane and hydrogen in the reaction is to be expected from thermodynamic considerations only, since the decomposition of all hydrocarbons should ultimately resolve itself into the methane equilibrium $CH_4 \rightarrow C+2H_2$ At 800° C and 1 minute heating period, Bone and Coward obtained from methane a gas of the composition C_2H_2 1 9%, C_2H_4 11 2%, C_2H_6 17 9%, CH_4 31 3%, and H_2 37 7% After 1 hour's heating only methane (63 8%) and hydrogen (36 3%) were found in the system

The dehydrogenation of ethane to ethylene is an equilibrium reaction which has been investigated experimentally by Pease and Durgan [55, 1928], and by Frey and Huppke [21, 1933] It is necessary to point out, however, that although ethane does resolve itself into hydrogen and ethylene at temperatures above 550° C, and the reverse reaction takes place at lower temperatures, this reaction nevertheless, is not a *true* equilibrium, because if ethane is heated for long periods at which dehydrogenation takes place, the system will ultimately resolve itself into the well-known methane equilibrium That this is true of most of the thermal reactions of hydrocarbons at their cracking temperatures was demonstrated theoretically and practically by Cantelo and others The equilibrium between ethane, ethylene, and hydrogen above 550–600° C is an example of an instantaneous equilibrium, and Pease and Durgan found that their results were to some extent obscured, especially at 700° C, by the formation of methane

Pease and Durgan investigated the equilibrium in the absence of catalysts, whereas Frey and Huppke made use of a chromic oxide gel catalyst and obtained values for the equilibrium constant at temperatures lower (450–500° C) than Pease and Durgan The last named investigators found that the values of the equilibrium constant

$$K = \frac{(C_2H_4)(H_2)}{(C_2H_6)}$$

(concentrations being in atmospheres), were as follows

600° C	0 0310
650° C	0 082
700° C	0 20

whereas Frey and Huppke gave the following figures

400° C	0 00015
450° C	0 00076
500 C	0 0032

These values give a straight-line plot of $\log K$ against I/T and show satisfactory agreement The data are satisfactorily reproduced by the equation

$$AF = -RT \log K = 31{,}244-28\ 88T$$

Fig 3 gives the equilibrium constants determined by Frey and Huppke in the dehydrogenation of the lower paraffins, i e ethane, propane, and butanes

A study on the velocity of the thermal decomposition of ethane into ethylene and hydrogen at 600–700° C in copper reaction tubes has been made by Marek and McCluer [43, 1931]

With regard to the production of higher hydrocarbons from ethane by thermal treatment, ethane is much more reactive than methane in this respect Thus, Hague and Wheeler [24, 1929] found, in experiments carried out on these two gases at different temperatures but using a constant reaction time (4 litres per hour of gas—measured at N T P flowing through a reaction tube 70 cm long × 2 2 cm inside diameter), that the temperatures for optimum yield of total oils were as follows

Methane	**1,000° C**	**—Total oil yield 3 7% of methane treated**
Ethane	**900° C**	**— „ „ 21 9% of ethane „**

The formation of liquid hydrocarbons (mostly of an unsaturated nature) was first noticed at 750° C., but at 800° C. and higher the distillate was almost pure benzene. The results obtained by Hague and Wheeler on the decomposition of ethane are given in the following table.

TABLE IV

Results of Hague and Wheeler. Decomposition of Ethane

Flow rate, 4 litres per hour.
Reaction tube, 70 cm. long × 2.2 cm. I.D.
Space velocity, approx. 49.

					Analysis of exit gas % vol.					
Temp. ° C.	Total oils %, wt.	Distillate to 170° C. % wt.	Carbon % wt.	% increase in volume	Higher olefines	Acetylene	Ethylene	Hydrogen	Methane	Ethane
700	nil	nil	nil	32.7	1.7	2.8	21.3	21.9	2.7	49.6
750	2.13			63.0	4.7	4.3	24.3	32.3	13.3	21.1
800	9.7	6.9		63.9	3.7	3.0	21.1	38.4	21.1	12.7
850	17.93	11.2			1.7	2.3	14.7	41.4	32.4	7.5
900	21.90	10.6	3.1	71.0	1.6	1.8	5.0	44.3	38.9	8.4
950	12.83	7.96	13.9	87.5	0.4	1.0	3.8	52.6	40.8	1.4
1,000	6.53	3.6	16.2	109.0	0.3	0.8	2.4	58.5	33.9	4.1

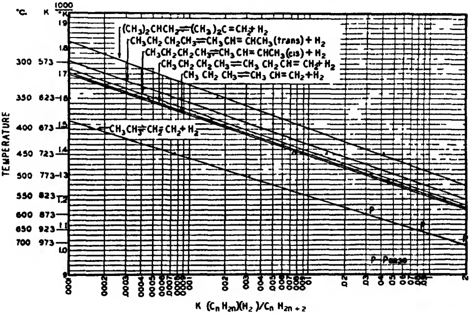


FIG. 3. Equilibrium constants—dehydrogenation of lower paraffins.

Concerning the chemical mechanism of ethane decomposition, Williams-Gardner [82, 1925] formulated the reactions on the assumption that there was a scission of the carbon–carbon bond in the ethane molecule, producing methyl residues which were stable at temperatures in the neighbourhood of 550° C. With increase in temperature these residues were thought to dissociate to hydrogen and the more unsaturated and probably less stable $=CH_2$ radicals, the system being in equilibrium with ethylene. With rise in temperature $—CH_3$ groups are hydrogenated to methane by hydrogen, while the reaction

$$C_2H_4 \rightleftharpoons =CH_2 + =CH_2$$

proceeds away from the ethylene side, the unstable $=CH_2$ residues undergoing either

(*a*) Decomposition into $\equiv CH$ residues and hydrogen, the former polymerizing to liquid products or decomposing into carbon and hydrogen,

(*b*) Hydrogenation to methane,

or (*c*) Direct decomposition to carbon and hydrogen.

These ideas may be represented as follows:

$$CH_3—CH_3 \rightleftharpoons 2CH_3— \rightleftharpoons 2CH_2 + H_2 \rightleftharpoons C_2H_4$$

Hydrogenation (at all temperatures)	$2(—CH_3) + H_2 \rightarrow 2CH_4$ $(=CH_2) + H_2 \rightarrow CH_4$
Dehydrogenation (650–850° C.)	$2(=CH_2) \rightarrow 2(\equiv CH) + H_2$ $(=CH_2) \rightarrow C + H_2$ $2(\equiv CH) \rightarrow 2C + H_2$
Polymerization (750–850° C.)	$n(\equiv CH) \rightarrow C_nH_n$ $n(\equiv CH) \rightarrow C_nH_{n-m} + \frac{1}{2}mH_2$
Equilibrium (850° C. and above)	$CH_4 \rightleftharpoons C + 2H_2$

Hague and Wheeler [24, 1929] suggested that in the production of higher products $=CH_2$ radicals formed from ethane combined and produced ethylene, from which butylene, butadiene, and, finally, aromatic hydrocarbons were formed.

An explanation of the thermal decomposition of paraffin hydrocarbons from the standpoint of free radicals has been given by Rice and his co-workers [57, 1931–4]. The relative strengths of the C–C and C–H linkages appear to indicate that decomposition of hydrocarbons takes place principally through the rupture of the C–C bond, any breaking of a C–H bond must be wholly negligible compared with that of a C–C bond. The free radicals thus produced can react in two ways: (1) decompose to form another free radical and hydrogen, or (2) take a hydrogen atom from the surrounding hydrocarbon molecule, since the probability that two free radicals will collide with each other is relatively small. The decomposition of the hydrocarbons can then take place according to chain reactions in which the free hydrogen atoms or free radicals combine with the hydrogen atoms of the surrounding hydrocarbon molecules.

For example, in the decomposition of ethane the primary reaction may be represented by the formation of two methyl radicals:

$$CH_3—CH_3 \rightarrow 2CH_3—$$

These can then react in secondary reactions to form ethyl radicals, methane, and ethylene

$$CH_3—CH_3+CH_3— \rightarrow CH_4+CH_3CH_2—$$
$$CH_3CH_2— \rightarrow CH_2=CH_2+H$$

Thus the chain reaction is

$$CH_3—CH_3+H \rightarrow H_2+CH_3—CH_2— \rightarrow H_2+CH_2=CH_2+H$$

The formation of free radicals in the decomposition of ethane at 850–950° C has been demonstrated experimentally by Rice and Dooley [58, 1933] in their well-known metallic mirror experiments. They found that neither hydrogen nor ethylene had any effect on the mirrors, but the gaseous products from the decomposition of ethane at 850–950° C caused the disappearance of the mirrors. Rice and Dooley therefore formed the conclusion that methyl radicals were the primary dissociation products of ethane.

Propane.

By the thermal decomposition of propane there have been produced the following: hydrogen, methane, ethane, ethylene, propylene, and various higher hydrocarbons, such as benzene and the higher aromatics. Propane is more amenable to thermal decomposition than either methane or ethane.

Pease [55, 1928] concluded that the initial decomposition of propane was monomolecular, the two main reactions being dehydrogenation and methanation, thus

(1) $C_3H_8 \rightarrow C_3H_6+H_2$
(2) $C_3H_8 \rightarrow C_2H_4+CH_4$

Frey and Smith [22, 1928] found that at 575° C, in the presence of silica, no carbon was formed and the reaction was unaffected by an increase in the surface area of the silica. These investigators proposed a further mechanism of decomposition, thus

(3) $2C_3H_8 \rightarrow C_3H_6+C_2H_6+CH_4$

and found that reactions (1) and (2) had fairly rapid velocities of the same order of magnitude, while (3) was much slower. Decomposition of propane in the presence of a nickel catalyst at 200–405° C led to the following changes

(4) $C_3H_8 \rightarrow 2CH_4+C$
(5) $C_3H_8 \rightarrow C_3H_6+H_2 \rightarrow CH_4+2H_2+2C$

of which the former takes place at all temperatures, and the latter becomes important only at higher temperatures.

The work of Hague and Wheeler on propane, conducted under the same conditions of reaction time as their experiments on the other gaseous hydrocarbons, showed that liquid hydrocarbons were first obtained at 700° C, and were still important products of decomposition at 1,000° C. Between these temperatures the yield reached a maximum at 850° C—corresponding to 23.1 % of the propane treated. At temperatures below 800° C the liquid products are unsaturated in nature, and butadiene is found in the products obtained at 750° C and above. Carbon was first noted at 750° C in the usual form of a foil-like surface deposit, but only above 850° C was carbon a considerable part of the products.

The results of Hague and Wheeler's tests on propane are reproduced in the following table.

TABLE V

Results of Hague and Wheeler: Decomposition of Propane

Flow rate, 4 litres per hour   Reaction tube, 70 cm long × 2.2 cm I.D.

Temp., ° C	*Total oil % yield wt*	*Distillate to 170° C % wt*	*Carbon, % wt*	*% increase in volume*	*Composition of exit gas, % vol* *% Higher olefines*	*% Acetylene*	*% Ethylene*	*% Hydrogen*	*% Methane*
700	1.01			52.5	14.2	3.4	19.7	11.8	14.1
750	6.87	4.25		88.8	13.3	7.1	20.5	13.3	26.8
800	16.98	10.14		105·0	3.4	2.9	19.7	20.8	38.8
850	23.09	11.65	0.89	106.2	2.3	2.5	14.5	26.6	46.2
900	20.10	9.73	4.98	119.0	1.4	1.8	9.8	33.4	45.8
950	10.35	5.42	11.32	144.0	0.5	1.1	6.1	44.0	41.5
1 000	5.54	2.25	18.32	159.0	0.5	1.1	5.8	51.3	36.1

These investigators concluded, as a result of their work, that at 700° C approximately 61 % of the propane decomposed follows the reaction

$$CH_3—CH_2—CH_3 \rightarrow CH_2=CH_2+CH_4$$

and the remainder reacts to give propylene and hydrogen, thus

$$CH_3—CH_2—CH_3 \rightarrow CH_3—CH=CH_2+H_2$$

At temperatures above 700° C the butadiene formed (no figures for which are given in Table V) was considered to be produced as follows

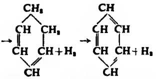
$$2C_2H_4 \rightarrow CH_2=CH—CH=CH_2+H_2$$

The mechanism proposed for the formation of aromatics was that ethylene polymerized to butylene, which, by elimination of hydrogen, gave butadiene. This was then considered to react with further ethylene in the following manner

(1) $CH_2=CH_2+CH_2=CH_2 \rightarrow CH_3—CH_2—CH=CH_2$
$\rightarrow CH_2=CH—CH=CH_2+H_2$

(2) $CH_2=CH—CH=CH_2+CH_2=CH_2$
$\rightarrow CH_2=CH—CH_2—CH_2—CH=CH_2$

$\rightarrow CH_2=CH—CH=CH—CH=CH+H_2$



Further, by analogy with the formation of diphenyl from benzene, it was supposed that butadiene could react with benzene, hydrogen being eliminated, to form naphthalene; and that anthracene and phenanthrene could be formed from naphthalene in a similar manner.

The work of Schneider and Frolich [66, 1931] on the pyrolysis of propane and other gases is of considerable importance. Experiments were made with the object of determining the primary decomposition products, and the method adopted was to vary the degree of decomposition within a range where accurate analysis of the products was possible, and then to plot the results in such a manner that extrapolation to zero per cent decomposition distinguishes the primary products from those produced by secondary reactions. These experiments were made by passing the gases concerned through a silica tube 61 cm. long × 1.3 cm diameter. No information is available concerning the reaction times employed—these being varied to give the different degrees of decomposition required.

The results obtained by Schneider and Frolich on propane decomposition are reproduced in Figs 4, 5, and 6, and show that at 725° C, 1 atm pressure, and zero per cent decomposition, propane breaks down to the extent of 48% according to the equation

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

while 42% is converted into propylene and hydrogen Ethane also appears to be a primary product, although the reaction responsible for its production is not clear Butadiene and higher hydrocarbons appear to be secondary products. At 650° C about 50% of the propane undergoes dehydrogenation, and somewhat less than 40% is converted into ethylene and methane Both ethane and butane appear to be primary products—probably by the reaction

$$2C_3H_8 \rightarrow C_2H_6 + C_4H_{10}$$

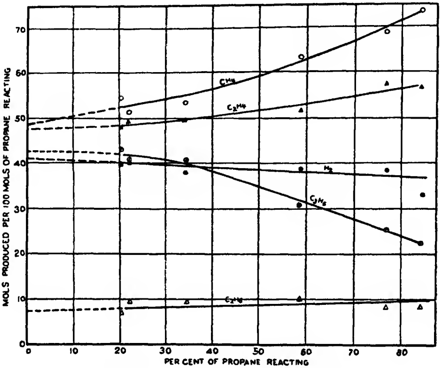


Fig 4 Decomposition of propane at 725 C and 1 atm pressure

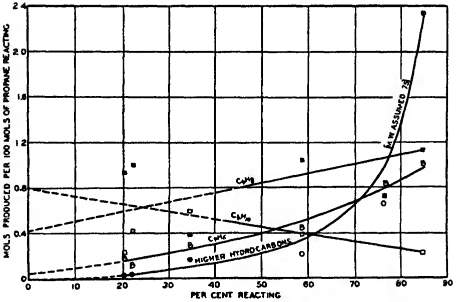


Fig 5 Decomposition of propane at 725° C and 1 atm pressure

Tropsch, Thomas, and Egloff [73, 1936] have reported work on the pyrolysis of propane at super-atmospheric pressure (51 kg/cm² or 725 lb per sq in), and 555–585° C Under these conditions the dehydrogenation reaction yielding propylene and hydrogen is naturally suppressed, and the products obtained indicated that the propane decomposed as follows

Dehydrogenation to propylene and hydrogen	6 8% (Reaction 1)
Demethanation to ethylene and methane	33 0% (,, 2)
Simultaneous demethanation and dehydrogenation	54 0% (,, 3)

Summarizing, therefore, the decomposition of propane has been observed to proceed as follows

Investigators	*Temp* ° *C*	*Pressure, lb per sq in*	*Reaction 1* %	*Reaction 2* %	*Reaction 3* %
Hague and Wheeler	700	Atmospheric	39	61	
Schneider and Frolich	725	,,	42	48	
,,	650	,,	50	40	
Tropsch, Thomas, and Egloff	555–585	725	6 8	33	54

primary or the secondary hydrogen atom of propane, are then as follows

(v) $CH_3{-}CH_2{-}CH_3 + R \rightarrow RH + CH_3{-}CH_2{-}CH_2{-}$
$\rightarrow RH + CH_2{=}CH_2 + CH_3{-}$

(vi) $CH_3{-}CH_2{-}CH_3 + R \rightarrow RH + CH_3{-}(CH)CH_3{-}$
$\rightarrow RH + CH_3CH{=}CH_2 + H$

(*In these equations* R *may be either* CH_3— *or H*)

Rice has found good agreement between the experimental results of Pease and Durgan [55, 1928] and the values predicted by his theory

On the other hand, Lang and Morgan have concluded, as a result of work on the pyrolysis of propane at partial pressures less than atmospheric (steam being used as a diluent), that there is no combination of equations in the Rice mechanism that will account for the relative quantities of products found These workers favour the Nef dissociation hypothesis [51, 1904, 1908] Nef considered that organic compounds exist in two states which he called 'active' and 'inert', and that, although the relative number of active molecules is small, the two exist in a state of dynamic equilibrium It is further stipulated that the active valences must be on adjacent carbon atoms, e g in the case of propane

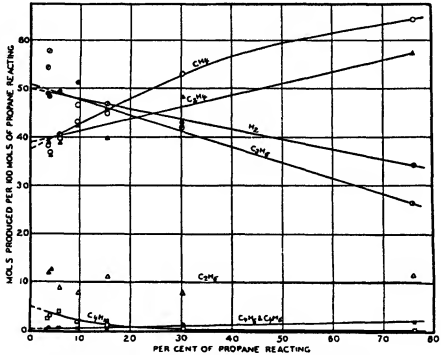


FIG 6 Decomposition of propane at 650° C and 1 atm pressure

Rice [57, 1931–4] has represented the decomposition of propane as follows

The principal reaction produces both free ethyl and methyl radicals

(i) $CH_3{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH_2{-} + CH_3{-}$

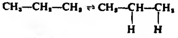
The secondary reactions are

(ii) $CH_3{-}CH_2{-} \rightarrow CH_2{=}CH_2 + H$

(iii) $CH_3{-}CH_2{-} + CH_3{-}CH_2{-}CH_3$
$\rightarrow C_2H_6 + CH_2CH_2{-}CH_3{-}$
$\rightarrow C_2H_6 + CH_2{=}CH_2 + CH_3{-}$

(iv) $CH_3{-}CH_2{-} + CH_3{-}CH_2{-}CH_3$
$\rightarrow C_2H_6 + CH_3CH(CH_3){-}$
$\rightarrow C_2H_6 + CH_3CH{=}CH_2 + H$

The two chain reactions, the relative extents of which depend upon whether the carrier group reacts with the

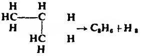


$$\underset{Inert}{CH_3{-}CH_2{-}CH_3} \rightleftharpoons \underset{Active}{CH_3{-}\underset{H}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH_2}}}$$

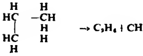
Inert *Active*

Nef also said that these active molecules may be considered to be in a kind of state of ionization, or dissociation, although not necessarily in the same category as the ionization of electrolytes

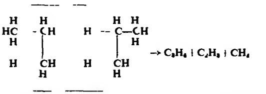
In applying the theoretical deductions of Nef to the thermal decomposition of propane, Lang and Morgan assumed that an increase in temperature displaces the equilibrium towards the formation of more active molecules, and also that in the active molecules the dissociation proceeds farther until the equilibrium is disturbed by the closing of the bonds on the alkylidene residue and union of the two other radicals from the dissociation of the molecule Lang and Morgan admit that the monomolecular dissociation of propane, which predominates at low partial pressures, can be explained satisfactorily by the mechanisms suggested above by other writers, but maintain that the bimolecular reaction is not similarly explained They propose the following process—based on Nef s active molecules



(A)

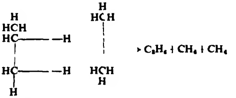


(B)



(C)

The bimolecular reaction could also, it was suggested, proceed as follows



(D)

The Dehydrogenation of Propane to Propylene As shown later, the dehydrogenation of propane is rapidly assuming commercial importance as a method for the production of propylene

The reaction involved

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

is a reversible equilibrium, and has been studied by Frey and Huppke [21, 1933] using a chromic oxide gel catalyst at 350–450° C and atmospheric pressure These workers obtained the following values for the equilibrium constant

$$K = \frac{(C_3H_6)\,(H_2)}{C_3H_8}$$

At 350° C = 0 00038
„ 400° C = 0 0022
„ 450° C = 0 0074

indicating that a lower temperature is required for a given extent of decomposition than in the case of ethane At the temperatures employed propane gave no side reactions

Boeckler [3, 1929] has made a study of propane decomposition over the temperature range 500–1,000° C, and investigated the effect of various catalysts The use of copper gauze, nickel gauze, and a mixture of zinc and copper did not affect the character of the decomposition products, but lowered the temperature necessary for their formation For a given propylene yield the temperature was lowered 50° C by copper gauze and about 30° C by a mixture of zinc and copper Nickel was a somewhat less effective catalyst than copper Pumice and stainless-steel turnings were without catalytic effect A catalyst mixture containing 78 5 molar % zinc and 21 5 molar % chromium markedly increased propylene formation, so that a larger yield of this hydrocarbon was obtained at 658° C by its use than was formed without the catalyst at 730° C with a rate of flow but one-fourth as great A similar mixture containing 30 2 molar % zinc and 69 8 molar % chromium was also active in promoting dehydrogenation to propylene, but it also encouraged complete decomposition of the propane Hydrogen formation exceeded that of propylene, which decreased rapidly as the temperature increased, while carbon deposition increased Addition of pumice to the latter mixture of zinc and chromium decreased its activity for both partial and complete dehydrogenation When the propane was diluted with 67% of nitrogen, an 11% yield of propylene was formed at temperatures as low as 520° C, and no methane was formed

In the presence of a copper pumice catalyst [45, 1932] at 500° C dehydrogenation to propylene is the predominating reaction, and only small amounts of ethylene and methane are produced The formation of propylene is favoured by short time of contact with this catalyst, prolonged contact increasing the yields of methane and ethylene

Butanes.

Normal Butane As in the case of propane, there are a number of possible methods of decomposition for normal butane These are as follows

(A) $CH_3—CH_2—CH_2—CH_3 \rightarrow CH_3—CH_2—CH{=}CH_2 + H_2$
(B) $CH_3—CH_2—CH_2—CH_3 \rightarrow CH_3—CH_3 + CH_2{=}CH_2$
(C) $CH_3—CH_2—CH_2—CH_3 \rightarrow CH_3—CH{=}CH_2 + CH_4$
(D) $2CH_3—CH_2—CH_2—CH_3 \rightarrow CH_3—CH_2—CH{=}CH_2 + {} + CH_3—CH_2—CH_3 + CH_4$
(E) $2CH_3—CH_2—CH_2—CH_3 \rightarrow CH_3—CH_2—CH{=}CH_2 + {} + 2CH_3—CH_3$
(F) $CH_3—CH_2—CH_2—CH_3 \rightarrow 2H_2 + CH_2{=}CH—CH{=}CH_2$

The actual products obtained are best represented by equations (A), (B), and (C), although there is no direct evidence of the exact mechanism that produces the products

The relative tendency for the above reactions to occur is evident from the results of various investigators collected in Table VI Hague and Wheeler's [24, 1929] work was conducted in silica tubes 70 cm long × 2 2 cm inside diameter, using a constant flow rate of 4 litres per hour, i e the same conditions as employed for their work on other paraffins, which has already been mentioned Hurd and Spence [29, 1929] used a pyrex reaction tube 1 in diameter, heated over 30 in of its length, and flow rate of 20 7–25 8 litres per hour, corresponding to contact times of 18–30 sec Frey and Hepp [20, 1933] employed a silica reaction coil of 166 c c capacity and contact times of 25 sec The other investigators mentioned unfortunately give no details regarding reaction times or flow rates

The figures of Table VI indicate that at the lower temperatures the formation of methane and propylene is the preferential reaction, but, as the temperature is increased, the tendency for the formation of ethylene and ethane is increased. Dehydrogenation to *n*-butylenes is also an important reaction

TABLE VI

Decomposition Products of n-*Butane*

Investigators	*Contact time, sec*	*Flow rate, litres per hr*	*Temp, ° C*	*Mols per 100 mols butane*		
				Methane and propylene	*Ethylene and ethane*	*Butylene and hydrogen*
Frey and Hepp [20]	25·2		875	60·0	29·0	10·7
Hurd and Spence [29]	30·0		600	52·5	45·0	4·0
Neuhaus and Marek [52]			600	48·5	34·5	16·0
Neuhaus and Marek [52]			650	48·0	37·7	12·3
Hague and Wheeler [24]		4	650	36·0	43·0	21·0
Hurd and Spence [29]	18·0		700	43·7	51·0	5·3

Experiments made by Tropsch, Thomas, and Egloff at 525–555° C and 725 lb per sq in pressure showed that liquid products in appreciable quantity were produced from *n*-butane under these conditions At contact times of 47 to 173 sec, butane decomposed as follows

1·4% according to reaction (A), i.e. dehydrogenation to butylene
36·6% according to reaction (C), i.e. formation of methane and propylene
30·0% according to reaction (B), i.e. formation of ethylene and ethane
31·9% according to reaction (D), i.e. formation of butylene, propane, and methane
3·2% according to reaction (E), i.e. formation of butylene and ethane

These results show that simple monomolecular dehydrogenation is suppressed by an increase in pressure—an observation agreeing with the Le Chatelier principle, and that the bimolecular reactions are facilitated The latter effect is also to be expected because the rate of a bimolecular reaction is proportional to the concentration (i.e. partial pressure) of the reacting substance

Experimental evidence in support of a mechanism for the decomposition of *n*-butane is lacking The chain mechanism of Rice accounts for the products of a number of hydrocarbons, but in some cases a chain mechanism is not adequate to account for the products For the decomposition of butane the chain mechanism is definitely out of line, because it does not predict any butylene or hydrogen, which are important products

The equilibrium dehydrogenation of *n*-butane has been studied by Frey and Huppke [21, 1933], using a chromic oxide gel catalyst over the temperature range 350–450° C Under these conditions small proportions of methane, ethylene, and ethane were produced by reactions involving the fracture of carbon—carbon bonds, in addition to the products of simple dehydrogenation These by-products were evidently formed by catalytic action, since the temperatures were too low to cause appreciable homogeneous decomposition Frey and Huppke found that the butylenes produced consisted of 1-butene and both *cis*-2-butene and *trans*-2-butene (Following Dillon, Young, and Lucas [8, 1930], the lower boiling 2-butene was designated the *trans* isomer) The following values of the equilibrium constants were determined (see also Fig 3)

Equilibrium constant, K	*Temperature*		
	350° C	*400° C*	*450° C*
$\frac{(CH_3—CH_2—CH{=}CH_2)(H_2)}{CH_3—CH_2—CH_2—CH_3}$	0·00045	0·0022	0·0075
$\frac{(trans\ CH_3—CH{=}CH—CH_3)(H_2)}{CH_3—CH_2—CH_2—CH_3}$	0·00083	0·0039	0·014
$\frac{(cis\ CH_3—CH{=}CH—CH_3)H_2}{CH_3—CH_2—CH_2—CH_3}$	0·00052	0·0025	0·0087

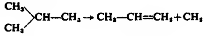
No isobutylene was produced in the dehydrogenation of *n*-butane

Regarding the formation of liquid products from *n*-butane, Hague and Wheeler found, under the experimental conditions already described, that these were first evident at 700° C and were still in evidence in tests at 950° C Between these two temperatures the yields attained maxima, the total oil yield at 850° C and the 'distillate to 170° C' yield at 800° C, with values of 24·6% and 12·9% by weight of the butane used, respectively The liquid products obtained at temperatures up to 750° C was largely olefinic in character, but at higher temperatures consisted essentially of benzene Naphthalene began to form somewhat above 800° C

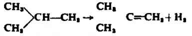
Frey and Hepp [19, 1932] have made a detailed examination of the volatile oils obtained by the pyrolysis of a mixture of 89% *n*-butane and 11% isobutane at 850° C in silica reaction tubes, and have identified 1,3-butadiene, pentenes, cyclopentadienes, hexadienes, methylcyclopentadiene, benzene, toluene, xylenes, and styrene

Isobutane

Hurd and Spence [29, 1929] working at 600 and 700° C, and Pease at 625 and 650° C, found isobutane and *n*-butane to have about the same thermal stability, the main difference in their behaviour being a greater liberation of hydrogen from the isobutane At 600° C Hurd and Spence found that 90% of the isobutane reacting did so according to the equations

(*a*)


$$(CH_3)_2CH—CH_3 \rightarrow CH_3—CH{=}CH_2 + CH_4$$

(*b*)


$$(CH_3)_2CH—CH_3 \rightarrow (CH_3)_2C{=}CH_2 + H_2$$

At 700° C, as well as at 600° C, their data showed that these reactions were still the major ones, although at the higher temperature an increased amount of ethylene was formed

As a result of similar experiments made at 600 and 650° C, Marek and Neuhaus [44, 1933] agree that the above reactions are the most important, demethanation accounting for the formation of primary products to the extent of 34·5%, and dehydrogenation to the extent of 63% Under super-atmospheric conditions (i.e. 725 lb per sq in) Tropsch, Thomas, and Egloff [73, 1936] found isobutane to be less reactive than *n*-butane, and to occupy, in this respect, a position between *n*-butane and propane. Thus isobutane at 555° C. and 725 lb per sq in gave 21·6% decomposition in 51 sec., while *n*-butane at the same temperature and pressure gave 43·4% decomposition in 47 sec Thus isobutane at 555° C. reacts only half as fast as *n*-butane.

The ease of dehydrogenation of isobutane is of particular interest, because it offers a convenient source of isobutylene —now used as a raw material in the production of iso-octane by processes of polymerization and subsequent hydrogenation Frey and Huppke [21, 1933] have shown that, using a chromic oxide gel catalyst at 350, 400, and 450° C, dehydrogenation takes place more easily in the case of isobutane than in the case of any of the lower paraffins, but side reactions are most marked These side reactions lead to the production of methane, and the products contain a deficiency of hydrogen Values for the dehydrogenation equilibrium constant are given in Fig 3 in graphical form and are as follows

Temp, ° C	$K = \frac{(C_4H_8)(H_2)}{C_4H_{10}}$
350	0 0017
400	0 01
450	0 042

The Thermal Behaviour of the Gaseous Olefines The olefines undergo thermal changes similar to the corresponding paraffins, but are also very prone to enter into polymerization reactions During breakdown, by heat or other agencies, methane is almost always formed, often in considerable proportions It arises probably by the splitting off of a terminal carbon atom Such splitting first forms two molecular fragments, a small group which becomes methane by hydrogenation, and a larger residue which can rearrange to a diolefine or absorb hydrogen to form a lower mono-olefine

Dehydrogenation and hydrogenation also occur during olefine reactions, and yield diolefines, acetylene, and paraffins Probably free radicals form during decomposition and are intermediate in many of the reactions occurring The proof of the existence of such free radicals offers the clearest explanation of many of the reactions of olefines and is almost a necessity to a rational mechanism for some changes Available evidence indicates that polymerization reactions begin with the addition of an olefine molecule to another of the same type, forming a dimer of the original substance In some investigations it has been possible to stop reaction at the dimer stage, but in many reactions higher boiling polymers have inevitably been formed As a preliminary to the formation of dimers, it is quite probable that there is activation, creating from the double-bond grouping a reactive radical with two free linkages Various molecular rearrangements also take place during the thermal treatment of olefines, for instance, naphthenes have been reported present in the liquid products obtained from olefines in the presence of some catalysts, or by the use of high pressures With regard to the relationship of structure to stability among isomeric olefines, Hurd [27, 1929] has presented the generalization that hydrocarbons containing alkyl groups attached to saturated carbon atoms are less stable than those containing alkyl groups attached to unsaturated carbon atoms Thus 1-butene is less stable than 2-butene, and iso-propyl-ethylene is less stable than trimethylethylene

The action of heat on olefines may produce changes of three types With mild heating, rearrangement or polymerization reactions predominate, and may be the only ones occurring. They produce olefine (and frequently naphthene) hydrocarbons of molecular weight greater than that of the original material Changes such as these are aided by super-atmospheric pressure At more elevated temperatures, while polymerization continues, decomposition also occurs, and leads to the production of lower molecular weight olefines and paraffins, and also carbon and hydrogen At the same time the higher olefines produced by polymerization tend to become converted, in part, to aromatic hydrocarbons At still higher temperatures practically no polymerization takes place, and the primary products are carbon and hydrogen

Catalysts have been very widely used in studying the thermal reactions of the gaseous olefines, some favour disruptive changes, while others have valuable polymerization activity

Ethylene

Very complete data are available concerning the thermal behaviour of ethylene over a wide temperature range, both in the presence and absence of suitable catalysts

When exposed to low temperatures polymerization is the predominating reaction in the absence of catalysts (and also when certain specific catalysts are used), and may be the only change which takes place At temperatures of 350–800° C changes both of polymerization and disintegration take place, while at high temperatures, e g above 950° C, decomposition reactions alone take place

From their calculations of the free energies of various hydrocarbons, Francis and Kleinschmidt [18, 1930] concluded that the lower olefines will polymerize at temperatures up to 425° C, but decompose at higher temperatures Similarly, the higher olefines tend to isomerize into naphthenes below about 425° C

As products of ethylene decomposition the most important are carbon, hydrogen, methane, ethane, and acetylene Polymerization yields, depending upon the conditions, gaseous and liquid products The liquids often contain higher olefines, but may, at high temperature, also contain aromatics Pressure greatly aids polymerization of all the gaseous olefines and causes this to take place at atmospheric temperature, yielding among the products naphthene hydrocarbons, which have not been reported in work at atmospheric pressure in the absence of catalysts

With regard to the mechanisms by which these changes occur, some investigators have postulated the extensive formation of free radicals as intermediate products, while others have presented schemes involving the intermediate production of either acetylene, butylene, or butadiene In 1931 Egloff, Schaad, and Lowry [13, 1930–1] wrote as follows

> 'We consider the most probable course of the reactions occurring when ethylene is subjected to the action of heat to be the following The first break of an ethylene molecule is probably in part at least to free methylene radicals, $=CH_2$ These lose hydrogen and form methine radicals, $\equiv CH$, or disintegrate completely to carbon and hydrogen—two products abundantly formed Hydrogenation of methylene radicals gives methane
>
> 'Because of its stability, methane once formed does not usually undergo further change It is therefore an abundant product of ethylene pyrolysis Ethane forms by direct hydrogenation of ethylene, the hydrogen being liberated by the simultaneous dehydrogenation of other molecules of ethylene or split from free radicals
>
> 'Combination of a radical with an ethylene molecule forms propylene, or this hydrocarbon may be formed by butylene breakdown The most simple way in which acetylene could be formed from ethylene is by loss of

hydrogen Possibly it is formed by combination of free ≡CH groups, or even by union of carbon and hydrogen resulting from ethylene breakdown '

With regard to the polymerization of ethylene, these authorities state that this appears to commence with the formation of butylene 'As butylene is the sole product obtained in careful work done at very low temperatures, it undoubtedly is produced by the direct combination of two ethylene molecules, and does not involve any intermediate steps ' Butadiene results by the dehydrogenation of butylene Further polymerization can be confined to hexene, formed by the addition of ethylene to butylene Continuation of this process gives the oils reported as 'higher olefines of undetermined structure' With regard to the steps by which ethylene is converted into aromatic hydrocarbons, Egloff, Schaad, and Lowry favoured the mechanism proposed by a number of workers involving the formation of butadiene, a cyclohexene, and benzene by dehydrogenation of the cyclic hydrocarbon This mechanism, given by Hague and Wheeler, has already been mentioned

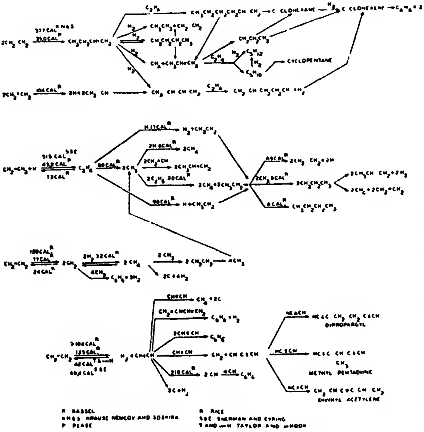


FIG 7 Thermal reactions of ethylene (Egloff and Wilson)

A valuable survey of the thermal reactions of ethylene has recently been made by Egloff and Wilson [14, 1935], who have tabulated these reactions in the convenient form reproduced in Fig 7

Non-catalytic Thermal Treatment of Ethylene at Atmospheric Pressure. There is considerable uncertainty as to the temperature at which ethylene first decomposes Some investigators have found no marked decomposition below 600° C, but others have observed incipient decomposition on prolonged exposure to a temperature of 350–355° C. These differences are to be attributed to differences in reaction time Day [7, 1886] found that ethylene began to react at 350° C and yielded polymerides, without the formation of any hydrocarbon with a C/H ratio different from that of the olefines On raising the temperature, however, to 400° C, the products were methane, ethane, and liquid hydrocarbons No carbon was deposited At 450° C ethylene contracted to the extent of 44% in 72 hours, and a liquid product was obtained The residual gas contained 8 4% methane, 64% ethane, and 27 6% olefines No hydrogen was obtained, but there was slight deposition of carbon

In 1930 Pease [54] decomposed ethylene at comparatively low temperatures in an attempt to study the reactions involved He found formation of butylene to be the only change which took place to any large extent when ethylene was passed through a pyrex tube of reaction volume 637 c c heated to 450–500° C The flow rate employed was 5–40 c c per minute Above 525° C ethane, methane, a little hydrogen, and liquid products began to appear Ethane was regarded as a primary product and methane a secondary reaction product

Bone and Coward [4, 1908] examined the behaviour of ethylene at higher temperatures, i e 570–950° C At 570–580° C they obtained hydrogen, methane, ethane, acetylene, and aromatic hydrocarbons, with little carbon

At 700–800° C methane was an important product, while the formation of aromatic hydrocarbons was reduced and the extent of carbon deposition increased At 950° C only 4% of the ethylene was converted into condensable products, there was extensive carbon deposition, and the reaction was very rapid—90% of the ethylene decomposing in 1 minute The results obtained by Hague and Wheeler [24, 1929] are of special interest They employed a quartz reaction tube and the contact-time conditions identical with those employed in paraffin decomposition Their results are reproduced in Table VII

TABLE VII

Thermal Decomposition of Ethylene (*Hague and Wheeler*) [24, 1929]

Temp, ° C	*Total liquid, % wt*	*Benzene fraction, % wt*	*Exit gas analysis, % volume*				
			Higher olefines	*Acetylene**	*Ethylene*	*Hydrogen*	*Methane*
700	13 3	6 6	9 2	8 2	55 2	5 9	8 7
750	25 5	13 1	4 4	4 8	40 5	13 1	28 8
800	28 9	10 7	1 4	4 2	16 1	27 9	44 0
850	15 5	7 8	0 4	1 1	6 6	35 6	50 0

* These figures are stated to be too high—due to inaccurate gas analysis

Of the liquids obtained at 700 and 750° C ($d = 0\ 8$), half distilled at 80–86° C, a small portion boiling at 72–76° C The gases contained butylene and butadiene

Experiments were also conducted in sealed quartz bulbs using a constant heating period of 3 hours Maximum production of higher olefines was noticed at 500° C, and methane first appeared at 550° C

Wheeler and Wood [80, 1930] have described experiments conducted over the temperature range 650–900° C At 650° C the principal product was butylene, but at 700° C butadiene and propylene were formed Evidence of the disruption of the ethylene molecule, to form compounds of lower carbon content, was first obtained at 750° C Examination of the liquid products formed at 700° C showed that 50% boiled below 110° C and was principally benzene, with some toluene and cyclohexene, neither naphthenes nor paraffins were present in this fraction The results of Wheeler and Wood [80, 1930] are reproduced in Table VIII

Acetylene was reported absent in the exit gases from these experiments

A further insight into the mechanism of ethylene decomposition is afforded by the work of Schneider and Frolich [66, 1931], who endeavoured to determine the primary products by cracking ethylene in silica tubes at a pressure of 0 2 atm By extrapolation of the results to zero per cent reaction, there were formed from each 100 moles of ethylene reacting about 41 moles of hydrogen, 36 moles of butadiene, 12 moles of propylene, and 3 moles of butylene The results also indicated that about 72% of the ethylene reacting formed butadiene and hydrogen as initial products

$$2C_2H_4 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2$$

Since a positive test for the presence of acetylene was always obtained, the excess of 5 moles of hydrogen may have come from a reaction producing acetylene Ethane and methane were found to be definitely secondary products, but it was observed that propylene was a primary product under the experimental conditions employed This conclusion, although at first sight rather improbable, has been substantiated by the work of Lenher [40, 1931], who found that propylene was the most important product of the polymerization of ethylene during the slow oxidation of ethylene with oxygen at temperatures of 450–520° C A number of experiments with high ethylene concentrations and oxygen concentrations of about 5% showed that below 520° C propylene and butylene are the only hydrocarbons formed in oxygen-activated polymerizations A slow oxidation experiment at 600° C yielded a hydrocarbon product consisting of 59 3% propylene, 2 2% butylene, and 28 4% amylenes In order to account for the formation of propylene as an initial product in the activated polymerization process, Lenher advances three possible mechanisms (*a*) by intermolecular collision, (*b*) by the formation of an excited intermediate molecule $C_4H_8^1$ which then reacts with a further molecule of ethylene, thus

$$2C_2H_4 \rightarrow C_4H_8^1$$
$$C_4H_8^1 + C_2H_4 \rightarrow 2C_3H_6,$$

and (*c*) the condensation of a free methylene radical with ethylene in the following manner

$$CH_2{=}CH_2 \rightarrow 2(CH_2{=})$$
$$CH_2{=}CH_2 + (CH_2{=}) \rightarrow CH_3CH{=}CH_2$$

Lenher considers that the last explanation is more probable than the others

Valuable contributions on the kinetics of ethylene polymerization have recently been made by Storch [70, 1935], who confirmed Lenher's observation concerning the marked accelerating effect of traces of oxygen, and found that 1 molecule of oxygen caused about 85 additional molecules of ethylene to polymerize At 377° C and 141 5 cm pressure, 0 02% oxygen resulted in about twice the yield obtained in the absence of oxygen with 2 hours' contact time Storch also conducted experiments in which elaborate precautions were taken to exclude traces of oxygen, because of the possibility that autocatalysis may be connected with the accelerating influence of oxygen The results of tests by Storch are reproduced in Table IX, and show the production of both propylene and butylene The ratio of propylene to C_4 hydrocarbons is 0 31, 0 83, and 1 01 for the 1-, 2-, and 3-hour products respectively, and leads to the conclusion that propylene is not a primary product Distillation data indicated the presence of both α- and β-butylene, but the evidence regarding the identity of 'cyclobutane' is very doubtful A similar remark may be made concerning 'cyclopentane' Storch concluded that butylene was the main primary product of ethylene polymerization

TABLE VIII

Decomposition of Ethylene (Wheeler and Wood)

Temp ° C	Total liquids, % wt	Distillate to 170° C % wt	Carbon, % wt	Change in volume %	Exit gas analysis % volume						
					C_4H_6	C_4H_8	C_3H_6	C_2H_4	H_2	CH_4	C_2H_6
650	1 5		nil	2 7	0 3	3 8	nil	89 9	0 7	0 5	2 0
700	12 2	8 0	nil	15 2	0 4	2 8	2 2	66 2	3 2	4 9	4 9
750	28 2	16 5	trace	−16 4	0 2	1 5	1 7	47 6	7 2	16 7	8 6
800	36 1	17 7	1 4	−11 8	0 15	nil	1 1	29 0	17 3	33 7	6 9
850	31 4	13 3	11 9	+1 3		0 5		12 2	35 8	49 7	3 3
900	13 4	5 4	13 4	+13 1		nil		4 6	51 0	55 2	2 2

TABLE IX

Polymerization Products of Ethylene at 377° C and 141 5 cm Pressure (Storch)

Time of contact—hours	1	2	3
Yield c c (at 27° C and 76 cm) per experiment	3 7	16 4	37 1
Pressure drop, cm	0 35	1 5	3 35
Propylene, vol %	13 8	28 4	30 5
Butylene, vol %	31 7	32 0	24 2
'Cyclobutane' vol %	12 6	2 1	5 9
Pentanes, vol %	4 1	6 1	6 6
'Cyclopentane, vol %	8 1	11 5	4 0
Hexene, vol %	12 6	8 9	14 4
Higher olefines, vol %	10 1		2 3
Unaccounted for vol %	7 0	11 0	12 1
Average contraction factor	2 28	1 83	2 03
Yield c c (at 27° C and 76 cm) calculated from contraction factor and pressure drop	2 8	18 6	33 5

In further experiments Storch found that the addition of small amounts (about 0 1 %) of ethyl mercaptan to ethylene prepared by fractionation of anaesthesia grade material decreased the rate of polymerization about tenfold

Non-catalytic Thermal Treatment of Ethylene at Elevated Pressures. It was found by Ipatieff [31, 1906–7, 1911] that, under a pressure of 70 atm , the polymerization of ethylene took place at temperatures at which, under atmospheric pressure, change was very slight Reaction began at about 325° C and proceeded with considerable speed at 380–400° C The product consisted of a small amount of solid and a greyish-green liquid made up of paraffin, naphthene, and olefine hydrocarbons The fractions of this liquid boiling up to 100° C were chiefly composed of paraffin and olefine hydrocarbons, while naphthenes were thought to be the main constituents of the portions boiling from 100 to 280° C From the boiling ranges, densities, and elemental analyses of the fractions Ipatieff reported the presence of pentane, hexane, octane, nonane, amylene, hexene, and various poly-naphthenes It seems possible, however, that the fractions he studied were not individual hydrocarbons but mixtures, since the criteria employed were insufficient for the identification of pure hydrocarbons

According to Nash and Stanley [50, 1930] ethylene is stable, in the absence of catalytic material and under pressure, at temperatures up to about 300° C At 325° C a gradual reduction in pressure took place, and with increasing temperature the condensation became more rapid Thus, on heating ethylene (initial pressure 51 atm at 20° C and 135 atm at 340–350° C) for 7 hours in a small steel autoclave, the pressure fell uniformly from 140 to 32 atm When cold the pressure was 7 atm and the gaseous product of the reaction was a small quantity of gas of the composition 68% C_2H_4, 7 4% of higher olefine, 0 6% hydrogen, and 23 8% methane The liquid reaction product was of a yellow colour with slight fluorescence, and on distillation gave the following fractions

40–100° C	17% colourless
100–700° C	35% ”
200° C /750 mm –200° C /13 mm	36% yellow
Above 200° C /13 mm	12% brownish yellow

Under certain conditions of heating under pressure ethylene is liable to decompose with explosive violence and give hydrogen, methane, and carbon This was first observed by Waterman and Tulleners in 1931 [78] Using an initial pressure of 32 kg per cm^2, an autoclave of 2,000 ml capacity was employed and heated slowly to 350° C , at which temperature it remained for 30 min Under these conditions slight liquid formation was observed but no explosive decomposition, whereas when an initial pressure of 48 kg per cm^2 was used, explosion took place when a temperature of 350° C was reached, corresponding to a pressure of 175 kg per cm^2 The gaseous product contained 89% methane, 6% hydrogen, and a little benzene The carbon produced closely resembled ordinary carbon black and filled the autoclave completely Analysis showed this to contain more than 99% carbon

This phenomenon has also been observed by Dunstan, Hague, and Wheeler [10, 1932], who found that the reaction is profoundly affected by various metals Using a flow type of apparatus and a mild-steel reaction tube, polymerization of ethylene was rapid at 380–400° C and 800 lb pressure, but carbon was deposited in an amount corresponding to 6 6 % of the liquid produced Using a copper liner in the reaction tube, carbon deposition became serious at pressures higher than 800 lb per sq in , and violent decomposition (resembling the flashing of acetylene) occurred, accompanied by a copious deposition of soft carbon Similar results were obtained in the presence of either oxidized or cleaned copper surfaces With stainless-steel and aluminium liners similar results were obtained, but carbon deposition was rather more marked with these metals than with copper Some allow steels, notably Hadfields Era 131 (chrome molybdenum steel, 0 4% Cr, 0 8–0 9% Mo, 0 4% Cu), gave less carbon deposition than copper, and allowed polymerization to liquid products to proceed satisfactorily at 380–500° C and pressures up to 1,200 lb per sq in At temperatures above 470° C a surface deposit of hard carbon was formed in the presence of Era 131 steel, but even at 490° C the carbon represented only about 1% of the liquids produced

The explosive decomposition of ethylene has also been observed by Egloff and Schaad [12, 1933] in the presence of a catalyst comprising $4NiO—2Al_2O_3—CuO$ An autoclave, filled with ethylene to 49 atm initial pressure, was heated and the pressure increased regularly until a pressure of 143 atm was reached at 330° C The pressure then suddenly rose from 143 to 340 atm , and the temperature rose 200° C The products of the decomposition were fluffy carbon and a gas containing 37 6% hydrogen and 54 2% methane

This explosive decomposition has not been observed in the case of either propylene and butylene, or when working with gaseous mixtures containing up to 25% ethylene at temperatures up to 500° C and pressures up to 2,500 lb per sq in The phenomenon does not occur with normal refinery gases A detailed explanation of this peculiar behaviour of ethylene is not forthcoming The polymerization is known to be highly exothermic, and the heat liberated must be dissipated, but it would appear that the reason for the explosive decomposition is chemical rather than physical

The conditions of temperature and pressure under which ethylene decomposes in this way are thus as follows

Observer	*Temperature, ° C*	*Pressure, atmospheres*
Dunstan, Hague, and Wheeler (copper tube)	390–460	54 5
Waterman and Tulleners	350	169 0
Egloff and Schaad ($NiO—Al_2O_3—CuO$ catalyst)	330	143 0

Regarding the conversions of ethylene to liquid products realized by simple thermal treatment, and the nature of the products obtained, much information has been published Egloff and Schaad give the following details

Properties of products	*Autoclave tests*	*Small continuous plant*
Pressure, atm	131–158 max	60–71
Temp , ° C , average	379–380	424–432
Time of heating, hours	1 78–3 45	0 73–0 85
Liquid products, % of ethylene changed	66–74	76–78
Density of product, 15 5/15 5° C	0 766–0 777	0 761–0 765
Engler distillations of product		
Initial boiling-point, ° C	40	44
10% distillate at	74	68
20% ” ”	98	86
30% ” ”	128	102
40% ” ”	153	122
50% ” ”	173	145
60% ” ”	195	169
70% ” ”	222	200
80% ” ”	257	237
90% ” ”	305	313
Final boiling-point	323	326

The product produced in the small continuous plant contained more low-boiling constituents than did that produced in the autoclave, where the reaction time was longer and the pressure greater and gave the following yields on Hempel distillation

Gasoline	35–210 C	78 5% volume	Yellow
Residue	above 210° C	21 5%	,,

The gasoline fraction had a bromine number of 81, and contained 44 5% olefines, 9 6% aromatics, the remaining 45 9% being naphthenes and paraffins The octane number, as determined by the procedure of Hubner and Murphy [26, 1931], was 76

In the experiments of Dunstan, Hague, and Wheeler, autoclave tests showed that at 400° C and 1,200 lb per sq in pressure conversions of ethylene to liquid products of up to 73% could be obtained Under these conditions, however, the residual gas contained only 15% olefines, indicating that these conditions were rather too drastic Lowering the temperature to 380–392° C resulted in yields up to 92% by weight In continuous plant tests at 380–390° C and 800 lb per sq in pressure, conversions up to 64% per pass were realized under appropriate conditions of reaction time Using a lining tube of copper, it was found that at this pressure it was necessary to operate at 440° C—that is to say, 50–60° C higher than when using mild steel to obtain comparable reaction rates

With regard to the liquid products obtained, those from autoclave operation were turbid and dark in colour, and contained 60–70% boiling below 200 C and 88–93% boiling below 300° C, depending upon operating conditions The products produced in continuous plants were quite transparent and light straw in colour, and contained 80–6% of material boiling below 200° C Analysis of these products indicated that they were largely olefinic, the paraffin hydrocarbon content increasing with rise in boiling-point The presence of naphthenes was indicated, but diolefines were considered absent Anti-knock value tests on the gasoline content of the polymers indicated that, *in blend*, this had a blending value rather inferior to that of benzene These tests were made on an Armstrong Whitworth Variable Compression Engine operated at 120° F jacket temperature Experimental work described by Sullivan, Ruthruff, and Kuentzel [71, 1935] is of particular interest, because it covers the polymerization of ethylene over a range of pressures from 500 to 3,000 lb per sq in, and 343–456° C At 500 lb pressure and 454° C a conversion of 59% was obtained at 8 min time of contact, and when the pressure was increased to 1,000 lb, giving a time of contact of 27 sec, the yield was 70% at the same temperature At all pressures and temperatures examined conversion increased rapidly with contact time up to a maximum, beyond this point further increase in time of contact resulted in little or no increase in liquid yield Thus at 800° F ethylene gave a conversion of 67% at 2,000 lb and 14 min time of contact, 72 3% at 27 min, and only 73 2% after 59 5 min At 455° C, increasing the time of contact beyond 22 min at 2,000 lb pressure resulted in decreased yields of liquid, indicating that polymer destruction by cracking was proceeding more rapidly than polymer formation by polymerization Typical results obtained by these investigators at 2,000 lb per sq in pressure are reproduced in Fig 8, and the conditions for maximum polymer yield are summarized in Table X The yield was not found to increase appreciably with increasing pressure, but the allowable throughputs increased enormously Thus at 3,000 lb the polymer production per unit time was over 10 times that obtained at 500 lb pressure

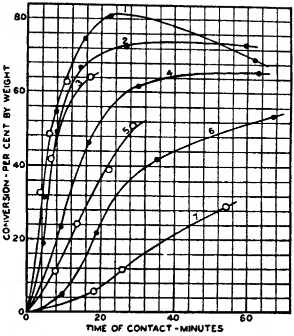


FIG 8 Polymerization of ethylene and propylene at 2,000 lb per sq in pressure

1 Propylene and ethylene at 850° F (454° C) 2 Ethylene at 800° F (427° C) 3 Propylene at 800° F (427° C) 4 Ethylene at 750° F (399° C) 5 Propylene at 750° F (399° C) 6 Ethylene at 700° F (371° C) 7 Propylene at 700° F (371° C)

TABLE X

Thermal Polymerization of Ethylene (Sullivan, Ruthruff, and W E Kuentzel)

Pressure, lb per sq in	*Temp °C*	*Reaction time, min*	*Liquid yield, %*	*Sp gr of liquid*	*Gasoline, %*	*Octane number of gasoline (C F R Research Method)*
500	454	8 1	59 1	0 7839	73 8	78
1 000	454	27 4	70 0	0 7824	69 5	68
2,000	454	22 4	80 8	0 7883	62 5	64
3,000	371	85 0	75 0	0 7950	40 2	62
3,000	399	43 0	74 8	0 7905	47 3	63
3 000	427	17 3	74 3	0 7897	55 0	62
3,000	454	9 6	71 4	0 7792	67 1	63

With regard to the nature of the products obtained under the various conditions examined, the low octane numbers of the gasoline fractions are noteworthy, especially when it is remembered that these are Research Method octane numbers and that the Motor Method octane numbers would be appreciably lower The gasoline contents of the crude liquid products are also low

Ipatieff and Pines [32, 1935] have described in detail the properties of ethylene polymers produced at 330° C and 64 atm pressure in an autoclave The product was found to contain 8% paraffins, 68% olefines, and 24% naphthenes Aromatic hydrocarbons were absent and only 25% of the product boiled up to 225° C The results of Podbielniak high-temperature distillation of the product are reproduced in Table XI The absence of aromatic hydro-

TABLE XI

Thermal Polymerization of Ethylene at 330° C (Ipatieff and Pines)

Fraction no	*Boiling-point, ° C, 738 mm*	*Total percentage over*	*Bromine number*	*Refractive index n_D^{25}*	*Olefines, %*	*Density at 25° C*	*Molecular weight*	*Carbon, %*	*Hydrogen, %*
1	36–60	2 1	117	1 3879	60				
2	60–75	3 9	113	1 3883	60	0 6716	85	84 7	15 05
3	75–90	4 9	105	1 3980	55				
4	90–115	5 8	88	1 4099	55				
5	115–135	9 3	81	1 4136	56				
6	135–155	13 3	70	1 4205	55	0 7381	127	85 17	14 96
7	155–175	17 1	61	1 4272	53				
8	175–195	19 1	66	1 4338	58				
9	195–205	19 9							
10	205–225	24 0	58	1 4443	61				
11	225–245	31 2	52	1 4469	63	0 7940	194	85 69	14 35
12	245–260	35 3	58	1 4511	76				
13	260–270	41 9	53	1 4544	70	0 8060	211		
14	155–170/15/mm	45 1	55	1 4591	74				
15	170–190/15/mm	49 6	43	1 4610	70				
16	190–207/15/mm	57 7	30	1 4632	56	0 8289	299	85 68	14 17
17	207–220/15/mm	62 1	28	1 4663					
18	220–235/15/mm	65 5	26	1 4661					
19	to 389/15/mm	99 9	17		67		630	85 98	14 18

carbons is evidenced by the figures obtained on organic analysis of the product, and also by the fact that after 96% sulphuric acid treatment of the fractions there was a product obtained which did not react with an acid nitrating mixture For a further proof a method of hydrogenation at 220° C in the presence of nickel oxide was applied to fractions 11, 16, and 19 The products obtained were entirely paraffinoid

The properties of this product should be compared with those of a similar product produced using phosphoric acid catalyst (see later)

Propylene.

Under the influence of heat propylene undergoes decomposition in a manner very similar to ethylene Its decomposition temperature is slightly lower than that of ethylene, however, since by replacing 1 hydrogen atom in the ethylene molecule by a methyl group the symmetry of the molecule is destroyed

The possible types of reaction involved in the case of propylene are as shown in Fig 9, reproduced from the published work of Egloff and Wilson [14, 1935], in which the energy of activation of the various scissions involved are taken from the figures of Rice [60, 1935] Propylene may polymerize to give hexene in a manner similar to the polymerization of ethylene to butene At temperatures of 400–405° C Engler and Rogowski [15, 1909] claimed a 50% conversion of propylene to cyclopropane, but the work of subsequent investigators does not favour this possibility This reaction may take place through the formation of an intermediate tri-methylene radical, which might also combine with a like molecule to form cyclohexane The two most probable types of decomposition for propylene are (1) into hydrogen and an allyl group, and (2) into a methyl radical and a vinyl radical Rice [60, 1935] estimated the values of 91,000 and 85,000 calories respectively for the energy of activation of these reactions The allyl radicals appear to combine forming cyclohexene, for Wheeler and Wood [80, 1930] obtained a monocyclic hydrocarbon with one double bond as the main product in the liquid obtained at 650° C When a methyl radical splits from propylene it reacts to form methane or ethane, depending on the concentration of the methyl radical and hydrogen, as shown by the experiments of Paneth At atmospheric pressure the rate of combination of methyl radicals will undoubtedly be high Similarly, at atmospheric pressure the formation of ethane is favoured in thermal reactions in which polymerization predominates As the decomposition proceeds, ethane dehydrogenates to form ethylene, and by several reactions the concentration of ethylene is increased until the thermal reactions of propylene are essentially those of ethylene at the temperatures at which methylene radicals, acetylene, and liquid aromatic hydrocarbons are formed The experiments of Wheeler and Wood [80, 1930] are of interest in this connexion, the results of which are reproduced in Table XII In these tests the gas was passed through heated quartz tubes, the reaction time varying from 20 sec at the lower temperatures to about 10 sec at the higher temperatures.

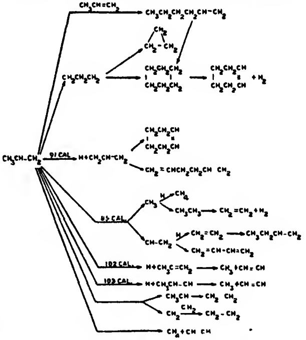


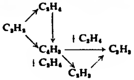
FIG 9 Thermal reactions of propene

Table XII

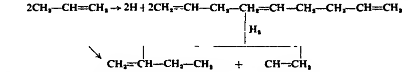
The Thermal Decomposition of Propylene (Wheeler and Wood)

Temp °C	Total liquids, % wt	Distillate to 170° C, % wt	Carbon, %	Change in volume, %	Exit gas analysis (% volume)						
					C_4H_6	C_4H_8	C_3H_6	C_2H_4	H_2	CH_4	C_2H_6
650	5 2	3 2	nil	+40 0	0 2	4 1	86 9	7 7	0 5	2 1	2 5
700	20 3	12 9	trace	+10 0	0 6	6 5	45 6	23 5	7 0	18 9	7 9
750	35 6	20 4	trace	+20 1	0 4	2 0	10 4	37 0	14 4	49 1	6 8
800	40 6	19 0	1 7	+30 1	0 3	0 5	1 5	28 1	23 6	70 7	5 4
850	33 8	14 6	9 5	+46 2				18 6	36 7	85 9	4 5
900	11 9	6 8		+64 2				8 0	66 5	86 1	3 1

These results seem contrary to those of other workers The scheme suggested by Schneider and Frolich was as follows



whereas Egloff and Wilson interpret the evidence to indicate decomposition to (1) hydrogen and allyl radicals, and (2) to methyl and vinyl radicals



$$2CH_3—CH{=}CH_2 \rightarrow 2H + 2CH_2{=}CH—CH_2—CH_2{=}CH—CH_2—CH_2—CH{=}CH_2$$

$$\xrightarrow{H_2} CH_2{=}CH—CH_2—CH_3 \quad + \quad CH{=}CH_2$$

$$2CH_3—CH{=}CH_2 \rightarrow 2CH_3 + 2CH{=}CH_2 \rightarrow CH_2{=}CH—CH{=}CH_2 + CH_3—CH_3$$

At 650° C the principal products were ethylene, ethane, and butylene, with comparatively small amounts of unsaturated liquid hydrocarbons Under the conditions of test the formation of butylene from ethylene or of ethylene from butylene could not occur at this temperature There was a noticeable difference in character between the liquids of lower boiling-point obtained from the decomposition at 650° C and at 700° C Whereas the former were mainly monocyclic hydroaromatic hydrocarbons, having one double bond in the ring, the latter were mainly benzene and toluene At the higher temperatures of formation the proportion of liquids of high boiling-point increased, showing that the more complex hydrocarbons had been formed at the expense of those of simpler composition The proportion of toluene to benzene formed from propylene at 700° C was greater than that formed from ethylene at the same temperature Naphthenes and paraffins were absent from the liquids boiling below 110° C, and were presumably absent also from the liquids of higher boiling-point

Hurd and Meinert [28, 1930] also found propylene to be decomposed rapidly at temperatures above 600° C in pyrex or quartz tubes The larger part of the propylene which reacted was broken down into carbon, hydrogen, methane, paraffins higher than methane (principally ethane), and ethylene Propylene and isobutylene were found to undergo about the same amount of pyrolysis when subjected to the same temperature and contact time Frey and Smith [23, 1928] employed a temperature of 575° C and a reaction time of 240 sec, and found that the longer time factor gave a greater yield of methane at the expense of butene, butadiene, and ethane

With regard to the primary products of propylene decomposition and polymerization comparatively little is known The work of Schneider and Frolich [66, 1931] conducted at a pressure of 0 2 atm, in which the products of primary reactions were obtained by an extrapolation method, shows that for each 100 moles of propylene reacting, 23–4 moles of both ethylene and butylene are formed as initial products Hence it must be concluded that about 48% of the propylene reacts according to the equation

$$2C_3H_6 \rightarrow C_2H_4 + C_4H_8$$

Likewise it appears that 10% goes to form ethane and butadiene, thus

$$2C_3H_6 \rightarrow C_2H_6 + C_4H_6$$

The combination of two allyl radicals would give hexadiene which, together with the high concentration of propylene, would decompose into butene and vinyl radicals, and these on hydrogenation would yield butylene and ethylene In the second type of decomposition methyl and vinyl radicals would combine with similar radicals to give butadiene and ethane Other combinations of these radicals would give 5 or 6 carbon-atom olefines, which were indicated in the products

According to Dunstan, Hague, and Wheeler [10, 1932] the principal primary reactions involved in the thermal decomposition of the olefines yield both 2 and 4 carbon-atom olefines, thus

$$(a)\ 2C_2H_4 \rightarrow C_4H_8$$
$$(b)\ 2C_3H_6 \rightleftharpoons C_2H_4 + C_4H_8$$
$$(c)\ C_4H_8 = 2C_2H_4$$

Under conditions involving secondary changes propylene yields ethylene and methane, 'probably by hydrogenation of the radicals formed by scission of the carbon chain at the single linking', thus

$$CH_3—CH{=}CH_2 + H_2 \rightarrow CH_2{=}CH_2 + CH_4$$

Non-catalytic Thermal Treatment of Propylene at Elevated Pressures. At elevated pressures polymerization is the predominant reaction in the thermal treatment of propylene at temperatures up to 400° C At higher temperatures decomposition and complex side reactions occur Evidence regarding the relative ease of polymerization of ethylene and propylene under increased pressure conditions is contradictory In the presence of catalysts, e g phosphoric acid, propylene is the more easily polymerized, but in the absence of catalysts the reverse appears to be the case [10, 1932, 81, 1935]

The liquid products obtained by the non-catalytic polymerization of propylene at 375° C and 214–54 kg per cm^2 pressure over a period of 12 hours have been described by Ipatieff and Pines [33, 1936] (Table XIII) Paraffins are present in the lowest boiling fractions, but as the boiling-point rises the percentage of paraffins diminishes until it becomes nil in the fractions boiling at 175° C and higher Olefines are present to the extent of about 50% in the fractions boiling up to about 185° C. In the product boiling at 215–225° C olefines are present to the extent of 8% only and are absent in higher boiling fractions Cycloparaffins are present in all but the lowest boiling fractions, while fractions

TABLE XIII

Thermal Polymerization of Propylene (Ipatieff and Pines)

Fraction no	*Boiling-point, ° C, 760 mm*	*Total percentage over*	*Bromine no*	*Refractive index n_D^{20}*
1	29–50	5.1	104	
2	50–65	8.9	106	1.3830
3	65–71	13.3	105	1.3958
4	71–87	17.1	99	1.3975
5	87–115	21.1	79	1.4036
6	115–140	26.7	61	1.4123
7	140–145	32.4	59	1.4199
8	145 155	36.7	53	1.4228
9	155–165	37.7	52	1.4269
10	165–175	40.7	50	1.4279
11	175–185	45.1	48	1.4318
12	185–195	47.8	48	1.4341
13	195–205	53.1	45	1.4383
14	205–215	55.7	49	1.4403
15	215–225	61.6	43	1.4440
16	225–245	64.5	44	1.4479
17	245–255	66.4	34	1.4500
18	255–266	70.8	43	1.4514
19	266–279	73.9	42	1.4538
20	279–291	78.5	41	1.4570
21	291–303	81.4	46	1.4589
22	303–317	85.3	39	1.4620
23	317–329	88.5	42	1.4648
24	329–346	90.8	33	1.4677
25	346–366	94.7	33	1.4728
26	Residue	99.4		

	Original product						*Hydrogenated product*				*Composition of original material*			
Boiling range, ° C	*Bromine*	*Molecular weight*	*Density*	*n_D^{20}*	*% Carbon*	*% Hydrogen*	*n_D^{20}*	*Density*	*% Carbon*	*% Hydrogen*	*Paraffins*	*% Olefines*	*% Cyclo-olefines*	*% Naphthenes*
65–71	105				85.07	14.95					25	55	0	20
140–145	59	137	0.7447	1.4199	85.56	14.55	1.4151		84.84	15.07	8	47	0	45
175–185	48	150	0.7860	1.4318	85.62	14.38		0.7655	84.95	14.94	0	45	0	55
215–225	43	178	0.7995	1.4440	85.81	14.01			85.47	14.56	0	8	37	55
170–182/14 mm	39	243	0.8315	1.4620	86.06	13.83			85.61	14.31	0	0	62	38
205–223/14 mm	33	309	0.8515	1.4728	86.01	13.74			85.77	14.0	0	0	63	37

boiling at 215° C and higher contain cyclo-olefines—presumably formed by the dehydrogenation of cycloparaffins According to Ipatieff and Pines [33, 1936] the thermal polymerization of ethylene proceeds more easily than that of propylene In the case of ethylene the polymerization proceeds satisfactorily at 330° C, but propylene polymerizes at 330° C to a negligible extent at the same pressure This agrees with statements made by Dunstan, Hague, and Wheeler [10, 1932] and by Sullivan, Ruthruff, and Kuentzel [71, 1935]

TABLE XIV

Thermal Polymerization of Propylene (Sullivan, Ruthruff, and Kuentzel)

Pressure, lb per sq in	*Temp ° C*	*Reaction time, min*	*Liquid yield, %*	*Sp gr of liquid*	*Gasoline, %*	*Octane number of gasoline (C F R Research Method)*
500	454	5.7	16.3	0.7661	80.3	78
1,000	427	22.6	46.9	0.7645	73.1	87
2,000	427	16.9	64.0	0.7653	69.5	75
2,000	454	10.6	62.8	0.7805	66.2	80
3,000	399	27.3	62.6	0.7682	59.5	75
3,000	427	16.4	61.0	0.7690	63.4	74
3,000	454	8.7	61.2	0.7784	67.1	74

Typical results obtained by the last-named investigators in the polymerization of propylene are reproduced in Table XIV, from which it is evident that the octane numbers of the polymer gasolines produced are higher than those from ethylene under the same conditions

In autoclave experiments at 400° C and 1,010 lb per sq in maximum pressure Dunstan, Hague, and Wheeler [10, 1932] obtained an 80% conversion of propylene to total liquid products

Butenes.

The three butenes, namely, 1-butene, 2-butene, and isobutene, are less stable under the action of heat than either propylene or ethylene In general, the larger the alkyl group substituted for a hydrogen atom in the ethylene molecule, the more unsymmetrical the resulting molecule and the greater the instability This is shown in the case of the two normal butenes, 2-butene being the more stable Undoubtedly, either of the normal butenes isomerizes into the other, so that a study of either is really a study of a mixture of both Only at low temperatures in the early stages of decomposition are differences in the relative stability of the normal butenes apparent

n-Butenes. The results obtained by Wheeler and Wood [80, 1930] in the pyrolysis of these gases at temperatures ranging from 600 to 900° C indicate that the products of decomposition from both isomers are similar The production of equal volumes of propylene and methane at

600° C indicates rupture of the terminal C–C linkage, followed by hydrogenation of the radicals so formed. The necessary hydrogen would be liberated during the simultaneous decomposition of some of the butene to form butadiene. Another simultaneous reaction is the formation of molecules containing 2 carbon atoms, mainly depolymerization to ethylene.

Liquid hydrocarbons were produced at 600° C, mainly, it was believed, through the combination of butadiene with an olefine. On this assumption calculation showed that the three primary reactions involved about equal weights of butene. An examination of the liquids formed when a mixture of the two *n*-butenes was decomposed at 600° C showed that cyclohexene and methyl-cyclohexene predominated, benzene and toluene being present in comparatively small proportion. Cyclohexadiene and methyl cyclohexadiene were also present. Only 18.5% of the liquids produced at this temperature boiled above 117° C. Of the liquids formed from 2-butene at 650° C, however, 29.6% boiled above 110° C and 16.6% above 150° C, and aromatic hydrocarbons predominated. Thus an increase in the temperature of formation of the liquids resulted in a greater proportion of higher boiling hydrocarbons and caused the conversion of hydro-aromatic into the more stable aromatic hydrocarbons. Naphthenes and paraffins were absent from the liquids boiling below 110° C. The results of Wheeler and Wood are reproduced in Table XV.

TABLE XV

Pyrolysis of n-Butenes (Wheeler and Wood)

Temp. °C	*Total liquid, %*	*Distillate to 170° C, %*	*Carbon, %*	*Change in vol., %*	Exit gas analysis, % volume C_4H_6	C_4H_8	C_3H_6	C_2H_4	H_2	CH_4	C_2H_6
				1 Butene							
600	12.9	6.5	nil	−23.4	0.9	54.1	7.6	3.2	0.8	8.1	1.9
650	29.8	20.3	nil	−10.7	1.7	19.8	24.5	14.2	6.2	37.2	7.1
700	35.8	23.6	trace	+30.0	1.4	2.1	19.6	22.3	11.9	62.1	10.6
750	39.6	22.4	trace	+43.9	0.2	1.3	5.6	31.4	17.3	78.5	9.7
800	39.4	19.9	1.0	+57.0		1.0	2.0	30.2	27.2	89.0	7.6
850	35.0	16.2	4.7	+73.9		1.0		20.6	50.5	95.7	6.1
900	13.9	7.8	7.1	+104.0		0.9		9.6	85.2	103.3	5.0
				2 Butene							
600	5.2	1.4	nil	25.4	0.8	65.0	2.6	1.3	0.9	2.8	1.2
650	27.0	17.2	nil	−7.5	1.7	20.0	17.8	8.9	4.9	31.4	7.8
700	37.0	25.8	trace	+27.4	0.9	2.6	19.2	19.8	11.1	62.0	11.8
750	39.6	23.2	trace	+38.9	0.4	2.1	5.3	27.9	17.6	76.5	9.1
800	37.9	18.6	1.4	+52.8		0.5	1.6	24.4	28.4	90.0	7.8
850	31.6	14.2	4.7	+68.3		1.2		16.9	48.4	96.1	5.7
900	12.4	6.1	5.4	+100.0		1.6		8.3	83.3	103.1	3.7

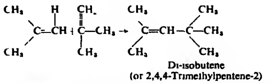
Isobutene. Isobutene is less stable to heat than either of the normal butenes, propylene, or ethylene. On the other hand, it is more stable than the corresponding paraffin—isobutane. Thus Hurd and Spence [29, 1929] found that at 600° C isobutene decomposed to the extent of only 1.2% in 18 sec., whereas isobutane decomposed to the extent of 13–19.5% in 17–21 sec. at the same temperature. For a 20% decomposition of isobutylene at 600° C a hot contact time of 200 sec. was required. At 700° C the rate of decomposition for both hydrocarbons was markedly increased, although the contrast was still apparent. For a hot contact time of 12–21 sec., isobutane was broken down to the extent of 70%, whereas with isobutylene decomposition varied from 30 to 50%. Still more striking a difference in the two cases is to be found in the course of the two reactions. Isobutane was found to decompose almost exclusively into gaseous hydrocarbons, which were of lower molecular weight than the original material. Isobutylene, on the contrary, changed quite materially into hydrocarbons of greater molecular complexity. Nearly half of the decomposed isobutylene gave rise to liquid hydrocarbons, whereas the remainder appeared in the form of gases. The gaseous products from both isobutane and isobutylene were similar to the extent that methane, hydrogen, and propylene were important products of the decomposition, with methane always predominating. Some of the results obtained by Hurd and Spence on isobutene are reproduced in Table XVI.

TABLE XVI

Decomposition of Isobutene (Hurd and Spence)

Temp., °C	*Contact time, sec.*	*% Decomposition*	*c.c. gaseous products per litre of isobutene decomposed* C_3H_6	CH_4	*Iso* C_4H_{10}	H_2	C_2H_4	C_2H_6 + *aromatics*	*Oil yield, % isobutene decomposed*
599	200	20.0	305	590	270	175	15	90	
652	27	22.7	172	286	176	150	35	31	39.6
652	13	11.1	144	135	198	54	108	99	63.0
700	12	30.2	218	586	133	242	43	66	46.6
700	18	47.7	228	655	61	260	59	69	63.0

The Non-catalytic Thermal Treatment of Butenes at Increased Pressures. Ipatieff [30, 1902–3, 34, 1907–8] was probably the first to polymerize isobutene by heating to 380–400° C at 70 atm. pressure. He thus obtained a mixture of liquid paraffin, olefine, and naphthene hydrocarbons which resembled the products he obtained by similar treatment of ethylene, except that the fraction boiling below 150° C was richer in olefines in the case of isobutene. Among the olefines present were thought to be the dimer and trimer of the original olefine. By heating isobutene at 200° C for 14 days in sealed glass tubes small yields of polymers have been obtained [39, 1930]. It would appear that polymerization of isobutene to di- and tri-isobutene and higher polymers occurs first, followed by decomposition and cyclization of the polymers, i.e.



Di-isobutene
(or 2,4,4-Trimethylpentene-2)

Experiments on the polymerization of isobutene (and also propylene and amylene) have shown that the reaction velocity varies directly as the square of the concentration, and that the velocity constant of polymerization depends upon the temperature. At high initial concentrations the polymerization of olefines is homogeneous, and although the mechanism of the reaction differs from the usual consecutive bimolecular reaction, the second kinetic order reaction is formally observed. The polymerization reaction velocity of olefines of normal structure rapidly decreases with increase in molecular weight, and the presence of two double bonds in the molecule increases the velocity of polymerization [37, 1934–5].

The Thermal Reactions of Acetylene.

The first experiments on the action of heat on acetylene were carried out by Berthelot [1, 1866, 1901], who formed the opinion that acetylene was an intermediate product in the pyrolysis of practically all the hydrocarbons which he studied Acetylene was found to decompose when passed through a porcelain tube at red heat and gave largely carbon and hydrogen Minor products were ethylene, methane, naphthalene, and tar To explain the separation of carbon, Berthelot assumed a progressive polymerization reaction, hydrogen splitting off in the process until only carbon remained Experiments under less drastic conditions indicated definitely the predominant trend in the action of heat on acetylene to be towards the production of aromatic hydrocarbons by polymerization At a much later date important researches on acetylene decomposition were carried out by Bone and Coward [4, 1908], who found that

(1) At moderate temperatures acetylene shows a strong tendency to polymerize, maximum reaction occurring at 600–700° C, and decreasing above this temperature, so that little polymerization occurs at 1,000° C

(2) At 800° C and above, the primary change is decomposition and considerable amounts of methane are formed, presumably by hydrogenation of $\equiv$CH radicals initially produced

At 480–500° C, with an exposure of 20 hours, about 82% of the acetylene was found to react Of this 48% polymerized, 39% decomposed into carbon and hydrogen, and the remainder (13%) was converted into methane, ethane, and ethylene At 800° C explosive decomposition —i e the so-called 'acetylene flashing'—occurred, producing much methane Methane was also produced in high yield when acetylene was heated with hydrogen at 800° C

Probably the most extensive work on acetylene pyrolysis, particularly with regard to the identification of the liquid products obtained, is that by Meyer and his co-workers [47, 1912–14, 1918, 1920], whose work should be consulted for further details Of interest is the work of Hague and Wheeler [24, 1929], conducted at atmospheric pressure and under the same conditions of contact time as their experiments on other hydrocarbon gases Their results are reproduced in Table XVII, and show that high yields of liquid products are obtained at 650–700° C The decomposition of pure acetylene as compared with that of acetylene produced in the thermal decomposition of other hydrocarbons shows differences arising from increased concentration Decomposition should take place through the same mechanisms, but the chances for methenyl radical formation are much greater in the case of undiluted acetylene These methenyl radicals should combine to give benzene Moreover, there is the possibility of 3 acetylene molecules polymerizing to give benzene without the intermediate formation of methenyl radicals

TABLE XVII

Polymerization and Decomposition of Acetylene
(Hague and Wheeler)

Temp, ° C	*Total liquids, %*	*Benzene fraction, %*	*Carbon, %*	*Exit gas analysis % (vol)*				
				Higher Olefines	*Acetylene*	*Ethylene*	*Hydrogen*	*Methane*
600	30 8			0 8	53 2	4 2	27 9	8 3
650	61 1	26 4	9 7	1 2	29 5	6 9	34 0	23 0
700	61 1	24 8	16 7	1 2	2 4	10 4	43 8	37 1
750	46 7	18 3	22 1	0 2	0 7	8 8	50 1	37 5

At low temperatures and atmospheric pressure acetylene polymerizes to higher gaseous and liquid derivatives, such as dipropargyl, methyl pentadene, and divinyl acetylene

The General Effects of the Variables involved in Thermal Decomposition of Hydrocarbons

The foregoing account of the thermal reactions of the gaseous hydrocarbons allows an accurate assessment of the effect of the various variables involved to be made Considering the effect of temperature first, it is evident that at very high temperatures, e g above 1,000° C, all the gaseous hydrocarbons decompose completely to carbon and hydrogen, if the heating period is sufficiently long That is, the methane equilibrium

$$CH_4 \rightleftharpoons C+2H_2$$

is the ultimate stage in the decomposition of all hydrocarbons, and if products other than carbon and hydrogen are required, then the heating time and/or the temperature must be so adjusted that the primary or secondary products of decomposition are withdrawn from the reaction zone before the final decomposition reactions set in

In the heat treatment of gaseous paraffins the least drastic conditions of temperature and reaction time yield gaseous olefines, and liquid products are only usually obtained by an increase in either temperature or contact time Aromatic liquids are obtained under more drastic conditions than liquid products of an unsaturated character

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THE GASEOUS PARAFFINS AS A SOURCE OF OLEFINES

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It has already been shown that the gaseous paraffins—methane to butane—yield olefines by thermal decomposition, and also by dehydrogenation The commercial and practical aspects of these means of producing olefines may now be considered in detail

The Production of Olefines by Thermal Non-catalytic Decomposition

Theoretically it is feasible to obtain high yields of olefines from the corresponding paraffins by heat treatment—the reaction involved being a simple dehydrogenation

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2$$

Methane is not amenable to such dehydrogenation because the production of ethylene from it involves a synthesis process in which two carbon atoms must become linked together

Unfortunately heat treatment alone does not have the desired results because, as already shown, the gaseous paraffins decompose in a variety of ways, each C—C linkage being broken in addition to the elimination of hydrogen from a terminal alkyl radical Consequently the thermal treatment of a gaseous paraffin results in the formation of both paraffins and olefines containing fewer carbon atoms per molecule than the parent substance, and the yields of olefines are, as a result, low As far as can be ascertained the highest yield of olefines yet obtained by the thermal treatment of either propane or butanes is about 60% by weight, the production of lower paraffin and hydrogen being about 40% by weight

Methane.

Most of the work reported on the thermal decomposition of methane is concerned with either the decomposition into carbon and hydrogen or with the production of aromatic liquids, and no work has apparently been carried out to determine the optimum yield of gaseous olefines obtainable The production of acetylene from ethane is dealt with later

Whenever liquid hydrocarbons are produced from methane by thermal treatment, the exit gas is found to contain small amounts of ethylene and/or higher olefines in addition to varying quantities of acetylene For example, Hague and Wheeler [31, 1929], in experiments at 900–1,050° C obtained an exit gas, after condensation of higher hydrocarbons, containing 0 3–0 9% of higher olefines and 2 1–3 7% of ethylene Similarly, Stanley and Nash [47, 1929], in experiments on highly purified methane at 1,000° C , obtained an exit gas containing up to 1 1% ethylene and 0 8% acetylene In these tests the space velocity was varied from about 24 to 143 volumes of inlet methane per volume of reaction space per hour

Cambron [6, 1932] has described detailed tests on a natural gas fraction of the following analysis

Methane	89 7% volume
Ethane	4 8% ,,
Propane	3 4% ,,
Butanes	1 5% ,,
Pentanes +	0 6% ,,

These tests were made in quartz and porcelain tubes containing a centrally disposed electrically heated carbon rod Temperatures ranging from 990 to 1,200° C were employed, and the effects of temperature and contact time variables were investigated

Cambron found that yields of ethylene and acetylene equivalent to 13 5% and 3 0%, respectively, could be obtained from the above natural gas fraction at 1,020° C , using a suitably short contact time Under more severe conditions the yield of ethylene decreased while that of acetylene increased

It is evident from these results that the production of ethylene and higher olefines from methane by thermal treatment is not a commercial feasibility As far as is known, the use of catalysts has not yet given any greater yields than those mentioned above As a source of olefines, therefore, methane may be disregarded

Ethane.

Ethane is a very convenient source of ethylene As already mentioned, the main reaction involved in thermal treatment at temperatures considerably higher than the initial decomposition temperature, is dehydrogenation, although other reactions take place to minor extents In the following correlation of the published work on the production of ethylene from ethane by non-catalytic thermal treatment, experiments made by heating ethane statically in a closed system have been ignored because, while they have given valuable information on the reaction mechanisms involved, are far removed from industrial practice, and give no indication of what may be realized in commercial operation

TABLE I

Results of Hague and Wheeler Decomposition of Ethane

Flow rate 4 litres per hour
Reaction tube 70 cm long × 2 2 cm I D
Space Velocity approx 49

Temp ° C	*Total oils % wt*	*Distillate to 170° C % wt*	*Carbon % wt*	*% Increase in volume*	*Higher Olefines*	*Analysis of exit gas % vol*				
						Acetylene	*Ethylene*	*Hydrogen*	*Methane*	*Ethane*
700	nil	nil	nil	32 7	1 7	2 8	21 3	21 9	2 7	49 6
750	2 13			63 0	4 7	4 3	24 3	32 3	13 3	21 1
800	9 7	6 9		63 9	3 7	3 0	21 1	38 4	21 1	12 7
850	17 93	11 2			1 7	2 3	14 7	41 4	32 4	7 5
900	21 90	10 6	3 1	71 0	1 6	1 8	5·0	44 3	38 9	8 4
950	12 83	7 96	13 9	87 5	0 4	1 0	3 8	52 6	40 8	1 4
1,000	6 53	3 6	16 2	109 0	0 3	0 8	2·4	58 5	33 9	4 1

Among the earliest work on the thermal decomposition of ethane to ethylene that is of any value is that of Hague and Wheeler [31, 1929], whose results are reproduced in Table I These investigators used silica and porcelain tubes 2 2 cm diameter and 70 cm long The heated length of the tube was 42 5 cm , but the volume of the constant temperature zone is unknown The total heated reaction volume is thus 162 c c., and the constant temperature volume must have been at least half this, i.e 81 c c. These figures ignore the volume of an internal thermo couple pocket which was used A constant inlet gas rate of 4 litres per hour (measured at N T P) was used in all the tests reported, and therefore the space velocity (volumes of inlet gas per volume of reaction space per hour) was $\frac{4,000}{81} = 49\ 4$, based on the assumed constant temperature zone volume Under these conditions Hague and Wheeler obtained the optimum conversion of ethane to ethylene (as shown in Table I) at 750° C , when the olefine content of the exit gas was 33 3%, and the increase in gas volume due to reaction was 63% Assuming the olefines formed to consist entirely of ethylene, these figures correspond to an ethylene yield of $33\ 3 \times \frac{163}{100}$ 54 3% by volume or 50 5% by weight Under these conditions the reaction time was about 20 seconds

Other workers have employed reaction time and space velocity conditions more in accord with industrial operations, in which high gas linear velocity is essential in order to obtain good heat transfer rates Thus, Sullivan, Ruthruff, and Kuentzel [50, 1935] have studied the pyrolysis of ethane for olefine production in a helical coil of KA2S tubing (18/8 Cr-Ni steel) of 14 ft total length and $\frac{5}{16}$ I D Reaction times of 0 5 to 2 6 sec and space velocities of 270–1,440 were employed The detailed results of these investigators are reproduced in Table II, and the effects of the more important variables are shown in Figs 1, 2, and 3

TABLE II

Production of Ethylene by the Pyrolysis of Ethane (Sullivan, Ruthruff, and Kuentzel) [50, 1935]

Run no	Mean reaction temp °C	Mean reaction temp °F	Inlet gas litres per minute	Reaction time sec	Space velocity	Exit Gas: Litres per minute	Exit Gas: % Unsaturateds	Exit Gas: Mol wt	Volume increase %	Conversion to ethylene: Volume %	Conversion to ethylene: Weight %
55	780	1 436	3 98	0 80	950	5 59	28 1	20 9	40 5	39 5	36 9
50	782	1 440	3 83	0 85	914	5 60	29 6	21 0	46 2	43 3	40 4
58	780	1 436	2 22	1 38	529	3 35	31 9	20 0	50 7	48 1	44 9
54	777	1,430	2 12	1 47	504	3 11	31 5	19 8	46 8	46 2	43 1
53	785	1 445	2 13	1 48	484	3 18	34 2	19 5	49 0	51 1	47 6
51	780	1 436	1 82	1 69	434	2 88	32 6	19 0	58 0	51 5	48 1
56	772	1 421	1 28	2 5	305	1 83	30 2	19 3	42 5	43 0	40 3
52	785	1 445	1 14	2 6	272	1 94	28 2	17 5	70 0	47 8	44 6
57	773	1 423	1 17	2 6	279	1 81	31 2	19 4	55 0	48 3	45 1
42	812	1 494	6 06	0 50	1 440	9 60	33 2	20 0	58 0	52 6	49 1
40	817	1 502	4 94	0 54	1 175	8 15	34 1	19 8	65 0	56 2	52 4
59	812	1 494	4 55	0 65	1,080	7 06	33 6	19 5	55 0	52 1	48 6
43	810	1,490	4 04	0 73	961	6 66	35 5		64 6	58 5	54 6
49	813	1,496	3 78	0 76	900	6 44	34 9	18 8	70 5	59 5	55 6
39	816	1 500	3 32	0 85	790	5 54	35 6		66 5	59 3	55 3
44	813	1,496	1 94	1 42	461	3 51	37 5	17 5	80 5	67 7	63 0
45	843	1,550	5 89	0 47	1,400	10 42	39 2	18 3	77 0	69 4	64 9
47	844	1 552	4 00	0 65	953	7 60	39 0	16 6	90 0	74 1	69 1
46	832	1,530	4 06	0 66	967	7 45	38 8	17 7	83 0	71 3	66 6
48	855	1,571	1 99	1 27	474	3 89	32 2	15 4	96 0	63 1	59 0

In Fig 1 the volume per cent conversion of ethane to ethylene is plotted against the per cent volume increase In the absence of any secondary reactions the volume increase should be numerically equal to the volume yield of olefines, and as Fig 1 shows, the deviation of experimental points from the theoretical curve is quite small but increase with increasing conversion This figure also demonstrates that temperature, per cent conversion, and reaction time *per se* have little influence on the course of the reaction The curve in Fig. 1 represents all the data obtained in the temperature range 1,440–1,550° F (782–843° C), and at reaction times varying from 0 5 to 2 6 sec

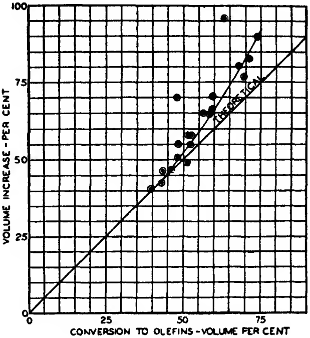

FIG 1 Volume increase *v* conversion to olefines in ethane pyrolysis

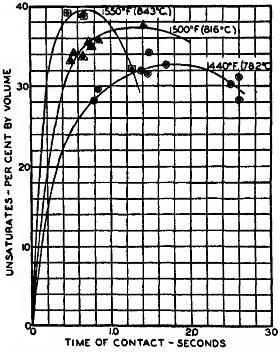

FIG 2 Unsaturates in exit gas *v* time of contact in ethane pyrolysis

In Fig 2 the olefine content of the exit gas is plotted against reaction time, and it is apparent that the greatest olefine concentration is obtained by operating at high temperatures and short reaction times Volume per cent yield of olefines is plotted against reaction time in Fig 3

Under optimum conditions 74% of the ethane treated was converted into olefines in one pass These figures demonstrate that olefine yield and olefine content of the cracked gas increase at any given temperature with increasing reaction time until optimum conditions are reached, after which a further increase in reaction time results in decreased olefine yield and lower olefine concentration in the cracked gas This decrease is due to the destruction of ethylene through secondary reactions giving carbon, hydrogen, and methane, and also aromatic liquids

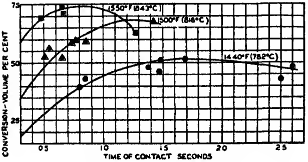

FIG 3 Conversion to olefines *v* time of contact in ethane pyrolysis

Further important work on the production of ethylene from ethane by pyrolysis has been carried out by Cambron and his co-workers [6, 1932, 7, 1933], using reaction tubes internally heated by glowing carbon rods No details are, however, available for the calculation of reaction times and space velocities obtained in these experiments Results obtained by Tropsch and Egloff [53, 1935] on the pyrolysis of ethane and other gases at 1,100–1,400° C are considered later

A possible method of obtaining greater yields of ethylene from ethane than those mentioned above is to operate at a sufficiently low temperature to obtain a low conversion of ethylene per pass, and to remove the ethylene before recycling the residual ethane In this way the production of methane and hydrogen would be considerably decreased

The data of Sullivan, Ruthruff, and Kuentzel give the following rates of ethylene production under the optimum conversion conditions

	780° C	*813° C*	*844° C*
Cu ft ethylene per cu ft reaction space per hour	223	535	704
Lb ethylene per cu ft reaction space per hour	16 5	39 6	52 1
Grammes ethylene per litre reaction space per hour	264	633	833

Propane.

As already mentioned, it is not feasible to convert propane exclusively into propylene and hydrogen to an extent sufficiently attractive for large scale operation by thermal non-catalytic decomposition, because lower paraffins and olefines are both formed The work of Hague and Wheeler [31, 1929] shows this very clearly For example, at 700° C propane gave an exit gas containing 14 2% higher olefines and 23 1% ethylene plus acetylene At 850° C the higher olefine content of the exit gas was only 2 3%, while that of ethylene was 14 5% Under these conditions the volume per cent yield of higher olefines (presumably propylene) was 21 7% and 4 8%, respectively, at these two temperatures In order to obtain high yields of propylene without the concurrent formation of ethylene, methane, and ethane, resort must be made to catalytic dehydrogenation (see later)

Similar results have been described by Frolich and Wiezerich [28, 1935] These are given in Fig 4

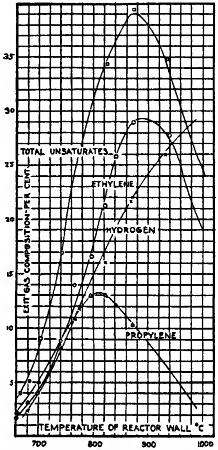

FIG 4 Pyrolysis of propane (Frolich and Wiezerich)

Using a quartz reaction tube, a contact time of 0 4 sec and a space velocity of *c* 7,500, the maximum concentration of propylene in the exit gas was 13 2%, and this occurred at a lower temperature (810° C) than the maximum concentration of ethylene (29 4%), which occurred at 890° C The ratio of ethylene to propylene in the cracked gas was roughly 2 to 1, increasing slightly with temperature, presumably because the propylene initially formed enters more readily into secondary reaction than does the ethylene However, if the cracking of propane is carried nearly to completion, the sum of ethylene and propylene in the exit gas is close to 40% over a wide temperature range Since the volume of gas is practically doubled by the cracking process, this means that the yield of ethylene plus propylene is of the order of 80% (by volume) on the basis of entering propane This is equivalent to 56% by weight

Tests made by Ebrey and Engelder [14, 1931] at a constant space velocity of 98 vols of inlet gas per volume of reaction space per hour, gave an ethylene+propylene concentration in the exit gas of 33 7% by volume, at a temperature of 760° C The maximum propylene concentration in the exit gas was 10 7% by volume—obtained at 660° C At 760° C the yield of ethylene+propylene was

42 5% by weight of the propane treated This low yield may be attributed to the low space velocity employed

One of the most complete published accounts of the pyrolysis of propane for the production of olefines is that by Sullivan, Ruthruff, and Kuentzel [50, 1935] Qualitatively the results obtained are similar in all respects to those obtained by the same workers on ethane (see above) A plot of volume per cent conversion of propane to olefines against per cent volume increase is satisfied by one curve, regardless of the time and temperature conditions employed to obtain the individual points The deviation of this curve from the theoretical is small but increases rapidly as conversion increases This is reproduced in Fig 5 As shown in Figs 6 and 7, the volume olefine yield and the olefine content of the cracked gas are both maximum when operating at high temperatures and short contact times On increasing the time of contact beyond that necessary for optimum results, the olefine content of the cracked gas and the olefine yield both decrease because of destruction of the olefines through secondary reactions The highest weight per cent conversion of propane to olefines obtained was 55% The detailed results of Sullivan, Ruthruff, and Kuentzel on the pyrolysis of propane are reproduced in Table III

Further work of value on the production of olefines by the pyrolysis of propane is that by Cambron and Bayley [7, 1933] These workers found that when pyrolysis is carried out under conditions of turbulent flow, the yields of olefines obtained at a given temperature are greatly increased over those obtained under conditions of streamline flow They also found that under conditions of turbulent flow higher rates of conversion to olefines are possible since the temperatures at which side reactions begin to be noticeable are considerably higher under these conditions Cambron and Bayley obtained turbulent flow conditions by inserting suitable baffles in their reaction tubes [8, 1935]

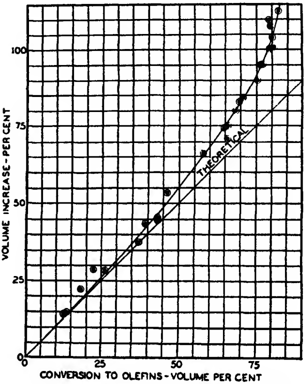

FIG 5 Volume increases v conversion to olefines in propane pyrolysis

TABLE III

Propane Pyrolysis in KA2S Coil [50, 1935]
(Sullivan, Ruthruff, and Kuentzel)

Run no	Mean reaction temp °F	Mean reaction temp °C	Inlet gas litres per min	Reaction time sec	Space velocity	Exit gas: Litres per min	Exit gas: % Unsaturateds	Exit gas: Mol wt	Exit gas: Mol wt olefines	Volume increase %	Conversion: Volume %	Conversion: Weight %	Grammes of olefines per litre of reaction space per hour
3	1,260	682	5 96	0 71	1,420	6 82	11 0	35 7	34 6	14 5	12 6	9 9	
2	1,246	674	3 98	1 03	950	4 61	11 7	35 8		14 8	13 6		
1	1,247	675	2 01	1 90	476	2 46	15 0	40 0		22 2	18 3	12 7	
4	1 310	710	5 72	0 67	1,365	7 36	17 4		31 6	28 6	22 4	16 1	
5	1,305	707	4 02	0 94	957	5 16	20 4		31 6	28 5	26 2	18 8	
6	1,313	712	1 96	1 78	467	2 81	24 4		32 1	43 4	39 3	28 7	236
7	1,407	764	8 30	0 42	1,980	11 4	27 1	30 0	32 8	37 5	37 2	27 7	
8	1,412	767	6 30	0 53	1,500	9 18	29 7	28 5	32 2	45 6	43 3	31 7	
9	1,410	766	6 34	0 53	1,510	9 14	29 9	28 5	32 2	44 6	43 3		
10	1,403	762	4 20	0 77	1,000	6 4	30 1	27 0	33 5	53 5	46 2	35 2	
11	1,412	767	2 13	1 39	508	3 72	37 0	23 8	31 6	74 5	64 6		
12	1,466	797	6 59	0 46	1,560	10 62	36 0	25 0	30 3	61 1	58 0	40 0	
13	1,465	796	4 13	0 71	997	7 06	38 5	24 3	32 4	71 0	65 8	48 5	
14	1,460	793	2 17	1 25	517	4 13	39 6	22 5	31 5	90 2	75 2	53 4	552
15	1,498	814	8 28	0 35	1,960	14 48	37 6	25 5	32 3	75 0	65 8	48 3	1,880
16	1,494	812	6 36	0 43	1,520	11 71	38 4	24 8	34 1	84 3	70 8	54 8	
17	1,495	813	4 24	0 62	1,010	8 29	39 5	22 6	30 2	95 4	77 1	53 0	
18	1,497	814	2 07	1 21	492	4 31	38 2	20 4	30 4	108 0	79 5	55 0	
19	1,491	811	2 73	0 95	650	5 47	39 6	21 6	29 8	100 2	79 3		
32	1,503	817	8 16	0 34	1,945	14 7	38 0	25 0		80 0	68 4		
33	1,497	813	4 23	0 62	1,010	8 26	39 2	22 2		95 2	76 4		
34	1,505	818	2 71	0 94	644	5 54	39 4	20 6		104 0	80 1		
35	1,505	818	2 17	1 14	517	4 56	37 6	19 8		110 0	79 0		
36	1,486	808	6 19	0 45	1,480	11 33	37 9	c 25		83 0	69 4		
37	1,499	815	4 13	0 62	997	8 30	40 2	23 0		101 0	80 8		
38	1,508	820	2 43	1 01	580	5 18	38 5	c 22		113 0	82 1		

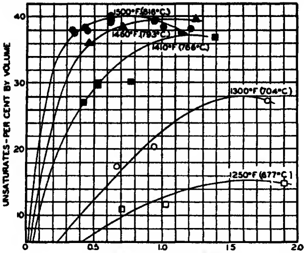

FIG 6 Unsaturates in exit gas v time of contact in propane pyrolysis

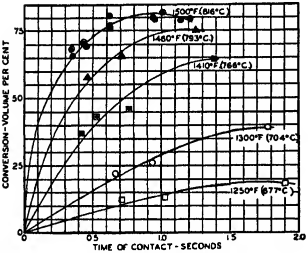

FIG 7 Conversion of olefines v time of contact in propane pyrolysis

Space velocities up to 4,000 and temperatures of 800–1,087° C were employed Under these conditions the optimum results obtained were as summarized below (Table IV)

The production of olefines by the thermal pyrolysis of propane at super atmospheric pressure has been studied by Tropsch, Thomas, and Egloff [55, 1936], whose results may be summarized as follows in Table V

TABLE V

The Production of Olefines by the Pyrolysis of Propane at Super-atmospheric Pressure

Run no	*A*	*B*	*C*	*D*
Temp ° C	555	555	585	585
Reaction time (sec)	95	144	52 5	86 8
% inlet propane decomposed	13 0	17 6	21 6	39 9
Liquid product				
U S gal per 1,000 cu ft input	0 1	0 4	0 5	0 9
Imp ,, ,, ,,	0 08	0 33	0 42	0 75
Gaseous products				
% by vol of propane decomposed				
H_2	6 1	4 9	9 8	6 6
CH_4	48 4	50 5	83 5	57 9
C_2H_6	36 3	20 5	20 5	30 8
C_2H_4	25 2	32 3	27 8	16 3
C_3H_6	32 4	28 8	35 6	23 5
Total olefines	57 6	61 1	63 4	39 8
Mean molecular weight of olefines produced	35 9	34 6	35 9	36 4
Yield of olefines				
% vol on propane decomposed	57 6	61 1	63 4	39 8
, , , input	7 48	10 75	13 65	15 9
% wt on propane decomposed	47 0	48 1	51 8	33 2
, , ,, input	6 1	8 47	11 2	13 2

These results are of particular interest in view of the high mean molecular weight of the olefines produced

Butanes

The olefines produced by the non-catalytic pyrolysis of *n*-butane and isobutane comprise ethylene, propylene, and butylenes—the more severe the conditions the lower the average molecular weight of the olefines produced That is, the behaviour of butanes is similar to that of propane in this respect

The effect of temperature on the products obtained from *n*-butane as determined by Frolich and Wiezevich is shown in Fig 8 In these experiments the contact time was 0 4 sec and the space velocity *c* 340, and, under these conditions, the temperature (650° C) at which maximum propylene concentration occurs (11 1 %) is somewhat lower than the temperature (730° C) for maximum ethylene (29 %) The highest concentration of butylene (8 1 %) was reached at

TABLE IV

Optimum Results Obtained by Cambron and Bayley in the Pyrolysis of Propane for Olefine Production

Expt no	*Temp ° C*	*Space velocity*	*Conditions of flow*	*Reactor*	*Expansion % vol*	*% wt*	*% vol*	*Olefines in exit gas, % vol*		*Olefine production rate*	
								Ethylene	*Propylene*	*Grams per litre reaction space per hour*	*Lb per cu ft reaction space per hour*
15	1,050	3,560	streamline	quartz	78 3	31 7	47 4	21 8	4 8	2,110	132
18	950	3,560	turbulent	,,	99 6	54 7	78 0	30 4	8 8	3,630	227
36	1,087	4,100	,,	,,	76 4	50 0	65 8			3,920	245
84	977	1,236	streamline	KA2S	66 9	38 8	54 0	22 5	9 8	895	55 8
81	949	1,250	turbulent	,,	81 2	50 2	70 0	28 0	9 6	1,160	69 5
97	860	1,295	,,	28 % Chromium alloy	84 0	50 2	72 8	28 3	11 4	1,320	82 0

about 670° C For maximum total unsaturateds in the exit gas, a temperature of about 690° C was required

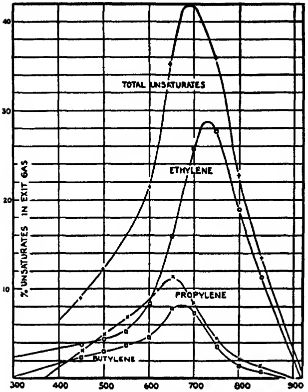

FIG 8 Pyrolysis of normal butane (Frolich and Wiezerich)

The experimental results of Hague and Wheeler [31, 1929] on butane have already been mentioned These were obtained at very low space velocities (*ca* 49), i e long times of contact The highest total olefine content in the exit gas was 42 5% vol (i e 19 7% higher olefines, 2 4% C_2H_2 (probably C_2H_4), and 20 4% C_2H_4), at a temperature of 700° C Under these conditions a 2 3% oil yield was obtained simultaneously and higher temperatures gave decreased olefine yields, but higher liquid yields Valuable results at higher space velocities, i e under conditions much nearer to commercial scale practice than those of Hague and Wheeler, have been obtained by Cambron and Bayley [7, 1933] These results, together with figures derived therefrom by the author of this paper, are detailed in Table VI It will be observed that the high space velocities used by Cambron and Bayley necessitated the use of temperatures up to 990° C, but under these conditions the output of olefines per unit of reaction space was very high

The production of gaseous olefines and liquid products by the pyrolysis of butanes at 725 lb per sq in (51 kg per cm ^{2}) has been studied by Tropsch Thomas, and Egloff [55, 1936], whose results have already been discussed on theoretical grounds At these pressures the temperatures required (525–550° C) for olefine production are much lower than those necessary at substantially atmospheric pressure, but the reaction times (40–120 sec) are correspondingly longer Under these conditions it was found necessary to limit the percentage decomposition per pass in order to reduce carbon formation, and in all tests liquid products were produced The results obtained by Tropsch *et al* have been used to calculate the data pertaining to them given in Table VII It is noteworthy that the olefines produced under these conditions had average molecular weights ranging from 43 to 48 (i e approximating to propylene) A suitable recycling arrangement would allow the production (see later) of *circa* 50% by weight of such olefines, plus 1–4 Imp gal of liquid product per 1,000 cu ft of butane treated These yields are very promising

General Considerations on the Production of Olefines by Non-catalytic Pyrolysis

The above account of the more important published work on the production of olefines by the pyrolysis of the gaseous paraffins may be briefly summarized as follows

1 Olefines may conveniently be produced by this means. Yields up to 50–60% by weight may be realized

2 The temperature and reaction time conditions required

TABLE VI

Pyrolysis of n-Butane (Cambron and Bayley) [7, 1933]

Reactor	*Expt no*	*Inlet gas rate, litres per hr*	*Size of reactor, cm*	*Re-action vol c c*	*Space velocity inlet gas*	*Temp ° C*	*Exit gas anal %, vol*				*Ex-pansion %*	*Yield of olefines*		*Olefines g per hr*	*Olefine prodn rate*		*Remarks*
							C_2H_4	C_3H_6	C_4H_8	*Total olefines*		*% wt*	*% vol*		*lb per cu ft reaction vol per hr*	*g litre reaction vol per hr*	
Empty quartz	21	203 8	18 5 × 2 0	58	3,520	852	9 3	10 2	1 4	20 9	24 2	17 0	26 0	85 4	94	1 475	
,,	22	204 6	,,	58	3,525	910	13 0	10 9	1 7	25 6	45 2	18 8	37 1	94 7	104	1,630	Formation of liquid products observed
,,	23	202 1	,,	58	3,480	950	16 7	10 5	2 7	29 9	63 0	30 6	48 7	152 1	168	2 625	
,,	23A	204 6	,,	58	3 525	990	20 7	10 0	2 2	32 9	78 4	34 8	58 8	175 7	193	3 020	
Baffled quartz	24	205 4	,,	58	3,550	840	12 2	13·9	2 9	29 0	43 1	27 9	41 5	141 5	156	2,440	
,,	25	202 1	,,	58	3 480	868	14 2	15 1	2 6	31 9	56 3	32 9	49 9	164 2	181	2 830	
,,	26	203 8	,,	58	3,520	895	15 7	17 0	1 8	34 5	67 6	37 5	57 8	189 2	208	3,260	Formation of liquid products observed
,,	27	203 8	,,	58	3,520	922	19 6	15 0	2 1	36 7	83 3	41 7	67 1	210 4	232	3 630	
,,	53	396 5	40 × 2 5	196	2,020	881	14 7	16 8	5 0	36 5	61 9	40 7	59 0	399·0	130	2 030	
,,	54	399 0	,,	196	2,030	913	17 2	18 4	4 3	39 9	80 8	48 0	72 0	473 0	154	2 420	
,,	55	397 5	,,	196	2,025	940	19 8	18 4	3 1	41 3	97 6	52 5	81 2	515 0	168	2,630	
,,	56	808·0	80 × 2 5	392	2 060	827	9 4	12 6	4 4	26 4	41 0	27 4	37 2	545 0	88 5	1 390	
,,	57	812·0	,,	392	2,080	858	11 7	14 7	5 0	31 4	58 0	34 8	50 2	700·0	114	1 785	
,,	58	808·0	,,	392	2,060	898	14 6	16 3	5 8	36 7	73 7	44 1	63 8	879 0	143	2,240	
,,	59	808 0	,,	392	2,060	915	16 4	17 3	5 3	39 0	88 1	50 0	73 4	995 0	162	2,540	

TABLE VII

Pressure Pyrolysis of Butanes (Tropsch, Thomas, and Egloff)

Material treated	*Normal butane*				*Isobutane*		*Commercial butane*		
Run no	*F*	*F*	*G*	*H*	*I*	*J*	*3*	*4*	*5*
Temp °C	525	525	555	555	555	555	350	550	550
Reaction time, sec	99	173	82 3	47	51	86 5	115	96	82
Pressure, lb per sq in	725	725	725	725	725	725	725	725	725
% of inlet gas decomposed	25 6	38 6	55 4	43 3	21 6	25 8	51 2	44 5	41 7
Liquid produced									
U S gal per 1,000 cu ft input	0 75	1 3	2 2	1 3	0 3	0 4	3 1	2 3	2 3
Imp gal per 1 000 cu ft input	0 62	1 08	1 83	1 08	0 25	0 33	2 58	1 92	1 92
Gaseous products									
% vol of C_4H_{10} decomposed									
H_2	1 5	1 9	2 2	nil	5 5	6 4			
CH_4	35 1	58 5	52 5	45 8	45 8	42 2			
C_2H_6	45 8	29 5	30 6	27 7	1 3	5 0			
C_3H_8	19 6	16 7	14 4	13 1	19 2	20 7			
C_2H_4	12 5	6 9	7 4	10 3	2 9	4 5			
C_3H_6	18 2	21 3	25 1	31 0	19 2	20 7			
C_4H_8	23 2	18 3	17 8	16 0	20 3	20 9			
Mol wt of olefines produced	44 8	45 4	45 1	43 4	49 3	48 4			
Yield of olefines % vol on									
C_4H_{10} decomposed	53 9	46 5	50 3	57 9	42 4	46 1	50 2	57 5	61 4
C_4H_{10} input	16 35	17 9	27 8	25 0	9 15	11 9	25 7	25 6	25 6
% weight on									
C_4H_{10} decomposed	41 7	36 4	39 2	43 4	36 1	38 4			
C_4H_{10} input	12 65	14 0	21 7	18 7	7 8	9 9			

are less severe than those necessary for liquid hydrocarbon formation

3 Olefines may be produced over a very wide temperature range (i e 600–1,000° C) by proper choice of the reaction times

4 The shorter the reaction time—i e the higher the space velocity employed—the higher is the temperature required for a given conversion

5 The olefines produced are invariably of considerably lower molecular weight than the parent paraffins—i e olefines are produced by the splitting of carbon chains in preference to simple dehydrogenation

6 The more severe the conditions employed the lower is the molecular weight of the olefines produced, i e ethylene is the predominating olefine product under severe pyrolysis conditions (Acetylene is also an important high temperature product—this is dealt with later)

7 The higher the molecular weight of the paraffin treated, the milder the reaction conditions required for a given conversion, or alternatively, the greater the conversion under given reaction conditions

The reaction conditions and the results obtained by selected workers in this field are summarized in Table VIII These refer to experiments in which conditions were controlled so as to prevent the formation of oils and substantial amounts of coke.

Thermal Considerations.

The pyrolysis reaction for the production of gaseous olefines is markedly endothermic, as shown by the following typical reactions

$C_2H_6 \rightarrow C_2H_4 + H_2$ — 32,000 cal per g mole (1920 B Th U per lb)
$C_3H_8 \rightarrow C_3H_6 + H_2$ — 32,000 „ (1309 , ,)
$C_3H_8 \rightarrow C_2H_4 + CH_4$ — 16 100 (658 6 , ,)
$n\ C_4H_{10} \rightarrow C_4H_8 + H_2$ — 32 000 , (993 1 , ,)
$n\ C_4H_{10} \rightarrow C_2H_4 + C_2H_6$ — 17,000 , (527 6 , ,)
$n\ C_4H_{10} \rightarrow C_3H_6 + CH_4$ — 17 600 , , (546 2 , ,)

As a result a large quantity of heat at a high temperature level must be transmitted to the reacting gas It is, therefore, essential to employ highly turbulent flow of the gas within the reaction tubes so as to obtain a heat transfer rate as high as possible Without such highly turbulent flow side reactions occur leading to the formation of coke and aromatic liquids, and the throughput capacity of the plant is considerably reduced

Plant Arrangement.

It is evident that the reaction coil must be heated, and the plant arrangement is simple A gas-fired furnace, designed on conventional lines, serves for both preheat and reaction heat duties, but care must be taken in the choice of suitable furnace tube materials Such steels as Krupps NCT3 and Hadfields HR3 (both containing 25% chromium and 20% nickel) are satisfactory for use at temperatures up to 1,000° C, while for lower temperatures there is a wide range of suitable tube steels—including austenitic stainless steels and molybdenum and chromium steels

It is frequently found that steels of different chemical composition have appreciably different catalytic affects upon the reactions involved The use of steels containing large quantities of nickel (but only a little, or no, chromium) is to be avoided because they accelerate carbon formation

Large-scale Installations.

As far as is known, the only large-scale plants in operation for the manufacture of olefines by the pyrolysis of gaseous paraffins are those of certain American chemical manufacturers, who utilize the olefines produced, particularly ethylene, for the production of synthetic organic chemicals The reason for the non-adoption of this process on any scale by the petroleum industry is the rapid development of combination pyrolysis—polymerization plants by which paraffins are converted into olefines and the olefines then polymerized in one plant These plants obviate the necessity of segregating the olefines produced and then subsequently polymerizing them

The Production of Gaseous Olefines by the Dehydrogenation of the Lower Paraffins

It has already been mentioned that the low yields of olefines obtainable from the gaseous paraffins by pyrolysis processes, due mainly to the fact that cracking (i e formation of hydrocarbon containing a smaller number of carbon atoms) is the predominating reaction, may be considerably improved in processes of catalytic dehydrogenation Thus the highest yield of olefines yet obtained from butane by pyrolysis is about 60% by weight, whereas by dehydrogenation it is theoretically possible to obtain an olefine yield of 96 5% by weight consisting entirely of butylenes This high yield of olefines is not obtainable in single pass operation, for reasons which are given later, but such a process offers other attractions (e g production of hydrogen for hydrogenation)

TABLE VIII

Summary of Published Results on Olefine Production by Thermal Pyrolysis

Investigators	*Material treated*	*Temp ° C*	*Reaction time, sec*	*Space velocity*	*Wt % yield of olefines*	*Pressure lb per sq in gauge*	*Olefine production rate*		*Remarks*
							G per litre reaction space per hr	*lb per cu ft reaction space per hr*	
Dunstan and Howes [13]	Natural and refinery gases	750–900		200–2,500	50–60	0 30	3 200-16,000	200–1,000	
Sullivan, Ruthruff, and Kuentzel [50]	Ethane	780–855	0 5–1 7	270–1,440	36 9–69 1	Atm	264–834	16 5–52 1	
Hague and Wheeler [31]	Ethane	750		49	50 5	Atm	33 7	2 1	Assumption made that the olefines produced had a mole wt of 28
Sullivan, Ruthruff, and Kuentzel [50]	Propane	674–820	0 43–1 9	467–1 980	up to 55	Atm	3,776–30,080	236–1,880	
Cambron and Bayley [7]	Propane	860–1 088		1 236–3,560	31 7–54 7	Atm	893–3 920	558–245	
Tropsch, Thomas and Egloff [55]	Propane	555–585	52 5 144		6 1–13 2	725			% decomposition per pass limited to avoid coke formation
Hague and Wheeler [31]	Propane	750		49	57 2	Atm	55 9	3 49	
Cambron and Bayley [7]	*n*-Butane	827–990		2 020–3,550	17–52 5	Atm	1,504–3,712	94-232	
Hague and Wheeler [31]	*n*-Butane	700		49	49 0	Atm	62 8	3 9	
Tropsch, Thomas and Egloff [55]	*n*-Butane	525-555	47–175		12 6–21 7	725			% decomposition per pass limited to avoid coke formation
	i-Butane	555	51–86 5		9 15–11 9	725			do
,	Comm butane	550	82-115		*c* 25% (vol)	725			do

TABLE IX

Maximum Conversion to Olefines by Dehydrogenation of Paraffins at 350–700° C *from the data of Frey and Huppke* [23, 1933] (*Percentage Conversion to Olefines* (*volume*))

	350 C	*400° C*	*450° C*	*500° C*	*550° C*	*575° C*	*600° C*	*650° C*	*700° C*
Ethane		1 0	2 8	5 8	9 5	13 0	17 8	28 2	40 8
Propane	1 9	4 7	8 7	16 3	28 2	37 0	43 9		
n-Butane	3 8	9 4	19 1	32 5	52 3				
Isobutane	4 2	10 0	20 1	32 8					

TABLE X

Maximum Concentration of Olefines in Exit Gas by Dehydrogenation of Paraffins (*per cent volume*) [23, 1933]

	350° C	*400° C*	*450° C*	*500° C*	*550° C*	*575° C*	*600° C*	*650° C*	*700° C*
Ethane		1 0	2 7	5 5	8 7	11 5	15 0	22 0	29 0
Propane	1 9	4 5	8 0	14 0	22 0	27 0	30 5		
n-Butane	3 7	8 6	16 0	24 5	34 3				
Isobutane	4 0	9 1	16 7	24 7					

The equilibrium

$$\underset{\text{Paraffin}}{C_nH_{2n+2}} \rightarrow \underset{\text{Olefine}+\text{Hydrogen}}{C_nH_{2n}+H_2}$$

lies well over to the left at temperatures below 350° C, but the extent of dehydrogenation increases with rise in temperature and proceeds extensively above 450° C Of particular interest is the work by Frey and Huppke [23, 1933] on the experimental determination of the dehydrogenation equilibrium in the case of ethane, propane, and the butanes, whose results have already been discussed They are also presented in Fig 3 of the article entitled 'Pyrolysis of Gaseous Hydrocarbons' (p 2013) These results enable the percentage conversions of the lower paraffins into the corresponding olefines to be calculated for any particular temperature From the values of *K* given in Fig 3 (p 2013), the extent of dehydrogenation theoretically possible has been calculated—as reproduced in Table IX, while the corresponding concentrations of olefines in the exit gases are set out in Table X

According to Frey and Huppke (loc cit) no molecular rearrangement occurs in dehydrogenation in the presence of suitable catalysts, with the result that *n*-butane yields *n*-butylenes only and isobutane gives exclusively isobutylene

It is evident from the above figures that it is thermodynamically possible to obtain from *n*- or isobutane, for example, an exit gas containing *c* 30% butylenes by dehydrogenation at 550° C, the other constituents being 30% hydrogen and 40% undecomposed butane In practice, however, there are various conditions which must be realized before the reaction involved can proceed satisfactorily The most important requirement is a suitable catalyst to speed up the dehydrogenation reaction so that it may proceed at a much greater rate than any cracking reactions Figures already presented show that in the absence of such a catalyst dehydrogenation proceeds only to a slight extent Other important requirements are choice of pressure and temperature conditions, and also choice of catalyst such that there is complete prevention of any cracking reactions which cause the deposition of cracked products and carbon on the catalyst and so reduce its activity Polymerization of the olefines formed must also be prevented, because this also causes the deposition of deleterious products on the catalyst

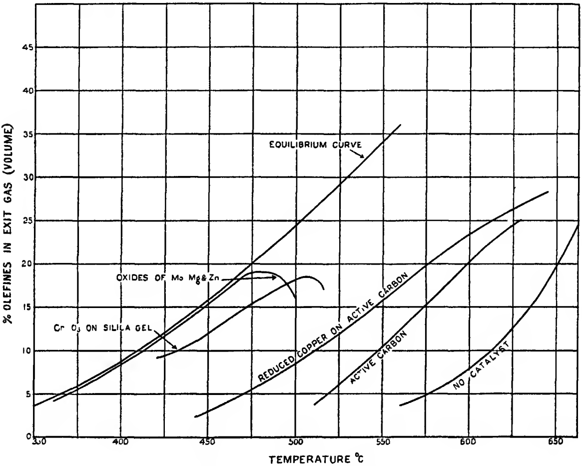

FIG 9 Dehydrogenation of normal butane (97% pure)

Catalysts.

Various catalysts have been used in the dehydrogenation of the lower paraffins According to Pease [44, 1923], copper is active in this direction, but loses its activity rapidly, while nickel, platinum, and palladium have been reported to bring about complex decomposition in addition to simple dehydrogenation [15, 1930–2]

The I G Farbenindustrie [17, 1927] claim the production of amylene by passing pentane over active carbon at 450–500° C, and Tausz and Putnoky [51, 1919] have dehydrogenated pentane, hexane, heptane, and octane over palladium at 300° C In their work on the determination of equilibrium constants, Frey and Huppke [23, 1933] used a chromic oxide gel catalyst prepared by precipitation from a chromic nitrate solution by ammonia in the presence of ammonium acetate The gel was black in appearance and vitreous in texture At temperatures above 450° C, however, this catalyst suffers from deterioration in activity Chromic oxide catalysts not in the gel form are reputed to give inferior results [37, 1933], while the best results are claimed to be obtained from chromic oxide gel catalysts made by precipitation from chromic nitrate solution by caustic soda or caustic potash Such gels retain their gel structure on drying and heating Catalysts of good catalytic activity may also be obtained by precipitation with ammonia in the presence of acetic acid, sulphuric acid, aluminium salts, or soluble silicates [37, 1933]

Mixtures of chromic oxide and zinc oxide have been claimed as satisfactory catalysts for the dehydrogenation of paraffin hydrocarbons higher than methane by Frolich and Boeckeler [27, 1934] The temperature range is quoted as

450–700° C. Catalysts containing zinc oxide and another oxide of a metal which has two or more valencies are favourably mentioned, such as 30 mole % zinc oxide plus 70 mole % chromium oxide, or other proportions of the same oxides, or zinc oxide and molybdenum oxide According to Frolich and Boeckeler [27, 1934], the space velocities allowable with such catalysts are in the neighbourhood of 780, but may range from 108 to 6,480 The catalysts must be reduced before use and it is often advantageous to dilute the ingoing paraffin hydrocarbon gases with nitrogen or water vapour—or else with hydrogen—which tend to prevent carbon deposition A process has been described by Frolich [24, 1932], in which gaseous paraffin hydrocarbons are dehydrogenated to the corresponding olefines, using the chromium oxide–zinc oxide catalysts described above, the resulting hydrogen is then removed by treatment with reducible metallic oxides (such as copper oxide) and the olefine polymerized The removal of hydrogen before the polymerization stage by treatment over a suitable catalyst with carbon monoxide has also been suggested [25, 1935] In this case the reaction involved is

$$CO+3H_2 \rightarrow CH_4+H_2O$$

and the catalyst employed is nickel in various forms

Dunstan and Howes [13, 1936] have described tests made on the dehydrogenation of *n*-butane and isobutane Their results on a variety of catalysts are shown in Figs 9 and 10 With the most satisfactory catalysts equilibrium conditions were established at temperatures up to 450–500° C. In general, above this temperature cracking took place with the formation of methane and ethane, carbon was also deposited The most effective catalysts examined by Dunstan and Howes comprised mixtures of molybdenum, zinc, and magnesium oxides, and ammonium chromate deposited on carriers, such as silica gel and active carbon In the temperature range 400–600° C the allowable space velocities varied from 250 to 2,000, the higher throughputs being obtained with the more active molybdenum and chromium catalysts

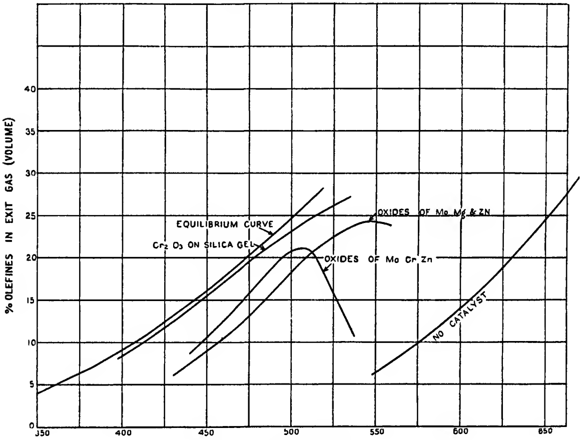

Fig 10 Dehydrogenation of isobutene

The patent literature contains several statements concerning effective catalysts for the dehydrogenation of ethane and higher gaseous paraffin hydrocarbons The most important of these may be summarized as follows

- Copper and porcelain catalysts [32, 1925]
- Various metals and alloys, also nickel, calcium, and platinum [33, 1933]
- Reaction chambers constructed of chromium steel [44, 1923]
- Porous materials such as active carbon and silica gel [52, 1934]
- Zinc, aluminium, and nickel oxides on supports [52, 1934]
- Heavy metals of group I, e g gold, silver, or copper, or their alloys [59, 1934]
- Stainless steels coated with tin, zinc, lead, aluminium, and chromium, with free elementary silicon [2, 1908]

Silicates, phosphates, and borates of copper, manganese, lead, and copper [58, 1935]
Vapours of mercury, lead, tin, and zinc [60, 1935]
High-temperature cokes [19, 1935]
Silicon carbide [18, 1935]

Large-scale Plant Operation.

Because dehydrogenation is an equilibrium reaction and because temperatures high enough for substantially complete conversion per pass are not allowable—due to secondary reactions, a recycle operation is necessary It is usually undesirable, with the catalysts at present available, to operate at temperatures in excess of 500° C This limits the extent of dehydrogenation as follows

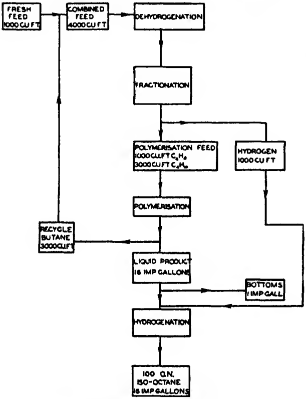

FIG 11 Flow diagram Dehydrogenation of isobutane (Ideal operation)

Ethane	9 5%
Propane	28 2%
n-Butane	52 3%
Isobutane	*c* 60%

Moreover, it is usually preferable to employ catalysts which do not give the theoretical conversion, and, in practice, on C_3–C_4 paraffin mixtures the decomposition per pass rarely exceeds 35% This necessitates the use of a recycle ratio of 65/35—i e the feed consists of 65 parts of recycle material and 35 parts fresh feed The olefines and hydrogen must be separated from the exit gas before returning this to the system, and a convenient arrangement is that shown diagrammatically in Fig 11, which relates to a typical treatment of butane

It is desirable to operate the dehydrogenation process at such a pressure that the feed to it may be handled in the liquid state—thus avoiding compressors—and also at such a pressure that simple separation or fractionation may be employed for the separation of the hydrogen from the paraffin-olefine mixture before passing the latter to polymerization

The plant requirements are not stringent Because of the fairly low temperatures required, the catalyst tubes may be constructed of normal carbon steels or the well-known steels containing small amounts of molybdenum and/or chromium The dehydrogenation reaction is markedly exothermic (990 B Th U per lb of paraffins reacting in the case of butane), and arrangements must be made for supplying this heat to the catalyst without danger of overheating This is the only important factor in the design of the equipment and must be given adequate attention

The dehydrogenation of the gaseous paraffins is receiving considerable attention in the petroleum industry at present, because it provides large quantities of raw materials for the manufacture of 100 octane number aviation fuels Thus butane fractions may be converted by this means into butylenes The latter may then be polymerized, by methods which are described later, into di-butenes, which, when hydrogenated, become converted into branched chain octanes of very high anti-knock value The following figures illustrate the yields obtainable in commercial operation

Feed material to dehydrogenation plant	*Propane*	*Butanes*	*Iso-butane*
Olefine yield (80% theory)			
Tons per 100 tons feed	76 4	77 3	77 3
Cu ft per 100 cu ft feed	80 0	80 0	80 0
Hydrogen yield (90% theory)			
Tons per 100 tons feed	4 1	3 1	3 1
Cu ft per 100 cu ft feed	90 0	90 0	90 0
Polymer yield (95% theory)			
Tons per 100 tons feed	72 6	73 4	73 4
Gallons per 1,000 cu ft feed	11 0	15 0	15 0
Polymer spirit 200° C E P			
Tons per 100 tons feed	64 3	66 1	66 1
Gallons per 1,000 cu ft feed	9 9	13 5	13 5
Hydrogenated polymer spirit, 200° C E P 100 octane number			
Tons per 100 tons feed			66 0
Gallons per 1,000 cu ft feed			14 2

The Production of Acetylene by the Pyrolysis of the Lower Hydrocarbons

Acetylene is produced in the pyrolysis of all hydrocarbons, but is mainly a high-temperature product For this reason the production of acetylene by pyrolysis has not received its due attention, and, moreover, the polymerization of acetylene to liquid hydrocarbons of gasoline boiling-range has not yet been fully explored Considerable data have been published on the synthesis of acetylene from methane by means of an electric discharge through the gas [49, 1932], or by passing methane through an electric arc [26, 1930] Cost estimates made by Storch [48, 1934] (based on a power cost of 0 25 cents per K W H) indicate, however, that such processes cannot compete with the production of acetylene from calcium carbide, with the latter at its present low price There are also several patented processes [22, 1931, 42, 1931] for the production of acetylene by the partial oxidation of methane, but so far these have made no headway

In 1932 Fischer and Pichler [20, 1932] published some data on the dehydrogenation of ethylene at temperatures from 1,000 to 1,400° C, and at reaction times varying from 0 004 to 0 005 sec Under these conditions the formation of hydrocarbons of higher molecular weight was always appreciable. On the other hand, little or no carbon was formed. The results obtained by these workers are summarized in Table XI, reproduced from a paper by Storch [48, 1934]. It is evident from these results that concentrations of acetylene in the exit gas as high as 32% were obtained, corresponding to ethylene conversions to acetylene as high as 92%. The percentage of ethylene decomposed is fairly constant, under the above-mentioned conditions, for any particular temperature, but there is a definite trend towards somewhat higher conversions at low ethylene partial pressures. The presence of hydrogen appears to retard the dehydrogenation rate. Pressure seems to affect the distribution of the products markedly, a lower partial pressure of ethylene resulting in a higher conversion to acetylene. Fischer and Pichler [20, 1932] have also given some results on the conversion of ethane to acetylene. These data are practically identical with those obtained for ethylene under the same conditions and indicate that the dehydrogenation of ethane to ethylene is much more rapid at 1,000° to 1,400° C than is the dehydrogenation of ethylene to acetylene. Acetylene was also produced in quantity by the pyrolysis of various petroleum fractions at 700–1,260° F [21, 1932], and 50–75% conversions of methane to acetylene realized by the pyrolysis of coke-oven gas at 1,500–1,600 and 0.004–0.005 sec. reaction time.

TABLE XI

Production of Acetylene by the Pyrolysis of Ethylene (Fischer and Pichler)

Expt. no.	Temp. ° C	Pressure (atm.) C_2H_4	Pressure (atm.) H_2	Pressure (atm.) N_2	% ethylene decomposed	Products as % of ethylene decomposed: Acetylene	Polymers	Methane	% acetylene in exit gas
8	1,000	1.0			8.5	16.5	83.5		1.3
2	1,000	0.1			13.0	32.3	53.1	8.5	3.6
11	1,000	0.5	0.5		6.4	12.5	45.3	42.2	0.4
19	1,000	0.5		0.5	9.9	30.3	51.6	19.2	1.4
9	1,100	1.0			20.9	23.9	64.2	9.6	4.3
3	1,100	0.1			26.0	95.0	[illegible]	2.3	18.8
12	1,100	0.5	0.5		20.0	43.0	38.0	19.0	3.9
20	1,100	0.5		0.5	27.0	43.4	49.6	7.0	5.2
10	1,200	1.0			46.2	29.4	60.3	9.5	10.6
4	1,200	0.1			54.4	67.4	25.2	7.3	23.6
13	1,200	0.5	0.5		45.1	47.5	36.7	15.8	9.4
21	1,200	0.5		0.5	54.4	42.0	48.7	9.4	9.3
5	1,300	0.1			82.2	72.0	22.6	4.6	31.8
7	1,300	0.017			93.4	66.3	30.2	3.5	32.0
10	1,320	0.05	0.05		80.6	75.4	19.4	4.3	24.4
12	1,300	0.0085	0.0085		85.8	76.3	17.1	5.6	23.5
14	1,280	0.025	0.075		62.8	84.8	2.9	8.9	10.9
18	1,300	0.0143	0.0857		61.6	81.2	13.2	5.6	6.8
9	1,400	0.017			98.5	59.0	39.0	2.0	28.8
11	1,380	0.05	0.05		95.2	74.0	22.3	3.7	27.0
13	1,400	0.0085	0.0085		98.7	73.5	23.5	2.7	24.6
16	1,400	0.025	0.075		97.0	87.4	11.1	1.5	16.4
19	1,400	0.0143	0.0857		91.1	92.3	3.1	4.6	11.1
20	1,410	0.0143	0.0857		100.0	90.0	2.0	8.0	11.2

Recently valuable contributions have been made by Egloff and his co-workers [53, 1935, 54, 1936] on the pyrolysis of the gaseous olefines and paraffins at 1,100–1,400° C and 50 mm. total pressure. Acetylene was in most cases an important reaction product. Considering their results on the gaseous paraffins first, it was found that at 1,100° C and 50 mm. total pressure, the highest yields of acetylene, expressed as per cent. by volume, were as follows, over a reaction time range of 0.8 to 100×10^{-3} sec.:

Ethane	10.0
Propane	25.0
***n*-Butane**	30.0

At 1,400° C. it was found that methane required from 10 to 20 times longer reaction time than ethane and propane to obtain maximum acetylene yields. A maximum of 12% by volume of acetylene was obtained from methane at 14.1×10^{-3} sec. reaction time. De Rudder and Biederman [46, 1930] have reported yields of 22% by volume, which they obtained using a reaction time of *c.* 100×10^{-3} sec. The pyrolysis of ethane and propane proceeded similarly at 1,400° C. as at 1,100° C. The maximum yields of olefines obtained at 1,400° C. were as follows:

	Ethylene	*Propylene*	*Acetylene*
From ethane			
Volume %	67	5.00	53
Reaction time 10^{-3} sec.	0.4	0.33	5.5
From propane			
Volume %	72	14.5	76
Reaction time 10^{-3} sec.	0.5	0.39	5.5

With regard to the olefines, the results obtained at 1,100° C. and 50 mm. total pressure were as follows:

	Ethylene	*Propylene*	*Butene 1*	*Butene 2*	*Isobutene*
Acetylene					
Volume %	21.0	21.8	35.0	26.0	40.3
Contact time 10^{-3} sec.	44.0	12.0	13.0	3.0	4.9
Ethylene					
Volume %		28.5	42.6	32.6	20.1
Contact time 10^{-3} sec.		12.0	13.0	5.8	4.0
Propylene+butylene					
Volume %	3.0				22.6
Contact time 10^{-3} sec.	2.2–44.0				2.8
Butadiene					
Volume %	1.5	2.6	17.4	23.3	10.9
Contact time 10^{-3} sec.	0.7–44.0	2.5–12.0	3.7	2.5	2.8

The highest yields of acetylene and ethylene obtained at 1,400° C. and 50 mm. pressure were as follows:

	Ethylene	*Propylene*	*Butene —1*	*Butene —2*	*Isobutene*
Acetylene					
Volume %	76.6	59.3	64.5	64.1	57.8
Contact time 10^{-3} sec.	2.3	2.2	0.9	1.9	1.8
Ethylene					
Volume %		26.4	38.2	9.9	10.3
Contact time 10^{-3} sec.		0.9	0.9	1.9	0.8

It is thus evident that acetylene can be produced by the pyrolysis of gaseous paraffins and olefines—particularly the latter—in attractive yields.

The high temperature required is a great disadvantage, however, especially when combined with sub-atmospheric-pressure operation. Metal reaction tubes are out of the question, and the only suitable materials for fabrication appear to be alundum and silicon carbide.

The Separation of Gaseous Olefines from Mixtures with Paraffins and Hydrogen

It is often desirable to segregate or concentrate olefines produced in pyrolysis processes, although usually the olefine-paraffin mixture is passed to polymerization or other treatment without intermediate purification.

The methods of separation available are as follows:

(*a*) Fractional distillation and partial liquefaction,
(*b*) Physical absorption with selective solvents,
(*c*) Chemical processes,
(*d*) Adsorption,

the applicability of which depends upon the gas mixture to be handled and the degree of separation required.

(*a*) Fractional Distillation, &c.

This can only be employed to separate constituents having boiling-points not closely similar. Usually it can be relied upon to yield fairly good separation between fractions containing different numbers of carbon atoms per molecule—i.e. a mixture of propylene and propane can be separated from a mixture of butanes and butylenes, but it is not usually feasible to separate olefines from the corresponding paraffins by this method. Much can be done, however, to concentrate olefines by the refractionation of selected cuts. Thus Carney [9, 1932] has reported it possible, for example, to separate 90% butylene (a mixture of *n*- and iso-butylene) by fractionation of a C_4 fraction, or to vary the content of the more reactive butylene, isobutylene, from 5% to more than 80% in a fraction containing only C_4 hydrocarbons.

The process of Linde-Bronn, which has been applied in Germany and Belgium to the separation of the constituents of coke-oven gas, is of interest as illustrating the potentialities of fractionation at low temperatures [4, 1917]. Coke-oven gas is cooled under pressure to separate first the easily liquefiable impurities, and also an ethylene-methane condensate. In this liquefaction step the coke-oven gas is cooled in a bath of liquid air or liquid nitrogen. Fractionation of the ethylene-methane condensate yields practically pure ethylene. Complete separation of methane and of carbon monoxide from the accompanying hydrogen can be accomplished by cooling the coke-oven gas, after removal of the ethylene-methane mixture, to a temperature about −209° C under 10 atm. pressure. This low temperature is secured with liquid nitrogen maintained under reduced pressure.

Although most fractionations are carried out at constant pressure and at varying temperatures—a process of 'isothermal vaporization'—i.e. fractionation at a constant temperature and gradually diminishing pressure has been used for effecting a partial separation of the constituents of a liquefied cracked gas [40, 1932]. Methods involving fractional condensation have also been employed [1].

A recent development is fractionation in the presence of a third substance which forms azeotropes. Sulphur dioxide has been proposed for this purpose. By adding sulphur dioxide to a mixture of C_4 hydrocarbons in an amount equivalent to the azeotropes of the butanes present, and then subjecting the mixture to fractional distillation, the butenes can be separated from the butanes [41, 1936].

(*b*) Absorption with Selective Solvents.

A partial separation of the various lower olefines from one another, and from the corresponding paraffins, can be effected by taking advantage of their different solubilities in various liquid solvents. The dissolved gases can be liberated from solution by heating. Generally, the solubility of the olefines in neutral solvents increases with increasing molecular weight and, possibly on account of their greater reactivity, they are sometimes more soluble than the corresponding paraffins.

Two types of solvents have been suggested:

(1) Certain organic solvents such as mineral oil fractions in which the higher olefines are preferentially soluble, but which also tend to absorb relatively large proportions of the paraffins.
(2) Certain solvents which dissolve the gaseous olefines by forming loosely bound addition compounds, but which do not dissolve saturated hydrocarbons.

In scrubbing with solvents such as mineral oil fractions, the use of elevated pressures is desirable, since the solubilities of the gas constituents are roughly proportional to their partial pressures. This method is only suitable for giving rough separations, but is used to a considerable extent. Some figures for the solubility of the lighter hydrocarbons in various hydrocarbons and oils are given in Table XII.

TABLE XII

Solubility of gaseous hydrocarbons and hydrogen in various hydrocarbons at 20° C

(Volumes dissolved at N.T.P. in 1 volume of solvent per atmosphere partial pressure — Bunsen absorption coefficient.)

Solvent	H_2	CH_4	C_2H_6	C_2H_4
Hexane		0.57	3.15	2.91
Heptane		0.69	4.25	3.15
Gasoline (sp. gr. 0.771)	0.086			
Kerosine (sp. gr. 0.839)	0.052		3.55	2.20
Benzene	0.066	0.47		2.95
Toluene	0.077	0.46		
Xylene	0.073	0.49		

As an example of what may be accomplished by scrubbing a cracked gas with kerosine, the following figures by Horsley [36, 1933, 1935] may be mentioned. Such a gas was washed at 22° C in countercurrent with 60 litres per hour of kerosine (b.p. 200–300° C.) in an unpacked tower 2 in. diameter and 12 ft. high, having an effective washing surface of 6.3 sq. ft. The gas was compressed before scrubbing to a pressure of 21 atm., and the gases dissolved in the kerosine were substantially regenerated by reduction of pressure, firstly to 7 atm. and subsequently to atmospheric pressure. The two gas fractions evolved were collected separately. Under these conditions the following gases were obtained, volumes referring to normal temperature and pressure:

	Ethylene	*Propylene and higher olefines*	*Methane*	*Ethane and higher saturated hydrocarbons*	*Hydrogen and inert gases*
Initial gas 9,000 litres per hour	26.5%	17.1%	29.9%	20.8%	5.7%
Residual gas 5,820 litres per hour	28.2%	2.4%	42.8%	18.1%	8.5%
1st stage let-down gas 1,000 litres per hour	36.4%	23.6%	16.4%	22.4%	1.2%
2nd stage let-down gas 2,180 litres per hour	17.6%	53.2%	1.7%	27.2%	0.3%

It is evident that the gas dissolved in the kerosene and evolved on reducing the pressure on the solvent to 7 atm.

contains a much higher concentration of ethylene than initially Similarly, it contains less methane and hydrogen The second stage let-down gas is a concentrated source of propylene

Acetone has been suggested as a solvent for ethylene [11, 1922], and also 95% ethyl alcohol [57, 1932] For the separation of butylene from butane, ammonia has been proposed [12]

The removal of acetylene from gaseous mixtures by scrubbing with esters or ethers of high boiling-point has also been suggested Suitable solvents are said to be glycol mono-formate, glycol mono- and di-alkyl ethers, esters of the mono-alkyl ethers of ethylene glycol [3], and also poly-glycols, their ethers, esters, and mixed ester-ethers [43, 1933]

(*c*) Chemical Process.

Perhaps the most obvious method for the separation of olefines from gaseous mixtures is absorption in a reagent capable of combining more readily with the olefines than with the other hydrocarbons present Such methods include direct hydration to the corresponding alcohols, esterification with sulphuric acid or with the hydrogen halides, and also selective polymerization These reactions, described in considerable detail by Ellis [16, 1934], suffer from the great disadvantage that the absorbed olefines are not recoverable and therefore need not be considered here

Aqueous solutions of silver, cuprous, and mercury salts are known to dissolve the gaseous olefines readily, probably by forming complex compounds The olefines can be recovered from these solutions by warming, with or without reduction of pressure Thus Horsley [34, 1927] has proposed the use of an acid solution of silver nitrate for the removal of ethylene from coal gas, and the use of solutions of mercury salts for the separation of olefines has also been suggested [10] Cuprous salts are much more popular, e g ammoniacal cuprous formate, acetate, or carbonate [30, 1929]

A typical liquor composition is as follows

Ammonia	7 5 g moles per litre
Copper	1 75 g atoms ,
Formate	1 5 g moles
Carbonate	1 8 g moles , "

This is preferably used at high pressures, e g 250 atm

Recently the following figures have been given to show that the solubility of ethylene is greater in ammonical solutions of cuprous nitrate, salicylate, phenolate, and cresolate [35, 1935]

Solubility of Ethylene	*Volumes per volume*
Amm cuprous formate	5 43 at 24 9° C
" , acetate	4 27 at 24 0° C
, , carbonate	3 33 at 23 5° C
" " nitrate	9 1 at 24 2° C
" , salicylate	14 1 at 19 0° C
, , cresolate	8 5 at 20 5° C
" , phenolate	9 5 at 21 5° C

Solutions of cuprous salts in aqueous hydroxy-alkylamines have also been proposed as selective solvents for the removal of olefines from gas mixtures, from which the latter may be recovered by heating or by reducing the pressure A satisfactory solution of such a composition may be prepared by dissolving 100 g of cuprous chloride in a mixture of 500 g of water, 75 c c of hydrochloric acid ($d = 1\ 16$), and 200 g of mono-ethanolamine [38, 1935]

The following are solubilities of the lower olefines and hydrogen in this solution—expressed in litres at N T P per kilogram of solvent

Absolute pressure, atm	*1*	*5*	*10*	*20*
Ethylene	8 4	15 8	21 2	24 2
Propylene	1 1	4 3	6 1	
Butylene	1 0			
1,3-Butadiene	11 0			
Hydrogen			0 08	0 17

The removal of diolefines from mixtures containing also mono-olefines by contacting the mixture in the liquid phase with finely divided cuprous chloride dispersed in an aqueous solution has also been patented [5, 1935]

(*d*) Adsorption.

Olefines can be preferentially adsorbed from gaseous mixtures on active carbon, silica gel, fuller's earth, or other highly adsorptive materials, and subsequently recovered by heating the adsorbent, with or without the use of superheated steam The olefines appear to be much more readily adsorbed than the corresponding paraffins, and methane and hydrogen are adsorbed to only a small extent Olefines of higher molecular weight are more easily adsorbed than ethylene, and hence this method allows ethylene to be separated from its homologues [29, 1926] The adsorption may be carried out under pressure [39, 1930]

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PYROLYSIS AND POLYMERIZATION PROCESSES FOR THE PRODUCTION OF LIQUID FUELS FROM GASEOUS HYDROCARBONS

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It is necessary to make a distinction between 'pyrolysis' and 'polymerization' processes, because recent American publications refer to all processes by which liquid hydrocarbons are obtained from natural and refinery gases as 'Poly' processes. In this paper polymerization processes are classed as those in which polymerization of olefines takes place as a major reaction, whereas processes in which chemical degradation is predominant and the liquids produced (if any) are essentially aromatic in character are termed 'Pyrolysis' processes. Processes in which both reactions occur, either in sequence or simultaneously, are called 'combination' pyrolysis-polymerization processes.

Pyrolysis processes have been adopted for the conversion of the gaseous olefines and paraffins into liquid products boiling essentially in the gasoline range and of a pronounced aromatic character. This type of operation is frequently referred to as 'Benzole Pyrolysis', because the liquid produced contains a considerable proportion of benzole. The chemical reactions involved have already been discussed.

Work conducted by the Anglo-Iranian Oil Company

Among the most valuable work done on this application of pyrolysis is that of Hague and Wheeler [17, 1934, 28, 1929], done on behalf of the Anglo-Iranian Oil Company.

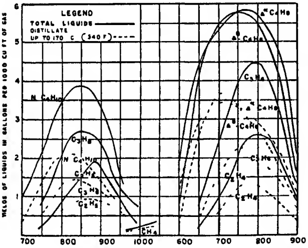


Fig. 1. Yields of liquid hydrocarbons obtainable by the high-temperature pyrolysis of the gaseous hydrocarbons. (Hague and Wheeler.)

The yields of liquid products obtained are shown in Fig. 1, and are also detailed below.

It will be observed that the liquid yield increases with rise in molecular weight of the gas treated in the case of both paraffins and olefines, and also that the yield is greater for an olefine than for the corresponding paraffin.

TABLE I

Yields of Products obtainable by the Benzole Pyrolysis of Pure Hydrocarbons

Atmospheric pressure operation. Constant reaction time. Space velocity = c. 49.0

Hydro-carbon	Temp. °C	Total liquids: Imp. gal. per 1,000 cu. ft.	Total liquids: % wt.	200° C. E.P. benzole: Imp. gal. per 1,000 cu. ft.	200° C. E.P. benzole: % wt.	Residue above 200° C.: Imp. gal. per 1,000 cu. ft.	Residue above 200° C.: % wt.
Paraffins							
Methane	1,050	0.44	8.8	0.3	4.7	0.14	4.1
Ethane	900	2.1	21.9	1.5	16.9	0.6	5.0
Propane	850	3.25	23.09	2.4	18.4	0.85	4.69
Butanes	850	4.6	24.55	3.4	19.8	1.2	4.75
Olefines							
Ethylene	800	3.15	36.1	2.4	28.8	0.75	7.3
Propylene	800	5.32	40.6	4.0	31.2	1.32	9.4
Butylenes	800	6.85	39.6	5.1	30.7	1.75	8.9

It is of interest to compare the above gallonage yields with those theoretically obtainable from the relationship

$$\text{Imp. gal. per 1,000 cu. ft. of gas treated} = \frac{\text{lb. per cu. ft. of gas treated} \times 1{,}000}{\text{sp. gr. of liquid product} \times 10}$$

which is graphed in Fig. 2.

To obtain products rich in benzene the temperature conditions are necessarily severe, but the yields obtainable are sufficiently high to attract attention. The temperatures required at substantially atmospheric pressure operation vary from 1,000 to 1,200° C. (1,832–2,192° F.) in the case of methane to 800 to 850° C. (1,472–1,562° F.) in the case of butane, although with suitable adjustment of space velocity (or reaction time) these temperature ranges may be extended somewhat in an upward direction.

By operating under temperature, pressure, and throughput conditions less severe than those required for the production of benzole, the liquids obtained are essentially unsaturated in character, and are of lower octane number than benzoles. Under reaction conditions suitable for benzole production, by making small variations in operating conditions, the freezing-point, boiling range, and unsaturated content of the product may be varied at will, and under the most severe conditions employed, 200° C. E.P. distillates consisting largely of benzene (C_6H_6, b.p. 80.8° C.) can be obtained.

In the benzole pyrolysis process the variables, temperature, pressure, and throughput rate are to a large extent complementary, although there is a minimum temperature below which benzole formation is not obtained. If super-atmospheric pressure is employed as a means of increasing plant throughput, the temperature remaining the same as in atmospheric pressure operation, then the same type of product will be obtained, but if, by the use of pressure, a lower reaction temperature is used, then the product will only be substantially benzene if the temperature is above about 800° C At lower temperatures products containing toluene, xylene, and higher aromatics are obtained Data are given in Table II showing how variation of reaction conditions affects the properties of the 200° C E P distillates obtained [18, 1936]

Exhaustive tests by the Anglo-Iranian Oil Company have shown that the benzoles obtained by the pyrololysis of gaseous hydrocarbons may be easily refined to yield spirits of good colour and of very satisfactory gum stability in conventional refining plant Sulphuric acid may be used as the refining agent The amount required is only in the order of 0 3 %, a quantity not greater than that required in the refining of cracked spirits The refined spirits have been subjected to prolonged engine tests in which gum formation has been encouraged, but the amount of gum deposition in the inlet manifold and on the inlet valves is negligible

The product may thus be described as a fully satisfactory benzole of natural gas origin

With regard to the knock ratings and blending properties of benzoles produced by pyrolysis, these are very similar to those of pure benzene and are referred to in detail later

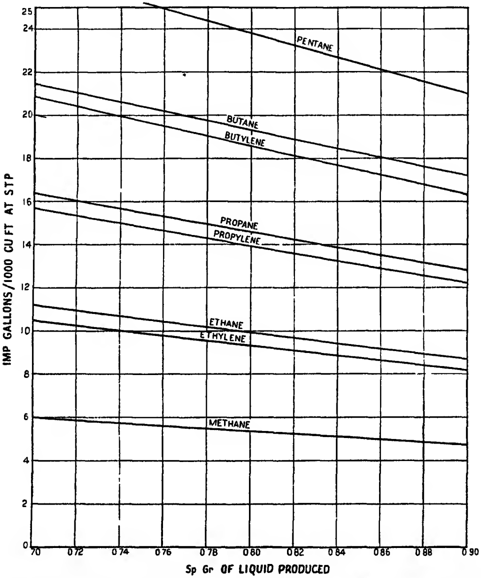


FIG 2 Theoretical yields (100% conversion) of liquids of sp gr 0 7 to 0 9 obtainable from gaseous hydrocarbons

Plant for Pyrolysis Benzole Production

The plant required for the production of benzole by the pyrolysis of gaseous hydrocarbons is very simple and only consists of conventional refinery equipment, although the choice of materials and reaction conditions is important. A typical flow diagram is reproduced in Fig 3

It is usually convenient to avoid the use of feed stocks in the gaseous state and to liquify in normal stabilizing equipment This allows the use of inlet feed pumps and the avoidance of compressors with their attendant high running maintenance costs Modern stabilizing equipment operates at pressures up to 500 lb. per sq. in , and there is usually no difficulty in obtaining feed stocks in the liquid

TABLE II

Properties of Pyrolysis Benzoles—Affect of Variation in Reaction Conditions

Inlet gas Straight-run gas $C_2H_6 = 15\%$, $C_3H_8 = 20\%$, $C_4H_{10} = 45\%$, $C_5H_{12} = 20\%$

Temperature (° C)	700	750	800	850	870	800	850	850
Inlet pressure (lb per sq in)	30	30	30	30	5	5	5	15
Space velocity (vol inlet gas per vol reaction space per hour)	209	209	209	209	210	182	182	400
Properties of product								
Sp gr at 60° F	0.796	0.849	0.873	0.875	0.880	0.845	0.873	0.875
I B P (° C)	39	51	69	70	69	66.5	67.5	63
10% distillate at (° C)	55	70.5	79	80	80	80	78.5	76.5
20% ,, ,	62	77	81	82	82.5	84	81	79.5
30% ,, ,	68.5	81	82.5	83	84	87.5	82	81
40% , ,	75	84	84	84	86	91	83.5	83
50% ,, ,	81	87	85	85	87.5	96.5	85	84
60% ,,	87	90	87	86.5	89.5	107	86	86
70% ,, ,	94.5	94.5	89.5	89	94	133.5	88.5	88.5
80% ,, ,,	109	102.5	95	93.5	102	169	93	93
90% ,, ,,	153	125	113	110	130	188.5	109.5	109
F B P (° C)	211	190	187	200	200	200	200	195
Aniline-point (° C)	<0	<0	0	0	<0	<0	<0	<0
Bromine number (g per 100 g)	74	56	25	22				30
Octane number (C F R Motor)	84.4	95.6	96.1	104.1	102	87.7	101.5	99
Freezing-point (Air Ministry test) (° C)	−38	−19	−17	−7				−15
Blending octane number								
20% in 52.5 octane number base	104.8				100.2			
30% ,, 65 , ,, ,,	91.6	93			92			
30% ,, 70 ,, ,	87.3	90.3			88.6			

state, except in the case of those containing large amounts of non-condensable gases such as ethylene In such cases compressors must be used The plant required comprises a preheat furnace, reaction coil (either heated or unheated), cooling device, tar separator, product receiver, and product stabilizer

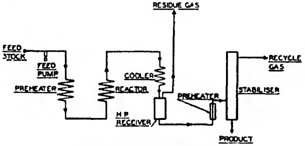


FIG 3 Flow diagram Pyrolysis of gaseous hydrocarbons for benzole production

Furnaces. The preheat furnace may be conventional pipe-still practice, although the selection of the furnace tubes and furnace insulation for use at temperatures above 500° C (932° F) and up to 880–900° C (1,616–1,652° F) needs care Up to temperatures of 500° C ordinary cracking furnace tubes may be employed, fabricated in mild steel, 0.5% molybdenum steel or 6% chromium steel, but, for the higher temperatures, steels containing higher percentages of nickel and chromium are required Stainless steels of the 18/8 chromium-nickel type are satisfactory for temperatures not exceeding 650° C, but reasonable life at temperatures up to 900° C (1,652° F) is only obtained by the use of 25/20 chromium-nickel steels, examples of which are Hadfields H R 3 and Krupps N C T. 3 Tests carried out on a semi-commercial plant over several years have demonstrated that such steels are perfectly satisfactory for continued service because of their excellent mechanical properties and resistance to decarburization and scaling

The reaction coil is preferably heated in pyrolysis processes as markedly endothermic as that involving benzole production, and is normally placed in the same furnace as the preheating tubes The reaction coil may, however, be unheated when handling olefinic feed stocks and mounted on an independent structure, in this case it is desirable to provide means for fairly rapid cooling, such as controlled induced or forced-air circulation In the production of benzole from saturated gases such as propane or butane the heat absorbed by reaction is approximately 1,000 B Th U per lb of inlet gas, excluding the heat required in preheating the feed to reaction temperature This figure is materially lower in the case of feed stocks containing unsaturateds because the latter undergo exothermic reactions during the initial stages of the pyrolysis process To avoid sagging of furnace tubes, these may be mounted vertically and supported only from the top

The formation of coke and carbon in the furnace tubes may be reduced to that normally met with in cracking plant practice by careful attention to the flow conditions of the gases being treated Highly turbulent flow and short heating periods are necessary Values of vd/ν, where v = gas velocity cm per sec, d = diameter of tube cm, ν = kinematic viscosity (Stokes), should be at least 10,000–20,000 for efficient heat transfer and to avoid coke deposition Recycle operation is also favourable with regard to prevention of coke formation

Various patents cover the use of linings for pyrolysis furnace tubes which inhibit carbon formation Such linings are effective for short periods, but eventually become coated with a thin layer of carbon and coke, and so lose their efficacy Similarly, any differences which exist between different furnace-tube materials with regard to catalytic or auto-catalytic effect on carbon deposition disappear after a comparatively short period when the inside of the tube acquires a thin coating of carbon

Proposals have been made from time to time to employ as furnace-tube materials for pyrolysis processes cheap steels, such as mild steel treated in various ways to give an outside surface of heat-resisting alloy. Such composite materials rarely possess adequate mechanical strength, and often give trouble due to excessive creep.

Coolers and Tar Separators. The exit gases from the preheat and reaction furnaces must be cooled to a temperature suitable for tar removal and stabilization. This is conveniently accomplished by injection of cold oil, by heat exchange with the inlet feed to the furnaces, or by a combination of atmospheric coolers and conventional water coolers. Tar separation may be effected by flashing into a separator under suitable temperature and pressure conditions or by the use of electrostatic detarrers at temperatures about 100° C.

Product stabilizers follow normal refinery practice.

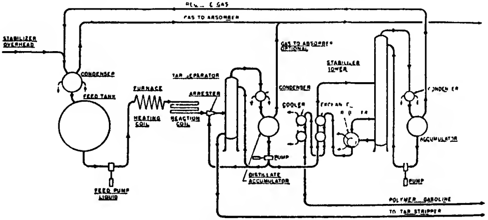


FIG. 4. Flow diagram. Alco pyrolysis unit.

Composition of Residue Gases from Benzole Pyrolysis Processes.

By the treatment of C_3 and C_4 hydrocarbons at pressures of 5–100 lb. per sq. in. and temperatures of 750–900° C. at suitable throughput rates, single pass treatment is sufficient and recycling can be avoided. Under these conditions the exit gas from the product stabilizers has the following average composition [17, 1934].

Hydrogen	10–25% volume
Methane	50–60% „
Ethylene	20–25%
Ethane	0–10% .

This gas is a refractory pyrolysis stock, but the ethane-ethylene fraction may be treated in this way after separation, or it may be subjected to polymerization. The hydrogen-methane fraction constitutes an ideal feed for hydrogen manufacture by well-known processes.

Properties of Tars Produced (i.e. liquids boiling above 200° C.).

The tars produced in the benzole pyrolysis reaction consist almost entirely of polynuclear aromatic hydrocarbons, naphthalene and anthracene predominating, and are solid crystalline masses at ordinary temperatures. They constitute valuable sources of the higher aromatic hydrocarbons, and by destructive hydrogenation may be converted, with good yield, into gasolines of 90–100 octane number having very low freezing-points and good blending properties [18, 1936].

Work by Other Investigators

Of the work conducted by other investigators on the production of aromatic hydrocarbons by the pyrolysis of gaseous hydrocarbons, the most important is that reported by H. M. Smith *et al.* [97, 1931], Cambron and Bayley [10, 1933–4], Stanley and Nash [99, 1929], Frolich and Wiezevich [24, 1935], Podbielniak [95, 1931], and Wagner [103, 1935].

The last-named has described the production of liquid aromatic hydrocarbons by rapidly heating olefine-containing gases to 1,100° F. (594° C.) or higher, and then allowing them to rise in temperature due to the exothermic nature of the reaction until a final temperature of 1,200–1,300° F. (649–705° C.) was reached. In this manner it was possible to obtain a highly aromatic distillate from which gasoline having an octane number of approximately 100 could be produced. It was also possible to produce relatively pure aromatic hydrocarbons (benzene, toluene, and naphthalene) by simple fractionation after a light acid refining treatment.

Podbielniak [95, 1931] conducted pilot plant-scale tests on the pyrolysis of stabilizer gases. The plant used comprised a furnace, having separate convection and radiant sections, a water-spray cooler for cooling the pyrolysed gas, a scrubber for the removal of carbon and suspended tar, and a compressor installation for the recovery of the light oils produced. The maximum capacity of the furnace was 25,000 cu. ft. per day. For the optimum yield of benzole and heavier aromatics from gases consisting mainly of propane outlet temperatures of 1,650–1,700° F. (899–927° C.) were necessary. No details regarding reaction times or space velocities employed are available. The yields of total oils realized ranged from 0·99 to 2·7 U.S. gal. per 1,000 cu. ft. (= 0·825–2·25 imp. gal. per 1,000 cu. ft.).

A gas containing 77·6% CH_4, 6·9% C_2H_6, 10·1% C_3H_8, and 5·4% C_4+ gave an oil yield of 0·41 imp. gal. per 1,000 cu. ft. at 899° C.

The published work of Stanley and Nash [99, 1929] is concerned entirely with the pyrolysis of methane. Temperatures of 1,000–1,200° C. were employed and the space velocities ranged from *c.* 500 to 10,000. The best yields of higher hydrocarbons were obtained at a temperature of 1,150° C., a reaction time of *c.* 0·6 sec., and a space velocity of 6,400. Under these conditions the best yield of light oil and tar was 11%, which compares well with Hague and Wheeler's figure of 8 8%

The work of Smith *et al* [97, 1931] is also concerned entirely with methane The best results obtained, over a temperature range of 1,000 to 1,260° C (space velocities not stated) averaged 0 3 gal of light oil plus 0 25 gal of tar per 1,000 cu ft of methane treated This is approximately equivalent to a 9 8% total oil yield The light oil contained about 86% benzene and about 2% of liquid boiling below 73° C—probably consisting partly of unsaturated hydrocarbons The tar contained naphthalene, anthacene, and pyrene

Frolich and Wiezevich [24, 1935] have described tests on propane at 88° C in which the maximum oil yield was 3 7 imp gal per 1,000 cu ft of gas treated Of this the yield of light oil was 1 27 imp gal The corresponding yields of Hague and Wheeler [28, 1929] were 3 25 and 2 4 imp gal, respectively A gas containing 60% propane, 18 6% ethane, and 13 4% propylene gave at 900–960° C, a total oil yield of 1 4–1 5 imp gal per 1,000 cu ft, of which 70–75% boiled below 220° C, and slightly less than 50% of the total product was benzene The exit gas increased in volume 60–70% and contained 30–40% unsaturated hydrocarbons Frolich and Wiezevich found that increasing pressure caused a change in chemical composition from the aromatic type obtained at substantially atmospheric pressure to a decidedly non-aromatic material resulting from operation at higher pressures

The work of Cambron and Bayley [10, 1933–4] was also concerned with the treatment of propane These investigators used temperatures ranging from 850 to 1,046° C, and space velocities from *c* 280 to 1,230 The best liquid yield was obtained at 950° C (space velocity *c* 800), and amounted to 29% by weight, of which 70% boiled within the gasoline range By recirculating the exit gas and using turbulent flow conditions approximately the same liquid yields were realized at 800–810° C The gasoline fraction contained about 64% benzene, 14% toluene, 7 8% styrene, and small amounts of cyclopentadiene, xylenes, and higher aromatics The liquids boiling above 200° C contained about 25% naphthalene and 12 5% anthracene together with smaller amounts of mono- and di-methyl naphthalene, acenaphthene, and phenanthrene

The Alco Pyrolysis Process for the Production of Aromatics.

Alco Products, Incorporated, are licensing agents for so-called 'Polymerization' processes developed by the Pure Oil Company, Chicago One of these processes is, according to the nomenclature adopted in this article, a pyrolysis process, and the products obtained consist primarily of aromatic hydrocarbons The process has been described [15, 1935] as a high-temperature—low-pressure operation, the conditions being 1,150–1,300° F (621–704° C) and pressures of the order of 50–250 lb per sq in gauge Feed stocks of a saturated or unsaturated nature may be processed

A flow diagram of the process is reproduced in Fig 4 A liquid feed is shown, but a gaseous feed could be handled by substituting compressors for the feed pump A feature of the process is that the reaction coil is unheated and situated outside the furnace, the operation being the same as that described by Wagner [105, 1933] The exit gases from the reaction coil are suddenly quenched by the recycling of overhead material from the tar separator, and the plant includes conventional product stabilizer equipment and an absorber operating on the residue gas Recycle material to the furnace is drawn from the reflux accumulator on the product stabilizer

The yields of distillate obtained by this process are shown in the results reproduced in Table III Saturated feed stocks behave similarly and give similar products

TABLE III

Typical Results—Alco Pyrolysis Process [15, 1935]
Once through operation—no recycle

Feed	*Absorber residue gas*	*Stabilizer overhead gas*
Properties of feed		
Sp gr (air — 1)	0 79	1 352
Unsaturateds, %	39 4	79 6
Conditions of operation		
Coil outlet, ° F	1,265 (685° C)	1,175 (635° C)
„ „ lb per sq in	60	55
Residue gas		
Sp gr (air = 1)	0 72	0 86
Unsaturateds, %	29	34 5
Cu ft per cu ft input	0 85	0 46
Distillate produced		
U S gal per 1 000 cu ft	1 75	9 8
Imp gal per 1,000 cu ft	1 46	8 15
Gravity, ° API	21 6	26 4
Sp gr	0 929	0 896
% boiling to 350° F (176 7° C)	76	68
Properties of 350 F E P distillate		
Octane number (C F R Motor)	102	86
I B P, ° C		49
10% distillate at (° C)		78
30% „ „		88
50% „		96
70% „ „		107
90% „		131
F B P, C		178
Estimated distillate yield by recycle operation, imp gal per 1,000 cu ft	3 3	9 1
Figures calculated from above data by the author of this paper		
Feed		
Mean molecular weight	22 9	39 2
„ „ of olefine content	28 (assumed)	39 2 (assumed)
Residue gas		
Mean molecular weight	20 8	25
„ „ „ of olefine content	28 (assumed)	28 (assumed)
Per 1,000 cu ft input	394	
Olefines in, cu ft	29 2	796
„ lb	247	82
Olefines out, cu ft	18 3	159
„ lb	13 6	11 8
Distillate, lb		73·0
Distillate yield, % of olefines destroyed (wt)	125	104
Distillate yield, % on input (wt)	22 0	71 0
Estimated distillate yield on recycling as % (wt) of olefines in change	105	100

Figures included in Table III indicate that this process gives a product the amount of which corresponds closely with the amount of olefines destroyed (i e olefines in minus olefines out) On the other hand, completely saturated feed stocks, consisting of propane and butanes, may be satisfactorily handled by this process

Regarding the products obtained, the octane numbers are high, ranging from 85 to 105 (C F R Motor method) The blending octane numbers in low octane number base

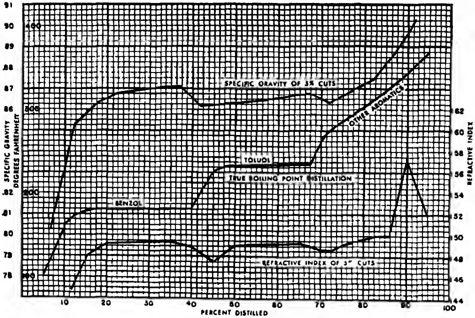


FIG 5 Properties of liquid product from Alco pyrolysis plant

spirits range from 105 to 125 The products are aromatic in character and therefore of rather low volatility Fig 5 shows a True Boiling-Point Distillation curve of the product and also specific gravities and refractive indices of 5% fractions [93, 1936] The benzene content is approximately 30%, and toluene approximately 24%

Thermal Processes for the Polymerization of Olefines

The Alco Polymerization Process.

The most important thermal polymerization process in use at present is that developed by the Pure Oil Company, Chicago, and licensed by Alco Products, Inc , and recently described by Cooke, Swanson, and Wagner [15, 1935], and independently by Wagner [105, 1933] The temperature range employed is 900–1,000° F (482–538° C) and the pressure 600–800 lb The feed is heated under these conditions in a conventional pipe heater and discharged into a reactor, which is cooled in order to absorb the exothermic heat of reaction, and the products are then chilled by injection of either cold gas or oil The reaction is normally checked at about 60–70 conversions per pass, necessitating a recycle ratio of about 1 5 to 1 A typical flow diagram is shown in Fig 5 It is usually preferred to operate on a liquified gas-feed, to eliminate methane and ethane from the feed as far as possible, and to concentrate the active olefine (propylene and butylene) Many advantages result from this procedure (1) lower power costs due to the large reduction in horse-power required for the compression of the gaseous feed, (2) reduction in plant capital cost due to reduction in size of the several pieces of plant equipment as a result of eliminating the inactive gas from the cycle, (3) uniform control of the reaction is simplified. The process of preparing the feed stock consists either in absorbing the higher molecular weight constituents of cracked gas and recovering them from the absorbing medium under high pressure in the liquid state, or in separating and fractionating directly under pressure, this requiring compression of the cracked gas and fractionation of the condensed portion When using these methods, the amount of ethylene in the charging stock is relatively small Typical results obtained by the Alco Thermal Polymerization process are detailed in Table IV

TABLE IV

Typical Results—Alco Polymerization Plant [15, 1935]

Feed	*Gyro residue gas*	*Liquid feed*
Properties of feed		
Sp gr (air = 1)	1 06	1 51
Unsaturateds, %	47 2	49 4
Recycle ratio	Once through operation	1 75
Residue gas		
Sp gr (air = 1)	0 87	1 01
Unsaturateds, %	18 4	22 0
Cu ft per cu ft feed	0 80	
Liquid products		
U S gal per 1,000 cu ft charge	4 4	11 8
Imp ,, ,, ,,	3 67	9 83
F P gasoline		
U S gal per 1,000 cu ft charge	3 7	8 8
Imp ,, ,,	3 08	7 53
Gravity, ° API	52 4	55 0
Sp gr	0 769	0 759
% of total liquid	84 0	75 0
I B P , ° C	35 6	32 2
10% distillate at (° C)	57	41
30% ,, ,		63
50% ,,	104	83
80% , ,,	150	
90% ,, ,,		162
F B P , ° C	215 6	203
Octane number (C F R Motor)		76
Fuel oil		
Gravity, ° API		8 0
Sp gr		1·04
U S gal per 1,000 cu ft	0 7	3 0
Imp ,, ,,	0 58	2 5
Conversion of unsaturateds to total liquids, %	78·0	86 7
Conversion of unsaturateds to gasoline, %	63	..

The following product properties have been given by Wagner [105, 1933] Octane ratings are referred to again later

	Condensate	*Gasoline*
Gravity, ° API	53 7	56 5
Sp gr	0 768	0 753
I B P , ° C	29	33
10% distillate at (° C)	43	53
20% " "	58	63
30% " ,	73	74
40% " ,	86	83
50% " "	98	94
60% " "	113	106
70% " "	126	120
80% " ,	164	138
90% , "	213	164
F B P , ° C		203
Residue, %	8 7	1 0
Reid vapour pressure, lb per sq in at 100° F	11 5	10 0
Octane no		
C F R Research method		96
C F R Motor method		78

Wagner has described tests on various cracked gases at 600–1,000 lb pressure and 647–951° F (342–511° C)

Work conducted by the Anglo-Iranian Oil Company [18, 1936]

A flow diagram of the semi-scale plant employed by the Anglo-Iranian Oil Company in their investigations of the non-catalytic polymerization process is reproduced in Fig 6 The feed stocks examined ranged from vapour-phase cracked gases to stabilizer overheads These were fed to the plant by compressor and pump, respectively, and passed through a preheat coil and reactor in series, and thence to a cooler, high-pressure separator, and product stabilizer The plant designed was capable of operation at temperatures up to 650° C and at pressures up to 4,500 lb per sq in , so that the reaction variables could be studied over a wide range

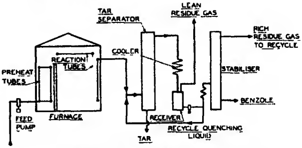


FIG 6 Flow diagram Anglo-Iranian Oil Company's semi-commercial thermal polymerization plant

As in the case of pyrolysis to benzole, it was found that desulphurization of the feed stock was desirable in order to avoid corrosion and the fixation of the sulphur in the product in the form of mercaptans and sulphides, with resultant increased refinery difficulties

It was not found necessary to heat the reactor, in fact, when operating at high conversions per pass, considerable difficulty was experienced in preventing the reactor temperatures getting out of control, and means for sudden chilling were adopted Careful temperature control was found necessary to avoid the formation of coke Another factor controlling the amount of coke deposition was the time of reaction When this was prolonged to get high conversions per pass, coke formation readily occurred, but by limiting the conversion per pass to 60–70% this was prevented This necessitates the use of a recycle system if

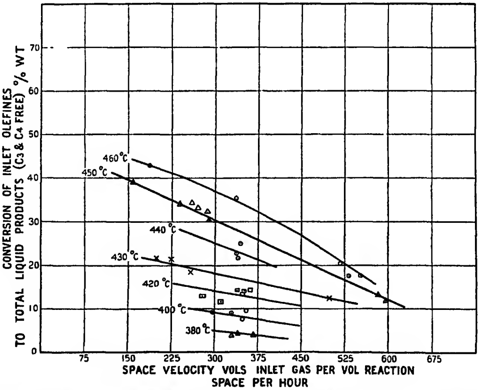


FIG 7 Thermal polymerization of stabilizer overhead The effect of inlet gas rate and temperature on conversion at 800 lb

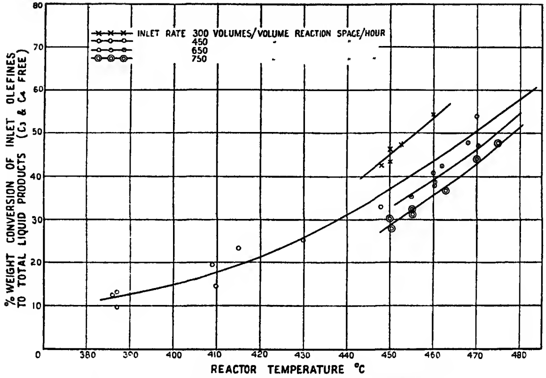


Fig 8 Thermal polymerization of stabilizer overhead Results obtained at 1,300 lb

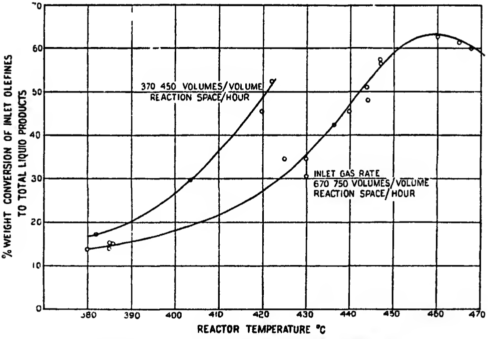


Fig 9 Thermal polymerization of stabilizer overhead Results obtained at 2,000 lb

the optimum yields are required, and agrees with the experience of Alco Products

A selection of typical results obtained are given in Figs 7–9 These show the effect of pressure, temperature, and reaction time on conversion, and refer to a stabilizer overhead feed stock

The process is an easy one to operate The reaction conditions are not unduly critical, and are determined by the nature of the product required and the capital and running costs of the plant. Under optimum conditions, the product contains about 80% by weight of 200° C end-point distillate, the remainder being a residue of little value as a high-speed Diesel fuel, but a satisfactory stock for cracking or destructive hydrogenation Unfortunately the gasoline produced under the most favourable conditions is little superior to normal cracked spirit in octane number, and has an optimum value of 75–80 (C F R Motor method) when produced at 480–550° C and 500–1,000 lb pressure In addition the lead responses are poor At lower temperatures the gasoline octane numbers are lower

The most important effect of pressure in the thermal polymerization process is to increase the throughput capacity of a given size plant, but another valuable effect is a reduction in the temperature necessary to effect a given conversion per pass

Typical properties of thermal polymers produced from stabilizer overhead gas at 1,000-lb pressure and 510° C are set out in Table V

TABLE V

	Crude polymer	*Crude 200° C E P distillate*	*Residue above 200° C*
Sp gr, 60° F	0 780	0 764	0 985
I B P (° C)	23	27	222
2% distillate at (° C)		35	
5% ,, ,,		46	
10% ,, ,,	60	58	236
20% ,, ,,	82	77	250
30%	95	91	266
40% ,,	100	99	280
50% ,, ,,	110	103	297
60% ,, ,,	130	114	317
70% ,,	150	123	335
80% ,, ,,	180	145	
90%	230	178	
F B P (° C)	320	198	
% 100 C	40	41	
% 140° C	64	77	
% 200° C	84		
% 300° C			52
Total distillate	97	98	75
Residue	1	1	25
Loss	2	1	
Aniline-point (° C)		272	below 15
Bromine number		75	20
Freezing-point (° C)		below 70	
Gum actual mg per 100 ml		35	
Reid vapour pressure at 100° F		4 5 lb	
Octane number (C F R Motor)		75	
,, ,, (C F R Research)		89	
Cetene number			19

The gasoline fractions of thermal polymers produced from cracked feed stocks such as stabilizer overhead fractions, containing both propylene and butylene, show no improvement in octane number on non-destructive hydrogenation However, the polymer gasolines may readily be refined to marketable products of most satisfactory quality [17, 1934]

Combination Pyrolysis—Polymerization Processes

Two proprietary processes are in operation involving successive steps of pyrolysis and polymerization to produce polymer products from saturated gases When cracked gases are treated by these processes the yields of polymer products are higher than those that would be obtained from the olefine content alone, and it appears definite that, under the conditions employed, cracking of paraffins to olefines takes place at the same time as olefines are polymerized The olefines formed by pyrolysis are polymerized and the yield is thereby augmented

The two processes concerned are

1. The 'Unitary' Process of Polymerization Process Corporation Licensing Agents, M W Kellogg Co
2. The 'Multiple Coil' Process of the Pure Oil Company Licensing Agents, Alco Products Incorporated

The 'Unitary' Process

The idea of conducting two distinctly different reactions, governed by different laws, under identical conditions of temperature and pressure is theoretically not attractive but the results claimed for the 'Unitary' process are of considerable interest, particularly the contention that, under the conditions employed, a certain amount of alkylation—i e direct union of paraffins with olefines—takes place

The process is described in the literature [70, 1935–6], and a simplified flow diagram is reproduced in Fig 10

The practicability of the operation was fully demonstrated by experimental work carried out at the Alamo Refinery of the Phillips Petroleum Company at Borger, Texas, which has been in commercial operation for an extended period The operating schedule between shut-downs for cleaning varies from 50 to 60 days The feed stocks which may be handled by the process vary from propane or butane, or any mixture of these, to a complex mixture of C_2, C_3, and C_4 hydrocarbons in which the unsaturated content may be as high as 80% The flow diagram shown in Fig 10 is representative, but the gas recovery system, not shown in detail, varies with the type of feed handled and the recycle ratio required According to the limited information available, the reaction conditions range from 800 to 1,100° F (427–593° C) and 800–3,000 lb pressure

TABLE VI

'Unitary' Polymerization Process Once through operation Pilot Plant results

Run no	*1217 1*	*1217–2*	*1217–3*
1 Reaction conditions			
Pressure, lb per sq in gauge	800	800	800
Temp, ° F	800	800	800
Temp ° C	427	427	427
2 Feed stock, g per hour	667	635	1,327
Analysis, g per hour			
CH_4	1	1	2
C_2H_6	19	18	37
C_3H_8	170	162	339
C_4H_{10}	85	81	169
C_5+	19	18	39
C_2H_4	5	4	9
C_3H_6	155	148	309
C_4H_8	172	163	342
C_5H_{10}	41	39	81
3 Liquid products, g per hour	213	211	546
4 Gaseous product, g per hour	454	424	781
Analysis, g per hour			
H_2	2	1	2
CH_4	6	5	12
C_2H_6	14	17	13
C_3H_8	120	113	161
C_4H_{10}	68	71	120
C_5+	19	18	39
C_2H_4	5	3	4
C_3H_6	92	79	123
C_4H_8	109	109	228
C_5H_{10}	19	8	79
5 Unsaturated hydrocarbons converted, g per hour	148	155	307
6 Liquid production as % wt of olefines converted	144	136	178
7 Liquid required from saturated hydrocarbons, g per hour	65	56	239
8 Potential liquid yield from saturateds	55	46	197

With regard to the results obtained by this process, in Table VI are reproduced figures relating to tests made on a pilot plant on a once through basis (i e no recycle) and on cracked C_3–C_4 feed stocks It is evident from these figures that the amount of liquid produced is greater than the amount of olefines converted—i e some of the liquid produced must have its origin in the paraffins in the feed Keith and Ward [70, 1935–6] have assumed that, if the paraffins decomposed to give olefines, which subsequently polymerized, the yields of polymer from these paraffins would not be greater than 93 4%, 79 5%, and 67 5% of the ethane, propane, and butane, respectively The figures given in Table VI for 'potential liquid yield from saturateds' are calculated on this basis Because the liquid yields actually obtained from the saturated hydrocarbons in the feed are slightly greater than the calculated yields, obtained in this way, Keith and Ward have assumed that alkylation reactions proceed

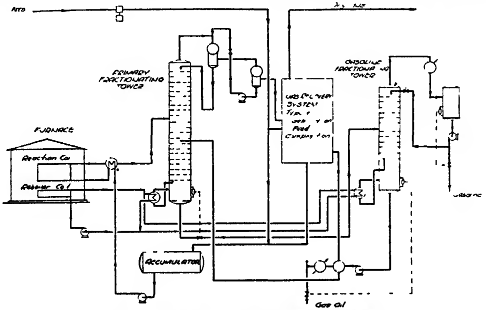


Fig 10 Flow diagram 'Unitary polymerization process

This contention is not proved by the figures in Table VI Firstly, the assumptions regarding the maximum polymer yield from the saturated hydrocarbons are not valid, because the primary or secondary products of the paraffin decomposition would certainly take part in the polymerization reaction before they had time to be converted into stable lower paraffins Secondly, if these assumptions are valid, the small differences between items 7 and 8 in Table VI would suggest that small experimental errors are involved The differences between items 7 and 8 vary from 1 5 to 3 1% of the feed, both quantities being in grams per hour—a quantity well within the normal experimental errors involved in analyses and plant balances of this type Keith and Ward [70, 1935–6] have also stated that the polymer products contain *iso* paraffin, but no evidence in support of this statement has yet been presented

Results obtained in recycle operation on stabilizer reflux feed are reproduced in Table VII Of particular interest is the high yield of liquid product obtained, and also the high gasoline content of the liquid product With regard to the extent of decomposition of the paraffin constituents of the feed stocks listed in Table VII, it is noteworthy that the figures given by Keith and Ward for total liquid yield correspond very closely to those which would be obtained if the paraffins decomposed to olefines and these olefines then polymerized (together with the original olefines present in the feed), to give a 90% liquid yield It can be assumed that all paraffins give a 60% wt yield of olefines on pyrolysis

Calculated yield figures, on this basis, are given in item 8 of Table VII These do not support the opinion that alkylation reactions occur to any appreciable extent

Properties of Products.

The properties reported for the products obtained by the Kellogg Unitary Process are summarized in Table VIII The properties of the gasoline fractions vary widely as functions of feed-stock composition and operating conditions The use of a feed stock high in unsaturateds (65–70% by volume) at high conversions to liquid per pass appears to result in a product higher in specific gravity and lower in paraffin content than does one in which the unsaturated content lies between 15 and 35% by volume Aromatics and mono-olefines appear to be predominant in products from highly unsaturated feed stocks The material resulting from operation on stabilizer reflux feeds containing 30–8% of unsaturateds has a specific gravity of 0 724 to 0 739 when stabilized to a Reid vapour pressure of 10 5 lb Its composition is paraffinic rather than olefinic or aromatic The products are very volatile, averaging 70–80% by volume boiling up to 100° C The neat octane numbers (C F R Motor method) are rather higher (79–82) than those normally obtained by olefine polymerization, but this is no doubt due to the low average boiling-point and molecular weight of the 'Unitary' products

The Alco Combination Pyrolysis—Polymerization Unit, i.e. 'Multiple Coil' Process.

In contradistinction to the Kellogg 'Unitary' Process, the process developed by the Pure Oil Company and Alco Products Incorporated, for the treatment of both saturated and unsaturated gaseous feed stocks involves separate pyrolysis and polymerization steps in separate furnaces and reaction coils, each step being carried out under its own optimum conditions [15, 1935]

TABLE VII

Unitary Process Recycle Operation on Stabilizer Reflux and Other Similar Feed Stocks

Run no	*772*	*861*	*903*	*942*	*961*	*1 191*		*1,792*	*1,803*	*1 754–4*
1 Reaction conditions										
Pressure, lb per sq in	800	1,200	1,200	1,200	1,200	1,200	2 200	2,200	2,200	2,200
Temperature, ° F	1,000	1,000	1,100	1 030	1,020	1 035	1,100	1,050	1,037	1,025
° C	538	538	593	554	557	593	566	566	558	552
2 Feed stock										
Net feed, % wt							C_2H_6 3.6			
C_3H_8	57	54	36.4	37.1	10.8	58.2	88.8	53	59.4	17.4
C_4H_{10}			24.3	22.8	75.5	41.2	(Iso) 7.6	47	15.7	59.8
C_3H_6	43	41.1	23.1	20.3	4.8				16.1	4.0
C_4H_8		4.9	16.1	19.8	8.9				8.8	18.8
Gross feed, % vol							CH_4 1.4			
C_2H_6	12.2	6.8	9.6	6.5	C_2 2.5		3.0			
C_3H_8	46.3	49.8	38.8	39.6	14.4		83.0			
C_4H_{10}	4.2	6.2	16.9	17.3	67.5		7.2			
C_2H_4	3.4	1.9	2.4	2.0			0.7			
C_3H_6	29.6	30.5	21.3	21.0	7.0		3.9			
C_4H_8	4.3	4.8	11.0	13.6	8.6		0.8			
3 'Net' yield, % wt	67.9	69.0	69.6	64.5	58.2	59.0	56.0	61.2	67.3	70.5
4 'Net' yield, % wt of unsaturateds in fresh feed	158	150	177	161	425					
5 U S gal of liquid product per 1,000 cu ft net gaseous feed	12.78	13.10	14.40	13.5	14.29		11.7	14.07	13.28	16.1
6 Imp gal of liquid product per 1 000 cu ft	10.65	10.9	12.0	11.25	11.91		9.75	11.73	11.07	13.4
7 Yield, % wt 392° F E P gasoline							52.1	59.4	65.1	65.6
8 Theoretical yield calculated as follows Liquid yield – % olefines in feed × 0.9 + % paraffin in feed × 0.6 × 0.9	70.2	70.6	69.5	68.4	58.9	53.8	54	54	63.4	62.3

TABLE VIII

Properties of Products 'Unitary' Polymerization Process

	Pilot plant products stabilizer reflux feed		*Comm plant product butane feed (clay treated)*	*Total product propane feed 2 200 lb 593° C*	*Gasoline fractions 2,200 lb pressure 552–566° C Various feed stocks*		
	Raw product	*Clay-treated gasoline fraction*					
Gravity, ° API	65.1	66.5	61.4	64.8	69.9	69.7	66.4
Sp gr	0.72	0.7146	0.7335	0.7208	0.7025	0.7032	0.715
I B P, ° C	38	41	35	34	34	38	40
5% distillate at (° C)	47	49	46	44	45	47	52
10% ,, ,,	51	52	49	47	48	49	56
20% ,, ,,	57	57	56	50	52	53	63
30% ,, ,,	63	61	64	56	56	57	68
40% ,, ,,	69	67	73	62	61	62	75
50% ,, ,,	73	72	82	68	67	68	82
60% ,, ,,	81	78	95	78	74	77	91
70% ,, ,,	91	85	109	93	86	88	103
80% ,, ,,	108	98	133	117	103	103	119
90% ,, ,,	147	126	183	162	134	134	151
95% ,, ,,	192	148	218	211	169	169	186
F B P, ° C	212	157	232	253	204	199	210
Total distillate %				97	98	98	98
Residue %				2.5			
Loss %				0.5			
% at 392° F (200° C)				94.5			
Reid vapour pressure	10.7			11.7			
Colour (Saybolt)		30+	30+				
Colour after 8 hours in the sun		30+					
Copper dish gum, mg per 100 c c		10.4					
Induction period (min)			120				
Induction period after adding 1 lb B A P gum inhibitor per 100 bbl			+240				
Octane number (C.F R Motor)			79				
Octane number (blending value 50% in A 3 reference fuel of 43.6 octane number)	92	90		91			

For example, in the treatment of a stabilizer overhead gas containing about 30% of olefinic constituents the gas is first of all subjected to a polymerization reaction under the most favourable conditions for the conversion of propylene and butylene to polymer gasoline In this step the charge—normally available in the liquefied state, is heated to the proper temperature, and enters the reaction coil which is designed to give the required temperature reaction time effect Cooling means are provided to keep the temperature within the proper limits The reaction products, immediately upon leaving the coil, are chilled to stop any further reaction, and simultaneously are cooled to a temperature low enough so that heavier products are dropped out in the tar separator Gases, distillate vapours, and chilling medium forming the overhead from this separator are refluxed for end-point control The total overhead passes to a cooler and accumulator where the chilling medium, polymerized distillate, and a portion of the gaseous constituents are condensed The uncondensed gases and vapours from the accumulator are passed directly to the gas-pyrolysis unit, where the saturated hydrocarbons are cracked to give the optimum yield of olefines

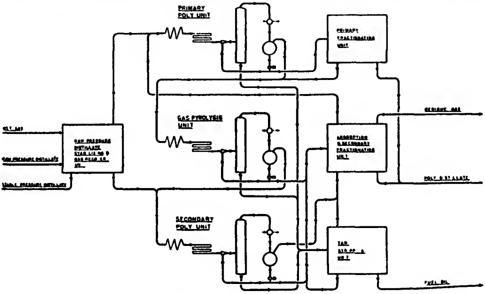


FIG 11 Alco multiple coil combination pyrolysis Polymerization plant

A portion of the condensate from the accumulator is used as the chilling medium previously referred to, and the remainder, equivalent to the condensed products of reaction, is pumped to the fractionating unit In this unit the polymer distillate is stabilized to desired specifications, and all gaseous compounds—including excess C_4 constituents not desired in the finished distillate—are taken overhead and form additional feed to the gas-pyrolysis coil

In the gas-pyrolysis coil the charge as recovered in the primary polymerization step is heated to a temperature in excess of 1,300° F A reaction time as short as possible is desired to prevent the unsaturateds once formed from entering secondary reactions leading to the formation of tar The products of reaction are chilled to a temperature low enough to liquefy compounds in the fuel-oil and tar range Gases, distillate vapours, and vaporized chilling oil pass overhead from the tar separator to a condenser and accumulator, where the chilling material is condensed The gas remaining after compression and cooling is charged to the secondary polymerization coil, and submitted to a high-temperature—low-pressure reaction The chilling of the conversion product, tar separation, condensing of chilling medium, is analogous to the method used in the primary polymerization step Since the reaction products contain a high percentage of hydrogen and methane, recovery of polymer distillate cannot be effected by condensation under the low operating pressure Recovery may be accomplished by compression and subsequent condensation However, in most cases it is believed that absorption is more economical All polymer distillate distilled from the absorption oil is accumulated and fed, together with the pyrolysis distillate, to the secondary fractionator The bottom product from this unit is stabilized to desired specifications, and the light overhead material is passed directly under its own pressure to the primary polymerization unit as recycle

The bottoms from the various tar separators are combined, heated, and then stripped of all fractions of gasoline of boiling range

A unit of the type described above is very flexible, and ensures a high yield of distillate for charging stocks varying widely in composition

A flow diagram of the Alco Multiple Coil Unit is reproduced in Fig 11 No details of the products are available, but it may be assumed that the gasolines produced in each separate step are the same as those produced in the Alco polymerization and pyrolysis units, respectively These have already been described

Catalytic Polymerization Processes

A recent development of considerable importance is the growth of catalytic polymerization processes for the production of gasolines and lubricating oils These are now in commercial operation The former application is alone considered here

The polymerization reactions of the lower olefines in the absence of catalysts have been fully described above, and it remains to consider the changes that are brought about by the use of catalysts of different kinds In general it may be said that the use of an efficient catalyst enables lower temperatures and pressures to be employed, and often, as a result of this, secondary reactions by which the polymerized olefines are converted into non-olefinic hydrocarbons are often suppressed On the other hand, some catalysts, particularly aluminium chloride, have pronounced isomerization activity, and yield products which are predominantly saturated in character

It is convenient to consider different types of polymerization catalysts separately and to compare their activities and peculiarities

The active polymerization catalysts may be classified as follows

(*a*) Metals and certain non-metals,
(*b*) Metal oxides,
(*c*) Neutral salts,
(*d*) Adsorbents, e g floridin, active carbon, silica gel, &c ,
(*e*) Metal halides,
(*f*) Inorganic acids, and acid inorganic salts,

and each may be considered with reference to the various gaseous olefines and gas mixtures containing these available for commercial use

(*a*) Metals and certain Non-metals.

Nearly all metals accelerate the decomposition of gaseous olefines into paraffins of lower molecular weight, carbon and hydrogen, consequently their polymerization activity is slight The marked activity of nickel and cobalt in this direction has already been indicated On the other hand, nickel is a satisfactory catalyst for the polymerization of acetylene in the presence of hydrogen at temperatures up to 300° C [94, 1934–5] Aluminium and magnesium also promote scission, but are much less active than nickel and cobalt Iron and copper also accelerate decomposition and likewise platinum and palladium In the case of iron, some polymerization activity on the lower olefines has been observed at 350° C and above, but this has always been accompanied by decomposition [106, 1927] Deposition of carbon upon it very soon stops its polymerization activity Molten sodium has a polymerizing effect on ethylene at 150° C Walker [106, 1927] obtained a colourless liquid polymer in this manner, but the sodium had no lasting activity because it was readily converted into ethylene sodium carbide Sodium is used industrially in the catalytic polymerization of diolefines and acetylene derivatives to produce synthetic resins, &c

Some metals, when employed in a finely divided condition, accelerate the polymerization activity of aluminium chloride and phosphoric acid and sulphuric acid

The patent literature contains many references to polymerization reactions carried out in the presence of metals claimed to have catalytic effect and employed in the form of coherent surfaces The following are typical examples

(i) Copper and silver [84, 1932] and gold [38, 1928]
(ii) Catalysts containing metals resistant to heat superficially coated with a metal selected from the group tin, zinc, aluminium, and chromium [40, 113, 1933]
(iii) Metals of the 8th group of the Periodic Table, capable of adsorbing gases in considerable quantity, e g platinum or palladium sponge [105, 1933]
(iv) Metals of the 8th group, either alone or admixed [14]

(*b*) Metal Oxides, &c.

Very few of the metal oxides exhibit catalytic effect on polymerization reactions unless they are used in the form of adsorbent gels Where catalytic effect is evident it is usually towards decomposition Thus titania has been reported [22, 1917] to cause decomposition of ethylene at 490° C On the other hand, Ipatieff [43, 1911–12] has claimed alumina to possess pronounced catalytic activity in the polymerization of ethylene at 70 atm and 375° C , whereas it decomposes isobutylene into hydrogen, propylene, and lower paraffins at 550–600° C [42, 1903, 58, 1907–8] Probably a difference in physical state of the alumina accounts for these contradictory observations

Egloff and Schaad [21, 1933] failed to observe any catalytic effect of alumina (prepared from both the nitrate and sulphate) in the pressure polymerization of ethylene at 380° C and 130–40 atm pressure

A claim has also been made for the condensation of liquid hydrocarbons rich in naphthenes with ethylene under pressure in the presence of oxides of the heavy metals, molybdic oxide being specially referred to [2, 1934]

A catalyst of the composition $4NiO–2Al_2O_3–CuO$ has been found to accelerate the explosive decomposition of ethylene at 330° C and 143 atm pressure [21, 1933]

Dunstan and Howes [18, 1936] have described tests made on the polymerization of a stabilizer reflux liquid containing 26% propylene and 45% butylene at 200–350° C and 150 lb pressure in the presence of various metal oxides Chromium oxides (CrO_3 and Cr_2O_3), molybdic oxide (MoO_3), uranium trioxide, vanadium pentoxide, and titania were found to possess little activity Alumina deposited on silica gel was found to be slightly active and not to deteriorate rapidly in use On the other hand, tungstic oxide (WO_3) was found to possess definite activity and at 230–250° C and 85–130 lb pressure gave an appreciable yield of liquid polymer However, the catalyst deteriorated rather rapidly, due to reduction to the lower blue tungstic oxide (W_2O_5)—which is inactive In this connexion it is of interest to note that calcium oxide is not reduced by ethylene, but ferric oxide (Fe_2O_3) is completely reduced at 500° C , zinc oxide at 800–900° C , and lead oxide at 600° C [106, 1927] Many heavy metal higher oxides, e g those of molybdenum, vanadium, and uranium, are easily reduced by gaseous olefines and paraffins to the corresponding lower oxides at quite low temperatures—e g 150–300° C

Waterman *et al* [107, 1934–5] observed that a catalyst comprising alumina on silica gel and activated at 350° C was active in the polymerization of isobutylene in the vapour phase at temperatures up to 40° C

(*c*) Neutral Salts.

Very few inorganic neutral salts possess any catalytic activity with regard to the polymerization of olefines The neutral phosphates possess some activity, and these are referred to in detail later in a discussion on phosphoric acid catalysts Zinc antimonate and copper borate have been mentioned as being effective catalysts, and also potassium dichromate [84, 1932] Cuprous chloride is an important ingredient in catalyst mixtures employed for the conversion of acetylene to vinyl acetylene [101, 1933], but has no polymerizing action on the lower mono-olefines [18, 1936] Some neutral salts have a promoter action in the polymerization of olefines by inorganic acids

(*d*) Adsorbents, e.g. Floridin, Active Carbon, Silica Gel, &c.

The pronounced polymerizing activity of the common adsorbents is well known. The first published work on the polymerizing action of floridin and other finely divided siliceous earths is that of Gurwitsch [27, 1923, 1926], who treated amylenes with these materials at normal temperatures and found that heat was evolved and diamylenes, triamylenes, and higher polymers were formed. In 1925 Lebedev and Filonenko [72, 1925] from a study of the polymerization of olefines by floridin at ordinary pressure, advanced the generalization that only those olefines are polymerized which are derivatives of the asymmetrical di- or tri-substituted ethylenes of the types $RR'C{=}CH_2$ and $RR'C{=}CHR''$, while the mono-substituted or symmetrical di- and tetra-substituted olefines do not polymerize even after long periods of time in the presence of this material. In agreement with this generalization these workers found that propylene was unattacked by floridin, whereas isobutylene was readily polymerized. At a later date (1928) Van Winkle [102, 1928–9] found that although propylene did not change in contact with activated floridin at ordinary temperatures and pressures, it did undergo condensation at increased pressure. After allowing liquid propylene to remain in contact with floridin for a few months, the dimers and trimers were formed, but after 1 year's contact the products contained no dimer but only higher polymers. The polymerization of isobutylene in the presence of activated floridin is, to some extent, a reversible reaction. Lebedev and Koblianski [73, 1930] found that isobutylene polymerized readily in the presence of floridin (activated by heating to 300° C) even at −80° C. At room temperature the polymerization was very rapid, but it was retarded at temperatures of 200° C and above. The products obtained by allowing liquid isobutylene to stand with floridin for 4 days at normal temperatures contained no di-isobutylene, but only higher polymers. With much shorter reaction times appreciable quantities of di-isobutylene were formed.

Lebedev and Koblianski [73, 1930] also made tests on the depolymerization of isobutylene polymers using the same catalyst. At 200° C the pentamer decomposed into a mixture of the trimer and the dimer, the tetramer into two molecules of the dimer, the trimer into the dimer and isobutylene, and the dimer into two molecules of isobutylene itself. In all cases some monomeric isobutylene was produced, attributed in the case of the higher polymers to progressive dissociation of the initial dimer and trimers. Di-isobutylene is the most stable polymer. Further work on the depolymerization of tri-isobutylene in the presence of activated floridin has been published by Lebedev and Livshitz [75, 1934], who found that dissociation began measurably at 50° C, with 99% decomposed at 180–190°C to give di-isobutylene and isobutylene. A part of the di-isobutylene formed was polymerized with the formation of a tetramer and higher polymers. Butene-2 yields 80·5% of polymerides when left in contact with floridin at normal temperatures for 6 months [76, 1935].

In the case of isobutylene, the extent of polymerization in the presence of floridin increases to a maximum as the temperature is decreased to −60° C, and the molecular weight of the product also increases. Polymers of molecular weight up to 12,000 have been produced by low-temperature polymerization with floridin [71, 1935]. The polymerization and depolymerization of amylenes under the influence of floridin has also been reported on [77, 1928].

An important contribution on the polymerization of propylene, in the presence of various adsorbents, to liquid hydrocarbons of gasoline boiling range has been made by Gayer [25, 1933], who found that at 350° C and atmospheric pressure dehydrated floridin possesses considerable catalytic activity. The activity was found to increase after treatment with hydrochloric acid, and a precipitated porous silica containing adsorbed alumina on its surface was found to be 20 times more active than the best sample of activated floridin prepared. On the other hand, synthetic ferric and magnesium silicates and precipitated silica were found to be quite inactive.

Selected results obtained by Gayer are reproduced in Table IX. Each of the catalysts mentioned deteriorated rapidly in activity, but the useful life was extended by the addition of small quantities of hydrochloric acid to the propylene undergoing treatment.

With regard to the liquid polymers obtained by Gayer, approximately 84% by weight boiled below 220° C, and the stabilized crude product had the following properties:

d_4^{20} 0·70–0·71
n_D^{20} 1·405–1·410

TABLE IX

Catalytic Polymerization of Propylene at Atmospheric Pressure in the Presence of Adsorbents (*Gayer* [25, 1933])

Expt no	*Catalyst*	*Temp °C*	*Catalyst g (K)*	*Time, hours*	*Propylene per hour, g (R)*	*Contact time, sec*	*Yield of polymer per hour, g (P)*	*Polymer yield, %*	*Propylene, g per g of catalyst per hour, r = R/K*	*Polymers, g per g of catalyst per hour, c = P/K*	*Activity at end of expt (c)*
1	Floridin dehydrated 5–6 hr at 300–325° C	350	150	2·3	8·3	80	0·5	6	0·055	0·003	0·0
2	Floridin dehydrated 4 hr at 500° C	350	150	24	8·3	80	0·5	6	0·055	0·003	0·001
3	Floridin dehydrated as in expt 2, treated with conc HCl—washed and dehydrated	350	150	32	9·7	69	2·4	24	0·061	0·016	0·008
4	Floridin as in expt 3—twice treated with conc HCl	350	120	72	9·3	71	2·9	32	0·078	0·024	0·018
5	Synthetic aluminium silicate	350	100	73	10·0	74	2·9	29	0·010	0·028	0·020
6	Alumina on silica	340	15	183	21·0	8	4·3	20	1·40	0·29	0·11
7	Alumina on silica (0·3% N amyl chloride in propylene feed)	340	15	183	20·8	8	6·5	31	1·38	0·44	0·28

Bromine number (g Br per 100 g oil) 150–5 Fractional distillation gave the following figures

° C	% wt
25–50	6 25
50–80	34 5
80–100	13 8
100–125	7 6
125–150	10 0
150–220	11 7

The octane numbers of the crude product and of a 90% steam distillate were 91 and 87, respectively, by the C F R Research Method No information is available concerning C F R Motor Method knock ratings

The product was not entirely olefinic, the olefine content of narrow fractions ranging from 52 to 100% The non-olefinic portion was probably paraffinic in character Gum contents were very low

According to Dunstan and Howes [18, 1936], alumina and silica gels are only slightly active compared with phosphoric acid catalysts

The patent literature contains several references to the use of adsorbents as catalysts in polymerization reactions of olefines of which the following may be mentioned

(i) Polymerization of olefines and condensation of olefines with aromatic hydrocarbons in the presence of a hydrosilicate possessing a large surface and high porosity [39, 1930]

(ii) Polymerization of olefinic gases in contact with solid adsorbents at 177–400° C and 600–1,000 lb pressure Mention is made of fuller's earth, activated charcoal, silica gel, bentonite, partially hydrated silica, and silicic acid compounds [104, 1933]

(iii) Polymerization of olefinic gases in the presence of an acid treated montmorillonite type clay [29, 1936]

(*e*) Halogens, Halogen Acids, and Metal Halides.

The most important polymerization catalysts belonging to this group are the metal halides—aluminium chloride, zinc chloride, and boron tri-fluoride These are very vigorous in their action and catalyse many deep-seated isomerization reactions, with the result that the products obtained are not true polymerization products

Aluminium Chloride and Zinc Chloride. In 1913 Ipatieff and Routala [57] studied the effect of catalysts such as zinc chloride and aluminium chloride on the polymerization of ethylene under pressure In the presence of zinc chloride at 70 atm polymerization proceeded at 275° C, the liquid consisting of pentane, *iso*-pentane, and the higher paraffins, as well as olefines containing 6–9 carbon atoms Freshly prepared aluminium chloride induced polymerization of ethylene at the same pressure at ordinary temperature, and at 200° C was so violent in its action that only a carbonaceous residue was formed Some years earlier Heusler [31, 1896] found that unsaturated hydrocarbons were polymerized by the action of aluminium chloride, and the polymerization of amylene in the presence of this reagent was studied by Aschan [4, 1902] and also by Engler and Routala [23, 1909–10] The last-named investigators showed that the lower boiling products consisted chiefly of paraffins, the cyclo-paraffins predominating in the fractions boiling above 175° C

In 1928 Szayna [100, 1928–9] found that, at atmospheric pressure, ethylene reacts with difficulty with aluminium chloride at 100 and 150° C, giving rise only to small amounts of condensed products Under similar conditions other olefines underwent extensive polymerization The lower boiling liquid products obtained were chiefly paraffins, while the heavier fractions consisted of cyclo-paraffins together with small quantities of unsaturated hydrocarbons

No explanation of the extraordinary activity of aluminium chloride in promoting the polymerization of olefines has been advanced, but there appears no doubt that this process is another example of the Friedel-Crafts reaction so applied to olefine hydrocarbons Any explanation of the reaction mechanism must take into account the formation of complex aluminium chloride-hydrocarbon compounds, which are, in the case of ethylene, decomposable by water to give unsaturated hydrocarbons of the olefine type

One of the most complete investigations on the polymerizing action of aluminium chloride is that described by Stanley [98, 1930], and by Nash, Stanley, and Bowen [89, 1930], the results of which may be summarized as follows

In the absence of any catalyst, ethylene did not polymerize at 60 atm pressure until a temperature of 325° C was attained The condensation to liquid hydrocarbons was fairly rapid at 350° C In the presence of stannic chloride and titanium tetrachloride only negligible amounts of liquid products were produced at temperatures up to 100° C, but in the presence of aluminium chloride polymerization was extensive even at room temperatures Zinc chloride was much less effective than aluminium chloride, and caused polymerization to begin at 230–275° C

At ordinary temperatures, the products obtained from ethylene in the presence of aluminium chloride were of two types (*a*) a free oil, and (*b*) a double compound of aluminium chloride and liquid hydrocarbons, from which the 'combined' oil was extracted after decomposition with iced water The free oil was found to consist of liquid hydrocarbons mostly of a saturated nature and containing from about 10 to 45 carbon atoms in their molecules The lower boiling fractions contained proportions of paraffin hydrocarbons, but the main part of the oil consisted of saturated hydrocarbons of the empirical formula C_nH_{2n}, and presumably cyclo-paraffins The 'combined' oil, liberated from the pasty aluminium chloride addition compounds, also consisted of complex hydrocarbons containing from 10 to 15 carbon atoms per molecule These appear to be unsaturated and contain somewhat less hydrogen than required by the formula C_nH_{2n} These oils are probably to be regarded as composed of unsaturated hydrocarbons of the olefine series and of the formula C_nH_{2n}, admixed with hydrocarbons of lower hydrogen content (probably unsaturated cyclic hydrocarbons) It was found also that, whereas the amount of the combined oils was limited by the quantity of aluminium chloride present, the amount of the free oils produced increased steadily with the duration of the experiment

At higher temperatures the condensation of ethylene under pressure in the presence of aluminium chloride was much more rapid, but the life of the catalyst was considerably curtailed As before, free oil and aluminium chloride double compounds were formed, but these differed considerably from the products obtained at lower temperatures The aluminium chloride complex tended to become more and more carbonaceous as the temperature was increased, and above 100–150° C it was not possible to obtain oil from this material, but only a relatively small amount of a heavy black tar The free oil produced at higher temperatures was a pale yellow, clear oil containing large proportions of low-boiling constituents in contrast to the free oil produced at lower temperatures. The low-boiling fractions consisted of paraffin hydrocarbons from pentane upwards, whilst the higher boiling fractions were deficient in hydrogen, and corresponded to the formulae C_nH_{2n-6}, C_nH_{2n-8}, and C_nH_{2n-10}. These latter substances probably belong to the class of polynuclear naphthenes. At higher temperatures lower paraffin hydrocarbons appeared in the residual gases from the experiments, their amount increasing with rise in temperature. The properties of ethylene polymers obtained by Nash, Stanley, and Bowen [89, 1930] at 10–15° C in the presence of aluminium chloride are detailed in Table X. Similar properties of oils produced at 150° C are given in Table XI. Of particular interest *is* the polymer gasoline fraction produced at the higher temperature. Its physical constants, coupled with its rather high octane number, indicates that *it* is iso-paraffinic in character, thus differing radically from ethylene polymers produced in the absence of a catalyst or in the presence of catalysts such as adsorbents, phosphoric acid, &c. The properties detailed in Tables X and XI demonstrate the remarkable catalytic activity of aluminium chloride and show definitely that polymerization is only the *primary* reaction involved.

With regard to the mechanism of the polymerization of olefines by aluminium chloride, Stanley [98, 1930] believes that the production of the numerous and complex products formed by the action of aluminium chloride on ethylene can be explained on the basis of three well-known processes, namely,

(1) polymerization to higher olefines,
(2) isomerization of the olefines to produce the corresponding cycloparaffins, and
(3) the splitting off of lower paraffin hydrocarbon molecules under the influence of aluminium chloride with the simultaneous production of hydrocarbons of lower hydrogen content.

TABLE X

Properties of Oils produced by the Polymerization of Ethylene in the Presence of Aluminium Chloride at 10–15° C

(*Nash, Stanley and Bowen* [89, 1930])

Boiling range °C	*Free Oil*		*Combined oil*	
	Fraction	*% of total*	*Fraction*	*% of total*
Up to 100/10 mm	1 A	19.1	1 B	12.0
100–125 „	2 A	9.1	2 B	4.5
125–150	3 A	9.4	3 B	6.7
150–175 „	4 A	9.4	4 B	7.3
175–200 „	5 A	9.6	5 B	11.0
200–225	6 A	7.3	6 B	9.7
225–250	7 A	6.7	7 B	10.1
Above 250	8 A	29.4	8 B	38.7
		100.0		100.0

Properties of Fractions

Frctn	d_4^{20}	n_D^{20}	*Mol wt*	*Br no (Francis)*	% C	% H	*Approximate formula*
1 A	0.7517	1.4207	152		84.39	14.95	$C_{11}H_{22}$ and $C_{11}H_{24}$
2 A	0.7807	1.4350	210	1.3	84.86	14.93	$C_{15}H_{30}$ and $C_{15}H_{32}$
3 A	0.7942	1.4448	244		84.96	14.80	$C_{17}H_{34}$ and $C_{17}H_{36}$
4 A	0.8052	1.4499	272	2.8	85.03	14.61	$C_{20}H_{40}$
5 A	0.8160	1.4555	309		85.03	14.75	$C_{22}H_{44}$
6 A	0.8249	1.4594	357	4.4	85.26	14.57	$C_{25}H_{50}$
7 A	0.8332	1.4622	384		85.20	14.51	$C_{28}H_{56}$
8 A		1.4721	591	6.9	85.36	14.35	$C_{42}H_{84}$
1 B	0.7521	1.4267	133	30.36	84.88	14.63	
2 B	0.8200	1.4649	198	38.44	86.11	13.46	
3 B	0.8357	1.4735	228	37.32	86.01	13.31	
4 B	0.8451	1.4795	262	35.40	86.07	13.33	
5 B	0.8526	1.4823	305	44	86.17	13.41	
6 B	0.8584	1.4848	344	46	86.27	13.31	
7 B	0.8636	1.4863	380	32	86.19	13.42	
8 B			729	28	86.07	13.33	

TABLE XI

Properties of Free Oils produced by the Polymerization of Ethylene in the Presence of Aluminium Chloride at 150° C [89, 1930]

		% by weight	d_4^{20}	n_D^{20}	*Mol wt*	*Aniline point, °C*	*Bromine number*	*Elementary analysis* % C	*Elementary analysis* % H	*Approximate formula*
1	I.B.P., 27° C/743 mm 27–50° C/743 mm	7.6	0.6247	1.3649	77					
2	50–100° C „	14.5	0.6625	1.3791	90	70.7	0.0			
3	100–150° C „	15.1	0.7078	1.4018	116	72.7	0.0			
4	150–200° C „	12.8	0.7460	1.4198	145	75.8	0.0			
5	200° C/743 mm–100° C/10 mm	3.0	0.7761	1.4340	174		0.0			
6	100–120° C/10 mm	4.2	0.8017	1.4472	190		0.0			
7	120–140° C „	3.8	0.8319	1.4630	212		0.0			
8	140–160° C „	6.6	0.8604	1.4801	226		0.0			
9	160–180° C „	7.4	0.8902	1.4969	254		0.0	87.06	12.84	$C_{18}H_{30}$
10	180–200° C „	5.2	0.9040	1.5043	275		0.0	87.20	12.52	$C_{20}H_{34}$
11	200–220° C „	4.0	0.9181	1.5143	293		0.0	87.66	12.31	$C_{22}H_{36}$
12	220–250° C „	7.0		1.5296	350		0.0	87.62	12.01	$C_{25}H_{42}$
13	Above 250° C „	8.8		1.5296	428		0.0			

Fraction boiling up to 200° C [5, 1933]

Sp. gr. 60° F	0.6884
I.B.P.	35° C
10% distillate at	52.5° C
20% „ „	62° C
30% „ „	70.5° C
40% „ „	82° C
50% „ „	94.5° C
60% „ „	108.5° C
70% „ „	124° C
80% „ „	138° C
90% „ „	161° C
F.B.P.	192° C
Total distillate	96.5° C

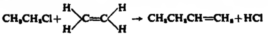
Aniline point	72.7–73.4° C
Aniline point after washing with 98% H_2SO_4	73.8° C
Loss to 98% H_2SO_4	2.0%
Octane number (S30 engine 212° F jacket temp.)	73

Of these three processes the first two can probably take place under the influence of aluminium chloride at quite low temperatures, whilst the third reaction becomes prominent at higher temperatures There is some evidence to show, however, that a slight splitting off of lower paraffins takes places at 10–20° C Stanley believes that polymerization to form higher olefines is the first step in the process and that these combine with the aluminium chloride as soon as they are formed to give complexes of the type $x(C_nH_{2n})yAlCl_3$ The next process is considered to be the isomerization of the higher olefines into cycloparaffins According to Francis and Kleinschmidt this isomerization is thermodynamically possible at all temperatures below about 400° C The process may be visualized as consisting of the isomerization of a higher olefine (momentarily liberated from combination with aluminium chloride in the complex), with the production of a cycloparaffin of the same molecular weight The cycloparaffin thus formed would be incapable of combination with the aluminium chloride, and therefore corresponds to the 'free' oils obtained On the other hand, the aluminium chloride rendered free from combination by the loss of an olefine molecule would be free to effect the polymerization of more ethylene to higher olefines, which themselves would be held in the form of an aluminium chloride complex The splitting off of lower paraffin molecules from more complex hydrocarbon molecules has been noticed by many observers, and, moreover, is the basis of the McAfee cracking process Grignard and Stratford [26, 1924] found that *n*-butane was formed on heating aluminium chloride at 120–150° C in the presence of either octane, di-isobutylene, decane or heptadecane According to Ipatieff and Grosse [50, 1936] the butane formed is the iso compound and not the normal isomer

Doubtless the mechanism of polymerization reactions induced by the other halides, e g zinc chloride, is similar to that in the case of aluminium chloride, but boron fluoride is reputed to bring about true polymerization in the presence of finely divided metals, e g nickel [48, 1935]

The polymerization of ethylene in the presence of aluminium chloride has also been studied by V N Ipatieff and A V Grosse [51, 1936] who, for the most part, agree with the conclusions of Stanley [98, 1930] These investigators found that aluminium chloride when really pure does not react with pure ethylene even under pressures up to 50 atm at 10–50° C, and that the presence of traces of hydrogen chloride or moisture is necessary for the reaction Examination of the products obtained in the presence of hydrogen chloride showed that the upper layer, i e free oil, was water white and consisted of paraffin hydrocarbons All fractions of this part of the product (except those boiling about 300° C) were stable to permanganate solution and to nitrating mixture, indicating the absence of unsaturated and aromatic hydrocarbons All fractions contained *traces* of alkyl chloride The lower layer of the product had the composition $5C_nH_{2n-x} \cdot AlCl_3$ (in which x varied from 2 to 6) and the separated hydrocarbons were cyclic unsaturated compounds of the type of terpenes—giving paraffins on hydrogenation

Ipatieff and Grosse consider that the mechanism of polymerization consists in the addition of hydrogen chloride to ethylene, leading to ethyl chloride which reacts with another molecule of ethylene (or higher olefine), losing hydrogen chloride



$$CH_3CH_2Cl + H_2C{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2 + HCl$$

The mono-olefines are considered to be transformed by cyclic or intramolecular alkylation into naphthenes, which, either as such or at the moment of their formation, are converted by means of a reaction of hydrogenation, dehydrogenation, or hydrogen disproportionization, into a mixture of paraffins and unsaturated naphthenes The latter combine with aluminium chloride—forming the lower layer Ipatieff and Grosse name such a polymerization—involving hydrogen disproportionization—a 'conjunct polymerization'

Many investigators have used so-called 'inert solvents' in reactions between aluminium chloride and olefines These solvents are usually low-boiling paraffin hydrocarbons In view of the discovery [49, 1936, 52, 1936] that olefines react with such paraffins in the presence of aluminium chloride, their results are not characteristic for olefine polymerization

Isobutylene and various higher olefines have been subjected to the action of aluminium chloride at various temperatures by Waterman and his co-workers In most cases pentane was used as a diluent Isobutylene at −78° C to +16° C gives a mixture of olefinic and cyclic hydrocarbons of molecular weight ranging from 132 to 4,800 The highest molecular weight products are obtained by working at the lowest temperatures At −78° C the reaction is often explosive and the products are highly viscous [52, 1936]

With regard to the pentenes, isopropyl ethylene and pentene-2 react slowly with aluminium chloride at −80° C in the absence of hydrogen chloride, but trimethyl ethylene and methyl ethyl ethylene polymerize much more rapidly In the presence of hydrogen chloride, chlorides are produced [78, 1934] At 0° C pentene-2 gives an 80% yield of partly cyclized hydrocarbon products [108, 1935]

Cyclo-hexene does not react with aluminium chloride dissolved in pentane at −78° C, 0° C, or −40° C At 70° C polymerization occurs with the formation of cyclohexyl compounds At −78° C in the presence of added hydrogen chloride chlorocyclohexene and a mixture of chloropolycyclohexyl compounds are produced [109, 1935]

The polymerization of acetylene, ethylene, and isobutylene by aluminium chloride has also been studied by Hunter and Yohe [35, 1933]

One of the most important contributions on the polymerization of olefines by zinc chloride, particularly with regard to the production of polymer gasolines, is that by Brandes, Gruse, and Lowy [6, 1936] dealing with propylene An autoclave was used for this work, and tests were made at temperatures varying from 150 to 300° C and at 1,500–3,400 lb per sq in (105 4–239 kg per cm²) maximum pressure Reaction time varied from 60 to 360 min, and $ZnCl_2/C_3H_6$ molecular ratios from 0 10 to 0 12 Conversions of propylene to liquid polymers of from 43 5 to 74 2% were realized with fresh batches of catalyst, but catalytic activity decreased rapidly The products produced were light straw in colour, and of sweet smell As the reaction temperature was increased from 150–160° C to 290–310° C, the quantity of gasoline fractions in the product decreased from 92 to 74 5%, and the quantity of product corresponding to the tripolymer of propylene also decreased from 56 to 19% The product was found to consist mainly of olefines and paraffins—although naphthenes were also present The product is thus essentially different from that obtained by Stanley [98, 1930] and by Ipatieff [51, 1936] from ethylene using aluminium chloride catalyst No information is available regarding the antiknock value of the above propylene polymers

Zinc chloride finds extensive use in the petroleum industry as a refining agent in the Lachman process for the treating of gasolines

The patent literature is of particular interest in that it reflects the enormous interest taken in the reactions of the lower olefines in the presence of zinc and aluminium chlorides Of importance are the various patents of Allenet [1, 1923], which are among the first devoted to this subject

These refer to the polymerization of the gaseous olefines with these materials in the presence of diluents at ordinary temperatures [1, 1923] Among the first proposals to make synthetic motor spirits and lubricating oils by such processes were those of Burrell and Dawe [8] and Brownlee [7] respectively, while Weizman and Legg [112] were among the first to refer to the production of naphthenic hydrocarbons by the action of aluminium chloride on butylene at low temperatures under pressure

Recently the production of polymer gasolines by the treatment of olefinic gases with aqueous zinc chloride solutions has been patented [87, 1936], and also polymerization in the presence of hydrogen halide and a metallic salt in aqueous solution [86, 1936]

The use of zinc and aluminium chlorides in the polymerization of olefines to hydrocarbons of lubricating-oil properties [67, 1933–6], and also in the condensation of olefines with aromatics [41], has also been extensively patented

Boron tri-fluoride Although boron tri-fluoride (BF_3) was first prepared in 1808, its possibilities did not attract commercial attention until about 1925 It is a gas which readily decomposes in contact with moisture, and is difficult to handle on account of its corrosive and poisonous nature Butlerov and Gorianov [9, 1873] appear to have been the first to observe the polymerizing action of boron fluoride They found that this material did not polymerize ethylene at ordinary pressure even at 200° C, but that propylene and butylene, on the other hand, were polymerized very readily at normal temperatures Otto [90, 1927] studied the polymerizing action of boron fluoride on the lower olefines at elevated pressures Ethylene polymerized extensively under pressure at ordinary temperatures, while its immediate homologues were even more easily converted into higher hydrocarbons The products were viscous and of high molecular weight This polymerizing action may be accelerated by the presence of finely divided metals such as nickel [32, 1927, 1931], or by the addition of halogen acids, such as HCl, HBr, HI or HF [33]

Of particular interest are claims [37, 1930, 91, 1935] that ethylene may be converted into butylene by the use of boron fluoride catalyst and very short reaction times at pressures of 50–60 atm and at room temperatures In this case also more energetic catalytic activity is obtained in the presence of halogen acids and/or finely divided nickel

The major application of boron fluoride as a polymerization catalyst now appears to be in the production of synthetic lubricating oils by the treatment of the gaseous olefines, and also in the production of oils of very high molecular weight—i e 5,000–6,000, for incorporation in lubricating oils Isobutylene is the preferred starting material [68, 1934–5]

Double Compounds of Halides with Organic Substances. Because of the corrosive natures of aluminium and zinc chlorides, and boron fluoride, double compounds of these materials have been discovered which can be substituted for them in polymerization reactions These double compounds are termed 'Ansolvo Acids' [82, 1927], typical examples being complexes of the organic acids, e g. oleic, formic, and naphthoic acid with zinc and aluminium chlorides and boron fluoride, and also similar complexes with ethers, ketones, nitrobenzene, nitromethane, and alcohols These double compounds are less violent in their action than the halides alone, and have, for this reason, been proposed as polymerization catalysts [11, 1936]

As far as is known no process is in commercial operation for the production of polymer gasolines from cracked gases using the halides as catalysts Their disadvantages, enumerated above, have so far prevented their adoption for this purpose They are corrosive and poisonous, difficult to handle and store, and their polymerizing action is usually too violent for gasoline production A further disadvantage is that no satisfactory method has yet been developed for ensuring a long catalyst life, and, moreover, the polymer gasolines obtained are of low knock rating

(*f*) Inorganic Acids and Acid Salts.

The inorganic acids, sulphuric acid and phosphoric acid, have pronounced polymerization activity under certain conditions Hydrochloric acid is also a well-known polymerization catalyst promoter (e g in the case of alumina and silica gels), but suffers from the disadvantage of causing chlorination Nitric acid possesses too vigorous an oxidizing action to allow its polymerization activity to be much in evidence

Phosphoric Acid as an Olefine Polymerization Catalyst. Phosphoric acid is one of the most successful polymerization catalysts yet developed, and is in commercial use on a large scale in the production of high octane number polymer gasolines from cracked gases The development has been carried out by Universal Oil Products Company [47, 1935], and also independently by the Anglo-Iranian Oil Company [18, 1936]

The polymerizing action of the phosphoric acids has been known for some time, but the application of such substances to the production of higher-boiling hydrocarbons from gaseous olefines was probably first mentioned in patents of the I G Farbenindustrie bearing application dates between 1926 and 1929

These make the following claims

(i) The polymerization of olefines under pressure in the presence of salts and oxy-acids of phosphorus, giving as examples calcium phosphate, di-potassium phosphate, calcium pyrophosphate, and also phosphorus pentoxide on a pumice support [83, 1932]

(ii) Polymerization of olefines by heat treatment under any suitable pressure in the presence of salts of the oxygen acids of phosphorus, boron, and antimony, with alkali metals or other metals as the basic constituent, or their reduction products, or the free acids themselves, in the solid form, or in the form of their anhydrides on carriers [65, 1927]

(iii) A process for the polymerization of lower olefines, which comprises treating the said olefines with catalysts comprising phosphoric acid, metaphosphoric acid, or other acids of phosphorus, as such or in the form of their salts, and in a solid or semi-solid state, and operating at temperatures below 400° C. [66, 1929–30].

These patents caused much interest in that they revealed the possible use of salts of phosphoric acid as polymerization catalysts, and they stimulated further research.

In 1932 a patent [34] was issued covering a process involving the selective polymerization of propylene and higher olefines in gaseous mixture containing ethylene, by passing the mixtures at atmospheric pressure over a metallic salt of phosphoric acid at elevated temperatures, e g 200° C The preferred catalyst mentioned was cadmium metaphosphate of the composition CdP_2O_6 The following year a proposal [2, 1932–3] was made to utilize as a motor fuel the mixture of polymers and alcohols obtained by passing a mixture of cracked gas and steam over phosphate catalysts, e g boron phosphate, at 200–350° C , and at high pressures—e g 30 atm

Patents by Universal Oil Products on the use of phosphoric acid and phosphate catalysts for the polymerization of olefines did not appear until May 1934, when several novel features were disclosed A proposal was made [59, 1932, 1934] to effect polymerization of olefines at temperatures between 50° and 200° C in the presence of an acid selected from the group consisting of orthophosphoric and orthophosphorous acids Orthophosphoric acid was preferred

This proposal was followed in 1935 by patents covering the use of so-called 'solid phosphoric acid' catalysts, these consisting of solid mixtures of phosphoric acid and various phosphates Examples of such catalysts are mixtures of phosphoric acid with a chloride and/or an oxide of an alkaline earth metal [61, 1933, 1935] and also mixtures of phosphoric acid with adsorbent materials of a siliceous nature such as kieselguhr [62, 1933, 1935] Further patents disclosed the use of catalysts of the above general compositions calcined prior to use at temperatures between 180° and 300° C , without any substantial heating above 300° C [63, 1934–5, 85, 1934–5], and also the use of catalysts comprising phosphoric acid, zinc oxide, and zinc chloride [64, 1933, 1935] The catalytic polymerization of ethylene, which is normally resistant to the action of the above catalysts, in the presence of readily reacting olefines, is also mentioned [53, 1934, 1936]

Recent I G patents have included catalysts comprising solutions of an anhydride of an acid of phosphorus in a liquid acid of phosphorus [13, 1934, 1936], and also acid esters of phosphoric acid—e g monocresyl phosphate, either in the presence or absence of copper or silver salts [12, 1934, 1936]

The development of phosphoric acid catalysts for polymerization is very closely connected with the catalytic vapour-phase hydration of olefines in the presence of steam to the corresponding alcohols, for which reaction practically identical catalysts have been proposed This is evident from the following summary of the most important patents dealing with this reaction

B P 368,668 J Y Johnson and I G (1932)
The production of ether by passing ethylene and steam over phosphate catalysts—particularly phosphates of the rare earths

B P 346,288 G F Horsley and I C I Ltd (1931)
Hydration of acetylene to acetaldehyde and crotonaldehyde by treating with cadmium phosphate catalyst (P_2O_5 CdO − 0 4–0 6) in the presence of steam

B P 369,216 (1932) I C I Ltd
Catalyst comprising a phosphate of cadmium, beryllium, zinc, aluminium, tin, or lead The preferred composition of cadmium phosphate is $\frac{P_2O_5}{CdO}$ = 0 9–0 725 Figures are given to show that cadmium phosphate is more active in this reaction than the phosphates of lead, zinc, aluminium, or tin

B P 378,865 (Appl date 1932) I C I Ltd
Catalytic hydration of olefines using boron phosphate catalyst .

B P 392,289 (1933) Distillers Company Ltd
Catalytic hydration, using phosphates of uranium, iron, or cobaltous cobalt—the amount of phosphoric acid being in excess of that required to form the orthophosphate, but not in excess of about 95% of the composition

B P 392,685 (1933) Distillers Company Ltd
Catalysts for hydration of olefines—compounded from phosphoric acid and either or both of the metals copper or manganese or their oxides , the amount of phosphoric acid present being in excess of that required to form the orthophosphate but not in excess of about 95% of the composition

B P 394,389 (1933) H Dreyfus
Phosphoric acid as a hydration catalyst—initially in the anhydrous condition

B P 396,724 (1933) Distillers Company Ltd
Boron phosphate as a hydration catalyst The amount of phosphoric acid being at least 10% in excess of that required to form the orthophosphate, but not in excess of about 95% of the composition

B P 404,115 (1934) Distillers Company Ltd
Catalysts for hydration reactions--containing a drying oil to improve mechanical strength

B P 407,722 (1934) H Dreyfus
Alkali and alkaline-earth metaphosphate catalysts

B P 407,944 (1934) I C I Ltd
Strontium metaphosphate catalyst

B P 408,313 (1934) I C I Ltd
A catalyst comprising ferric metaphosphate associated with a metaphosphate of a divalent metal, e g barium, strontium, cadmium, copper, or ferrous iron

B P 408,982 (1934) Distillers Company Ltd
The production of *iso*propyl alcohol using a solid catalyst compounded from phosphoric acid with one or more of the metals manganese copper, iron, cobalt, or uranium with or without boron, or their oxides or compounds, the amount of phosphoric acid being in excess of that required to form the orthophosphates, but not in so great a quantity as to depart from the solid nature of the catalyst

B P 413,043 (1934) Distillers Company Ltd
A catalyst rendered mechanically stable by incorporating with an organic substance or substances capable of forming true or colloidal solutions in water and which, after subjection to relatively elevated temperatures (of the order of 200° C), leaves or leave as residue in the catalyst substantially carbon only, e g starch, glucose, gelatin, glycerol, &c

B P 415,426 (1934) Distillers Company Ltd
Catalysts compounded from phosphoric acid with calcium and/or barium and/or strontium, magnesium, the amount of phosphoric acid present being in excess of that required to form the metaphosphates of the elements employed

B P 415,427 (1934) Distillers Company Ltd
Catalysts compounded from phosphoric acid with calcium, barium, strontium, and/or magnesium oxides—the amount of phosphoric acid being materially in excess of that required to form the orthophosphate, but materially less than that required to form the metaphosphate

B P 422,635 (1935) Distillers Company Ltd
Catalysts rendered mechanically stable by incorporating, during preparation, a non-drying oil such as castor oil, anhydrides, aldehydes, ketones, &c

B P 423,877 (1935) I C I Ltd
A catalyst consisting of cadmium phosphate together with a small quantity of one or more of the metaphosphates of barium, strontium, titanium, chromium, and tellurium

B P 435,749 (1935) I C I Ltd
Catalysts comprising one or more molecular proportions of aluminium metaphosphate associated with about one molecular proportion of a metaphosphate of calcium, cadmium, zinc, divalent copper, nickel, tin, or lead

U S P 2,052,095 (1936) Distillers Company Ltd
Catalysts comprising phosphoric acid and the phosphates of a metal taken from the group Mn, Cu, Fe, Co, and U, the amount of phosphoric acid being in excess of that required to form the orthophosphates of the metal or metals selected

In addition to being similar with regard to catalyst requirements, the processes of catalytic hydration and polymerization are also closely similar with respect to optimum temperature and influence of pressure, although the products are different It has been observed many times in the literature that, in the hydration reaction, if the olefine partial pressure or the total working pressure is increased, the rate of alcohol formation is augmented, but polymer formation becomes troublesome, because this also is favourably affected by increase in pressure In order to prevent polymer formation and still cause the reaction to occur in the desired direction, it is necessary to increase the partial pressure of the steam and maintain the partial pressure of the olefine at a relatively low value By this means good yields may be obtained

The proper choice of catalysts for the vapour-phase hydration of olefines under pressure to form alcohols is a very important factor because, as stated by Marek and Hahn [81] in 1932, 'catalysts active in promoting the hydration reaction are likewise active toward promotion of the undesirable polymerization reactions, since the latter often proceeds at a more rapid rate'.

The following statement is also made by Marek and Hahn

> 'In contemplating the use of high ratios of steam to olefine in vapour-phase hydrations for the purpose of restricting olefine polymerization, sight must not be lost of the fact that excessive steam ratios may impair catalyst activity by flooding the active surface with water molecules For this reason a mean should be struck between high ratios of steam to prevent polymerization and low ratios to prevent loss of catalyst activity '

To complete the comparison between polymerization and hydration reactions it is necessary also to consider the reverse of hydration of olefines to alcohols—namely, the dehydration of alcohols to the corresponding olefines

Phosphoric acid has been used for the preparation of ethylene from ethyl alcohol since this use was first discovered by Pelouze [92, 1833] In 1933 Lindinger and Moser [80, 1923] found that a mixture of alcohol and phosphoric acid would give off ethylene when heated to 205° C They concluded that the formation of ethylene was due to the action of the pyro-acid into which the ortho-acid was being dehydrated, and that a more complete conversion would be obtained at a higher temperature By passing ethyl alcohol vapour over finely divided pumice soaked in phosphoric acid heated to 250–300° C, a yield of 90% ethylene was obtained, which was 99 5% pure At a later date Newth demonstrated that syrupy phosphoric acid heated previously to 200° C was more efficient than glacial phosphoric acid (meta-acid) or phosphorus pentoxide Weber and Walton [111, 1930] have concluded that orthophosphoric acid previously heated to 250° C for 4½ hours gave the best yields of ethylene

It is thus evident that orthophosphoric acid (containing some pyro-acid) is an efficient catalyst for the dehydration of ethyl alcohol to ethylene and also for the hydration of ethylene to ethyl alcohol In view of the marked similarities between hydration and polymerization, it is also evident that phosphoric acid should also be a very effective catalyst for the latter reaction—a contention supported by the above-mentioned patents

The choice of suitable phosphoric acid catalysts for polymerization is helped somewhat by the above patent specifications Some of these frequently mention the advantages of catalysts containing free, i e uncombined, phosphoric acid, whilst others mostly claim metaphosphates containing, presumably, no free acid It should be noted here that the hydration reaction is invariably carried out in the presence of large quantities of steam, and that the effective catalysts may actually be orthophosphates, or possibly pyrophosphates, or the corresponding acids The reaction conditions most in favour for the hydration of olefines are as follows Temperature, 200–300° C, pressure, atmospheric to 2,000 lb, olefine/steam ratios 1 to 1 up to 3 to 1—but at atmospheric pressure may be as high as 10 to 1

It may thus be expected that under the same conditions, but in the absence of steam, polymerization of olefines would proceed at an attractive rate in the presence of a suitable phosphate or phosphoric acid catalyst As already mentioned, the temperature should be kept as low as possible, to prevent secondary isomerization reactions which lead to the formation of products of inferior knock rating

Chemical and Physical Properties of Phosphoric Acids. There are many acids of phosphorus—differing widely in their physical and chemical properties—some stable and others either volatile or easily decomposed, and it is necessary, in order to produce a catalyst of long active life and a polymer product free of phosphorus compounds, to choose the particular phosphorous acid with some care

Fortunately, as shown in Table XII, choice is limited to the hydrates of phosphorus pentoxide—namely, ortho-, pyro- and meta-phosphoric acids

TABLE XII

The Acids of Phosphorus

Name	*Formulae*	*M p (° C)*	*Action of heat, &c*
Ortho phosphoric	$H_3PO_4(P_2O_5—3H_2O)$	36 6–42 5	Dehydrates to mixture of meta- and pyrophosphoric acids
Meta-phosphoric	$HPO_3(P_2O_5—H_2O)$	Sublimes	Polymerizes to give a polymer of lower vapour pressure
Pyro-phosphoric	$H_4P_2O_7(P_2O — 2H_2O)$	61	Dehydrates to meta-phosphoric acid
Permono-phosphoric	H_4P_2O		Unstable
Di permono phosphoric	$H_4P_2O_8$		Unstable
Hypo-phosphoric	$H_4P_2O_6$ or $H_2PO_3(P_2O_4—2H_2O)$	$(H_2PO_3 = 55°$ $+ 2H_2O = 80$ $+ H_2O = 70)$	Phosphine evolved at 180° C At temperatures above the melting point spontaneously decomposes
Ortho phosphorous	$H_3PO_3(P_2O_3—3H_2O)$	70 1–74 0	Evolves phosphine at 140° C
Meta-phosphorous	HPO_2		Reacts with water to form ortho-phosphorous acid
Pyro-phosphorous	$H_4P_2O_5(P_2O_3 - 2H_2O)$		Reacts with water to form ortho-phosphorous acid
Hypo-phosphorous	H_3PO_2	17 4 26 5	Evolves phosphine at 100° C

Of these the former is a regular article of commerce, and is cheaper than the pyro-acid, whilst the meta-acid is inactive catalytically (see later)

The most suitable phosphoric acid to employ is therefore orthophosphoric acid, which may be obtained commercially in the anhydrous state, in 50% or in 90% solutions in water.

The presence of phosphorus pentoxide in polymerization catalysts is precluded because this substance sublimes at 180–250° C, and its vapour pressure may reach 760 mm at 250° C At higher temperatures, however, polymerization of the oxide causes the vapour pressure to fall considerably Phosphorus trioxide is of little use, because it boils at 173° C at 760 mm pressure, whilst phosphorus tetroxide sublimes at about 180° C

As shown in Table XII, orthophosphoric acid is dehydrated by the action of heat to give both pyro- and meta-acids, both of which are much too volatile for commercial use The dehydration of orthophosphoric acid may be briefly summarized as follows

When a dilute solution of orthophosphoric acid is evaporated at temperatures up to 150° C, a syrupy liquid is obtained which consists entirely of orthophosphoric acid and between 150° and 160° C it loses water slowly

At 240° C orthophosphoric acid loses water so that the ratio P_2O_5/H_2O = 1 2¾ to 1 2½—as compared with 1 3 for pure ortho-acid At higher temperatures more water is liberated until a product is obtained consisting mainly of metaphosphoric acid The literature is not conclusive regarding the minimum temperatures required for the formation of pyro- and meta-acids, but it is generally supposed that the conversion to pyrophosphoric acid is not complete at 230° C, whereas it is so at 260° C, and that meta-acid begins to form at about 290° C It is probable that, during the dehydration of orthophosphoric acid, there is a state of equilibrium between the three acids—dependent on the temperature and the partial pressure of any water present Thus dehydration is greatly suppressed by the presence of water vapour A consequence of dehydration is the formation of lower acids more volatile than the original ortho-acid Therefore, if dehydration is allowed to occur, greater loss of acid—due to volatility—might be expected, although experimental evidence is at variance with this deduction to some extent

Prevention of Phosphoric Acid Dehydration It has been stated [18, 1936] that whereas catalysts of the above type are active when prepared from either ortho- or pyro-phosphoric acid, those incorporating the meta-acid are inactive Furthermore, the activity of all phosphoric acid catalysts diminishes in use in polymerization reactions unless special steps are taken, and all such used catalysts contain meta-acid (HPO_3)

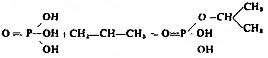
These observations show that, as is to be expected from the above comments on dehydration, the cause of catalyst decline is the formation of meta-acid, and the obvious way to prevent this is the admixture of small quantities of water vapour in the gas before passage over the catalyst In this way it is possible to keep the water content of the catalyst substantially constant, the amount of water mixed with the inlet gas just compensating for that lost from the catalyst by dehydration The amount of water required is approximately 2–10% by volume of the inlet feed, the water being measured in the form of steam By injecting water or steam in this way catalyst deterioration by the formation of meta-acid is prevented The amount of water should not exceed the above limits, otherwise alcohol formation is appreciable and often the mechanical strength of the catalyst is impaired

With catalysts of high free acid content dehydration leads to the formation of large quantities of meta-acid, which change the catalyst from a hard cake to a wet, pasty mass

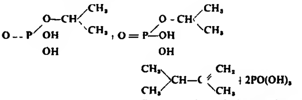
The use of steam to prevent phosphoric acid dehydration has been fully described by Dunstan and Howes [18, 1936], and also by Ipatieff [60, 1935] The scheme is, however, not novel, and was suggested in 1931 for maintaining sulphuric acid catalysts at constant strength at 140–160° C [16, 1931–2]

Formation of Volatile Phosphorus Compounds. A further consideration with regard to the use of phosphoric acid as a polymerization catalyst is the possibility of the formation of volatile compounds by interaction of the phosphoric acid with the olefines being treated This undoubtedly occurs with some phosphoric acid catalysts—particularly with catalysts consisting of phosphoric acid impregnated active carbons—and has also been observed by Sanders and Dodge [96, 1934] in the dehydration of ethyl alcohol to ethylene using phosphoric acid as catalyst at 300° C In this connexion the mechanism of polymerization suggested by Ipatieff [45, 1935] has a direct bearing Ipatieff [45, 1935] postulates the formation of intermediate alkyl phosphates which break down again as soon as formed

For example, in the case of propylene, *iso*propyl phosphate is supposed to be formed, thus



which decomposes as follows



Di-*iso*propyl Orthophosphoric acid

Ipatieff has demonstrated that when propylene is heated with phosphoric acid a homogeneous liquid is formed which contains esters such as the above, and that the liquid, on subsequent heating, liberates hydrocarbon polymers It is believed that some such intermediates must be formed When a phosphoric acid-active carbon catalyst is employed for the polymerization of olefines in the presence of small amounts of added steam, to prevent dehydration, the condensed water contains a little free phosphoric acid and a considerable quantity of combined phosphoric acid

Alkyl phosphates are volatile compounds as shown by the following figures

Dimethyl ethyl phosphate	b p	203 3° C	at 760 mm
Methyl diethyl phosphate	,	208 2° C	,,
Triethyl phosphate	,,	215–216° C	,,
Tripropyl phosphate	,	138° C	at 47 mm
Tri-*iso*propyl phosphate	,	218–220° C	at 763 mm
Tri *iso*butyl phosphate		135–136° C	at 8–10 mm

Experience indicates that loss of phosphoric acid from catalysts—presumably due to the formation of volatile phosphorus compounds—is more pronounced in the case of catalysts comprising phosphoric acid on inert carriers such as active carbon or coke than with other catalysts Furthermore, loss of phosphoric acid occurs only when the concentration of phosphoric acid on the inactive support is more than 20% [18, 1936] The loss of phosphoric acid from catalysts comprising acid cadmium phosphate, kieselguhr, and phosphoric acid, &c, is slight

The Composition of Phosphoric Acid Polymerization Catalysts. Of the various materials commonly used in catalyst masses only carbons and cokes have been found unreactive with phosphoric acids at temperatures up to 300° C, although even in the case of these substances there is the remote possibility of reduction of the phosphoric acid to phosphine, especially if the carbon or coke contains any oxides, such as ferric oxide

When any other materials, such as oxides, aluminates, silicates, carbonates, &c, are mixed with phosphoric acid and heated to give a hard mass, chemical reactions occur to give phosphates This even takes place in the case of silica, and in this case compounds of the type $(SiO_2)x(P_2O_5)y$

are formed—these are probably silicyl phosphates and are very stable towards heat

The literature evidence for the formation of stable compounds between siliceous materials and phosphoric acid is as follows

1 Phosphoric acid has practically no effect on glass at ordinary temperatures, but at 100–150° C the attack is marked and silicyl phosphate and metaphosphates are produced [36, 1908] At 400° C phosphoric acid has a strong corrosive action on quartz glass [71, 1905]

2 When a dried mixture of gelatinous silica and metaphosphoric acid is fused and extracted with hot water, transparent crystals are obtained, the composition of which corresponds to SiO_2–P_2O_5, which has been considered to be silicyl metaphosphate—$SiO(PO_3)_2$ [30, 1883–4, 1887]

3 Silica dissolves in orthophosphoric acid, and forms crystals of the composition SiO_2–P_2O_5

Silicates and aluminates react with phosphoric acid as mixtures of the corresponding oxides and give mixed phosphates, examples of such silicates are pumice and floridin

The work described in the literature leads to the conclusion that the catalytic activity of all phosphate catalysts is greatly affected by the presence of free phosphoric acid—probably in the ortho condition Therefore, unless the acid is present in a quantity more than sufficient completely to combine with the support under the reaction conditions of temperature and water-vapour pressure, an inactive, or only weakly active, catalyst is obtained

On the other hand, the catalyst activity is to a large extent dependent upon the composition of the phosphates present, some being practically ineffective and others very efficient [18, 1936]

There is, of course, a very definite upper limit to the amount of phosphoric acid which can be incorporated in a catalyst suitable for commercial use. As the amount of acid is increased the hardness of the catalyst diminishes, and a definite limit to the acid content is imposed for this reason In the case of some catalysts, however, total acid contents as high as 75–80% can be tolerated

The preparation and properties of phosphate catalysts of many types have been described in detail by Dunstan and Howes [18, 1936] These include a wide range of metal phosphates containing various amounts of free phosphoric acid

As already mentioned, the patents of Universal Oil Products Company pay particular attention to catalysts comprising mixtures of phosphoric acid with the alkaline earth oxides and chlorides, and also with siliceous materials such as kieselguhr

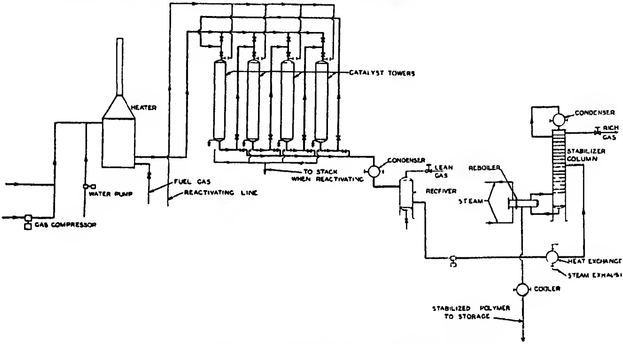


FIG 12 Universal Oil Products Company catalytic polymerization process

Typical compositions are as follows

(i) 73 7% wt of 89% phosphoric acid
6 3% „ zinc oxide
10 4% „ zinc chloride
7 6% „ aluminium hydrate
Calcined at 180–200° C.

(ii) 72% wt of 100% phosphoric acid
6% „ magnesium chloride
2% „ alumina
5% „ magnesia
5% „ starch
10% „ kieselguhr
Calcined at 250° C

(iii) 82% wt of 89% phosphoric acid
18% „ kieselguhr
Calcined at 250° C

Regeneration of Phosphate Catalysts. In use all phosphoric acid or phosphate catalysts become clogged with volatile high-boiling polymers, which, if allowed to stay on the catalyst, cause the latter to become disintegrated and very soft In addition to this volatile material, there is also formed on the catalyst a fairly large amount of practically non-volatile asphalt-like material which causes the catalyst volume to increase and also causes caking This latter material is not so deleterious in its effect as the former, but at least partial removal is necessary after the catalysts have been in use for prolonged periods A small amount of asphaltic material on the catalyst is beneficial in giving the catalyst greater activity and a higher degree of mechanical strength

The first step in any regeneration is the removal of the volatile high-boiling polymers which tend to disintegrate the catalyst, and this is readily accomplished by flushing with a stream of nitrogen or flue gas at 300° C for 4–12 hours When asphaltic material has accumulated, this can only be removed by treatment with flue gas containing small amounts of oxygen—at temperatures up to 350° C In this manner the asphaltic material is removed by oxidation or partial combustion Care is necessary in this step to prevent the development of local hot spots in the catalyst—otherwise acid is lost by volatization

With regard to the frequency of such regeneration treatments Egloff and Nelson [20, 1936] have stated that, when approximately 20 gallons of polymer gasoline per pound of catalyst has been produced, treatment with controlled amounts of air is applied to restore activity

Plant employed. One of the attractions of the phosphoric acid catalytic polymerization process is the mild conditions of temperature and pressure employed, and consequently the cheap and simple plant required The temperatures employed vary from 150 to 300° C (302–572° F), and the pressures are normally those at which the gaseous or liquid feed stocks are available—generally 120 to 300 lb per sq in

A flow diagram of a typical installation by Universal Oil Products Company is reproduced in Fig 12 The feed is preheated in a conventional furnace to a temperature of 204° C (400° F), mixed with the requisite amount of water or steam to prevent catalyst dehydration, and passed through a series of four catalyst towers, each 3 ft 6 in diameter × 25 ft high, and containing the catalyst Owing to the exothermic nature of the polymerization reaction, a temperature rise of *c* 70° C (158° F) occurs in the catalyst towers The residue gas from the reactors, together with the polymer formed, passes through a condenser to a receiver where lean gas is separated and the polymer condensate is pumped to a conventional stabilizer, where the vapour pressure may be controlled to suit market requirements

The pipe-work interconnecting the towers is arranged in such a way that any one may be taken off stream for regeneration treatment and the towers may be used in any order of sequence The reactivating line shown in the flow diagram is for flushing the catalyst with flue gas and also for treating with controlled quantities of air for burning off asphalt and carbon

With reference to design figures, it is possible to obtain at least 90% conversion of olefines to total polymers in continuous operation with an active catalyst at an inlet gas rate of 2–5 cu ft per lb of catalyst per hour, measured at N T P

An average figure for the 200° C E P spirit content of the crude polymers is 85–90% by volume Steam injection should be in amount equivalent to 2–10% by volume of the inlet gas (measured at N T P)

The Polymerization of Individual Olefines with Phosphoric Acid Catalysts Data are available in the literature on the polymerization of all the lower olefines in the presence of liquid phosphoric acid or solid phosphoric acid catalysts. Of these isobutylene is the most reactive and ethylene the least

Ethylene This has been polymerized under pressure in autoclave experiments in the presence of liquid phosphoric acid at 250–330° C, [54, 1935], and also with acid cadmium phosphate catalysts at 300–350° C [18, 1936]. Continuous plant tests have also been made using 'solid phosphoric acid' catalysts at 520 lb pressure and 296–324° C [46, 1936] In the presence of liquid phosphoric acid at 250–330° C ethylene gives a product consisting of a mixture of paraffin, olefine, naphthene, and aromatic hydrocarbons The concentration of paraffins is greatest in the lowest boiling fractions, but aromatics only appear in fractions boiling above 225° C Olefines are present in practically all fractions (*c* 20–30% by volume) and naphthenes in those boiling above 110° C The products obtained contained 60–5% by weight of spirit boiling up to 225° C

An important product of the reaction was isobutane, the formation of which increased with rise in temperature At 250° C 2 5% by weight of the ethylene reacting was converted into isobutane, and at 330° C 18 8% The difference between the polymerization of ethylene in the presence and absence [54, 1935] of phosphoric acid consists in the presence of aromatic and paraffin hydrocarbons in the former, whereas no traces of aromatics, and only small quantities of paraffins, were discovered in the latter The first step in the process in contact with phosphoric acid appears to be the formation of ethyl phosphates, which, being unstable at elevated temperatures, decompose to give ethylene polymers and naphthenes (cf polymerization in the presence of aluminium chloride) The naphthenes become dehydrogenated to aromatics, and paraffins are formed by the hydrogenation of olefines, i e intermolecular hydrogenation and dehydrogenation reactions take place

The results of continuous plant tests on the polymerization of ethylene at 520 lb pressure and 296–324° C in the presence of a phosphate catalyst are detailed in Table XIII The high gasoline octane number of 82 is noteworthy

TABLE XIII

Polymerization of Ethylene at 520 lb per sq in Gauge Pressure [46, 1936]

	A	*B*	*C*
Operating conditions			
Temp , ° C	296 (565° F)	324 (615° F)	324 (615° F)
Contact time, sec	790	420	320
Inlet gas rate, cu ft per hr per lb catalyst	1 5	2 5	3 4
Ethylene polymerization to liquid polymer, %	73	72	65
Polymer per 1,000 cu ft ethylene			
U S gal	8 0	7 9	7 1
Imp gal	6 67	6 6	5 92
400° F E P gasoline per 1,000 cu ft ethylene			
U S gal	4 7	4 7	4 6
Imp gal	3 92	3 92	3 8
Properties of crude polymer			
Gravity, °API at 60° F	48 8	48 7	48 8
Sp gr at 60° F	0 7848	0 7852	0 7848
I B P , ° C	37	42	44
5% distillate at (° C)	48	56	61
10% " "	57	63	70
20% " "	74	81	87
30% " "	98	100	104
40% " "	133	131	127
50% " "	178	169	157
60% " "	209	204	184
70% " "	239	234	211
80% " "	267	262	241
90% " "	314	303	279
95% " "	337	333	311
F B P , ° C	340	335	329
Reid vapour pressure at 100° F (37 8° C)	8 8	8 3	8 1

Properties of Steam Distilled Polymer

Gravity, °API at 60° F	67 4
Sp gr at 60° F	0 711
Colour (Saybolt)	30+
Gum content, copper dish	10 mg per 100 ml
Gum content+0 025% wood distillate inhibitor	2 „ „
Octane number (C F R Motor)	82
Blending octane number (25% in Reference Fuel A3 of 44 octane number)	96
Reid vapour pressure	6 5 lb at 100° F (37 8° C)
I B P	41° C
5% distillate at	52° C
10% „ „	58° C
20% „ „	66° C
30% „ „	74° C
40% „ „	82° C
50% „ „	93° C
60% „ „	106° C
70% „ „	121° C
80% „ „	142° C
90% „ „	163 C
95% „ „	183° C
F B P	203° C

Bottoms from Steam Distillation

Sp gr at 60° F	0 897
I B P	192° C
F B P	369° C

Propylene Propylene has been polymerized in contact with liquid phosphoric acid at 204° C and S I atm gauge pressure [44, 1935], and also at 330–370° C and 100–40 atm pressure [55, 1936] At the lower temperature propylene polymerizes to a liquid consisting almost entirely of mono-olefines, presumably of iso structure The liquid boils from 40 to 230° C and is almost entirely gasoline The evidence for the chemical nature is fourfold The polymer is practically entirely soluble in 96% sulphuric acid at 0° C , the bromine numbers of fractions agree with those calculated for mono-olefines, the carbon-hydrogen ratios agree with the formula C_nH_{2n}, and non-destructive hydrogenation yields a product containing only paraffins

At the higher temperatures (330–370° C) secondary reactions take place, resulting in a liquid product containing only 85% of unsaturated hydrocarbons Paraffins are present in the lower boiling fractions (that boiling at 25–63° C containing 80% paraffins), but the amount decreases with rise in boiling-point Cyclo-paraffins occur in fractions boiling at 155° C and above, while aromatics are found only in the very highest fractions The degree of unsaturation of the products obtained from the catalytic polymerization of propylene is much greater than in the case of thermal polymerization

Butylenes Of the three butenes, isobutylene polymerizes the most readily and butene-1 the least, in the presence of liquid phosphoric acid At 130° C the products obtained consist almost entirely of mono-olefines, but the mixture is very complex By reducing the polymerizing temperature the complexity of the product is reduced, and at 30° C isobutylene gives a product containing only di-isobutylene and tri-isobutylene It has been observed that butene-1 and butene-2 are polymerized much more readily in the presence of isobutylene than in its absence Similarly, the butylenes exert a promoting effect in the polymerization of propylene The butylenes undergo isomerization in the presence of phosphoric acid [56, 1934]

Results obtained on Cracked Gases Much information has been published by members of the staff of Universal Oil Products Company concerning the polymerization of cracked gases and their fractions using catalysts of the type described above The data summarized in Table XIV is typical of the results obtained on lean residue gas, stabilizer overhead, and stabilizer reflux The yields of polymers mentioned in Table XIV should be compared with the theoretical figures given in Fig 2

Properties of Products

It has previously been stated [18, 1936] that all phosphoric acid or phosphate catalysts, operating under the same conditions, give essentially the same product, the gasoline fractions are also of the same octane number (i e 78–82 C F R Motor Method) True boiling-point distillation curves of the products obtained from feed stocks containing both propylene and butylene show no decided flats corresponding to pure compounds, but, on the other hand, catalytic polymers obtained by the treatment of

TABLE XIV

Catalytic Polymerization of Cracked Gases

	Residue gas from liquid-phase cracking			*Stabilizer reflux from liquid-phase cracking*			*Stabilizer overhead gas from vapour-phase cracking*			*Stabilizer reflux from vapour-phase cracking*		
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
Properties of gas treated												
Propylenes and butylenes %	17 3	18 6	16 8	37 5	37 5	37 5	43 9	42 6	42 7	70 4	69 2	69 4
Ethylene, %	6 6	7 2	7 0	nil	nil	nil	20 2	21 6	21 2			
Operating conditions												
Pressure, lb per sq in gauge	200	200	200	100	100	100	100	100	100	200	200	200
Temp , ° C	204	232	232	204	204	204	232	232	232	204	204	204
Inlet gas rate, cu ft per hr per lb catalyst	2 1	1 3	0 5	4 9	3 4	2 1	1 7	0 9	0 3	3 7	2 4	0 8
Olefine polymerization												
Propylene and Butylene, %	64	79	95	72	81	89	84	94	96	70 4	69 2	69·4
Ethylene, %	13	16	31				9	25	32			
Polymer yield												
Crude polymer, U S gal per 1,000 cu ft	2 9	3 8	4·0	6 0	6 9	7 2	7 6	8 5	8 4	12 4	14 2	15 0
„ „ imp „ „	2 4	3 16	3 3	5 0	5 7	6 0	6 3	7 1	7 0	10 3	11 8	12 3
Gasoline (c 200° C E P)												
U S gal. per 1,000 cu ft	2 7	3 5	3 7	5 4	6 2	6 5	6 3	7 1	7 0	9 7	11 1	12 0
Imp. gal per 1,000 cu ft	2 25	3 9	3 1	4 5	5 2	5·4	5 25	5 9	5 8	8 1	9 2	10·0

cracked C_4 fractions under mild conditions consist mainly of dibutenes and tributenes

The anti-knock blending value of catalytic polymer spirit is of particular importance In Figs 13–15 are plotted the C F R Motor Method octane members of this material and other synthetic gasolines in three different base spirits [18, 1936] The blending value of any polymer spirit expressed in terms of 'blending octane numbers' (see note on p 2075) is naturally greatest in base spirits of low octane ratings, and Fig 16 shows how the blending octane numbers of catalytic polymer spirit range from 125 to 82 according to the nature of the base spirit and the concentration of polymer spirit used The octane numbers of fractions of catalytic polymer spirits show little variation with boiling-point, as shown in the following figures referring to material produced from reflux liquid using granular acid cadmium phosphate catalyst

Fraction b p (° C)	*C F R Motor Method octane numbers*		
	Neat	*30% in 52·5 octane no base spirit*	*70% in 52·5 octane no base spirit*
25–50		70·4	89·6
50–75	83·2	69·8	78·7
75–100	81·9	71·2	79·3
100–125	81·9	72·2	78·9
125–150	80·8	72·2	78·5
150–175	82·3	70·5	79·0
175–200	80·6	69·6	78·4
200–225	80·2	68·2	78·5

The octane number of the spirit produced from a cracked C_4 fraction is 78–82, and does not change from this value if the isobutene content of the feed (25% by volume) is removed prior to catalytic polymerization

Details of the properties of typical polymer products are given in Table XV

Selective Catalytic Polymerization.

A recent development is the catalytic polymerization, using phosphate catalysts of the types referred to above, of C_4 fractions containing considerable amounts of isobutylene, whereby di-isobutylene and tri-isobutylene are produced These when hydrogenated under non-destructive (i e reducing) conditions give iso-octanes and isododecanes of *c* 95–100 octane number, which are valuable constituents of aviation fuels, being saturated in chemical nature and gum free

It is not feasible to fractionate di-isobutylene from catalytic polymers produced from feeds containing ethylene and propylene in addition to isobutylene, because in this case the yield of di-isobutylene is low and its recovery uneconomic The reason for this is that the isobutylene condenses with the lower olefines to give products that are not di-isobutylene and which do not give 100 octane number products on hydrogenation

The Refining of Catalytic Polymer Gasoline.

Polymer gasolines produced from desulphurized cracked gases using phosphate catalysts are normally suitable for the American market after re-running to the desired end-point and the addition of the requisite amount of gum inhibitor To mask the slightly yellow colour dyes are often added as well.

TABLE XV

Properties of Typical Catalytic Polymers (Phosphate Catalysts)

Feed	*Stabilizer reflux* [18]	*Cracked C_4 fraction* [18]	*Residue gas* [47]	*Stabilizer reflux* [47]
Crude product				
Sp gr 60° F	0·750	0·750	0·734	0·750
Reid vapour pressure at 100° F			8·5	9·5
% distillate to 200° C (392° F)	82	83	*c* 90	*c* 80
Gasoline fraction				
Sp gr at 60° F	0·750	0·740	0·732	0·738
I B P , ° C	44	27·5	57	61
10% distillate at (° C)	84	81·5	90	90
20%	96	111	100	102
30%	102	120	107	112
40%	115	125	114	122
50%	125	130	120	130
60%	136	144	127	140
70%	154	172	138	151
80% ,,	168	185	151	162
90%	181	192·5	169	182
F B P ° C	198	197	205	212
Loss %	2	4		
Aniline point ° C	38	41		
Colour Saybolt			30	25
Octane no (C F R Motor)	80–82	82	82	82
Gum content (copper dish) mg 100 c c			5·0	72
Gum content + 0·025% wood distillate inhibitor				0·02
Residue fraction				
Sp gr , 60° F	0·858	0·872		
I B P ° C	215	222		
10% distillate at (° C)	229	235		
20%	234	240·5		
30%	239	245·5		
40% ,,	243	250		
50	251	255		
60%	260	262		
70%	277	270		
80%	305	286		
90%		314		
F B P ° C	348	320		
% distillate at 300° C	78	86		
Aniline point ° C	47	53·8		

Conclusions arrived at as a result of refining tests may be summarized as follows

1 200° C E P distillates from the crude polymer are practically water white, but very unstable to normal gum tests A finished spirit of specification gum content and gum stability has not been produced by the normal acid treatment applied to the total polymer The potential gum content of the polymer spirit increases rapidly with boiling-point

2 200° C E P distillate from crude polymer spirit may be stabilized against gum formation to an extent satisfactory for normal conditions by the addition of inhibitors

3 Blends of crude polymer with normal cracked spirit can be refined to give a finished product of good colour and gum stability by conventional acid treatment followed by redistillation and final neutralization The amount of acid required is very small

Alternatively, the crude polymer may be fed to the cracking plant primary tower as reflux—in which case the polymer bottoms pass to cracking stock and the polymer spirit is blended with cracked distillate for refining The polymer bottoms crack readily to give a spirit of 80 octane

Catalytic polymer bottoms (i e the fraction boiling above 200° C) is at the moment of little use as a Diesel fuel, the cetene number being only about 35, and is obviously better employed as a depolymerization stock

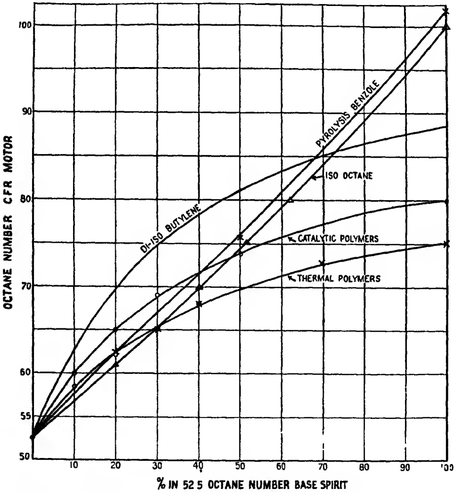


Fig 13 Octane numbers of blends of synthetic fuels in 52 5 octane number base spirit (C F R motor method)

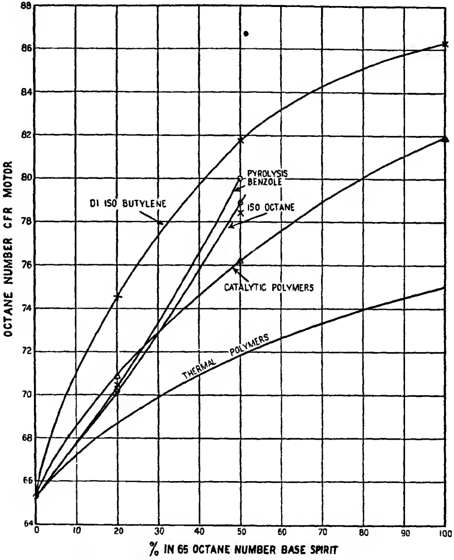


Fig 14 Octane numbers of blends of synthetic fuels in 65 octane number base spirit (C F R motor method)

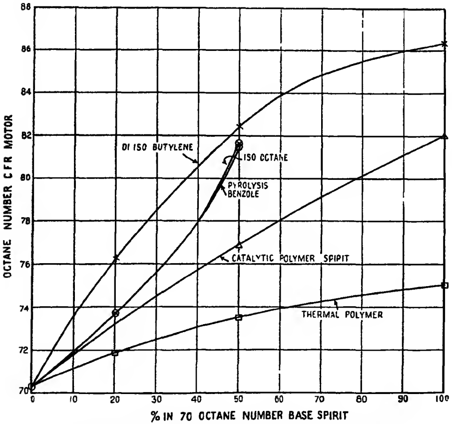


Fig 15 Octane numbers Blends of synthetic fuels in 70 octane number base spirit (C F R motor method)

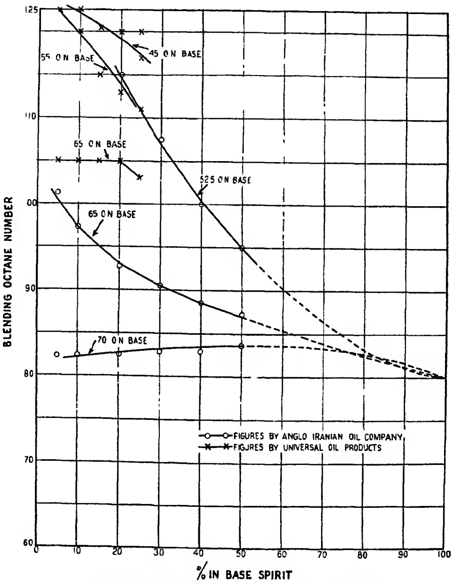


Fig 16 Blending octane numbers of catalytic polymers in various base spirits

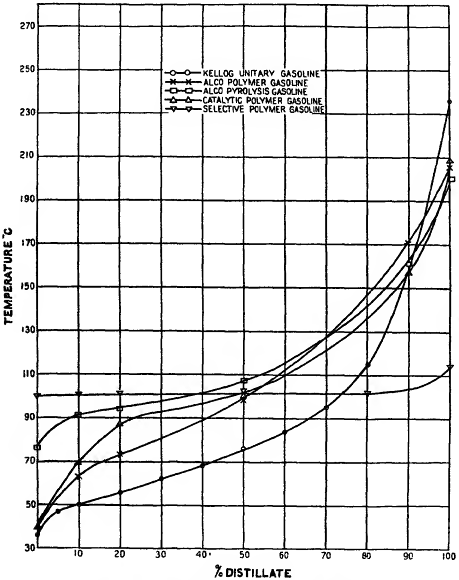


FIG 17 Pyrolysis and polymerization gasolines A S T M distillation curves

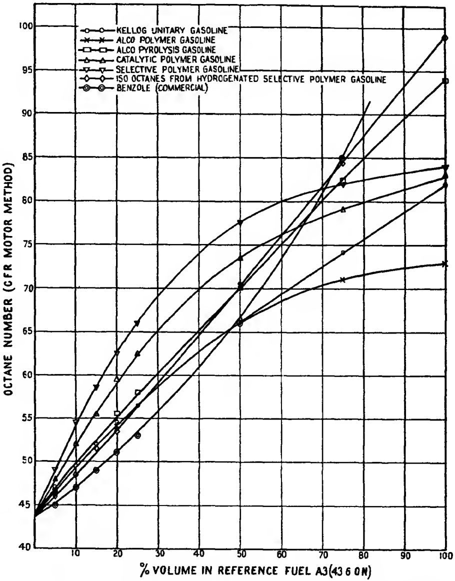


FIG 18 Octane numbers of blends of polymer spirits in A 3 reference fuel (C F R motor method)

Sulphuric Acid as a Polymerization Catalyst

A recent development of considerable importance is the polymerization of isobutylene to di-isobutylene in the presence of sulphuric acid and the hydrogenation of the polymer to iso-octane This is dealt with fully in another article

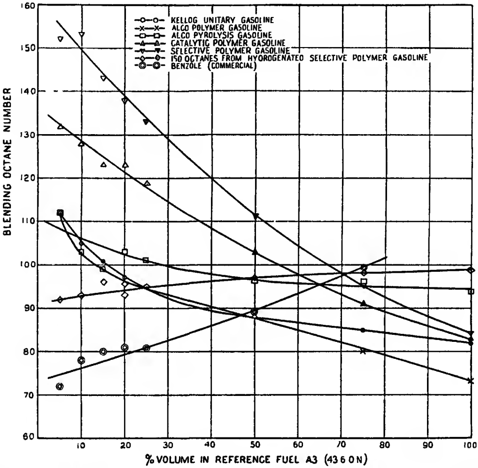


FIG 19 Blending octane numbers of polymers in A 3 reference fuel (octane number = 43 6, C F R motor method)

A Comparison of the Processes now available for the Production of Synthetic Gasolines from the Gaseous Hydrocarbons

The processes described above for the production of synthetic gasolines from waste petroleum gases vary in their applicability and in the nature of the products they give For the treatment of paraffinic gases containing no olefines there are four alternatives

1 Pyrolysis to aromatic—e g The Alco Pyrolysis Process
2 Pyrolysis to olefines—followed by polymerization—these steps being carried out separately—e g The Alco Multiple Coil Process
3 Simultaneous pyrolysis—polymerization—e g The Kellogg Unitary Process
4 Dehydrogenation to olefines—followed by polymerization

Of these the only one not yet fully developed is No 4, in which the dehydrogenation process is still in the experimental stage

For the treatment of the olefine constituents of cracked gases the following processes are available —

1 Pyrolysis to aromatics—e g Alco Pyrolysis Process,
2 Thermal polymerization—e g Alco and Kellogg Processes,
3 Catalytic polymerization—e g U O P Process,

while the paraffin constituents of cracked gases may be handled by the processes listed above

The gases amenable to treatment by these operations include ethylene and the higher gaseous olefines, and the paraffins propane and butane No satisfactory methods for the treatment of methane and ethane are yet available, although active development work is in progress

The greatest yields obtainable from a cracked or straight-run gas are realized by suitable combinations of dehydrogenation and catalytic polymerization processes

The products obtained by the various processes are compared, with respect to distillation range and anti-knock values, in Figs 17–19 [19, 1936]

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NOTE

The 'Blending octane number' of a spirit is calculated as follows

Octane number of blend = Octane number of base × Concentration + Blending octane number of added spirit × Concentration e g if a 50/50 blend of base spirit and a polymer spirit has an octane number of 74 and the base spirit alone has an octane number of 52 5, then the 'Blending octane number' of the polymer spirit at this concentration is given by

$$74 = 52\ 5 \times 0\ 5 + \text{Blending octane number} \times 0\ 5$$

$$\text{Blending octane number} = \frac{74 - 26\ 25}{0\ 5} = 95\ 5$$

SECTION 31

CRACKING

A BRIEF HISTORY OF PETROLEUM CRACKING

By **BENJAMIN T BROOKS, Ph D**, *Consulting Chemical Engineer*

CRACKING processes are those processes employed to convert petroleum oils of high molecular weight and high boiling-point range to products of smaller molecular weight and lower boiling-point range Some polymerization or condensation to higher boiling oils or tars invariably occurs in cracking processes, but the term 'cracking' is almost universally employed as descriptive of processes for the decomposition of hydrocarbon oils

The origin of the term 'cracking' is almost as old as the industry itself In 1869 S F Peckham [38, 1916] in an article entitled 'On the Distillation of Dense Hydrocarbons at High Temperatures, technically termed Cracking' stated that 'dense petroleums which yield practically no illuminating oil by ordinary treatment, by distillation under pressure are subjected to what is technically termed "cracking" and made to yield from 28 to 60% of oil fit for burning ' Peckham employed pressures of 30 to 40 lb per sq in

The cracking of petroleum oils has been carried out for the manufacture of gaseous products, e g in the manufacture of Pintsch gas and oil gas as produced in California, since about 1904, to a limited extent to increase the yield of kerosine and since 1913 to produce gasoline from oils boiling above gasoline range The present discussion makes no attempt to evaluate the much-debated questions of patent priority, nor to analyse the differences between processes known under various names, which have been argued at great length in many cases before the courts Rather, the present review aims to present mainly those relatively outstanding developments which have been carried out on a large scale irrespective of nice questions of patent law, the abandoned or very imperfect designs of many patentees, and debatable fine distinctions of language which have thrown a fog of verbiage about this subject in the last 20 years

It is perhaps misleading that cracking processes installed by many companies bore names implying some distinctive principle or novel features, which in many instances was not the case However, to distinguish fairly between all of them would be to assume the functions of a court Any one who has read the testimony of the cracking patent infringement suits in the United States courts will appreciate this difficulty In this discussion the names associated with important commercial installations will be used Some questions of priority and invention have been settled by the courts, and will be briefly noted, but many others remain unsettled

The need for optional flexibility of yields of gasoline could not be said to have been urgent prior to about 1911 Up to that time there had generally been a surplus of gasoline, and as late as 1913 much gasoline was still marketed in the United States under the name 'stove gasoline' It is possible that many of the processes described in the patent literature prior to 1911 could have been developed into practical operating processes had the need existed

The first cracking process to be successfully operated on a large industrial scale primarily for the object of increasing the gasoline yield was the pressure distillation process developed by William M Burton and his associates at the plant of the Standard Oil Company of Indiana at Whiting, Indiana, in 1912 and installed on a large scale in 1913 Prior to this time much experimental small-scale work had been carried out and many patents had been issued which became important only in the light of the experience with cracking processes acquired subsequent to 1913

The Period prior to 1913

The earlier work on cracking prior to 1913 has been well reviewed by Lomax, Dunstan, and Thole [38, 1916] In the early days of organic chemistry, 1860 to 1890 the decomposition of all sorts of organic substances by passing them through hot tubes was a common procedure Such work was generally only of a very rough qualitative character Petroleums and various hydrocarbons were subjected to the common method Such work may be considered to be suggestive of vapour-phase or atmospheric pressure cracking Of this early work that of Berthelot [8, 1866–7] on the formation of benzenoid hydrocarbons stands out and is of interest to-day in view of the new industrial interest in this field of work

One of the early cracking processes which appears actually to have been carried out on a small industrial scale was that of distilling heavy oils under pressure of about two atmospheres' in a steel boiler capable of withstanding pressures up to 7 atm This process, patented by James Young in 1865, was later described by him [56, 1867] as having been practised for the production of illuminating oils The well-known experimental work of Thorp and Young [51, 1871–3] on the decomposition of paraffin wax by distilling under pressure was carried out in order to gain further information regarding Young's process Young noted that the bottom of the still had to be frequently cleaned, an operation later to be carried out in the Burton shell stills after each run

Some years later, in 1886, the distillation of heavy petroleum oils under pressures of 3 to 6 atm was carried out in the Riebecksche Montanwerke [45, 1885] The Riebeck plant was located at Halle, Germany Brown coal tars and petroleum were distilled under pressures up to 6 atm [46, 1887], according to the Krey patent [35, 1885] The distillation was carried out in a cast steel retort or still with a valve interposed between the still and the condenser Engler [16, 1888] described the Krey operation as carried out at the Riebeck plant and stated that by varying the pressure light oils of the character desired could be produced ('durch Variation des Druckes es vollig in der Hand hat, leichte Oele von beliebiger Beschaffenheit herzustellen') It is of interest to note that a heavy residual oil from Oelheim yielded 75% by weight of a distillate containing 48% by volume of material distilling below 200° C, or within the distillation range of present-day motor fuel

The size of the pressure still employed at the Riebeck plant is indicated by tests described by Grotowsky [22, 1888] showing that batches of about 480 kg or about 130 gal were distilled Krey states that 2½ distillations were carried out in 24 hr [36, 1887]

The well-known publications of Engler [17, 1897] on cracking, and his analytical investigations of the products formed were of academic interest and perhaps were of indirect value years later as having shown the character of the hydrocarbon mixture distilling below 200° C or within the gasoline distilling range Since Engler examined products made by the Krey method in 1897 it is evident that the Krey method was operated for some 12 years or more, even though on a scale which to-day seems very small indeed

In the meantime a number of researches were published and several processes patented for the conversion of petroleum oils to benzenoid hydrocarbons by cracking at relatively high temperatures In 1885 Redwood [44, 1885] described the attempts then being made at Baku in the refinery of the Nobel Brothers, to produce benzene hydrocarbons, and stated that the work could only be regarded as experimental None of the numerous processes proposed for the conversion of petroleum oils to benzene and related hydrocarbons was industrially successful up to the period of the World War, although benzene and other benzenoid hydrocarbons were recovered in relatively small quantities as by-products of the manufacture of oil gas by cracking at high temperatures It will be remembered that benzene was *discovered* by Faraday in 1825 and first described in his paper 'On New Compounds of Carbon and Hydrogen, and on certain other products obtained during the decomposition of oil by heat' Fish and vegetable oils were used In 1884 Armstrong published his well-known paper on the 'Manufacture of Gas from Oil' [3, 1884], followed later by a study, by Armstrong and Miller, of the liquid products formed [4, 1886] The Pintsch oil-gas process was patented in 1873, but the operation was later modified in most plants to produce Blau gas Blau gas was made by cracking oil in Pintsch retorts at lower temperatures, i e 600–700° C, instead of 800–900° C Cracking under these conditions gave a smaller yield of a richer gas, and after condensing most of the benzene and higher boiling oils the gas was compressed to obtain a liquid mixture which was gasified on releasing the pressure This was manufactured widely in Europe and America, principally for lighting railway coaches, for many years The easily liquefiable products, as shown by Armstrong and Miller, included benzene, toluene, xylenes, mesitylene, naphthalene, &c, also amylenes, hexylenes, and the like The conversion of petroleum hydrocarbons to aromatics by high-temperature cracking continued to be carried out incidental to gas manufacture until the war time demand for benzene and toluene stimulated efforts to increase the yield of benzene and toluene The development of gas-polymerization processes in recent years (1932–6) has aroused new interest in the production of aromatics from refinery cracking still gases and from propane and butane There are at present indications that the demands of the chemical industry for aromatic hydrocarbons, particularly toluene and naphthalene, may outstrip the ability of the by-product coke industry to supply them Their manufacture from petroleum gases promises to relieve the situation

During the period immediately following the issue of the Young patent numerous patents were issued which are of considerable interest in the light of to-day's knowledge and experience with cracking, but which were apparently never carried out on a scale sufficiently large to have made any impression on refinery practice or to have left any tangible record of their actual operation To this class belongs the well-known patent of Benton [7, 1887] who proposed heating oil in a coil to 371–537° C under a pressure of 500 lb per sq in The coil was connected to an evaporating or flashing chamber and thence to a condenser The process of Dewar and Redwood, like that of Krey, was evidently designed for very small-scale operation [14, 1889–90] One of the most interesting of the patents of this period was that issued to Carl Pielsticker [43, 1890–2] Although the Pielsticker patent is generally regarded as a paper patent it is nevertheless of interest His process provided for continuous operation, oil being pumped through a heating coil where it was heated under pressure The heating coil discharged into a chamber provided with a draw-off for heavy residuum and an upper outlet to a condenser 'When it is intended to produce lighter gravity oils, a valve is placed between the outlet of the retort and the condenser which may be left open only so far as to create a certain pressure of gases inside the retort' (chamber) He also appreciated that 'by passing the oil through the coil with great velocity the deposition of the carbon or heavy matter which would soon choke up the coil was prevented' The length of his pipe coil was 200 ft of pipe having diameters of 1 to 2 in Special provision was made for closing the return bends of the coil so that the tubes could be cleaned Pielsticker was 20 years ahead of the need of cracking So far as American practice is concerned the earliest type of pipe stills to be used in large-scale work were the Trumble units installed in the Shell Company plant in California about 1910

In 1904 Ipatieff [30, 1904] published experimental results which are of great interest in the light of later developments His work showed that in cracking petroleum under pressures within the range 120 to 340 atm, the evolved gases become continually poorer in hydrogen, in spite of the higher temperatures involved at the higher pressures A little later Ipatieff [31, 1911] showed that ethylene was readily polymerized when heated to 400–50° C under pressure in contact with finely divided iron or copper Much experimental work has been done on the influence of metals and other catalysts on the decomposition of hydrocarbons which, however, has had little or no industrial result and need not be reviewed [42, 1910, 53, 1911]

The effect of anhydrous aluminium chloride in cracking or splitting hydrocarbons was noted as early as 1877, when Abel [1, 1877] patented treating petroleum hydrocarbons with this reagent at temperatures above 100° C The polymerizing action of aluminium chloride on olefines was noted by Heusler [25, 1896], Engler [18, 1910], and others Practical refinements of this process came later (see below)

While the earlier cracking processes had for their object increasing the yield of illuminating oil, the need for greater yields of motor fuel was foreseen at least as early as 1908 In that year Noad and Townsend [41, 1908] started a development which was followed up for several years by the New Oil Refining Process Although finally abandoned the work done is of interest Solar oil distillate was cracked at 1,000–1,200° F [538–649° C] by passing it with steam through heated horizontal tubes 12 ft long and 9 in diameter loosely packed with iron turnings The cracked distillate was refined by treating with sulphuric acid and alkali and steam distilled, a practice widely followed later

Many other patents were issued during this period which are mainly of interest to the legal profession

The Period 1913–36

The Burton Process.

On 1 March 1913 the Standard Oil Company of Indiana announced a new 'motor spirit' It was to cost the consumer 3 cents a gallon less than straight-run gasoline

A laboratory inspection report stated that the 'new motor spirit resembled gasoline in distillation range, was yellow in color and had a pungent odor' It was expected that the product might find a use in stationary engines and motor trucks Some experienced refiners doubted if such a product could be marketed The original Burton patent was filed on 3 July 1912 and construction of the first unit was started in the summer of 1912 at the Whiting, Indiana, plant of the Standard Oil Company of Indiana On 7 January 1913, the first of the Burton patents was issued, U S P 1,049,667

The first large still was 8 ft in diameter and 20 ft long, made of $\frac{1}{2}$-in mild steel plate As a result of the successful operation of this unit, 60 similar stills were built These first units were heavy riveted shell stills of 200 to 250 bbl capacity Gas oil or similar distillate was the charging stock used, the oil being heated to about 750 F and the pressure maintained originally at about 75 lb A little later the pressure regularly employed was 95 lb The distillation was slow, the stills being provided with long air-cooled vapour lines for the purpose of returning the heavier oil [28, 1914] The operating cycle was about 48 hr per batch, the yield being about 50% of 48–52° distillate After emptying, the stills were cooled sufficiently to allow workmen to enter them and scrape the carbon from the bottom The settling of coke particles on the hot bottoms was reduced by inserting false bottoms of thin movable steel plates [29, 1914] Late in 1914 E M Clark, an associate of Burton and Humphreys and later a vice-president of the Standard Oil Company of New Jersey, patented [10, 1914] the cracking of oil in a circulating system, the oil being pumped through a heating coil to a chamber from which vapours were withdrawn to a condenser and residual oil recirculated to the heating coil A little later Clark [11, 1921] patented the process of cracking oil in an apparatus resembling a water-tube boiler, the process being generally known as the 'Burton-Clark process' and the apparatus 'Burton-Clark tube stills' Circulation of the oil was obtained in this type of still by thermosiphon effect, more rapid cracking and distillation was possible on account of the large heating surface, and less coke was deposited on the heating surfaces (tubes), permitting longer runs without cleaning As described in 1925 by Howard [27, 1925] a total of 350 bbl of gas oil could be handled during an operating cycle of 53 hr in a still of 200 bbl charging capacity, fresh oil being supplied during the operation

In the meantime the greatly increased demand for gasoline during the World War caused the widespread installation of the Burton process in American refineries At the Neodesha, Kansas, refinery of the Standard Oil Company of Kansas, A S Hopkins improved upon the Humphreys air-cooled run-back line by adding fractionating columns which refluxed the heavier oils back to the stills [26, 1916]

As late as 1928, 1,200 Burton or Burton-Clark stills were still in existence, but by 1930 only 191 units were reported still in operation The largest installations were those at Bayway, New Jersey, Neodesha, Kansas, and Whiting, Indiana In 1920 more than 15,600,000 bbl of gasoline were produced by this process

On 17 May 1918 Dr Burton was awarded the Willard Gibbs Medal by the Chicago section of the American Chemical Society, and on 13 January 1922 he received the Perkin Medal from the American Section of the Society of Chemical Industry It is a tribute to the supervision of this operation and the discipline of the operators that, according to Dr Burton, 8 years elapsed, with several hundred stills in operation, before a fatal accident occurred

In the refining of cracked gasoline very high treating losses were common The belief was common at this time that unsaturated hydrocarbons were undesirable constituents of motor fuel The odour of the product even after drastic refining was different from that of straight-run gasoline and therefore considered objectionable by some This idea of the greater desirability of the saturated paraffins, in gasoline, is reflected in the Burton patent, by Burton's curious insistence that placing the valve on the cold side of the condenser was conducive to the formation of normal paraffins rather than unsaturated hydrocarbons Treatment of the crude pressure distillate with sulphuric acid followed by rerunning, usually with steam, and sweetening with alkaline plumbite was the usual procedure Cracked gasoline was sometimes blended with straight-run gasoline before treating in order to ease the action of the rather large proportions of sulphuric acid then commonly used

During the 12 years from 1913 to 1925 the Burton process and its improved forms practically monopolized the manufacture of cracked gasoline During this period, however, much experimental and semi-commercial scale development work was being carried out on processes which were later to become well known As early as 1913 Roy and Walter M Cross began experimental work in Kansas City, finally licensing their first commercial unit in 1920 The Texas Company erected the first large Holmes-Manley unit in 1917, followed in 1919 with a battery of units at Port Arthur, Texas The Dubbs process was also being developed during this period Work on vapour-phase or low-pressure cracking was also being vigorously carried out The work of the New Oil Refining Process Company has been referred to Probably the best known of the vapour-phase processes at this time were those associated with the names of William A Hall, Charles J Greenstreet, and Walter F Rittman

At the time the first Burton units were installed very little was known of the tensile strength and other properties of steels at the temperatures required for cracking, and some experienced refinery operators regarded the original Burton shell stills as too hazardous to warrant their installation Bacon and Clark [5, 1914] showed that cracking was more rapid and the yields of gasoline appeared to be higher and the gasoline formed less unsaturated by distilling heavy oils under pressures within the range 100–300 lb This patent, assigned to the Gulf Refining Company, was not followed up by plant development until several years later when pressure cracking had become widely practised The proposal of the Cross brothers at this time to employ pressures of 600 lb was all the more daring in the light of the engineering skill and metallurgical knowledge then available

The Coast process was first installed at the Cosden Refinery in Tulsa, Oklahoma, in 1917 It was very similar to the original Burton shell still process, having shell stills 8 by 40 ft One difference was that in the Coast process a pressure-control valve was interposed between the still and the condenser A number of other auxiliary features were described by Coast [12, 1918] such as a layer of molten lead on the still bottom, a mechanical device to keep coke from accumulating on the still bottom, or introducing gas or steam into the hot oil vapours, &c , but none of these features became of importance In 1924 the Standard Oil Company of Indiana brought suit against the Mid-Continent Refining Company for infringement of the Burton patents, and the suit was settled out of court by the payment of a substantial sum by the defendants

The Fleming process also resembled the early Burton process in that a body of oil was heated and distilled at moderate pressures The Fleming still was developed at the Martinez Refinery of the Shell Company of California in 1920 The still was set in an upright position, instead of being horizontal The bottom was not heated, but the side walls of the still were heated This arrangement sought to increase the heating surface somewhat and to take advantage of the lesser tendency of coke particles to deposit on an upright surface The stills were 10 by 30 ft in size The charging stock was introduced into the top of the dephlegmator The pressures employed were 110 to 120 lb and a unit was on stream 40 to 60 hr averaging about 70 bbl of gasoline from 200 bbl of charging stock The sale and manufacture of the units was taken over by the M W Kellogg Company The largest Fleming installation was that at the Marland Refining Company, now known as the Continental Oil and Refining Company, at Ponca City Oklahoma

The Jenkins process generally resembled the Burton-Clark process Whereas the latter depended upon thermosiphon action for the circulation of oil through the tubes, Jenkins [34, 1917] inserted a motor driven propeller in one leg of the still to produce more rapid circulation of the oil in the tubes A predetermined amount of residual oil was continuously withdrawn from the front cross drum and flashed in an expansion chamber, in order to minimize the accumulation of coke in the still The process was owned by the Jenkins Petroleum Process Company and the Graver Corporation acted as sales representatives and builders The pressures employed were 125 to 200 lb By 1928 about 50 units were in operation

The Isom process is the name given to the cracking process developed by E W Isom, Vice-President of the Sinclair Refining Company Development work was started comparatively early, and Isom s first patent was issued in 1918 [32, 1918] The unit consisted essentially of about 50 4-in tubes 20 ft long set vertically and connected to a horizontal insulated cylindrical shell 9 by 31 ft in size The vapours passed to a reflux tower into which the charging stock was pumped Pressure was reduced before condensation of the gasoline A unit (in 1928) processed about 1,200 bbl of gas oil per day, producing about 31 % gasoline

The Cross Process

In the earlier Cross installations a clean gas oil charging stock, normally 32-6° API gravity, was first heated to about 350° F in a heat exchanger in the dephlegmator and then heated in two sets of heating coils arranged in series to an exit temperature of about 875 to 950° F The oil then passed to a reaction chamber, a pressure of about 600 lb being maintained on the oil in the coils and reaction chamber It was believed that the pressure employed kept practically all of the material from changing phase, thus requiring less heat input to reach and sustain cracking temperatures This feature was strongly emphasized in the early years of the Cross process The high pressure maintained in the process permitted kerosine to be used or included in the charging stock However, the first commercial units were arranged only for single-pass operation, the yield being 30 to 40% gasoline, 50 to 55% re-cycle stock, 5 to 10% residuum, and about 5% gas The product was called synthetic crude The large proportion of cracking per pass necessitated distillate charging stocks

The reaction chamber, one of the conspicuous features, consisted of a heavy steel forging about 40 ft long and a little over 4 ft in diameter It was set in a horizontal position and was well insulated Most of the coke was deposited in the chamber Some time later the outlet from the chamber was changed to the bottom, so decreasing the amount of coke formed that the operating cycle of about 8 days was increased to 20 to 25 days The hot liquid and gas was, in the first type, discharged together through a pressure valve directly to a condenser

The evolution of the Cross process is well shown by the accompanying diagrams (Fig 1) published by H W Sheldon [49, 1933] The reaction chambers for the first Cross units were made in Germany in the famous Krupp gun shops, each chamber being made from a single forging, but later these chambers were manufactured by the Midvale Steel and Ordnance Company The accompanying diagrams show what may be termed the Cross *processes* of different periods All the more successful processes were greatly changed and improved as the art progressed

The Cross units were the first to be arranged to include Gray vapour-phase clay treaters Bubble-cap fractionating towers were added to the Cross units in 1924, and by the inclusion of Gray clay-treating units a year later, first at the plant of the Barnsdall Refining Company at Barnsdall, Oklahoma, the combined units were able to produce end-point gasoline which required no re-running, and no further refining other than sweetening In 1926 hot oil recirculation pumps were added, which added considerably to the fuel economy of the process Air preheaters were used on both Cross and Dubbs heating furnaces prior to 1930

The first large experimental Cross unit was operated at Rosedale, Kansas, prior to 1916 The first licensed commercial unit was installed in 1920 at the plant of the Indian Refining Company at Lawrenceville, Illinois In the following year the Pure Oil Company installed four units at Heath Ohio, and the Roxana Company erected two units at Wood River Illinois

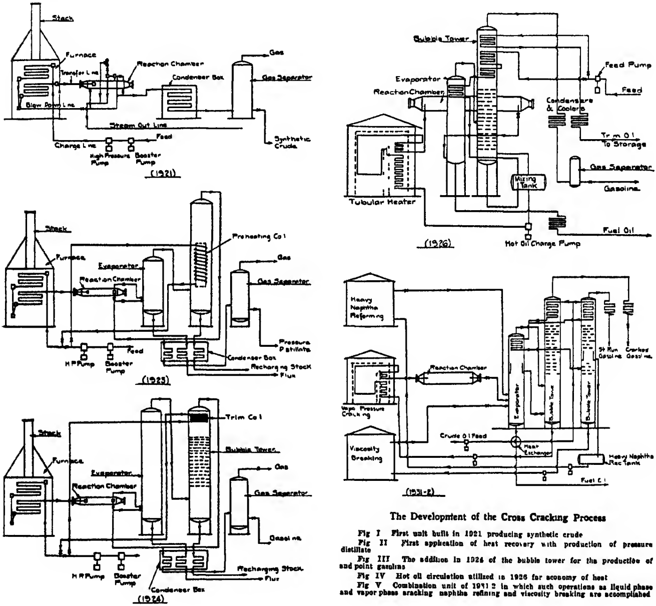
In 1921, following about 12 years of experimental work, the Cross brothers assigned their patents [13, 1916–19] to the Gasoline Products Company of New York The company was originally capitalized at $500,000 and all the stock was reported to be held in trust by Charles H Sabin, President of the Guaranty Trust Company, J E Otis of the Central Trust Company of Chicago, and Grayson M P, Murphy

The Dubbs Process.

The Dubbs process has been one of continual development and improvement It grew out of a method invented by Jesse A Dubbs [15, 1915] for the dehydration of petroleum emulsions by heating under pressure Provision was made for the distillation of a portion of the oil under pressure The original process was carried out on a small commercial scale near Santa Barbara, California, in 1909 Some years later a small cracking plant was operated in Independence, Kansas The character of this plant and its method of operation in 1919 was described in the report of a committee of the Western Refiners Association [55, 1919] The oil was pumped through a heating coil, consisting of 20-ft lengths of 4-in pipe The hot oil was discharged into four 20-ft lengths of 10-in pipe connected in series by return bends and set horizontally and well insulated The larger pipes were maintained about half full of oil, vapours being removed through goose necks to a manifold and finally to a condenser The operating pressure was normally about 135 lb

The first licensed commercial unit was installed in the plant of the Roxana Petroleum Company at Wood River, Illinois, in 1921 The earlier Dubbs units provided for the introduction of fresh charging stock either at the top of the dephlegmator or directly into the line leading into the heating coil In either case it was thus blended with 4 to 6 parts of recycle stock condensed in the dephlegmator The earlier units depended for oil circulation upon the head of oil flowing from the elevated dephlegmator, a conspicuous feature of these installations The oil left the heating coil at about 900° F passing into the expansion drum or 'reaction chamber' from which the vapours passed to the dephlegmator On account of the low pressures employed, the early Dubbs process, like the Burton, did not use kerosine as charging stock

It will be remembered that at this time, 1921–2, the welding of thick steel was not satisfactory and the expansion drums, which were large, accordingly limited the operation to low pressures Satisfactory hot oil pumps had to be developed As noted in the diagrams of the Cross process, the early Cross operation was a single-pass process, bubble-cap fractionating towers and hot-oil circulating pumps being added later In the early Dubbs units the dephlegmators were relatively small and the distillate contained about 60% gasoline



The Development of the Cross Cracking Process

Fig I First unit built in 1921 producing synthetic crude

Fig II First application of heat recovery with production of pressure distillate

Fig III The addition in 1924 of the bubble tower for the production of end point gasoline

Fig IV Hot oil circulation utilized in 1926 for economy of heat

Fig V Combination unit of 1931 2 in which such operations as liquid phase and vapor phase cracking naphtha refining and viscosity breaking are accomplished

FIG. 1.

The Dubbs process was the first to process heavy residual oils This was made possible by the *dilution of the heavy charging stock* by the distillate condensed in the dephlegmator, by the large reaction chamber where the hot residues were permitted to coke, and particularly by the fact that only 6 to 10% of cracking was effected per pass, thus minimizing coke formation in the heating tubes.

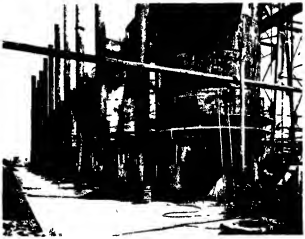
Refluxing the distillate and recycling clean distillate to the cracking system was an early feature of the Dubbs development, and also of the Holmes-Manley Behimer

The first Burton cracking unit built at the Whiting, Indiana, plant of the Standard Oil Company of Indiana in 1912

First Cross Process Plant built at Rosedale, Kansas, 1916

The first commercial Cross unit, Indian Refining Company at Lawrenceville, Illinois, 1921

First commercial Dyro installation at Cabin Creek, West Virginia, 1916



Fleming cracking units operated at the Ponca City Refinery of the Continental Oil Company (formerly Marland Refining Company) from October 1922 to July 1929

process of the Texas Company The principle of 'clean circulation' was one of the few cases of patent infringement and validity to be definitely settled by the courts The Universal Oil Products Company brought suit in 1929 against the Root Refining Company, operating a Winkler-Koch unit, for infringement of the patent generally known as the clean circulation patent, issued to C P Dubbs, U S Pat 1,392,629 (1921) Decision favourable to the Universal Oil Products Company was awarded by the United States District Court, Wilmington, Delaware, and confirmed by the Circuit Court of Appeals, Third Circuit, which decision became final on 21 October 1935, when the United States Supreme Court refused review of the case

The units could be operated to produce substantially only coke, uncondensed gas, gasoline, and pressure distillate bottoms, or by withdrawing heavy fuel oil from the reaction chamber, greater daily throughput and longer operating cycles could be attained The reaction chambers were in some cases made quite large, those installed at the plant of the Marland Refining Company (now Continental Oil Company) at Ponca City, Oklahoma, in 1926 being 10 by 40 ft in size Two reaction chambers were usually provided for each unit, one being emptied while the other was in operation In 1928 Morrell, Farragher, and Mekler introduced a special cement coating for the interior of reaction chambers to prevent their corrosion

The disposal of the coke produced in the Dubbs process was a problem in some cases, since the coke was softer and contained much more oil and sulphur than the coke made in old-fashioned coking stills It was sometimes ground and burned locally as plant fuel, and in some cases it was bricquetted with satisfactory results However, it had been noted by others that coke appeared to be formed by condensation reactions in the heavy tarry residuum About 1928 some Dubbs operations were changed by not allowing the hot residuum to remain in the reaction chamber, the formation of coke and its accumulation in the chambers being largely eliminated [50, 1929] By 1930 Dubbs plants were reported as operating continuously for as long as 500 hr

These studies of coke formation, beginning about 1927, had a profound effect upon cracking processes, all the well-known processes up to that time maintaining, in one form or another, a large body of hot oil in the system In fact it had been widely believed that the maintenance of a large body of hot oil in the system was necessary to form satisfactory yields of gasoline and keep coke out of the heating tubes This idea was reflected in the commonly used name, reaction chambers' The idea of a body of hot oil was completely discarded in the de Florez process, in 1928, and this feature rapidly became common practice in other processes Where reaction chambers existed the operation was changed to run at low liquid levels in the chambers, and flash-distil the hot residuum further to improve the matter of clean oil recirculation Flash distillation of hot residuum had been practised in connexion with the Holmes-Manley process from a much earlier date

In 1925 the average daily capacity, of charging stock, of the cracking units then in operation was 329 bbl per day In 1931 this had been increased by new units of larger capacity and the retirement of old units to an average of 1,416 bbl. per day The number and capacities of the more important cracking processes in 1931 are given in the Table in the next column

The Dubbs patents were acquired by the Universal Oil Products Company which was largely owned by J Ogden Armour In 1916 a suit was filed against the Standard Oil Company of Indiana for infringement of the first Jesse A Dubbs patent, noted above No decision was ever reached in this famous case, a settlement being finally made between the interested parties

1931 Census of Cracking Plants in the United States, and Average Capacities

Type of process	*No of units*	*Total capacity, bbl per day*	*Average capacity*
Burton	793	164,249	207
Dubbs	185	252,250	1,366
Cross	150	245,800	1,638
Tube and Tank	118	385,460	3,266
Holmes-Manley	115	233,900	2,033
Jenkins	46	66,150	1,438
de Florez	6	13 550	2,258
Gyro	20	16,000	800
Isom	115	179,150	1,557
Others	320	394,272	1,232

Carburol Process.

The formation of coke in reaction chambers and its control by maintaining very low liquid level in the chambers has been referred to The logical limit in this direction appears to be exemplified in the Carburol process developed in Germany and first described by K Bender in 1929 [6] In this process the pressure-release valve is placed between the heating coil and the first separating drum A small plant was installed in Stuttgart in 1928 The equipment is fabricated by the Rhein-Metall Borsig, Germany

Winkler-Koch Process.

The cracking system illustrated in Fig 2 is also characterized by omission of a reaction chamber The complete arrangement varies according to whether crude, topped crude, or gas oil is employed as charging stock The process has been installed during the last 10 years in numerous plants in the United States and Europe The Winkler-Koch units incorporated complete crude skimming with cracking at the Root Refining plant about 1928

Holmes-Manley Process

The Holmes-Manley process was developed by the Texas Company, who built the first unit in 1917 The most conspicuous feature of this process was a series of four reaction chambers in an insulated brick setting and maintained at moderate cracking temperatures by applying heat The unit comprised a cracking coil including an economizer and preheater section, four reaction chambers, 5 by 41 ft in size and 3-in walls, electrically welded The reaction chambers were provided with scrapers A fractionating column for overhead distillate and a flash tower for hot residuum were also provided The older units operated at 250 lb pressure, which was later increased to about 400 lb By 1928 the Texas Company operated about 100 of these units and about 50 were licensed to others

Tube and Tank Process.

The Tube and Tank process was developed by the Standard Oil Company of New Jersey, which company owned the Ellis patents, these units being developed following an extensive experience with the Burton process The process was originally carried out at moderate pressures, but as better welded chambers and better alloy tubes became available the operating pressures were increased to 350 lb , then to 450 and 750 lb , and finally to 1,200 lb In 1929 the Standard Oil Company of Ohio installed a plant operating under 1,000 lb pressure and 915° F Chrome-nickel steel tubes were used In 1931 the Associated Oil Company installed a unit at Avon, California, having a daily capacity of 10,000 bbl

In August 1922 the Standard Oil Company of New Jersey brought suit against the Pure Oil Company, operating the Cross process, for infringement of the Ellis patents The case was never brought to trial and was dismissed following an agreement with the Gasoline Products Company entered into in 1923 In 1915 the New Jersey Company had entered into an agreement with the Standard Oil Company of Indiana, owner of the Burton patents, and later the Texas Company was included In 1925 the United States Government brought suit against the group involved in these cross-licensing agreements In this suit the government unsuccessfully sought to show that the patents relied upon by the defendants were not valid in that they were anticipated by prior art

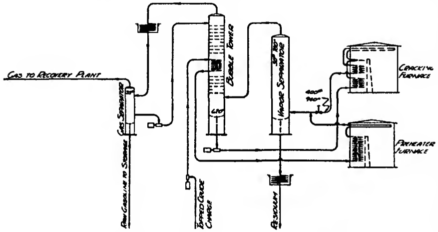


FIG 2 Winkler-Koch unit, adapted for topped crude charging stock

Emerson Process.

The Emerson process started with experimental work by V L Emerson in Philadelphia in 1916 In November 1920 the first two of twelve Emerson stills had been erected in the Schaffer Oil Company plant at Cushing, Oklahoma These stills were rated as producing about 50 bbl of gasoline per day Mr Shaffer, of this company, was one of the financial supporters of the process Early in 1921 twelve Emerson stills were erected at the Gulf Refining Company plant at Port Arthur, Texas One feature of the process was the distillation of oil from the so-called 'Secondary Still' under about 100 lb pressure, which probably accounts for the gasoline made After a brief period the operation of the Emerson stills was discontinued

Vapour-phase Processes.

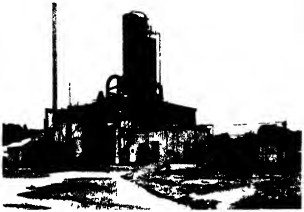
The work of Noad and Townsend [41, 1908], and Neilsen [40, 1908, 1911, 1913] on the process operated in England by the New Oil Refining Process Company has been referred to This work began about 1908 It consisted essentially in passing a mixture of oil and water or steam in the proportions of about 2 to 1 respectively through tubes containing scrap iron and heated to a dull red heat

Work on the Greenstreet process, in America, appears to have started about the same time This process also consisted in cracking oil vapours mixed with steam Greenstreet [21 1914–19] applied for his first patent in 1911 Commercial units were later installed in refineries of the Paragon Refining Company at Toledo, Ohio, the British American Oil Company at Toronto, Canada, the Interocean Refining Company at Baltimore, Maryland, and the Consolidated Oil Refining Company at East St Louis and at Cleveland, Oklahoma The largest unit had a capacity of about 1,500 bbl of gas-oil charging stock per day, yielding 25 to 40% gasoline in one pass This size unit had 6 heating coils arranged in parallel, each coil consisting of 425 ft of 2-in pipe The pressure, presumably on the inlet side, varied from 75 to 150 lb , and the exit temperature of the vapours leaving the furnace was 900° to 1,200° F [37, 1923]

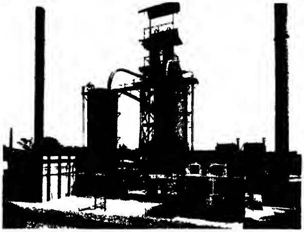
The Hall process appears to have been the first process used on a commercial scale for cracking oil in the vapour phase at low pressures without the use of steam William A Hall, the inventor of the process, described it in an address before the Institution of Petroleum Technologists in London on 18 February 1915 [23] Hall made very interesting and valuable contributions High vapour velocities were maintained in the cracking coil, which consisted of 300 ft of 1-in pipe In the course of his work Hall and his associates one of whom was Luis de Florez, discovered that under certain conditions relatively small differences in the heating conditions to which the oil vapours were subjected made large differences in the proportion of oil cracked and in the nature of the products Hall states 'Supposing the external temperature in the centre of the nest (of tubes) is 560° C , a change from 20° C below that point to 20° C above may make a difference of 50% in the production of gas, and a great difference in the gravity of a spirit boiling below a given point, but still more marked is the difference in the unsaturated portions I have seen a spirit produced containing 90% of unsaturated hydrocarbons, and another only 30%, both from the same oil, with the same point of cut and the same pressure, in fact, with all conditions the same except this comparatively small difference in temperature ' In a Hall unit installed for the Texas Company in 1916 particular attention was given to close temperature regulation by means of automatic controls on the gas admitted to the furnace

Responding to the exigencies of the war period Hall turned his efforts to the production of benzene and toluene by employing higher temperatures than are suited for gasoline production

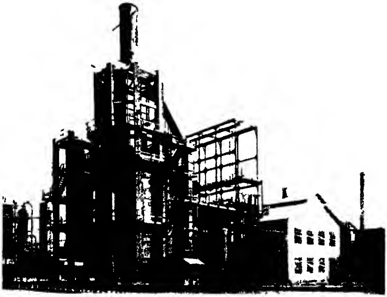
It is of interest in view of the later work of Frey and his associates [20, 1932] that when the hot cracked vapours were discharged from the cracking coil into an expansion chamber a *temperature increase* of about 30° C was observed even though the pressure dropped from about 60 lb to about atmospheric pressure Hall attributed this to a mechanical effect, but Frey has shown that under these conditions exothermic reactions occur Thus when propane and butane are cracked at about 850° C (1,560° F) the



Jenkins unit showing forced oil circulation and dephlegmators



Dubbs cracking unit in 1926



De Florez vertical tube cracking unit at the Port Arthur plant of the Texas Company in 1929

exothermic reaction ensuing after the gases leave the cracking coil causes a temperature increase of about 94° C [33, 1917]

In addition to the Hall unit tested by the Texas Company in 1916–17, a small demonstration unit was operated at Greenpoint, Long Island, in 1913, the results of which are summarized by Dr C F Chandler [9, 1916] However, the Hall process did not continue to be operated in the United States A small Hall plant was in operation for a short time at the Standard Oil Company of New Jersey at Bayway, New Jersey

It is particularly interesting that Hall noted as early as 1915 that motor fuel made by his process did not knock when used in automobile engines He stated that although the mixture of air and fuel ignites very readily the flame does not propagate itself through the mixture as rapidly as with ordinary gasoline, in other words, his motor fuel was a slow-burning fuel Hall also appears to have been the first to have noted the formation of gum, which is of course excessive in highly unsaturated gasoline, and proposed refining the gasoline by filtering through fuller's earth or distilling it with a small proportion of this material A series of patents were issued to Hall during the period 1914–18 [24]

The Rittman process was a development which had its beginning in studies of oil cracking which Dr Walter F Rittman made at Columbia University in 1914 under the direction of Prof M C Whitaker Dr Rittman continued his investigations in the U S Bureau of Mines These investigations led to the erection of a plant at Pittsburgh, Pa , in 1915 in co-operation with the Aetna Explosives Company The purpose of the Pittsburgh Rittman plant was the production of benzene and toluene The construction of this plant and its operation is described by Dr Rittman and his associates, C B Dutton and E W Dean [47, 1915] In contrast with Hall, Rittman employed short tubes, 12 to 14 ft long and larger diameter, 12 to 16 in Later work was done with 8- to 12-in tubes 11 to 12 ft in length Pressures of 100 to 150 lb and temperatures of 500° to 575° C were employed A Rittman unit for gasoline production having a capacity of 1,000 bbl per day of charging stock was built in 1916 for the Germania Refining Company Other units were built for the Gulf Refining Company at Port Arthur, Texas, the Indian Refining Company at Lawrenceville, Ill , the Empire Refining Company at Okmulgee, Oklahoma, and the Midwest Refining Company at Casper, Wyoming The operation of all of these plants was discontinued after a relatively brief period of operation

A vapour-phase cracking plant, having a daily capacity of about 8,000 bbl of charging stock, was built by the Gulf Refining Company at Port Arthur, Texas, in 1917 following the process patented by Dr C M Alexander [2, 1921–2] The charging stock used was a light distillate containing about equal parts of kerosine and gas oil Like Rittman, Alexander employed relatively short tubes, 20 ft long and 6 in in diameter, set vertically The oil was vaporized in pipe stills and the vapour distributed to manifold pipes, from which it passed to the cracking tubes through small orifices No pressure was used and the temperature maintained in the range 900–1,000° F The operation of the plant was discontinued in 1919

A process was operated by the General Petroleum Corporation of Los Angeles in 1917 and 1918 for the production of benzene and toluene A second plant using the same process was built by the Standard Oil Company of California at Richmond, California, in 1917 The General Petroleum Corporation acquired the patent of C H Washburn in 1916, but the improvement and actual operation of the process was carried out under the direction of Leslie [37, 1923] The two plants cost approximately $5,000,000, and were installed to have a daily capacity of about 100,000 lb of pure toluene Leslie states that there was 'a striking similarity between Washburn's method as described in his patent and that of Greenstreet' Both used gas oil and steam The yield of toluene was stated to be 6%

In November 1927 the Texas Company, which had acquired the Hall patents, and the Gulf Refining Company owning the Alexander patents, agreed to pool their patent interests in vapour-phase cracking This agreement was preliminary to the building of a new type of low-pressure cracking unit by the Gulf Refining Company under the direction of Luis de Florez The first unit was built at Bayonne, New Jersey, in 1927

As interest in motor fuel of higher octane value became greater much more interest in low-pressure or vapour-phase cracking processes was aroused In 1927 the first commercial unit of the 'Gyro' vapour-phase process was installed by the Pure Oil Company at Cabin Creek, W Va , and in 1929 Max B Miller and Company, licensers of the Gyro process, announced that a cross-licensing agreement on vapour-phase cracking patents had been entered into between that company and the Texas Company, Standard Oil Company of Indiana, Standard Oil Company of New Jersey, Gulf Refining Company, and the Gasoline Products Company

In 1929 five Gyro plants were in operation and four were in course of construction, having a combined daily capacity of 150,000 bbl of gas-oil charging stock The Gyro process (Fig 3) made provision for preheating the reduced crude oil by the hot gases from the cracking furnace, and obtained distillate charging stock for the cracking coils by utilizing the heat of the cracked products The hot cracked oil vapours were quickly cooled from about 1,100° F to about 700° F by directly contacting the vapours with oil, arresting polymerization of the highly unsaturated cracked products More detailed description of the Gyro process will be found in the article on 'Vapour-Phase Cracking', in this section

Another type of vapour-phase cracking process is that developed by the Petroleum Conversion Corporation and called the 'True Vapour-Phase Process' A small development plant was erected in Texas City, Texas, in 1924 The process consists essentially, according to A P Sachs [48, 1930], of heat accumulators very similar to blast furnace stoves which are first heated and gas then passed through The hot gas leaves the heating stoves at 1,600–1,800° F and mixes with hot oil vapours and 'carrier gas' which are thereby heated to about 1,000° F Condensible products are removed and the residual gas is partly recirculated and partly burned as fuel One of these units having a capacity of 9,000 bbl per day charging stocks was erected by the Shell Petroleum Company in Wood River, Illinois, in 1929 Later units have included alloy tube heaters in place of the heating stoves

A great deal of experimental work has been done in the attempt to catalyse the cracking of petroleum oils, and numerous papers have been published dealing with experimental results which would be profitless to review In a small vapour-phase cracking plant which was operated for several years by W G Leamon at Newark, Ohio, the vapours were passed into a chamber containing what was alleged to be a catalytic material The plant was described by Truesdell [52, 1928] Following several years of experimental work by E Houdry, a commercial unit having a charging capacity of about 200 bbl per day was erected in 1934 by the Vacuum Oil Company at Paulsboro, New Jersey As described by W F Faragher [19, 1933], cracking is effected by an active catalyst The oil is vaporized at atmospheric pressure at about 775° to 875° F, mixed with a small proportion of steam and passed through the catalyst chamber A yield of 37% on once-through operation on Mid-Continent gas oil is reported The residual oil is stated to be suitable for thermal cracking

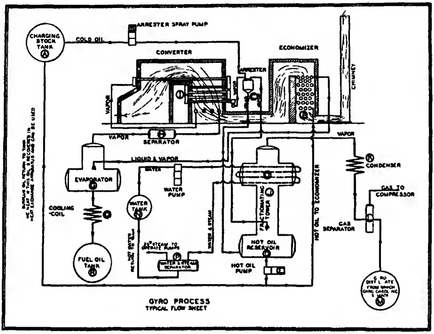


Fig 3 Gyro flow sheet of 1929

The Gulf Refining Company erected a large-scale plant at Port Arthur, Texas, in 1915 for the manufacture of gasoline from light gas-oil distillate by heating with anhydrous aluminium chloride The process used was developed by A M McAfee A battery of 30 large special stills similar in general appearance to the early 'cheese-box' stills was erected shortly thereafter Anhydrous aluminium chloride was made as required from chlorine, bauxite, and coke The aluminium chloride was obtained in fine granular form and pumped into the stills mixed with oil The aluminium chloride was not recovered, the carbonaceous residues being flushed out with water, the granular carbon washed and burned by means of a mechanical stoker in a nearby power plant The aluminium chloride process was never adopted by other refineries The patents covering the process were in litigation with the Texas Company for 15 years until the United States Circuit Court of Appeals for the fifth circuit decided in favour of McAfee and the Gulf Refining Company in May 1928

Summary

The general trend of change in cracking conditions has been from the low pressures of vapour-phase cracking and the 75 lb pressure first used by Burton, to the higher pressures, up to about 1,000 lb per sq in Cracking temperatures also have been raised in recent years to obtain gasolines of higher octane value The higher gas losses resulting from higher cracking temperatures, together with the steadily increasing importance of anti-knock values, have given greater importance to the use of these gases in so-called gas polymerization processes

Like other branches of refinery engineering there has been continued improvement in design materials, and efficiency of cracking equipment The older types of apparatus mentioned in the present review, now largely obsolete, are of interest in indicating the problems that have been met The history of cracking, like the history of petroleum distillation, clearly shows the trend from simple methods to a stage now characterized by the best engineering and research

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THERMOCHEMISTRY OF PETROLEUM HYDROCARBONS

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THE reactions which hydrocarbons undergo with thermal or catalytic treatment are in general very complex because of the enormous numbers of possible compounds involved The literature on the subject, especially the patent literature, has become extensive The bulk of this is the result of observations upon experiments conducted necessarily at least partly in an empirical manner In the petroleum industry, as in some other important industries, the technology is far in advance of the science

Nevertheless, theoretical considerations are making an important contribution to the chemistry of cracking These include studies of mechanism and equilibria during thermal or catalytic treatment of pure hydrocarbons or known mixtures, determinations of heats of combustion, heat capacities of hydrocarbon solids, liquids, and vapours, latent heats of fusion and vaporization, and more recently spectroscopic determinations of thermodynamic properties Comprehensive calculations upon free energies of hydrocarbons and related compounds have appeared from time to time These serve the double purpose of summarizing up-to-date experiments both scientific and technological so that they may become more readily available for practical use, and also of pointing out the numerous gaps due to inaccurate or completely lacking data, so as to stimulate research to fill up the gaps Such research is going forward at an accelerating rate so that a review is not entirely up to date when it comes off the press Sixty-five per cent of the references in this article are to 1933, 1934, or 1935

Previous reviews on the free energies of hydrocarbons are by Smith [72, 1927], Francis [19, 1928], Francis and Kleinschmidt [21, 1929], and Parks and Huffman [58, 1932] Since the appearance of the book by Parks and Huffman, opportunity for improving the calculations has been provided by researches on thermodynamic properties from spectroscopic data, by studies on equilibria of olefines with paraffins or with alcohols, by precise determinations of heats of combustion in the U S Bureau of Standards and elsewhere, and by some other new data to which reference will be made as it is used The literature on heat capacity of vapours of liquid hydrocarbons is still very meagre, and not much advance has been made recently in this direction It can be shown, however, that errors in heat-capacity equations have less effect upon the accuracy of free energy calculations than relatively small ones in heats of combustion, so that in many cases very rough estimates of heat capacity are tolerable

Chemical thermodynamics is sometimes depreciated because it tells nothing about rate of reaction, a prime consideration from the point of view of production Furthermore, many hydrocarbon reactions would not take place at all if it were not for the sluggishness of some other reactions In general, thermodynamics tells little about intermediate mechanisms, especially those involving free radicals or other 'imaginary' compounds not capable of isolation for direct experimental study

On the other hand, the mechanism, a favourite tool of many organic chemists, may be overrated in importance in some cases The composition of high-temperature tar such as gas tar, for example, is almost independent of the original hydrocarbon source And an example will be given below (explosion of ethylene) of a simple empirical reaction for which no suitable mechanism has been proposed, yet which gives products corresponding exactly with thermodynamic equilibrium

In predicting or evaluating results of thermal or catalytic treatment we must consider whether such treatment is mild or drastic In the former case mechanisms are important, in the latter case relative stability of hydrocarbons as indicated by thermodynamics becomes the controlling factor Consequently, in a study of mechanism of cracking, varying rates of flow are employed, and extrapolation to zero time (infinite rate) is presumed to show the initial reaction products, whereas in a study of equilibria the extrapolation is in the other direction, to zero rate (or infinite time), taking care to avoid excessive side reactions

The above distinction between mild and drastic reaction on the basis of time must be made, of course, with reference to temperature and catalytic environment I have made equilibrium studies at 100° C requiring more than a month for a reasonable approach to equilibrium, and but for the excessive time required would have preferred a much lower concentration of catalyst, which complicated the analysis and interpretation

On the other hand, an explosion, taking place usually in a small fraction of a second, results in products corresponding very closely to equilibrium conditions at or below the flame temperature For this reason explosions are rarely of much value for studying mechanism, apart from equilibria, unless some extraordinary precautions in experiment and interpretation are taken

This article is not the place for discussion of thermodynamics of explosions in general, which involve oxidation rather than cracking, although the latter reaction may take place to some extent as an intermediate mechanism Only two common hydrocarbons, acetylene and ethylene, are explosive alone, and the latter only under substantial pressure and preheated [2, 1934, 16, 1934, 17, 1933] Thus, Smolensky and Kovalevsky [73, 1935] found complete decomposition of ethylene according to the equation

$$C_2H_4 \rightarrow C+CH_4$$

in spite of the lack of a simple mechanism At the low temperature, 300° C , and high pressure (probably 34 atm) the equilibrium percentage of hydrogen would be only about 1%, which might easily escape detection Since hydrogen (possibly monotomic) was undoubtedly an intermediate in this reaction, its subsequent disappearance proves the importance of equilibria in explosions The explosibility of these two unsaturated gases is due to their endothermic character Propylene and some of the aromatics also are endothermic, but so slightly so that their decomposition would raise the temperature of their elements only slightly, not enough to reach their decomposition temperatures unless strongly preheated Nevertheless in the case of propylene, heating to 400° C under pressure in the presence of only 20% air resulted in a violent explosion (unpublished work of the author).

Free Energies of Some Hydrocarbons

In order to simplify the equilibrium relations between the hydrocarbons the free energies of several of them will be computed with the most recent data in nearly the same manner as in the earlier reviews The free energy of a substance is a measure of its thermodynamic stability (the more negative the more stable) It is related to the equilibrium constant for its formation from its elements by the equation, $\Delta F = -RT\ln K$, where R is the gas constant, 1 9885 cal, T is the absolute temperature in degrees Centigrade, and $\ln K$ is the natural logarithm of the equilibrium constant It is related to the heat of formation and change of entropy in formation by the equation, $\Delta F = \Delta H - T\Delta S$ The nomenclature in this article will be the same as that employed by Parks and Huffman [58, 1932]

As Parks and Huffman have pointed out (p 50), it is unnecessary to determine the thermodynamic properties of all the hydrocarbons to which we wish to apply the results It is only necessary to have accurate data on some of the lower members of a homologous series in order to make reliable extrapolations, supported if possible by certain properties of an occasional higher hydrocarbon The effect of branching chains, of unsaturation and position of unsaturation, of ring formation, &c, can be ascertained from typical examples and then applied with confidence to other compounds not available in pure form for individual study

The temperature range for the calculations will be limited to 298 1 to 1,500° K, since no hydrocarbon has any appreciable stability above the latter temperature

Heat Capacities of Gases

Most experimental determinations of heat capacity of gases in the past have been at ordinary temperatures, 0 to 100° C [60, 1924], and extrapolations to higher temperatures for use in thermodynamic calculations have been very uncertain especially in view of the poor agreement in determinations made by different investigators by different methods Those of some of the simpler gases have been determined by the flame temperatures of explosions This method is limited to stable gaseous products of explosions, which excludes hydrocarbons, and to inert gases Recently Lewis and von Elbe [50, 1934] have developed a method of determining the heat capacities of *reactant* gases by the same kind of experiment Undoubtedly the most accurate method for simple gases over a wide temperature range is one derived from spectroscopic data by Bryant [8, 1933] and others

In the case of most of the diatomic gases and also steam, the curvature of the lines up to about 1,400° K is too slight to justify using quadratic equations Carbon dioxide, methane, and acetylene have plots showing a negative curvature, but by limiting the range of temperature to about 1,400° K, which is sufficient for the calculations to a slightly higher temperature, much simpler equations can be derived than those proposed by Bryant, and because of the shorter range the agreement with the theoretical is fully as good Similar data for ethane and ethylene can be derived from data given by Frost [27, 1933] The data for heat capacity of higher hydrocarbons are meagre, but the negative curvature of the lines for the lower ones suggests a T^2 term of the order of $-0\,0_5 5nT^2$ Accordingly the general equation of Parks and Huffman [58, 1932, p 68, eq 39] for gaseous hydrocarbons is modified in that respect The special equations for methane and ethane are only slightly different from this equation as applied to them A corresponding one for olefines is so chosen that the difference between that and the paraffins is always the same as for ethane and ethylene, namely, $\Delta C_p = 0\,55+0\,0065T$ The heat capacities used in this chapter for gases and graphite, as well as those of some of the other simpler gases derived similarly, are as follows

Substance	*Molar heat capacity, C_p*	*Reference*
H_2	$6\,73+0\,0005T$	14
O_2	$6\,44+0\,002T$	40, 49
N_2	$6\,54+0\,0012T$	39
NO	$6\,66+0\,0014T$	38
CO	$6\,48+0\,0014T$	39
H_2O	$7\,00+0\,0028T$	30
CO_2	$5\,60+0\,0128T-0\,0_5 54T^2$	43
CH_4	$4\,1+0\,0167-0\,0_5 3T^2$	8
C_2H_2	$8\,2+0\,011T-0\,0_5 3T^2$	8
C_2H_4	$2\,15+0\,0305T\ \ 0\,0_4 17$	27
C_2H_6	$2\,7+0\,037T-0\,0_4 1T^2$	27
C_nH_{2n+2}	$3\,0+0\,018nT-0\,0_5 5nT^2$	
C_nH_{2n}	$2\,45-0\,0065T+0\,018nT-0\,0_5 5nT^2$	
C	$0\,2+0\,008T-0\,0_5 3T^2$	53

Methane

The calculations of Kassel [42, 1933] for methane (using the Dennison-Villars frequency, which he seems to prefer) from spectroscopic data show excellent agreement in the moderate temperature range, 300 to 600° K with the equation given by Parks and Huffman [58, 1932, p 56] from numerous direct experimental data for the equilibrium of methane with its elements, and with carbon dioxide, steam, and hydrogen The same heat of combustion data were used in both calculations But at higher temperatures there is a marked divergence in the direction of more positive free energies (lower stability for the hydrocarbon) This is due probably to the higher values for the heat capacity of methane used by Parks and Huffman (p 54) Using the above equation for heat capacity and the same equilibrium data in the low-temperature range, the following equation can be computed (corresponding to a slightly curved line in Fig 3, p 55, of their book)

$$\text{C (graphite)}+2H_2 \rightarrow CH_4,\quad \Delta F^0_{298} = -12{,}270,$$

$$\Delta F^0 = -15{,}530+9\,56T\ln T-0\,0035T^2-42\,5T \qquad (1)$$

This equation agrees with the values resulting from Kassel's computations [42, 1933] within 30 cal over the entire range 298 1 to 1,500° K It also agrees with the equilibrium values of Pring and Fairlie [63, 1912] and Coward and Wilson [11, 1919], though not quite as well with those of Randall and Mohammed [65, 1929] The value for ΔH^0_0 in the above equation, $-15{,}530$, differs from that computed by Rossini [69, 1934], from Kassel's data, $-16{,}180$, because in the above equation it is only an integration constant depending upon the heat-capacity equation chosen, which cannot be expected to hold accurately for temperatures down to absolute zero

In the temperature range 800 to 1,200° K in which methane enters into thermal reactions, equation (1) can be simplified without much loss in accuracy to

$$\Delta F^0 = -21{,}470+26\,0T \qquad (1a)$$

Acetylene

The free energy values of acetylene computed by Kassel [42, 1933] from spectroscopic data agree well with the equation derived from heat capacities

$$2\text{C (graphite)}+H_2 \rightarrow C_2H_2,$$

$$\Delta F^0 = 54{,}076-1\,07T\ln T+0\,00275T^2-0{\cdot}0_6 5T^3+IT, \qquad (2)$$

provided I is set equal to $-8\,45$

Mayer, Brunauer, and Mayer [54, 1933] have calculated the ('practical') entropy of acetylene at 298° K as 46 7, but suggest the possibility that 1.1 units should be added to it. The latter would still be a trifle lower than the estimate of Kassel (50 833−2.755). A mean of Kassel's value and the higher one of Mayer, Brunauer, and Mayer would give −8.3 for the integration constant in the above equation. This gives $\Delta F^0_{298} = 50,000$. And in the temperature range, 900 to 1,300° K., where acetylene reactions begin to be significant, the equation may be simplified to

$$\Delta F^0 = 53,350-12.7T \qquad (2a)$$

Ethylene

Kassel [42, 1933] also computed the free energy of ethylene from spectroscopic data, but was obliged to combine them with an old value for heat of combustion. The latter can be evaluated much more accurately now from Rossini's value [68, 1934] for ethane combined with the heat of hydrogenation of ethylene as determined by Kistiakowsky and co-workers [47, 1935], namely 32,575±50 cal. This value has been checked closely by Rossini [69*a*, 1936]. Cf. also Smith and Vaughan [72*a*, 1935], Kassel [44*a*, 1936]. This gives for the heat of combustion of ethylene 337,080 cal. at 25° C. or 337,240 cal. at 18° C., a change of +3,240 cal. as compared with the value chosen by Kassel. This increases by the same amount the free energies of ethylene at all temperatures as derived from the table of Kassel. It seems advisable to choose his calculation including a torsional frequency of 950 cm $^{-1}$ since Frost [28, 1934] finds evidence favouring this choice. With this change the values are in excellent agreement with the equation derived from heat capacities,

$$2C\ (\text{graphite})-2H_2 \rightarrow C_2H_4,$$
$$\Delta F^0 = 14,884+11.66T\ln T-0.00675T^2+0.0_{6}67T^3+IT, \qquad (3)$$

provided that I is set equal to −60.96. However, the integration constant will be changed slightly after the calculations for ethane.

Ethane

In the case of ethane we have no direct spectroscopic determinations of free energy, but the excellent thermal data for hydrogenation of ethylene by Kistiakowsky and co-workers [47, 1935] and the numerous equilibrium determinations for the same reaction furnish a satisfactory basis for accurate computation from the free energies of ethylene. For the reaction

$$C_2H_4+H_2 \rightarrow C_2H_6$$
$$\Delta H^0_0 = -31,000$$
$$\Delta C_p = -6.18+0.006T$$
$$\Delta F^0 \quad -31,000+6.18T\ln T-0.003T^2+IT \qquad (4)$$

The integration constant is evaluated from the equilibrium data in Table I. The original values of Frey and Huppke [23, 1933] are modified as suggested by Kistiakowsky and co-workers [47, 1935].

The values of I are in good agreement considering the wide range of temperature studied. It seems preferable to omit the fourth and fifth values in the average, although they would not affect it much. The values of Travers and Pearce at 863 and 893° K. might well be given extra weight because they are the means of 29 and 39 experiments respectively, but the mean of these two nearly coincides with the general mean.

The integration constant gives the change of entropy, $\Delta S^0_{298} = -28.88$ from the equation

$$\Delta S^0 = \Gamma_0(1+\ln T)+\Gamma_1 T-I, \qquad (5)$$

where the Γ's are the coefficients in the equation for ΔC_p. The entropy of ethane can be found in three ways. One value (54.31) results on combining the above change in entropy with the entropy of hydrogen (31.23) and the 'practical' entropy of ethylene (51.96), which is found by subtracting 2×2.755 from the total entropy (57.472) given by Kassel, to correct for nuclear spin.

TABLE I

Equilibrium Data

T	K	$-R\ln K$	$-I$	*Reference*
673	0.000082	18.693	10.855	Frey and Huppke [23, 1933]
723	0.00056	14.876	10.515	„ „
773	0.0024	11.986	10.662	„
773	0.00315	11.445	(10.120)	Vvedenskii and Vinnikova [81, 1934]
823	0.0074	9.749	(11.093)	Travers and Pearce [78, 1934]
843	0.0153	8.304	10.634	„ „
863	0.0244	7.375	10.643	„
873	0.031	6.905	10.627	Pease and Durgan [61, 1928]
883	0.0359	6.606	10.769	Travers and Pearce [78, 1934]
893	0.0446	6.180	10.777	„
923	0.082	4.970	10.809	Pease and Durgan [61, 1928]
973	0.20	3.198	10.939	
		Mean	10.72±0.09	

A second method employs the third law of thermodynamics, as did Parks and Huffman [58, 1932, p. 60]. Their estimate of entropy of the gas from the boiling-point, 184.5° K. to 298° K., namely 5.13 units, can be revised in the light of the values of Eucken and Parts [18, 1933] for heat capacity at low temperatures, giving an entropy increase of 5.42 units over this range, or a total of 53.8 units.

Mayer, Brunauer, and Mayer [54, 1933] have calculated the entropy of ethane as 55.5 units from spectroscopic data. The discrepancy in the three estimates is a little greater than expected. An approximate mean of 54.5 is selected. The entropy of carbon is 1.36 according to Jacobs and Parks [36, 1934] instead of 1.3 as used previously, so that for the formation of ethane

$$\Delta S^0_{298} = -41.9$$
$$\Delta H^0_{298} \quad -20,600\ (\text{Rossini [69, 1934]})$$
$$\Delta F^0_{298} = -8,110$$
$$\Delta F^0 = -16,116+17.84T\ln T-0.00975T^2+$$
$$+0.0_{6}67T^3-71.94T, \qquad (6)$$

and approximately

$$\Delta F^0 = -24,900+51.0T \qquad (6a)$$

As in the case of methane the value of ΔH^0_0 is not the same as given by Rossini [69, 1934, p. 29], −16,990.

For consistency the equation for the formation of ethylene is modified

$$\Delta F^0 = 14,884+11.66T\ln T-0.00675T^2+$$
$$+0.0_{6}67T^3-61.22T \qquad (7)$$
$$\Delta F^0_{298} = 15,850,$$

and approximately (for the cracking range, 700 to 1,000° K.)

$$\Delta F^0 = 9,100+19.0T \qquad (7a)$$

The accurate free energies of the simpler gases are given in Table II at 50° intervals.

TABLE II

Free Energies of Simple Gases

Temp °K	Steam H_2O	Oxides of Carbon CO	CO_2	Methane CH_4	Acetylene C_2H_2	Ethylene C_2H_4	Ethane C_2H_6
298.1	54 637	33 001	−94,443	−12 301	50 006	+15 847	−8,118
300	54 617	−33,042	−94 444	−12,264	49 977	15,872	−8,038
350	54 075	−34,117	−94 478	−11 261	49 285	16 557	−5 891
400	53 515	35,199	−94 511	−10 212	48 596	17 295	−3,662
450	−52 940	−36 284	94 543	−9 114	47,910	18,077	−1,365
500	52,353	37 371	94 574	7 978	47,228	18 894	+987
550	51 754	−38 457	−94 603	−6 813	46 548	19 739	3,384
600	51 144	−39 542	−94 631	−5 621	45 871	20 615	5,823
650	−50 525	−40 626	−94 658	−4 407	45 199	21,504	8 286
700	49 898	−41,709	94,684	3 172	44,534	22 413	10 780
750	−49,262	−42 787	94 709	−1 923	43 875	23 336	13,294
800	−48 610	−43,860	−94,732	−657	43 220	24 272	15 826
850	47 971	−44 930	−94,754	+620	42 569	25 219	18 373
900	47 320	−45,995	−94 775	1 906	41,921	26 176	20 933
950	46 662	47 057	−94 795	3 201	41,276	27 141	23 504
1 000	−46 000	−48 117	−94,813	4 504	40,635	28 114	26,084
1 050	45 335	−49 173	−94 830	5 813	39 996	29 092	28 670
1,100	−44 667	−50 226	94 845	7 127	39 361	30 074	31 259
1 150	−43 993	51,275	94 859	8 445	38 730	31 060	33,851
1 200	−43 316	−52,320	−94,872	9 766	38 101	32 049	36 445
1 250	−42 637	−53 361	−94 884	11 088	37,475	33 040	39,040
1 300	−41 957	−54 400	−94,894	12 414	36 853	34 033	41 627
1 400	−40 590	−56 470	−94 911	15 074	35 615	36 024	46 812
1 500	−39 211	−58 530	−94 923	17 742	34 387	38 017	51 980
Ref	30	41	43	42	42	42	

Higher Normal Paraffin Hydrocarbons

Rossini [69, 1934] has estimated the heats of combustion and formation of all the normal paraffin hydrocarbons in the gaseous state. His figures are based on accurate determinations of the heats of combustion of methane [68, 1931], ethane, propane, *n*-butane, and *n*-pentane by himself [68, 1934], and of *n*-heptane and *n*-octane by Jessup [37, 1934]. Banse and Parks [3, 1933] determined the heats of combustion of *n*-octane and *n*-dodecane at 19° C. Converted to 25° C. and the gaseous state these values are 1,317,100±1,300 for *n*-octane and 1,947,100±2,000 for dodecane. The latter especially is appreciably higher than the value assigned to it by Rossini by extrapolation. It seems preferable to use a higher slope term in the general equation than that used by Rossini [69, 1934] (157,000 kg.-cal.). The expression, 58,840+157,260*n*, agrees with all the above determinations well within the assigned limits of error, except in the case of methane and ethane. This seemingly trivial change in the increment of the heat of combustion equation makes a substantial change in the resulting values for free energy. The increment is nearly the mean of that of Rossini and that, 157,550, corresponding to the estimate of Banse and Parks [3, 1933] for liquid hydrocarbons. The slight deviation in the case of propane is in the right direction (same as that of ethane) and may be real. It is retained, but in the other cases the smoothed out values for the heats of combustion are employed. The corresponding equation for heats of formation of vapours is

$$\Delta H^0_{298} = -9{,}470-5{,}290n \tag{8}$$

In Table III the latent heats of vaporization of ethane (extrapolated) and butane are from Dana, Jenkins, Burdick, and Timm [13, 1926], that of propane from Sage, Schaafsma, and Lacey [70, 1934], and those of pentane and hexane from Cragoe [12, 1929]. A correction for the Joule Thomson effect on expansion from the vapour pressure to dilute gas is given in these cases. It was estimated by the method of Newton and Dodge [56, 1935] for ethane and butane, and read from the diagram of Sage, Schaafsma, and Lacey [70, 1934] for propane. A ratio of 0.42 was then assumed for consecutive members of the series. The latent heats of *n*-heptane and *n*-octane are from Rossini's paper, and those for the higher members from the value 86 cal. per gram, which is approached as a limit by the lower members.

The entropy change ΔS^0_{298} was computed from the entropies given by Parks and Huffman [58, 1932, p. 64] using $S = 1.36$ for carbon instead of 1.30. Their value for liquid butane, 54.9, was used in preference to theirs for gaseous butane because the latter included a value for entropy of vaporization, 20.44, which is nearly 1 unit too high according to the results of Dana and co-workers [13, 1926]. The entropy of liquid propane, 47.0, is estimated from the equation $S^0_{298} = 23.3+7.9n$ which fits their data better for the lower members of the series. It is unfortunate that such an estimate must suffice for an important member of the series, but the resulting free energy value is in line with those of the higher members.

The free energies of formation, ΔF^0_{298}, are calculated by the equation, $\Delta F = \Delta H - T\Delta S$. The vapour pressures at 25° C. are from Beattie, Hadlock, and Poffenberger [5, 1935] for ethane, from Dana and co-workers [13, 1926] for propane and butane, from *Int. Crit. Tables*, **3**, 220–5, for pentane to octane, and from Ashworth [1, 1924] for nonane to dodecane. The fugacities (f) of the lower members were estimated from the vapour pressures and activity coefficients according to Newton [55, 1935]. The free energies of formation of the gases are found from those of liquids by the relation $\Delta F^0\text{ (evapn.)} = -RT\ln f$.

For the normal hydrocarbons above ethane the free energies as liquid agree with the equation

$$\Delta F^0_{298} = -7{,}430+880n \tag{9}$$

within experimental error, and values of this equation will be used in preference to the individual values of Table III. The slope term of this equation is somewhat less than that in the corresponding one of Parks and Huffman. The difference is due chiefly to the more recent data on heats of combustion.

As the free energies of evaporation follow the equation

$$\Delta F^0_{298}(v) = -3{,}140+680n, \tag{10}$$

those of the vapours may be expressed by the sum

$$\Delta F^0_{298}(g) = -10{,}570+1{,}560n \tag{11}$$

Combining with equation (8)

$$\Delta S^0_{298}(g) = +3.68-22.98n, \tag{12}$$

and combining this with the entropy of the elements, $n\mathrm{C}+(n+1)\mathrm{H}_2$, which is 31.23+32.59*n*, we get

$$S^0_{298}(g) = 34.91+9.61n \tag{13}$$

We are now in a position to derive a general equation for the free energies of normal paraffin hydrocarbons as vapours as functions of temperature.

For $n\mathrm{C}+(n+1)\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2}(g)$

$$\Delta H^0_{298} = -9{,}470-5{,}290n \tag{8}$$

$$\Delta C_p = -3.73-6.93n-0.0005T+0.0095nT-0.0_52nT^2$$

$$\Delta H^0 = -8{,}336-3{,}628n-3.73T-6.93nT-0.00025T^2+0.00475nT^2-0.0_667nT^3$$

$$\Delta F^0 = -8{,}336-3{,}628n+3.73T\ln T+6.93nT\ln T+0.00025T^2-0.00475nT^2+0.0_633nT^3-28.88T-20.66nT \tag{14}$$

$$\Delta F^0_{500} = -11{,}123+6{,}433n$$

$$\Delta F^0_{700} = -11{,}324+11{,}475n$$

$$\Delta F^0_{1000} = -11{,}201+19{,}165n.$$

TABLE III *Free Energies of Higher Paraffin Hydrocarbons*

Formula	ΔH^0_{298} (g)	ΔH^0_{298} (v)	ΔH^0_{298} (l)	ΔS^0_{298} (l)	ΔF^0_{298} (l)	v p atm	Fugacity	ΔF^0_{298}
C_2H_6	−20,600	1 360+900	− 22,860		− 6 152	41 37	26 3	−8,110
C_3H_8	−25,390	3,480+380	− 29,250	−82 0	−4,806	9 39	7 8	−6,022
C_4H_{10}	30,630	5,030+160	− 35,820	−106 69	−4,016	2 42	2 22	−4,488
C_5H_{12}	−35,920	6,320+70	−42,310	−132 18	−2,907	0 67	0 65	−2,653
C_6H_{14}	−41,210	7,490+30	−48,730	−155 97	−2,235	0 197	0 194	−1,274
C_7H_{16}	−46,500	8,750	−55,250	−180 86	−1,336	0 060		+325
C_8H_{18}	− 51,790	9,850	−61,640	−205 95	− 247	0 0184		+2,123
C_9H_{20}	−57,080	11,020	−68,100	− 230 64	+653	0 0066		3,628
$C_{10}H_{22}$	−62,370	12,225	−74,595	−254 63	1,310	0 0021		4,960
$C_{11}H_{24}$	−67,660	13,430	−81,090	−278 82	2,026	0 00072		6,318
$C_{12}H_{26}$	−72,950	14,635	− 87,585	−304 11	3,069	0 00022		8,050
$C_{14}H_{30}$	− 83,530	17,045	− 100,575	− 353 09	4,681			
$C_{15}H_{32}$	−88,820	18,250	107,070	−379 58	6 083			
$C_{20}H_{42}$	− 115,270	24,275	−139 545	− 502 53*	10,260			
$C_{25}H_{52}$	− 141,720	30,300	− 172,020	− 628 98*	15,484			
$C_{33}H_{68}$	−184 040	39,940	−223,980	−826 60*	23,430			

*As liquid

Since equation (14) is very awkward to use, it may be simplified for the cracking range, 700 to 1,000° K, as follows

$$\Delta F^0 = -11,260-6,440n+25\ 6nT \qquad (14a)$$

The slightly higher coefficient of the nT term (which becomes dominant at high temperatures) than that derived by Parks and Huffman [58, 1932, eq 42, p 69] is due to the quadratic term in the heat-capacity equations used here, so that the hydrocarbons are relatively less stable at high temperatures

Branched Chain Paraffins

The discussion of branched chain paraffin hydrocarbons by Parks and Huffman [58, 1932, pp 69–75] is excellent, and there are no more recent data by which their estimates can be improved If we assume with them for the reaction

$$n\text{-}C_nH_{2n+2} \rightleftharpoons i\text{-}C_nH_{2n+2}$$

(the difference between the two sides of the equation being in general just one branch), that

$$\Delta H^0_{298}(l) = -540,$$

then
$$\Delta F^0_{298}(l) = +800$$

And if we assume that the entropies of vaporization of isomers at 298° K are the same, the heats of vaporization would differ by the same amount as do the free energies, which Parks and Huffman estimated as 200 cal, giving

$$\Delta H^0_{298}(g) = -740 = \Delta H^0_0+\Delta C_pT$$
$$\Delta F^0_{298}(g) = +600 = \Delta H^0_0-\Delta C_pT\ln T+IT$$

The values of ΔH^0_0, ΔC_p, and I are unknown, but, since the specific heats of adjacent members of the normal paraffin vapours do not differ by more than an amount corresponding to 0 5 cal per mol, we may assume that the differences in molar heat capacities of isomers are probably no greater Then

$$\Delta H^0_0 = -740\mp150$$
$$I = 4\ 5\pm3{\cdot}0$$
$$\Delta F^0_{1000} = 3,760\mp250$$
$$\Delta F^0 = -740+4\ 5\mp0\ 3T \qquad (15)$$

This estimated difference at 1,000° K is a little less than that of Parks and Huffman [58, 1932, p 74] Its value depends almost wholly upon their estimate of entropy difference of liquid isomers, which seems well established, and which becomes the slope term in the above equation Uncertainty in heat capacity of vapour is largely cancelled Combining with equation (14*a*)

$$\Delta F^0 = -11,260-6,440n-740r+4\ 5rT+25\ 6nT, \qquad (16)$$

where r is the number of branches

In the case of isobutane, the simplest branched chain hydrocarbon, the calculation of Halford [31, 1934] gives $S^0_{298} = 71\ 9$, which is only about 1 6 units less than the revised value for *n*-butane instead of the usual 4 5 units difference If the difference in heat of combustion is normal, as seems probable, it would appear that the free energy is almost identical with that of *n*-butane at all temperatures Rossini [696, 1935] finds $\Delta H^0_{298\,1} = -1,630$ cal This would give $\Delta F^0 = -1,630+1\ 6T$, $\Delta F^0_{1000} = -30$, cf also Roth and Pahlke [69c, 1936] for isopentane

Olefines

The thermal data for the olefines can be estimated now with considerably increased precision as a result of the determinations by Kistiakowsky, Ruhoff, Smith, and Vaughan [48, 1935] of the heats of hydrogenation of propylene and all four butenes These values can be combined with the combustion data of Rossini [68, 1934] for the paraffins to give heats of formation and combustion of the olefines, and with the equilibrium determinations of Frey and Huppke [23, 1933] to give free energies of hydrogenation to the corresponding paraffins, and also free energies of formation from the elements These calculations are presented in Table IV

TABLE IV *Thermal Data of Gaseous Olefines*

Olefine		Propylene	Butene-1	Trans-butene-2	Cis-butene-2	Isobutene
Heat of hydrogenation	298	−30 115	−30 341	−27,621	−28 570	−28,389
	0° K	−28 540	−28 766	−26,046	−26 995	−26 814
Heat of formation	298°	+4 725	−289	−3 009	−2 060	−2,781
Heat of combustion	298	492 375	649 910	647 190	648 140	647,420
Integration constant (hydrogenation)		−8 23	−7 66	−10 55	−10 09	−7 58
Simplified free energy equation (Hydrogenation)		−31 590 +34 5T	−31 816 +35 1T	−29 096 +32 2T	−30 045 +32 65T	−29 864 +35 2T
(Formation)		1 010 +42 3T	−5 200 +67 3T	−7 920 +70 2T	−6,975 +69 75T	−7 160 +67 2T
Equation no		(17)	(18)	(19)	(20)	(21)

The heats of hydrogenation at 0° K were derived from the same equation used for the ethane-ethylene equilibrium.

$$\Delta H^0_{298}=\Delta H^0_0-6\ 18T+0\ 003T^2$$

And the integration constant is that resulting from the equilibria of Frey and Huppke and appearing in the equation

$$\Delta F^0 = \Delta H_0^0 + 6.18T\ln T - 0.003T^2 + IT$$

The equations were simplified to linear equations for the cracking range, 700 to 1,000° K , and combined with the corresponding equations for propane and butane from (14*a*) (assuming the same equation for free energy of isobutane as for *n*-butane) to find free energies of formation

The heat of hydrogenation of di-isobutene can be estimated more accurately than that of any other liquid olefine, from its heat of combustion determination by Banse and Parks [3, 1933], assuming that that of 2,2,4-trimethyl pentane, its hydrogenation product, is 3×540 cal lower than that of *n*-octane This gives $\Delta H_{298}^0 \quad -28{,}600$, which is almost the mean of the values for the four butenes, $-28{,}730$ We shall not err greatly therefore if we take the mean equation for hydrogenation of the butenes

$$\Delta F^0 = \quad 30{,}200 + 33.8T \tag{22}$$

to apply to the vapours of the higher olefines (Kistiakowsky and co-workers [46*a*, 1936] find heats of hydrogenation for higher olefines decreasing with branching but not with increasing molecular weights Cf also Bent and co-workers [5*a*, 1936], Crawford and Parks [12*a*, 1936]) Combining with (14*a*) we find the general equation for free energy of formation of the olefines (above propylene)

$$\Delta F^0 \quad 18{,}940 - 6{,}440n - 33.8T + 25.6nT \tag{23}$$

Cyclic Hydrocarbons

There is little more recent research which can be used to improve the excellent Chapter V of Parks and Huffman's book What there is seems excellent confirmation of their results Thus Southard and Brickwedde [74, 1933] have determined the entropy of naphthalene as 39.89 units at 25° C , within 0.01 unit of the value of Huffman, Parks, and Daniels [33, 1930] They give the free energy as 48.5 kg -cal per mol (instead of 45.2 by Parks and Huffman [58, 1932, p 90],) which seems to be a mistake for 45.5, since they used the same data except for the entropy of carbon The newer value for the latter, 1.36, would give +45,360 cal for the free energy of naphthalene at 25° C

Mayer, Brunauer, and Mayer [54, 1933] computed spectroscopically the entropy of benzene vapour, 65.1 units, agreeing exactly with the value calculated from Huffman, Parks, and Daniels' [33, 1930] experimental determination

Halford [31, 1934] calculated the entropy of toluene vapour as 76.3, or 0.6 units higher than that resulting from Kelley s determination [45, 1929] This change would make the integration constant in its free energy equation more negative by the same amount

Rossini [67, 1933] has determined the heats of fusion of some aromatic compounds If his values are substituted for those of Huffman and co-workers [33, 1930, 32, 1931] in the case of *o*- and *m*-xylene, and pseudocumene, the entropies at 25° C would be changed by +0.9, 0, and −1.2 units respectively, causing corresponding changes in free energies of −270, 0, and +360 cal These are, of course, trivial

Purdum and Pease [64, 1933] determined the equilibrium between benzene and cyclohexane vapours at six temperatures in the narrow temperature range, 251 to 274° C Similar determinations by Zharkova and Frost [84, 1932] at 230°, 250°, and 275° C ($\log K_p = 1.972$, 1.127, 0.147 respectively) show excellent agreement with those of Purdum and Pease The slight discrepancy with the equation proposed by Parks and Huffman [58, 1932, p 94] is due probably not to uncertainty in the integration constant, which can be derived from the entropy and heat capacity equations by the relation (5), but to a slight error in the heat of reaction A change of −350 cal in the latter gives the equation

$$\Delta F^0 = -44{,}150 + 18.2T\ln T - 0.008T^2 - 30.73T, \tag{24}$$

and approximately

$$\Delta F^0 = -53{,}700 + 96.6T \tag{24a}$$

Equation (24) agrees exactly with the entropy data of Parks and co-workers [59, 33, 1930], and within ±0.4 units in the integration constant (or in entropy of reaction) with all the results of Purdum and Pease, and of Zharkova and Frost Those of Burrows and Lucarini [9, 1927] would give values about 540 cal or 1 unit in entropy more negative It is, of course, uncertain whether the above slight change in heat of reaction should be assigned to the heat of combustion of benzene or of cyclohexane We shall assume the latter

Similarly, Frost [27, 1933] has determined the equilibria of toluene with methyl cyclohexane, and of benzene with diphenyl The former gives

$$\Delta F^0 = -43{,}335 + 19.71T\ln T - 0.01045T^2 - 37.8T \tag{25}$$

and approximately $\Delta F^0 = -52{,}400 + 97T, \quad (25a)$

which are only slightly different from the above equations for hydrogenation of benzene According to Frost the equilibrium constant for hydrogenation of toluene is about three-tenths as much as that of benzene, this ratio being nearly independent of temperature

The corresponding equilibria for hydrogenation of ethyl benzene and of propyl benzene as well as of toluene were studied by Vvedenskii, Vinnikova, Zharkova, and Funduiler [82, 1933] The results are in the form

for toluene $\log K_p = 10{,}970/T - 20.387 \pm 0.053$
for ethyl benzene $\log K_p = 9{,}620/T - 18.041 \pm 0.049$
for propyl benzene $\log K_p = 9{,}875/T - 18.560 \pm 0.084$

These equations can be reduced readily to free energy equations, but we lack the free energy values for ethyl benzene and propyl benzene unless we assume that the former are the same as for *m*-xylene, and arrive at the latter by addition of the values of the former and the increment for paraffin hydrocarbons, $-6{,}440 + 25.6T$ The equation for toluene agrees well with that given by Frost above, and those for the higher alkyl benzenes indicate constants about seven-tenths as great as for toluene or one-fifth as great as for benzene

Frost's data [27, 1933] for diphenyl correspond with the equation $\Delta F^0 = 2{,}700 + 1.4T, \quad (26)$
a comparatively small value, which is nearly independent of temperature Vvedenskii and Frost [80, 1932] had previously found that the equilibrium for formation of diphenyl benzene from diphenyl and benzene at about 900° K corresponds to $\log K_p$ - 0.5 or $\Delta F^0 = -2{,}000$, also a small value

The equations for heat capacity of aromatic vapours given by Parks and Huffman [58, 1932, p 93] agree with the data at moderate temperatures, but at high temperatures, which are especially interesting for aromatics, there is probably a negative T^2 term as in the case of paraffins However, the use by Parks and Huffman of a linear equation for the heat capacity of carbon instead of the more accurate quadratic equation compensates as well as is now possible for the neglect of unknown T^2 terms in the equations for aromatic vapours

They sımplıfied theır equatıons for hydrocarbon vapours to lınear equatıons for the range 400 to 900° K Since, however, there is very little cracking below 700° K (427° C), especially when aromatics are involved, the linear equations will be a trifle more accurate if derived from the longer ones over the range 700 to 1,000° K in which most of the reactions occur In this range the lines are a little steeper The following equations are derived in this manner from those of Parks and Huffman [58, 1932, eq 61–9], but corrected for the newer value for entropy of carbon (Jacobs and Parks [36, 1934]) and also for the abovementioned slight changes in the cases of toluene and cyclohexane The equations for methyl cyclohexane and diphenyl are new, and derived from Frost's data [27, 1933] In the case of anthracene the equation of Parks and Huffman [71, 1931] would give a slightly higher value and higher slope per carbon atom than that of naphthalene As this is improbable in view of the reverse relationship of naphthalene to benzene, the equation for anthracene vapour is simply 1 4 times that of naphthalene (to make its value per carbon atom identical)

TABLE V

Free Energies of Cyclic Hydrocarbons

Cyclohexane	$-36{,}500+139\ 6T$	(27)
Methyl cyclohexane	$-43{,}300+162\ 3T$	(28)
Benzene	$17{,}200+\ 43\ 0T$	(29)
Toluene	$6{,}800+\ 67\ 6T$	(30)
m-Xylene	$300+\ 93\ 5T$	(31)
Naphthalene	$28{,}600+\ 66\ 0T$	(32)
Anthracene	$40{,}000+\ 92\ 4T$	(33)
Diphenyl	$37{,}100+\ 87\ 3T$	(34)

Free Energy Relations among the Hydrocarbons

The free energies per carbon atom of most of the important hydrocarbons as vapours are plotted in the accompanying figure as functions of temperature This figure is similar to those published previously Francis [19, 1928], Francis and Kleinschmidt [21, 1929], Parks and Huffman [58, 1932] except that a smaller temperature range, 600 to 1,100° K (327 to 827° C), is used in order to permit a larger scale so that the numerous lines may be distinguished This range includes practically all cracking of importance Two hydrocarbons, methane and acetylene, are almost crowded off the diagram, but this need cause no uncertainty, since in this range methane is much the most stable (lowest free energy) of the hydrocarbons, and acetylene is much the least stable (thermodynamically) The reduction to 'free energy per carbon atom' is necessary to put hydrocarbons of different carbon content upon a comparable basis in cracking reactions

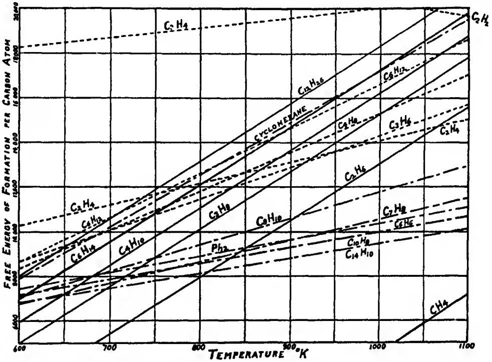

FIG 1

The thermodynamic relations of the hydrocarbons as liquids are similar, and could be computed for any individual case from the relative partial pressures of the reagents and products, but a general diagram which would show these relations properly cannot be constructed

The chief differences in the figure as compared with that of Parks and Huffman [58, 1932] (allowing for the diminished temperature range) are lines for the paraffins, especially methane, which are a little higher and steeper, a higher but less steep line for ethylene, and a lower and less steep line for acetylene The curves for methane and the C_2 hydrocarbons have been placed much more accurately than formerly by spectroscopic data and accurate heats of combustion

Free energies are plotted on the basis of unit fugacity (approximately 1 atm), and in general the tendency in cracking is for a hydrocarbon with a higher line to give one with a lower one at the temperature used Many cracking reactions are conducted under pressure, however, and under such conditions the relations are modified, depending upon the relative numbers of molecules in the reagents and proposed products Thus polymerization and hydrogenation (assuming hydrogen is present) of olefines are favoured by pressure This is well understood qualitatively The magnitude of this effect is such that in changing the pressure (more strictly the fugacity) from p_1 to p_2 there is a shift in effective free energy of

$$\Delta F = -\Delta nRT \ln p_2/p_1 \tag{35}$$

(the superscript of ΔF is here omitted because we are now considering other than unit fugacities) in which Δn is the change in numbers of molecules in the reaction. If, for instance, Δn is 1, and the pressure is doubled, at 800° K the change in effective free energy would be 1,100 cal. per *molar* quantity of the substances as written in the equation.

Cracking in general and especially the synthesis of aromatics is not favoured by high pressure, since there is always an increase in the number of molecules, for example,

$$C_{2n}H_{4n+2} \rightarrow C_nH_{2n+2} + C_nH_{2n}$$
$$C_6H_{14} \rightarrow C_6H_6 + 4H_2$$
$$6CH_4 \rightarrow C_6H_6 + 9H_2$$

In the latter two cases the increase of 4 mols in volume means an increase of 4,400 cal. (at 800° K.) or 733 cal. per carbon atom when the pressure is doubled. Dunstan, Hague, and Wheeler [16, 1934] in their comprehensive review on cracking discussed this point from a practical standpoint, and showed that with even a moderate pressure (3.5 atm.) the yield of aromatics is decreased.

Francis [20, 1931] demonstrated the profound effect of pressure in increasing the yield of carbon black by deposition from a flame (an equilibrium reaction), but computed that the yield would not continue to rise with pressure without limit, but decrease again because of the suppression of decomposition of methane.

Usually, however, the chief purpose in using pressure in cracking is not to control reactions, but to employ the reagents in high concentration (usually liquid) so as to attain economical heat transfer, and a reasonable throughput by weight without the high velocity and consequent high temperature necessary in vapour phase cracking.

Most of the conclusions of Francis [19, 1928] and of Parks and Huffman [58, 1932] in regard to possible hydrocarbon reactions are verified. One of them, stated by Francis and quoted by Parks and Huffman, which discourages the production of an olefine from a paraffin of the same number of carbon atoms, should be modified in the case of ethylene and propylene since the slightly higher values now found for free energies of the paraffins makes the dehydrogenation a little more favourable. Dunstan, Hague, and Wheeler [16, 1934] report conversions of 58% by weight of either ethane or butane into olefines, while Tropsch and Egloff [79, 1935] obtained 66% dehydrogenation of ethane by using a short time, 0.0035 sec. at 1,100° C. or 0.0004 sec. at 1,400° C. In the case of higher olefines, however, it is probably more promising economically to isolate or concentrate the desired olefines from cracking still gases.

Another reaction, the synthesis of acetylene from methane, which was considered very unfavourable, has been accomplished by Frolich and co-workers in two ways, by using an electric arc [24, 1930] at whose temperature the free energy is very favourable, though acetylene itself is not stable thermodynamically. The other method [25, 1930] was by using a moderately high temperature, 1,120° C., with diminished pressure, below 0.1 atm., at which the yield of acetylene becomes appreciable, 11%, even though the equilibrium constant is small. In both cases a very short time of contact was necessary to prevent decomposition of the product.

Storch and Golden [76, 1933] likewise made acetylene from methane at a temperature of 1,500° C. with a yield of 40% using carbon dioxide as a diluent instead of low pressure. According to equations (1*a*) and (2*a*) the equilibrium yield at that temperature would be nearly 99% if there were no side reactions (mainly decomposition to the elements).

Thermodynamics does not indicate just what reaction will take place in most cases. The ultimate equilibrium in all cases of hydrocarbon cracking corresponds to the elements, carbon and hydrogen, with varying amounts of methane depending upon the temperature and pressure, and this condition is sometimes nearly attained with explosions of acetylene or ethylene (see introduction to this article). But usually the products consist of a mixture only slightly nearer to equilibrium than the reagents, the actual reaction depending sometimes upon an available mechanism and sometimes upon a catalyst.

In the diagram one is impressed with the parallelism of the lines for the aliphatic hydrocarbons. In the case of those members above ethane this is a necessary consequence of the form of equation (14*a*). This parallelism would seem to bar the production of higher members of the series from lower ones, e.g. liquids from gases. Such a synthesis is possible to a certain extent, however, because of at least five considerations.

1. There may be some conversion by reactions of the type

$$2C_4H_{10} \rightarrow C_2H_6 + C_6H_{14}$$

for which the free energy is substantially zero at all temperatures, so that temperature and probably pressure also would have little effect.

2. Possibly the decomposition of part of the reagent furnishes energy for the building up of larger molecules, for example,

$$6C_2H_6 \rightarrow C_6H_{14} + 11H_2 + 6C$$

High temperatures and low pressures would favour such a reaction.

3. The bombardment of molecules with alpha particles [51, 1926], ultra-violet radiation [46, 1930], or electric discharge [52, 1930] may supply energy in a form immediately available in building up larger molecules.

4. Storch [75, 1933] obtained yields of ethane as high as 95% by heating methane with a carbon filament in a bulb immersed in liquid nitrogen.

5. The reaction may be carried out indirectly in two or three stages of the type

$$C_3H_8 \rightarrow C_3H_6 + H_2 \tag{a}$$
$$2C_3H_6 \rightarrow C_6H_{12} \tag{b}$$
$$H_2 + C_6H_{12} \rightarrow C_6H_{14} \tag{c}$$

Reaction (*a*) is possible to a substantial degree above 915° K. (642° C.) and is favoured by low pressure, while reaction (*b*) is possible at atmospheric pressure below about 618° K. (345° C.), and with pressure at considerably higher temperatures. The yields are, of course, much better if most of the hydrogen is removed between the two reactions. Reaction (*c*) is of no importance, but is included simply to show that higher paraffins can be synthesized indirectly.

This indirect procedure is well understood, and there have been recent experimental researches which employ it, for example, Frolich and Wiezevich [26, 1935] and Sullivan, Ruthruff, and Kuentzel [77, 1934]. From an economic standpoint the three steps are objectionable, but there seems little possibility of obtaining a good yield of aliphatic liquid products in a single step from paraffin gases, because of the diverse conditions required.

On the other hand, if olefine gases are available in high concentration as by-products of cracking, they may be polymerized to liquid hydrocarbons preferably with catalysts under pressure and at not too high temperatures. Polymerization is receiving much interest recently [26, 77, 79, 83, 1935], and has been reviewed comprehensively by Bowen and Nash [6, 1933].

If we apply equation (23), the free energy for the general equation

$$2C_nH_{2n} \rightarrow C_{2n}H_{4n}$$

would be

$$\Delta F^0 = -18{,}940 + 33.8T \qquad (36)$$

Although the situation is complicated because the products of polymerization are seldom straight chain olefines, the difference in free energy is not great. This equation seems to imply that polymerization is impossible above 287° C at which equation (36) becomes zero, and this supposition is contradicted by innumerable researches. Actually there is no inconsistency, since (*a*) usually pressure is employed in order to accelerate the reaction, and this would shift the equilibrium also towards polymerization, (*b*) in the cases of ethylene and propylene the general equation does not quite apply, and these olefines are thermodynamically less stable and (in that sense) more easily polymerized, (*c*) even at atmospheric pressure, a fair yield of polymer (up to 38% dimer or 32% trimer) is possible when the free energy change is unfavourable or zero.

Gayer [29, 1933] and Whitmore and Marschner [83, 1935] polymerized propylene at atmospheric pressure at about 350° C obtaining up to 34% yield of polymers. At that temperature, according to equations (17) and (23), the free energy change is 210 cal for the formation of dimer, 1,373 for trimer, and more positive values for higher polymers, although, of course, these values are uncertain by a few hundred calories.

The decrease in amount of higher polymers, especially beyond C_{12}, may be due partly to the less favourable free energy relations. Thermodynamics permits the observed formation of C_6, C_7, and C_8 hydrocarbons, but does not explain it, nor the apparent absence of hydrogen, C_1, C_2, and C_4 hydrocarbons. Such facts must be explained by mechanism.

The lesser slope of the lines for the aromatic hydrocarbons indicates that at temperatures above 800° K (527° C) they may be synthesized directly in moderate yield (because of decomposition side reactions) from any hydrocarbon material except methane, which requires a still higher temperature (and gives a still lower yield). The presence of aromatics in coal tar and gas-house tar is due to these reactions.

The formation of aromatics from naphthenes is relatively a simpler process, mere dehydrogenation in most cases, and may be accomplished at temperatures as low as 275° C, provided the hydrogen pressure is not allowed to accumulate.

The initial reaction in the cracking of a paraffin hydrocarbon can be represented generally by the reaction

$$C_nH_{2n+2} \rightarrow C_mH_{2m+2} + C_{n-m}H_{2(n-m)},$$

giving a lower paraffin (or hydrogen if $m = 0$) and an olefine. From equations (14*a*) and (23) the free energy of this reaction in the vapour phase is

$$\Delta F^0 = 18{,}940 - 33.8T, \qquad (37)$$

the reverse of equation (36) for polymerization. This applies to all higher values of n and m and becomes negative (making the reaction favourable thermodynamically) at temperatures above 560° K or 287° C. Its values are modified only slightly by the special equations for the hydrocarbon gases, so that the free energy of reaction gives little information as to the point of initial bond rupture, and indeed several such reactions may run concurrently. Thus, for example, Dintzes and Frost [15, 1935] find that demethanation and de-ethanation of *n*-octane proceed with equal velocity. Frey [22, 1934] has reviewed the pyrolysis of pure saturated hydrocarbons.

However, if hydrogen is to be the initial product, the free energy of reaction is given by equation (22) which becomes negative only at temperatures above 893° K (620° C). Of course some hydrogen can be formed at somewhat lower temperatures. Certainly, hydrogen is an initial product in many cracking reactions as shown, for example, by Schneider and Frolich [71, 1931]. The mechanisms of cracking are discussed much more extensively in the article by Frolich and Fulton on 'The Theory of Cracking'.

It is of interest to calculate the composite equilibrium in a fairly simple case, the cracking of propane at 650° C illustrated in Fig. 3 of the above-mentioned paper by Schneider and Frolich.

Let us assume that the only products are hydrogen, methane, ethane, ethylene, and propylene. If we write the reaction

$$aC_3H_8 \rightarrow hH_2 + mCH_4 + eC_2H_6 + e'C_2H_4 + pC_3H_8 + p'C_3H_6,$$

where the literal coefficients on the right side indicate the partial pressures in atmospheres, and a is the number of mols required to balance the equation, we have the following relations

$$h + m + e + e' + p + p' = 1 \quad \text{(total pressure)}$$
$$h + 2m + 3e + 2e' + 4p + 3p' = 4a \quad \text{(to balance H}_2\text{)}$$
$$m + 2e + 2e' + 3p + 3p' = 3a \quad \text{(to balance C)}$$
$$e + e' = m$$

(because there is no other C_1 hydrocarbon than methane)

$$\frac{me'}{p} = 450 \qquad \text{(from Table II and equation (14}a\text{))}$$

$$\frac{hp'}{p} = 1.15 \qquad \text{(from Table IV and equation (17))}$$

$$\frac{he'}{e} = 0.0855 \text{ (from Table II)}$$

Solving these seven equations partly by combination and elimination and partly by trial, we find

$h = 0.00922$ $e = 0.0455$ $p = 0.000439$
$a = 0.52296$ $m = 0.4678$ $e' = 0.4223$
$p' = 0.05472$

Reducing a to 1.0, the reaction becomes

$$C_3H_8 \rightarrow 0.01761H_2 + 0.89455CH_4 + 0.087C_2H_6 + $$
$$+ 0.80755C_2H_4 + 0.00084C_3H_8 + 0.10461C_3H_6$$

This equation is consistent with the result of extrapolating the curves far to the right (infinite time), except that hydrogen does not decrease as rapidly as the equation would indicate, probably because of further reactions involving carbon and higher hydrocarbons. The bulk of the reaction is to methane and ethylene, however, with about 9% ethane, as indicated by the equation.

Isomerization is an interesting pyrolytic reaction in some cases. One type is the possible conversion of olefines to naphthenes, such as hexene to cyclohexane. According to equations (23) and (27) the free energy of this conversion is $-16{,}800+19\ 8T$ which becomes zero at 849° K (576° C) The naphthene is favoured at lower and the olefine at higher temperatures, but the lines intersect at such a small angle that the computed equilibrium constant varies only from 8 3 at 700° K down to 0 2 at 1,000° K, so that appreciable yields might be obtained in either direction throughout the cracking range Aluminium chloride probably catalyzes this and similar reactions at moderate temperatures

Another type of isomerization is that of normal paraffins into branched chain structures Petrov and co-workers [62, 1935] have investigated such reactions of *n*-heptane and *n*-octane at 300 to 400° C and found maximum conversions of only 27% and 23 3% respectively Callingaert and Flood [10, 1935] claim *n*-heptane gives only 4% isomerization These results are consistent with the conclusion reached above that the straight chain hydrocarbon has a slightly lower free energy than its isomers The former investigators observed a moderate shifting of the double bond of hexene-1 to the 2 or 3 position, in agreement with the previous results of Norris and Reuter [57, 1927] Hurd and Goldsby [34, 1934] and Ipatieff, Pines, and Schaad [35, 1934] also found shifting of the double bond in both directions in the case of the butenes In general the isomer with the double bond nearer the middle seems to be slightly the more stable

Free radicals are favourite intermediates in explaining some pyrolytic reactions Such radicals as triphenyl methyl have a quasi-stable existence and therefore a determinable free energy, but they are not concerned in the present discussion We might make a rough estimate of the free energy of the methylene radical, $-CH_2-$, by supposing that it bears the same relation to that of methane as that of ethylene (more strictly ethylidene $CH_3CH=$) does to that of ethane This would give

$$\Delta F^\circ = 12{,}500-6T \qquad (38)$$

Like acetylene, its stability should increase with temperature, and even in the cracking range should exceed that of most hydrocarbons, but because of its free valencies its high reactivity prevents its isolation Rice and Dooley [66, 1934] have concluded that it is not formed in the pyrolysis of methane, although the methyl radical is formed, but Kassel [44, 1935] contends that methyl cannot possibly be the intermediate, and that methylene is more probable We cannot evaluate the free energy of neither methyl nor of methine, ethyl, &c, even approximately nor would it be of much significance if we could, since to complete the reaction the reverse of the free energy of the radical would be involved, and this would cancel out (cf Patat [60*a*, 1936], Voge [79*a*, 1936])

Origin of Petroleum

The thermodynamic relations of the hydrocarbons justify some considerations upon the origin of petroleum Brooks [7, 1934] presented a comprehensive discussion of this subject from a chemical viewpoint His conclusion was that there is no valid evidence for a higher temperature in the formation of petroleum than one which would permit life, say 100° F, and implied that it may have been formed from complex organic matter by fermentation This is contrary to the ideas of some others who have been led by the extreme complexity of petroleum to suppose that the complexity was due to thermal cracking of fats or waxes or other organic matter His points related to thermodynamics are (1) that no hydrogen, carbon monoxide, or olefines have ever been found in natural gas associated with petroleum, although these gases are always found in cracking reactions (assuming the presence of oxygen containing material in the case of carbon monoxide), (2) that usually no solid carbonaceous material is associated with petroleum as would be the case if there were cracking, (3) that petroleum often does contain naphthenes and aromatics, which are characteristic of high temperature cracking, but no liquid olefines

Some hold the idea that a longer time at a lower temperature is equivalent in cracking to a shorter time at a higher temperature, since this is true over a limited range of temperature However, it would not be true of moderate temperatures, 100 to 250° C, as compared with ordinary cracking temperatures, 400 to 800° C, even in 'geologic time', since the types of hydrocarbons which are stable are different Most petroleum deposits do not correspond in composition to equilibrium conditions at any temperature, since they usually contain appreciable quantities of naphthenes To illustrate this point, calculations are made in Table VI of the equilibrium percentages at atmospheric pressure of *n*-hexane, a hexene, cyclohexane, and benzene, representatives of the four classes of hydrocarbons on the assumption that no carbon–carbon bonds are broken The temperature range is 550 to 600° K (277 to 327° C), at which the transition from paraffin to aromatic takes place Cyclohexane rises to a maximum percentage of only 1% and then decreases again, while the olefine remains negligible at all temperatures Pressure would shift all equilibria towards paraffins

TABLE VI

Equilibrium Percentages of Hydrocarbons

Temp	*n-Hexane*	*Hexene*	*Cyclohexane*	*Benzene*
550° K	85%	0 006	0 8	14
570°	69	0 01	1 0	30
600°	34	0 01	0 6	65

Of course, the presence of aromatics, if produced by cracking, implies the presence also of hydrogen which would be formed as a by-product We must consider the possibility that petroleum was formed by slow 'cracking' at about 600° K (327° C) giving substantial amounts of aromatics and paraffins, together with hydrogen, some of which was lost by diffusion or oxidation, and that subsequently at lower temperatures the remaining hydrogen recombined with some of the aromatics forming naphthenes rather than the still more stable paraffins, because of the much simpler mechanism This process would be sound thermodynamically if it were not invalidated by other chemical and geological evidence The principal difficulty from the chemical standpoint is the uniform absence of hydrogen from natural gas, since (*a*) in some of the more recent deposits the hydrogenation would be expected to be incomplete, (*b*) complete loss of hydrogen by diffusion is improbable in view of the frequent presence of helium in natural gas, (*c*) loss of hydrogen by oxidation is likewise improbable because of the common presence of hydrogen sulphide, which is more readily oxidized than hydrogen

Barton [4, 1934] also discussed 'Transformation of Petroleum in Nature' He showed that generally the more recent petroleum deposits are heavier or more naphthenic than older ones, and reasoned that 'proto-petroleum' is naphthenic, and in the course of geologic time becomes more paraffinic, although with Brooks he insists on a very low temperature (generally below 50° C) In the absence of hydrogen as source material to bring about this enrichment with hydrogen, Barton postulated interaction of methane with the naphthenic oil Typical of this process is the reaction

$$CH_4 + C_6H_{12} \text{ (cyclohexane)} \rightarrow C_7H_{16},$$

the free energy of which is found from equations (1*a*), (27), and (14*a*) to be

$$\Delta F^0 = +1{,}630 + 13\ 6T \qquad (39)$$

This is sufficiently positive at all temperatures to make the reaction impossible thermodynamically as well as kinetically in view of the extreme inertness of methane even at much higher temperatures than those postulated

These considerations lead the author of this article to accept Brooks' conclusion (p 187) that 'organic materials as stable as the paraffins once formed and sealed in the sedimentary rocks, undergo no further chemical change whatever under the conditions of temperature and pressure existing in sedimentary rocks even of great geological age and depth' The difference in composition of younger and older deposits of oil is due more likely to differences in the source material or in the original reactions than to a progressive change in the oil

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THE THEORY OF CRACKING

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CRACKING is the term commonly used for the thermal decomposition of hydrocarbons, particularly as practised in the refining of petroleum, where the operation is mainly used for the production of motor fuel The purpose of cracking is primarily to produce low-boiling constituents by breaking down the larger molecules A secondary consequence arises from the fact that the products are, by virtue of their structure, less susceptible towards knocking in gasoline engines than most straight-run gasolines of a corresponding volatility Although the chemistry of cracking is complicated, due to the highly complex nature of petroleum, and not well understood, it has been possible from a commercial viewpoint to establish such controlling factors as reaction rate, equilibrium phenomena, &c , which are necessary for practical refinery operation For this reason the actual reaction mechanisms have been more or less neglected by the oil industry until the past few years, when it became generally recognized that such fundamental knowledge is an essential aid in successfully applying the art

Studies of the pyrogenic behaviour of pure compounds, comprising the various simpler types known to be present in petroleum, have and still are being actively pursued so that at the present time it is possible to obtain by analogy some idea of the mechanisms involved in the cracking of the more complex mixtures With the continual improvement in analytical technique, rapid advances towards a more comprehensive generalization of the theory of cracking may well be expected in the near future

In view of the rapid advances in the cracking industry and the great amount of research currently being done in this and allied fields, it stands to reason that there have been developments which have changed the authors views on some of the points presented in this discussion, which was submitted in 1935 By way of illustration, reference is made in this chapter to the possibility of complicated bimolecular primary reactions taking place in the thermal decomposition of the lower molecular weight paraffins Recent advances in the study of free radicals and of reaction kinetics have led to a more simplified concept of the mechanism of these reactions This subject was discussed in considerable detail by the senior author at a meeting of the New York Section of the British Society of Chemical Industry on April 3, 1936 In other cases, new facts might either have been introduced to further substantiate the views presented or might have served to modify some of the opinions ventured On the whole, however, the authors feel that the theory presented here incorporates the best existing knowledge on the mechanism of the cracking operation

Chemical Composition

The various classes of hydrocarbons behave differently towards thermal dissociation, particularly with respect to thermodynamic stability and in the nature of their dissociation products It is therefore important to consider the various types found in petroleum These vary with the source of the crude, but it is a general rule that the lower fractions consist of various isomeric paraffin hydrocarbons ranging from methane upwards. The intermediate fractions are partly paraffinic and partly single-ring aromatics and naphthenes with or without short side chains, while the heavier components, with the exception of wax which may be present, consist of single and condensed rings with side chains of varying lengths Although simple paraffin hydrocarbons of high molecular weight are found in appreciable amounts, particularly in the so-called paraffin-base crudes, Mabery's classic work has shown that the greater portion of the paraffinic constituents exist as radicals linked to ring compounds, the rings being either naphthenic or aromatic in character No investigator has yet reported the existence of any significant quantities of olefines in crude oil

Analysis of the various types of crude oils show that they contain on the average two atoms of hydrogen or slightly less per atom of carbon Actually the ratio of hydrogen to carbon is higher in the lighter fractions (as exemplified by the lower paraffins) but decreases gradually as the molecular weight increases This progressive decrease in the hydrogen-to-carbon ratio with increase in boiling-point is an important factor in the cracking and hydrogenation of petroleum

Primary and Secondary Reactions

The reactions undergone during the thermal decomposition of hydrocarbons are conveniently divided into two classes designated as primary and secondary reactions A primary reaction in general is one in which the parent hydrocarbon is either in equilibrium with the decomposition products or forms non-reversible fragments, while secondary reactions include all those which the products of a primary reaction undergo A determination of what products are formed as the result of a primary reaction is very useful in interpreting reaction mechanism which would be otherwise obscure A useful means of identifying these initial products, applicable to the simpler hydrocarbons, has been found in the extrapolation of the mol composition of the reaction products to zero conversion [32, 1931] which holds in all cases where the reaction velocity of the secondary reactions is of a lower order [19, 1934]

Two important unimolecular primary reactions can occur [1, 1866] equilibrium involving hydrogen, and [2, 1867] an irreversible splitting of the carbon-to-carbon bonds Equilibrium involving hydrogen, for example

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2 \text{ (for paraffins)}$$

$$C_nH_{2n} \text{ (cyclic)} \rightarrow C_nH_{2n-2,\,4} \text{ \&c (cyclic)} + 1, 2, \text{ \&c } H_2$$

is thermodynamically possible and has been shown to occur by numerous investigators

The major primary reaction comprises splitting the carbon-to-carbon bond This is more likely to occur than the former, since the activation energy for a carbon-to-carbon rupture is about 71 kg -cals against about 93 3 kg -cals for a carbon-to-hydrogen rupture These are the values now in use by Rice and his co-workers [27, 1931] They are somewhat higher than those originally determined by Fajans [9, 1922]

In addition, there are indications of more complicated bimolecular primary reactions For example, careful studies of the pyrolysis of simple paraffins indicate that overall reactions of the following general type can occur to a considerable extent

$$2C_3H_8 \rightarrow C_2H_6 + C_4H_{10}$$

Secondary reactions embrace all those reactions which are generally termed recracking and differ from primary reactions in definition only In addition to these reactions, however, polymerization becomes an important factor The formation of a branched olefine from two olefines and cyclization can occur under cracking conditions Specific examples of these various reactions will be taken up in more detail later

The Pyrolysis of Paraffins

As a general rule, it has been found that for hydrocarbons of the same molecular weight, paraffinic chains have the greatest tendency to crack in the temperature range covered by commercial liquid- and vapour-phase cracking (400 to 600° C)

The carbon-to-carbon rupture can theoretically be considered to take place in three ways

$$(1)\ R\,CH_2\ CH_2\ CH_2R' \rightarrow RCH_3 + CH_3R' + C$$

$$(2)\ R\,CH_2\ (CH_2)_2\ CH_2R' \rightarrow RCH{-}CH_3 + CH_2{=}CHR' + H_2$$

$$(3)\ R\,CH_2\ CH_2\ CH_2R' \rightarrow RCH{=}CH_2 + CH_3R'$$

Sachanen and Telicheyev [31, 1929] show that the rupture takes place exclusively according to the third reaction The absence of carbon in the primary reaction products definitely excludes (1), and any hydrogen formed does not occur according to (2), but from dehydrogenation

The primary reaction products have been established, especially for the lower members of the series For example, in the cracking of ethane only two primary products have been identified so far, i e ethylene and hydrogen, which are formed according to the reaction

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

The known primary products of propane are propylene, ethylene, methane, and hydrogen which are formed according to the following reactions

$$(1)\ C_3H_8 \rightarrow C_3H_6 + H_2$$

$$(2)\ C_3H_8 \rightarrow C_2H_4 + CH_4$$

Normal butane forms butylene, propylene, ethane, ethylene, methane, and hydrogen as primary products

$$(1)\ C_4H_{10} \rightarrow C_4H_8 + H_2$$

$$(2)\ C_4H_{10} \rightarrow C_3H_6 + CH_4$$

$$(3)\ C_4H_{10} \rightarrow C_2H_6 + C_2H_4$$

As the series ascends the number of possible initial reaction products increase making it more and more difficult to distinguish primary reactions The extent to which any of these reactions occur is largely dependent on temperature and the extent of dissociation This is illustrated in Figs 1 to 4, where cracking data for butane and isobutane, as typical examples, have been assembled Fig 1 from the data of Neuhaus and Marek [24, 1932], and Fig 2 from the data of Pease [26, 1930], represent the change in the composition of the reaction products with change in extent of decomposition and temperature, respectively Fig 3 from the data of Marek and Neuhaus [23, 1933], and Fig 4 from data of Hurd and Spence [20, 1929], illustrate the effect of the same variables on the cracking of isobutane

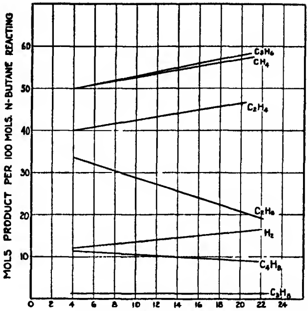


FIG 1 Cracking of *n*-butane at 650° C

The olefines formed are capable of existing in their various isomeric forms For example, in the case of butylene it has been shown that there is an equilibrium between 1 and 2 butylene and that the latter occurs in both the cis and trans form [11, 1933] In the rupture of the carbon-to-carbon bond it is quite probable that the olefine has the double bond in the alpha position first Further activation brings about a migration at least to the beta position to satisfy equilibrium conditions

By the use of hydrogen active catalysts, equilibrium constants for the dehydrogenation of some of the simpler

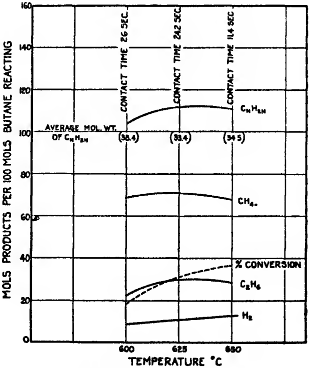


FIG 2 Cracking of *n*-butane.

paraffins have been obtained [12, 1933], at various temperatures from which it is seen that the extent of the C–H bond dissociation tends to increase with temperature Particularly the branched paraffins with a tertiary carbon lose hydrogen very readily Actually, however, in cracking, olefine formation by dehydrogenation ceases to be an important factor as the molecular weight increases, practically all of the decomposition occurring through the rupture of the carbon-to-carbon bonds

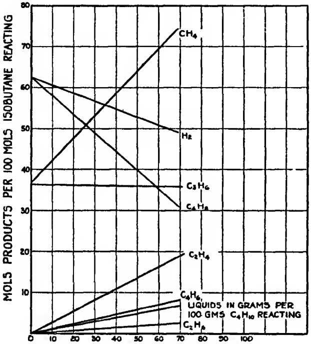


Fig 3 Cracking of isobutane at 650° C

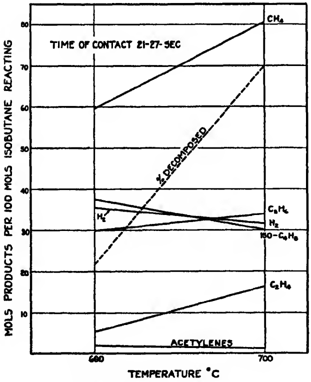


Fig 4 Cracking of isobutane.

The point of the rupture for normal paraffins in general seems to follow the law of chance with all of the theoretically possible complementary paraffins and olefines being found in the reaction products On the other hand, there is evidence in the case of the higher paraffins of the central carbon bonds being the most susceptible towards splitting [29] Thus it has been shown that at lower temperatures hexadecane forms octane and octene with practically no gas formation At higher temperatures, however, the reaction products tend to become more complex [15, 1924] The same general rule seems to hold true for branched paraffins where any of the carbon bonds of a primary, secondary, or tertiary carbon may break

Besides recracking, polymerization of the olefines formed becomes an important secondary reaction in the pyrolysis of paraffins, especially at higher temperatures and pressures At high temperature the liquid end products are predominantly cyclic For a more extensive discussion of the decomposition of paraffinic hydrocarbons the reader is referred to a detailed literature survey by Egloff and coworkers [7, 1930], and a recent review by Frey [10, 1934]

Pyrolysis of Olefines

Although the occurrence of olefines in crude oils is insignificant, nevertheless they play a most important role in cracking, since they are formed as one of the chief products of the primary reactions of paraffins and alkylated cyclics Olefines are in general more resistant to heat than the corresponding paraffins, although certain exceptions to this rule have been observed [18, 1934] Allene, di-alkyl, and 4-methyl 1-pentene, for example, decompose at appreciably lower temperatures than the corresponding paraffins Like the paraffins, the stability of olefines decreases with increasing molecular weight

Olefines may dehydrogenate to produce diolefines Very little is known of the kinetics of this reaction even for the simple olefines, but it can be assumed to parallel the paraffin to olefine step in the range of corresponding molecular weight As in the case of the paraffins, dehydrogenation of the olefines in comparison with the carbon-to-carbon rupture becomes less probable as the molecular weight increases

When an olefine undergoes carbon-to-carbon rupture, two courses are possible, with the formation of either a paraffin and a diolefine or two olefines, as for example

$$RCH_2\ CH_2\ CH_2CH{=}CHR' \rightarrow RCH_3 + CH_2{=}CH\ CH{=}CHR'$$
$$RCH_2\ CH_2\ CH_2CH{=}CHR' \rightarrow RCH{-}CH_2 + CH_3CH{=}CHR'$$

The indications are, at least for the lower cracking temperatures, that the formation of two olefines is the predominating reaction

The most important role played by olefines in pyrolysis is their ability to polymerize into both cyclics and higher molecular weight olefines It was early considered [1, 1866, 2, 1867] that cyclics are chiefly formed through the polymerization of three mols of acetylene The evidence that this reaction occurs at the higher temperature levels, where appreciable quantities of acetylene are formed, appears to be plausible, but some other explanation is required for extensive cyclization at lower temperatures, where acetylene formation is negligible

Recent facts [4, 1918, 5, 1934, 32, 1931] point to cyclization through the olefines Schneider and Frolich [32, 1931], have shown that at 725° C. and ½ of an atmosphere pressure, the main product obtained on cracking ethylene is butadiene Reference to Fig. 5 will show that approximately 36 mols of butadiene and 41 mols of hydrogen (amounting to about 72% of the ethylene reacting) are formed as initial products The fact that butadiene appears as a primary reaction product and in quantities about 14 times as large as butylene point to its formation from 2 mols of ethylene with the elimination of 1 mol of hydrogen

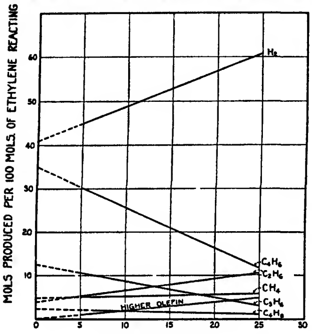


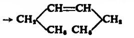
Fig 5 Pyrolysis of ethylene at 725° C and ½ atmospheric pressure

$$2C_2H_4 = C_4H_6 + H_2$$

as proposed by Davidson [4, 1918] Dunstan, Hague, and Wheeler [5, 1934], on the other hand, show from their experiments where appreciable butylene is formed (probably due to different temperature levels) in the reaction product from the cracking of ethylene that the apparent mechanism is first polymerization to butylene followed by dehydrogenation

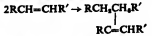
The formation of cyclics from butadiene proceeds by further polymerization with the olefine, apparently by the following mechanism

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2$$



from which aromatics are produced by dehydrogenation As will be seen later, this tendency to cyclize is one of the important factors in tar and coke formation.

The other type of polymerization occurring may be represented, for example, by the formation of a branched olefine from two simpler olefines as illustrated by



$$2RCH{=}CHR' \rightarrow \underset{\textstyle RC{=}CHR'}{RCH_2CH_2R'}$$

More complex changes in structure, however, usually occur Whitmore [35, 1932, 36, 1934] recently proposed a general theory based on the octet theory which agrees with experimental facts at least for polymerization of olefines by catalysts containing H ions The first step involves the addition of a hydrogen ion to the extra electron pair in the double bond, leaving one carbon with only 6 electrons This structure can then undergo changes which are characteristic for an atom with a deficiency of electrons, among which is polymerization This involves the addition of the positive organic fragment to another molecule of olefine The result is a larger fragment which can either unite with an additional olefine or lose a proton to give an olefine molecule after rearrangement

Table I contains a summary of the decomposition products of some of the simpler olefines as given by Hurd [18, 1934]

Pyrolysis of Cyclo-paraffins and Cyclo-olefines

In addition to the so-called naphthenes and unsaturated cyclo-compounds there are included in this group the same cyclo-compounds with aliphatic side chains The thermal stability of the alkylated cyclics, however, is usually determined by the stability of the side chains, which are generally much less stable than the rings

The pyrolytic behaviour of the unsubstituted cyclics is not well known owing to their relatively high heat stability When decomposition does take place at the higher temperatures where opening of the ring can occur, the primary products formed are so much less stable than the parent compound that disintegration to hydrogen, methane, and complex carbonaceous materials immediately follows Consequently these reactions become highly complex and are associated with excessive coke formation For this reason most of the studies of the behaviour of cyclics have been carried out with the aid of catalysts and the information thus obtained does not always apply to heat effects alone

Egloff and co-workers have published a comprehensive literature survey covering this class of compounds [8, 1931] It is apparent from their summary that the following reactions can occur

(1) Carbon-to-carbon rupture, resulting in opening of the ring

Table I

Mols of Major Gaseous Products from 100 Mols of Decomposed Olefine at 650° C

Olefine	*Contact time, sec*	*Extent of decomposition*	$C_nH_{2n}+2$	H_2	*Smaller olefines*	C_2H_2	*Isomeric olefines*	*Liquids % by wt of olefine decomposed*
Ethylene	350–450	26	24	10		13		Some
Propylene	30	16	42	8.3	31	3		20–5
Isobutylene	27	33	47	15	20	3.5		40
1-butene	11	57	44	3.7	33(C_3H_6) 16(C_2H_4)		20	30
2-butene	13	44	28	5.5	19(C_3H_6) 4(C_2H_4)		25	30

(2) Hydrogenation and dehydrogenation.
(3) Polymerization and depolymerization.
(4) Isomerization

A consideration of the three to eight carbon nuclear rings shows that the stabilities of compounds of each type are widely dissimilar and that reactions common to one ring will not take place in another

Cyclopropane, cyclobutane, cycloheptane, and cyclooctane will undergo a splitting of the carbon bonds Strangely enough, the stability increases with the number of carbon atoms in the ring

Cyclohexane dehydrogenates at lower temperatures than are required for ring splitting However, production of aromatics cannot in general be said to take place primarily by simple dehydrogenation in the absence of catalytic effects

Cyclopentane is highly resistant both as to ring splitting and dehydrogenation in accordance with the claims that the naphthenes present in cracked naphtha are mainly 5 carbon nuclear [31, 1929]

The main reaction product of cyclopropane has been found to be propylene Cycloheptane produces methyl cyclohexane Cyclo-octane goes to bicyclo-octane and cyclohexane produces cyclohexene which in turn dehydrogenates to benzol or splits to form butadiene and ethylene

Unsaturated ring compounds, as for example cyclopentadiene, are analogous with chain compounds containing the same type of unsaturation The conjugated doubly unsaturated cyclics readily polymerize

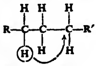
Pyrolysis of Aromatic Hydrocarbons

The nucleus of aromatic hydrocarbons is considered to be stable in the temperature range covered by commercial cracking, since excessive temperatures are required for the ring to open in the absence of a catalyst The stabilities of substituted aromatics, on the other hand, are dependent on the relative stabilities of the side chains, which may be olefinic or paraffinic in character Egloff and Moore [6, 1917] studied the decomposition of an aromatic base oil containing about 70% xylene and 30% higher alkylated benzenes at a temperature of 500 to 800° C and 11 atm pressure. The trend of decomposition was shown to be in the following order

Higher alkylated benzenes
Lower alkylated benzenes
Toluene
Benzene

Mechanism of the C–C Rupture

So far in this discussion cracking reactions have been considered statistically without consideration of the actual mechanisms involved Several theories have been advanced in an attempt to visualize how the carbon-to-carbon rupture takes place and at the same time quantitatively account for the various reaction products If the splitting of a paraffin into an olefine and a complementary paraffin is considered as a primary step, then the hydrogen bound to the beta carbon of one of the fragments must migrate to the alpha carbon of the other fragment, thus.



which does not appear plausible

The search to overcome this difficulty has led to the development of a number of theories which, although applicable to much of the existing data, are still considered incomplete and subject to further proof Some of these will be briefly outlined

Burk has postulated a partial ionization process in which one radical may transfer its allegiance to another [3, 1931] The Polanyi-Wagner equation for unimolecular velocity constants $\left(K = Ve - \frac{t}{RT}\right)$ was modified to be appropriate for the thermal decomposition of straight chain paraffins where it was shown to fit existing data for low conversions

Kassel [21, 1933] considers it possible to give a nearly complete account of decomposition in terms of 1–1, 1–2, and 1–4 unsaturation, although the data on the kinetics of decomposition are still insufficiently complete to prove or disprove this assumption This theory accounts for the formation of more than two products in a primary decomposition without the assumption of free radicals

Rice has developed cracking by the intermediate formation of free radicals into a working theory He assumes that when a hydrocarbon decomposes it dissociates into two free radicals which react with the surrounding hydrocarbon molecules, thereby initiating a chain reaction in which methyl, ethyl, and hydrogen act as the carriers Larger radicals are assumed to decompose to yield one or more molecules of an olefine and either a methyl group, an ethyl group, or atomic hydrogen If the relative chances of reaction of primary, secondary, and tertiary hydrogen atoms are 1 2 10 respectively, the decomposition products of all paraffin hydrocarbons can be calculated quantitatively [27, 1931, 28, 1932] Normal butane, for example, is considered to decompose according to the following scheme

$$P_1\quad CH_3CH_2CH_2CH_3 \rightarrow CH_3{-} + CH_3CH_2CH_2{-}$$

$$P_2\quad CH_3CH_2CH_2CH_3 \rightarrow 2CH_3CH_2{-}$$

$$S_1\quad CH_3CH_2CH_2{-} \rightarrow CH_2{=}CH_2 + CH_3{-}$$

$$\left.\begin{matrix} S_2 \\ S_3 \end{matrix}\right\}\text{Same as } A_1 \text{ and } A_2 \text{ where R–CH CH CH}$$

$$A_1\quad CH_3CH_2CH_2CH_3 + R{-} \rightarrow RH + CH_3CH_2CH_2CH_2{-} \rightarrow$$

$$RH + CH_2{=}CH_2 + CH_3CH_2{-} \begin{array}{l} \nearrow CH_3CH_2{-} \qquad A_1' \\ \searrow CH_2{=}CH_2 + H \quad A_1'' \end{array}$$

$$A_2\quad CH_3CH_2CH_2CH_3 + R \rightarrow RH + CH_3CH(CH_2CH_3){-} \rightarrow$$

$$RH + CH_3CH{=}CH_2 + CH_3{-}$$

$$R = CH_3{-},\ CH_3CH_2{-},\ H$$

P_1 and P_2 represent the primary reactions, S_1, S_2, and S_3 represent the secondary reactions and A_1 and A_2 the chain mechanisms Table II [27, 1931] illustrates the agreement between experimental and calculated results

Variables affecting Pyrolysis

Since the controlling factors in a cracking operation have been found to be reaction rate and equilibrium phenomena it is important to know the effect of time, temperature, and pressure on these factors

Within narrow limits, time and temperature are practically interchangeable, i e a longer time at a lower temperature will bring about the same overall result as a higher temperature and a correspondingly shorter time Considerably beyond these limits there is a lower temperature where the hydrocarbon is stable and a higher temperature region where the reaction cannot be controlled, no matter how short the contact time Temperature influences the course of the primary decomposition to some extent For example, increase in temperature increases the olefine content of the primary products (low pressure), but the main effect of temperature is its influence on reaction velocity

Pressure should have little effect on reaction velocity since the overall cracking reactions calculate as if of the first order Very high pressures, on the other hand, probably lower reaction rate as indicated by the work of Hugel and Artichevitch [17, 1928] It does, however, permit the use of higher temperatures by virtue of raising the boiling-point, when liquid- or mixed-phase cracking is desired, and thus indirectly aids in increasing reaction velocity Pressure greatly influences the composition of the products of cracking Where low pressures favour a high gas- to liquid-product ratio, high pressures tend to depress gas formation This is due in part to inducing polymerization of the gaseous olefines

These variables will be discussed in greater detail in connexion with gas-oil cracking

TABLE II

Decomposition of n-Butane

Upper part Pease and Durgan's Results Lower part Calculated

Temp, ° C	*Decomp %*	CH_4%	H_2%	C_2H_6%	C_2H_4%	C_3H_6%
600	18 5	33 5	4 5	11	51	
625	22 0	31 0	5 0	13	51	
650	26 0	30 0	6 0	12	52	
550	5–10	29 0	21 0		21 0	29 0
600	5–10	28 5	21 5		21 5	28 5
650	5–10	28 0	22 0		22 0	28 0

The relative amounts of H_2 and C_2H_6 cannot be predicted The figures for C_2H_4 and C_3H_6 have been calculated assuming that reaction A_1 is negligible The products will contain a small amount of propane produced by S_2 and S_3

Pyrolysis of Hydrocarbon Mixtures (Gas-oil Cracking)

In the cracking of petroleum where any or all of the various classes of hydrocarbons previously mentioned are present, the situation is quite different from cracking isolated members of each series Here the course of cracking is governed in general by the relative stability of the various constituents, their reaction rates and equilibrium phenomena

Examination of the thermodynamic stability of hydrocarbons as expressed by their free energy of formation from the elements shows that all petroleum hydrocarbons with the exception of methane and possibly ethane are potentially unstable at temperatures above 200° C At the lower temperatures up to approximately 300° C, however, the reaction rates are so slow that no perceptible decomposition takes place, even in the case of the most unstable molecules As the temperature increases, the hydrocarbons, with the exception of acetylene, become more and more unstable, each series having different temperature coefficients The stability of acetylene, on the other hand, increases with temperature Paraffin and polymethylene are more stable at the lower temperatures, while aromatics are more stable at the higher temperatures Above 600° C no hydrocarbon other than acetylene is thermodynamically stable with respect to the elements [25, 1932].

The fact that the stability of acetylene increases with temperature, however, is considered to be of little importance as far as most of the present cracking processes are concerned, because free energy relationships are such that acetylene apparently is not formed to any appreciable extent at the temperatures involved

Such thermodynamic considerations lead to the important conclusion that, with the temperatures employed in practice, the cracking of a hydrocarbon into smaller hydrocarbons is essentially a non-reversible process On the other hand, reactions involving liberation of hydrogen by simple dehydrogenation are reversible

While free energy relationships determine whether a certain type of reaction is possible, those reactions which do take place in cracking of a complex mixture of hydrocarbons are largely governed by relative reaction rates In general, it has been found that in the temperature range 400 to 600° C (covering most commercial liquid- and vapour-phase cracking processes) the various classes of hydrocarbons previously discussed separately may be listed as follows in the order of increasing stability This comparison is based on representative compounds of equal molecular weight

(1) Paraffins	C_nH_{2n+2}	(chains)
(2) Olefines	C_nH_{2n}	"
(3) Diolefines	C_nH_{2n-2}	"
(4) Naphthenes (6 carbon nuclear)	C_nH_{2n}, C_nH_{2n-m} (rings and condensed rings)	
(5) Naphthenes (5 carbon nuclear)	C_nH_{2n}, C_nH_{2n-m} (rings and condensed rings)	
(6) Aromatics	C_nH_{2n}, C_nH_{2n-m}	(rings)

The stability of the higher members of any given series, with the exception of the naphthenes, increases with decreasing ratio of hydrogen to carbon in the molecule Furthermore, it is a general rule that side chains are somewhat more stable than the ends of straight chains

The relative order of stability just outlined refers strictly to the temperature range specified At higher temperatures, 600 to 700° C or perhaps even lower, diolefines become more stable than naphthenes Thus it is possible by cracking at such high temperatures to convert naphthenes into diolefines which in turn give aromatics by subsequent polymerization and liberation of hydrogen [14, 1930]

The variation of reaction velocity constants with temperature are shown in Fig 6 as assembled by Geniesse and Reuter [16, 1932], for a typical gas oil, several naphthas, and a few pure hydrocarbons The curves show the rates of decomposition to increase as the molecular weight increases

As the temperature of these complex hydrocarbon mixtures is increased in the cracking process, noticeable decomposition usually begins to occur at temperatures above 300° C This point of incipient cracking, however, is dependent not only upon the temperature but also upon the nature of the most unstable hydrocarbons present in the charge stock Beyond this point reaction rate doubles for an increment of 14° C at 450° C, and gradually falls off to an increment of 21° C at 600° C [16, 1932]

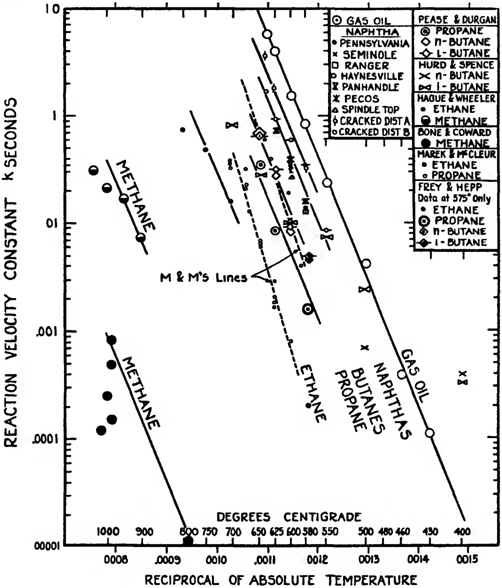


Fig 6 Variation of reaction-velocity constant with temperature

According to the relative stability of the hydrocarbons, it is therefore apparent that aliphatic hydrocarbons break first, followed by the other types as the temperature is increased, by the various reactions previously outlined As the temperature increases above 700° C more or less complete break-down occurs, characterized by excessive formation of coke and hydrogen Acetylene begins to appear at this stage

The nature of petroleum coke and the mechanism of its formation are not well understood, as evidenced by the widely different viewpoints On one hand, it is believed that coke is mainly made up of free carbon, while on the other to consist of highly condensed hydrocarbons Mechanisms which will explain the formation of each type are consequently widely different The fact of the matter is that a considerable portion of the so-called coke is chloroform and naphtha soluble and therefore cannot consist of elementary carbon In line with the mechanism discussed in this article, coke formation is largely the result of progressive cracking, polymerization, and condensation reactions leading through tar to a more and more complex product of decreasing hydrogen content

The olefines resulting from the primary reactions, particularly those of higher molecular weight, polymerize readily and in this way there are produced new compounds whose molecular weight tends to exceed that of the original stock It is important to note, however, that the unsaturated molecules possess less hydrogen on a carbon atom basis than the original hydrocarbons from which they are formed and consequently the same holds for the polymerization product On prolonged exposure to high temperature the polymerized material undergoes recracking with the formation of new unsaturated compounds which give rise to further polymerization

Progressive reactions of this type, along with condensations of the ring compounds, lead to the formation of more and more complex compounds of decreasing hydrogen-to-carbon ratio and with this decrease the material becomes more refractory, i e resistant to temperature The final products are therefore

(1) Gaseous and low-boiling liquid compounds, relatively high in hydrogen

(2) Liquid reaction products of higher molecular weight, tar, and petroleum coke, possessing a low ratio of hydrogen to carbon

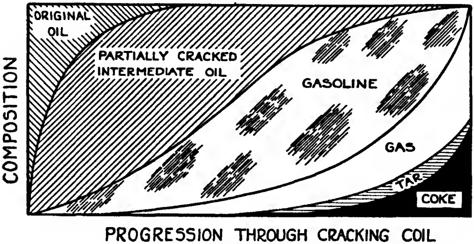


FIG 7 Degree of cracking as a function of time of contact

This is illustrated in a qualitative way by Fig 7 [33, 1929], which shows the changes taking place as the cracking progresses

Hence it is seen that the complete cracking process is a sequence of decomposition and polymerization reactions, the character of the final products being determined by the nature of the hydrocarbons present in the original charging stock, by the temperature and pressure of the operation as well as the time of exposure to cracking conditions

Polymerization is a bimolecular reaction and its rate therefore is, under parallel conditions, proportional to the square of the pressure The rate of polymerization also increases with temperature but apparently much less rapidly than the rate of simple molecular break-down If the temperature is high and pressure low, there is a tendency for polymerization to take place with simultaneous liberation of hydrogen By increasing the pressure, however, the hydrogen evolution is counteracted

This effect of pressure has been demonstrated with ethylene and propylene At atmospheric pressure a large amount of hydrogen is evolved and benzene is found in appreciable quantities together with other high-boiling materials There is little evidence of the formation of non-aromatic products If the pressure is increased gradually while the temperature is kept constant, hydrogen formation decreases with a simultaneous decrease in the aromatic character of the products, until at a pressure of several thousand pounds the liquid material formed is decidedly non-aromatic, even when the temperature is maintained as high as 600° C [13, 1931]

Vapour-phase, Liquid-phase, and Mixed-phase Cracking

Petroleum hydrocarbons may be cracked either in the vapour phase or in the liquid phase Vapour-phase processes usually are operated at temperatures of the order of 600° C at atmospheric pressure or somewhat above In the so-called liquid-phase cracking the pressures range from a few hundred pounds to 1,000 lb per sq in At temperatures of from 400 to 500° C, McKee has shown that in this temperature range [22, 1928], the bulk of the naphtha hydrocarbons formed are above the critical temperature and that in most cases mixed-phase cracking results At the higher pressures, however, true liquid-phase cracking is approached due to a solution of the lighter ends in the liquefied heavier ends As the temperature is raised the pressure must also be increased in order to accomplish this Most of the so-called liquid-phase processes, however, are operated at pressures not sufficiently high to prevent a substantial portion of the cracked products from accumulating as vapour

The properties of petroleum hydrocarbons discussed in previous sections leads to the obvious conclusion that vapour-phase cracking, operated at low pressure and short time of contact, does not particularly favour polymerization and recracking with resulting coke formation This is illustrated by the fact that both gaseous and liquid products from vapour-phase cracking may contain as much as 50% or more of unsaturated compounds

As the pressure on the cracking unit goes up, coke formation increases, at first rapidly, then more slowly until coke formation passes through a maximum and then decreases with further rise in pressure This peculiar result may be explained when it is considered that with rising pressure there is a gradual change from a true vapour-phase system into one containing increasing quantities of liquid As has been mentioned, polymerization is a bimolecular reaction, its rate increasing theoretically with the square of the partial pressure of the unsaturated compounds and therefore in the beginning approximately with the square of the total pressure in the system With continual increase in pressure the cracked products will be condensed and dissolved in the liquid phase in increasing quantities. In this way the highly unsaturated compounds of medium and higher molecular weight, which are the ones that polymerize most readily, are kept out of the vapour phase and remain in the liquid phase where dilution with the cracking stock slows down the rate of polymerization, the net result being a tendency to conserve the lower molecular weight products With rising pressure the progressive polymerization and recracking reactions, which according to the previous discussion lead to products of gradually decreasing hydrogen-to-carbon ratio and eventually to the formation of petroleum coke, are therefore at first accelerated, but the extent to which they lead to the production of coke passes through a maximum and finally decreases.

The effects of changes of conversion per pass, temperature, and pressure are illustrated by Table III from the work reported by Sydnor [34, 1934] These data substantiate the above conclusion that while there is increase in polymerization at the higher pressure, the result is more fuel oil and less coke Higher gasoline yields are obtained at the lower pressure Increase in temperature at constant conversion per pass and pressure results in a decrease in the ultimate yield of gasoline due to increased gas formation.

Because of the high temperature and low pressure employed, the vapour-phase product is rich in aromatics High conversion to gas is also experienced In comparison the yield of unsaturates and the gas loss for a given charge stock ordinarily are low when the cracking process is operated in the liquid phase

In order to control polymerization and recracking in the liquid-phase process, it is best from a chemical standpoint to reduce the time factor by removing the products after the reaction has progressed to a reasonable extent The residuum after this operation, which has a lower hydrogen-carbon ratio and hence is more refractory, should be subjected to more vigorous conditions than the original stock. In practice, however, the residue is recycled, due to the mechanical ease of such a procedure The increased formation of aromatics resulting from higher temperature cracking is desirable because it reduces the knocking tendency of gasoline With excess production of aromatics, however, the gasoline yield decreases materially, becoming less and less with rising temperature, while coke and gas formation increases.

TABLE III

Ultimate Yields secured by Cracking a 33 7° API Mid-Continent Gas Oil [34]

(All gasoline yields and volatilities calculated to a 100% butane recovery basis)

Pressure, lb per sq in	*200*			*750*			
Temperature (soaker), ° F	*860*	*900*		*860*		*900*	
Conversion per pass	7 5	7 5	20 0	7 5	20	7 5	20 0
Gasoline (400° F end-point), % vol	69 3	67 0	62 0	63 0	59 5	61 5	57 9
Fuel oil (12° API), % vol	24	27 1	23 4	30 0	32 4	29 6	32 0
Gas, % by wt	11 2	11 4	18 0	11 4	11 4	12 6	12 6
Coke, % by wt	2 0	0 2	2 0	0	0 8	0	0 8
Recovery, % by wt	100	100	100	100	100	100	100
	Yields corrected to coke-free basis						
Gasoline (400° F end-point), % by vol	67 4	66 8	60 2	63 0	58 8	61 5	57 2
Fuel oil (12° API), % by vol	28 1	27 5	27 5	30 0	34 0	29 6	33 6
Gas, % by wt	10 2	11 3	16 9	11 4	11 0	12 6	12 2

These data represent complete decomposition of the cycle gas oil into gasoline, fuel oil, coke, and gas in all cases

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COMBINATION CRACKING UNITS

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PROMINENT among the recent developments in refining practice has been the trend towards the close association of cracking with a variety of other operations Out of this trend the individual type of unit operation termed 'Combination' has been evolved The Combination Process is appearing with increasing frequency in current construction Its advent is of general significance in marking a definite departure from the long-practised segregation of the individual cracking and distillation operations

The term 'Combination' is applied to the association of such functions as initial distillation of crude, viscosity breaking, and naphtha reforming, with the main cracking operation, in self-contained systems Usually it involves also the production of ultimate yields of final products The refiner thus has available the facilities for carrying out the processing of crude oil to completion, including cracking, in one operation The advantages are the conservation of waste heat from the cracking system, reduced labour and investment requirements per unit of fresh feed capacity, the reduced handling of intermediate products, and maximum yields of high anti-knock gasoline The importance of these, both in the erection of completely new plants, and in supplementing existing capacity, explains the increasing adoption of combination operations by the industry

While the advantage of associating other functions with cracking has long been recognized, the prevailing methods and the lack of knowledge of fundamentals were factors of restriction for many years These limiting conditions restricted the combinations to elementary forms such as effecting crude topping, steam generation, and similar operations, with the waste heat of cracking systems Indeed, the long-existing size limitations of cracking systems and the lack of precise design data practically excluded more advanced combinations, and favoured complete separation of individual operations

The responsibility for the evolution of present-day Combination Units may be attributed to the research which has been diligently pursued by refiners and engineering firms in the industry In addition to means of applying laboratory results precisely to equipment of commercial size, the research and development work has yielded fundamental operation and design data which were invaluable For the complex combination systems this satisfied an important requirement, by increasing the degree to which precise design could furnish adequate capacity and flexibility of interrelated parts, without resort to the use of inordinate safety factors

The design of each unit is a separate problem defined by the processing requirements and the raw stock Accordingly, it has been indispensable that optimum operating methods and design, developed on laboratory or semi-plant scale equipment, be applicable with accuracy to the commercial design To this end, the research has embraced the field from development of fundamentals to extensive correlations of the small-scale and plant equipment The results achieved are reflected in the commercial installations, now in use, whose actual performance has duplicated within almost negligible limits the performance for which they were designed Finally, the flexibility necessary for optimum operation has been secured, without material overcapacity of individual parts

Consideration of representative types of combination operation is properly introduced by an example of one of the simpler forms, designed for the handling of reduced crude A diagram of this type of installation is presented in Fig 1 Generally, the operations comprise primary cracking, vapour-phase cracking, fuel-oil flashing, and naphtha stabilization

Fresh reduced crude feed is introduced to the fuel flash tower to be preheated with hot flashed vapours, and is collected on a trap-tray, with included heavy condensate, to be passed through the primary cracking section of the heater which discharges into the high-pressure evaporator The feed for the vapour-phase section of the heater is taken from the base of the bubble tower, the boiling range of this stock being regulated by the temperature of the evaporator top, so as to exclude high-boiling fractions unsuitable for the vapour-phase temperatures After passing through its section of the heater, and attaining a temperature of about 960° F , the vapour-phase cracked stream emerges to join the discharge from the primary cracking coil and enter the evaporator The composite fuel oil in the evaporator, under about 200 lb pressure, is released to the fuel oil flash-tower, under low pressure, where it is reduced down to the desired viscosity and the evolved cycle stock vapours are returned to the cracking system The stabilizer operates as an integral part of the system, using recycle gas oil reflux as the source of heat

It will be noted that the heater is of the dual combustion chamber type, separate radiant sections being provided for the two streams, to facilitate control of radiant-heat absorption, although both are served by a common convection zone This arrangement affords the flexibility of two individual furnaces, yet permits the advantageous use of the convection surface and confines the total surface within a single setting

Results of Cracking

Mid-Continent Reduced Crude, 23 2° API, comprising 60–65% of Original Crude

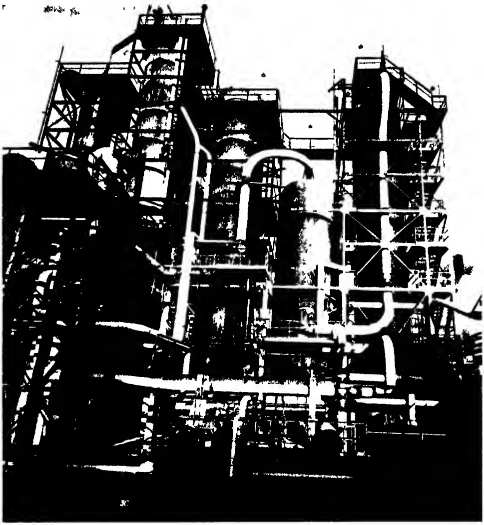
Yields

	%
Gasoline	42 31
Fuel oil	49 03
Gas and loss	8 66
Total	100·00

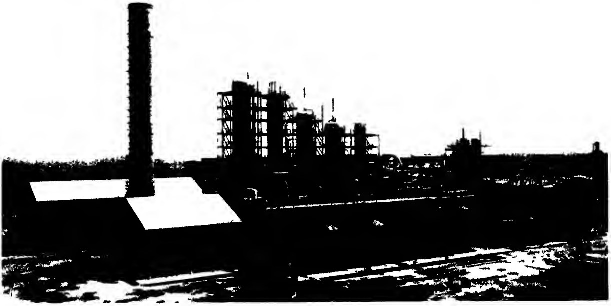
Products

	Gasoline	*Fuel oil*
End-point, ° F	400	
Octane no CFR—M	70	
Viscosity at 122° F (Furol)		196
B S & W (%)		0 24

The operating results of this installation on a reduced crude may be illustrated by the above data, typical of approximately 300 hrs of operation.



View of towers on combination cracking unit Throughput of plant 20 000 barrels per day



Combination cracking unit for the complete processing of crude oil to gasoline and fuel oil Throughput, 32,000 barrels per day

While representing the desirable plant operating conditions, these results do not define the range generally characteristic of the operation The operation is effective on a reduced crude, or similar residual stock, by virtue of the combined fuel-oil flashing and primary cracking steps, and in a more or less recognizable form it appears in other systems

More complex forms of the combination units, as employed for running crude to ultimate products, are shown in Figs 2 and 3 These units represent the advantageous association of crude topping, primary cracking, vapour-phase cracking, fuel-oil flashing, naphtha reforming, clay treating, and naphtha stabilization From crude oil charge, they produce a stabilized gasoline of low gum content and of the desired anti-knock rating, fuel oil, and gas, directly from the system Light fuel or furnace oils may also be trapped out directly if desired The compactness of the equipment serving these functions permits very large quantities of crude to be accommodated without excessive size, which is reflected in outstanding degree in the processing of 20,000 bbl of crude to completion, daily, by one of these units The advantage realized through the elimination of handling of intermediate products is obvious

From the diagrams, it will be noted that the crude oil feed, after preheating with waste heat, is flashed to separate light and heavy straight-run naphtha cuts, the former being ready for incorporation in the finished gasoline, and the latter to be subjected to reforming In the unit shown in Fig 3, provision is made for the additional separation of a kerosine cut in the crude distillation The reduced crude remaining from this pre-distillation is preheated by contact with hot vapours in the fuel-oil flash tower, but Figs 2 and 3 show different methods of its subsequent handling The unit in Fig 2 further preheats and distils the reduced crude, by introduction to the high-pressure evaporator prior to primary cracking The other unit, however, passes the reduced crude direct from the fuel-oil flash tower through the primary cracking coil, and back into the fuel-oil flash tower, thereby favouring segregation of the cracked and virgin stocks

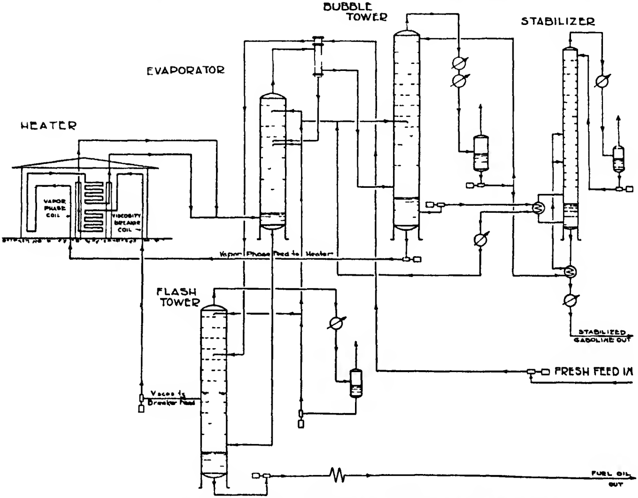


FIG 1 Combination unit employing vapour-phase cracking and viscosity-breaking for residual stocks

These units employ a redistilled circulation system, for the vapour-phase cracking, similar to the one observed in the installation in Fig 1 In both cases the circulating stock is carefully controlled in boiling range for suitability for the vapour-phase temperature employed, and it is made up of fractions distilling over into the bubble tower, from the evaporator, along with an amount of similar quality condensate from the fuel-oil flashing operation In passing through the vapour-phase cracking coil, temperatures upward of 950° F are attained, and the emerging stream is, in one case, soaked in an insulated vessel

The naphtha-reforming operation is applied to the heavy

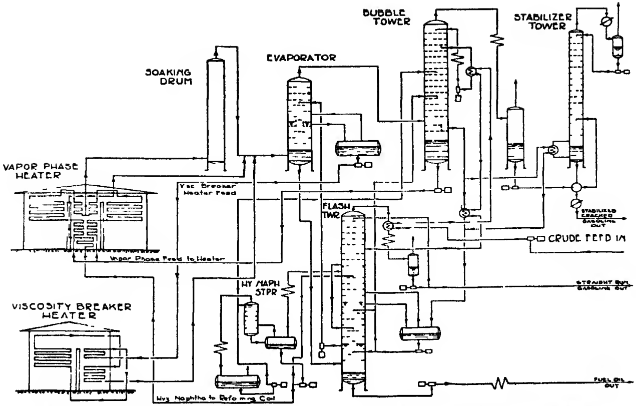


Fig 2 Combination unit for crude feed providing preliminary distillation, naphtha reforming, and cracking to completion

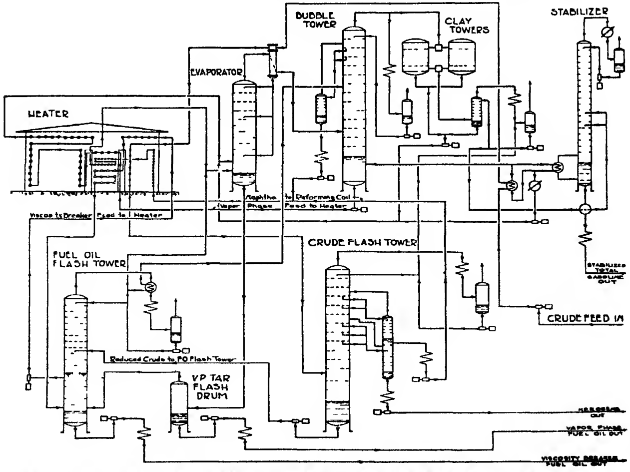


Fig 3 Combination unit for crude feed producing ultimate yields of products direct and employing a single heater and a cycle somewhat modified from Fig. 2

straight-run naphtha cut by digesting this material in a coil at temperatures over 1,000° F, and under pressures of 500 lb and higher—the total products from this heat treatment being discharged into the high-pressure evaporator, and handled subsequently with the vapour-phase cracked vapours The unit in Fig 3 is provided with a withdrawal point for heavy naphtha on the cracking fractionator, which permits inclusion of this stock with the feed to the reforming coil The total vapours leaving the cracking system comprise cracked naphtha produced in the primary cracking, vapour-phase cracking, and reforming, and can be subjected advantageously to Gray refining treatment in the vapour phase, as is shown in Fig 3 The light, straight-run naphtha not requiring such treatment is segregated and combined with the heavier product after treating

The heating facilities employed in these more complex combination operations present numerous unusual features The heating of the three or more individual streams, characteristic of such operations, as well as the handling of extraordinarily high throughputs, have favoured the use of the multi-stream heaters shown in the accompanying figures This trend has carried with it the necessity of precise design, as well as unique arrangements to preclude limiting interference between individual streams or the necessity for large over design in securing a practical degree of flexibility

Fig 2 will be seen to present an individual heater for primary cracking, and another for naphtha reforming and vapour-phase cracking together In the case of the latter, the two radiant sections serve similar functions in vapour-phase cracking parallel streams The vapour-phase feed to this heater amounts to more than 1,300 bbl per hr In Fig 3 the unit utilizes a single heater only, whose duties comprise the heating of the four separate streams required by the operation It will be observed that the separate radiant sections serve separate functions, while still others are served by the convection zone

The performance of these latter types of Combination Unit, since they have been put in service, has been fully in accordance with their theoretical advantages The following representative data are typical of the results secured on the running of a 36–37° API Mid-Continent Crude through one of the larger units above described, and they illustrate the results obtainable commercially

Yields

	%
Straight-run Light Gasoline	15 7
Cracked Gasoline, stabilized	50 5
Total Gasoline	66 2
Fuel oil	24 8
Fuel gas and loss	9 0
Total	100 0

Fuel Consumption

Total for unit—per cent of Crude Charge 5 10%

Products

	Composite gasoline	*Fuel oil*
Grav, °API	61 0	9 4
Viscosity at 122° F (Furol)		175
B.S & W, %		0 54
Octane no CFR—M	70	
I B P, ° F	84	
20%	164	
50%	254	
90%	382	
E P	401	
% Rec	96 0	

The comparatively recent advent of this type of operation has, in the light of its demonstrated capabilities, supplied the refiner with a new tool which fulfils a definite need Accordingly, it is to be expected that the future will witness an increased tendency towards establishing the main cracking operation as the basis around which all heat treating and distillation operations will be closely centred With continued design proficiency, the advantages now being realized from a limited number of combination units should accrue to a greatly increased extent to the industry in general

VAPOUR-PHASE CRACKING

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IT appears that Dalton [3] in 1809 and Faraday in 1825 were among the first to experiment in the field of high-temperature cracking of hydrocarbons Working with the electric arc, they produced, among other substances, benzene, ethylene, and related compounds Silliman in 1855 pointed out many possibilities in this field as a result of his classic research on petroleum In 1862 the grand prize at the London Industrial Exposition was won by Breitenlohner with a burning oil made by high-temperature vapour-phase cracking Many of the fundamental principles of high-temperature cracking were expounded by Berthelot [2, 1866, 1877], Thorpe and Young [19, 1877], Nikiforoff, and others before the beginning of the twentieth century

Probably the first cracking process designed to produce a light motor fuel was developed in 1906 by Cowper-Coles, who passed heavy hydrocarbon vapours through small metal tubes heated to high temperatures The next 10 years saw many other vapour-phase cracking processes developed Among the most noted were those of Noad, Sabatier, Testelin and Renard, Laing, Greenstreet, Lamplough, Turner, Hall, and Rittman Of these processes those of Hall, Greenstreet, and Rittman were employed commercially during the World War and for the period thereafter when high gasoline prices made them possible An excellent résumé of the literature pertaining to this early development is to be found in Bulletin 114 of the United States Bureau of Mines and in an article by Lomax, Dunstan, and Thole [12, 1916]

Apart from the troubles encountered with high gas loss, poor economy, and the treating problems involved in handling the distillate produced, these processes were failures because of carbon deposition If the carbon deposited in the heated tubes, the tubes quickly burned out, and, if the operator kept it out of the tubes, then it plugged up vapour lines and fractionating equipment Weaver [21] seems to have been the first to apply successfully on a commercial scale an effective cure for this trouble He injected part of the cold charge as a fine spray into the hot vapours leaving the cracking zone, thus stopping instantly the cracking reaction and preventing the formation of carbon This principle, first used in 1925 by the Gyro Process Company in constructing its low-pressure, high-temperature units, was rapidly adopted by all companies as a means to enable them to raise their cracking temperatures To-day it is universally used as a control in cracking to prevent secondary reactions leading to excessive gas production and coke formation after the hot oil has left the cracking furnace

Although such processes as the Cross, Dubbs, Tube and Tank, Holmes-Manley, &c , are still popularly known as liquid-phase processes, they are actually operating at temperatures above the critical point and might therefore more properly be regarded as vapour-phase processes The present discussion will be limited to low-pressure, high-temperature processes, typical of which may be mentioned the Gyro [14, 1929], deFlorez [4, 1929], and Knox [16, 1934] processes

In Fig 1 is shown a typical Gyro Process flow diagram The charging stock to the Gyro unit is introduced into the main fractionating tower, where it is stripped of any gasoline fractions Along with the recycle (partially cracked gas-oil fractions) the remainder of the charge is passed through a vaporizing (and viscosity-breaking) section of the furnace and discharged into an evaporator at 75–100 lb pressure The bottoms from the evaporator are passed to a flash tower and there stripped of their gas-oil fractions The evaporator vapours pass through the high-temperature cracking coils, leaving the furnace at about 1,100° F The reaction is checked by spraying into the vapours a light side stream cut from the main fractionating tower This quench oil has an end-point of about 525° F and does not deposit carbon when completely vaporized From the arrester the vapours pass to the fractionating tower, although it is desirable to interpose between the arrester and fractionating tower a drum where fuel-oil fractions can be separated from the system Vapours leaving the fractionating tower are handled in the conventional manner for the recovery of gasoline distillate and dry gas

In Table I are given results obtained by charging 26–27 API gravity East Texas topped crude to a typical Gyro unit

TABLE I

Yields	*Bbl per day*	*%*
East Texas topped crude	2,700	100 0
Finished gasoline	1,026	38 0
Fuel oil	1,142	42 3
Gas and loss	532	19 7

Conditions	*Temp , ° F*	*Press lb gauge*
Vapours out of evaporator	790	94
Vapours out of cracking coils	1,066	31
After quenching in arrester	716	30
Top of fractionating tower	351	25

Inspection Data

	Finished gasoline	*Raw distillate*	*East Texas topped crude*	*Fuel oil*	*Dry gas*
Grav API	57 5	55 2	26 9	9 9	Sp gr 0 985 % olefines 46 0 by absorption in bromine water
I B P , ° F	84	88	445		
10%	125	126	525		
20%	153	164	575		
50%	248	268			
90%	370	394			
End-point	399	430			
Colour (Saybolt)	25	yellow			
Octane Number A S T M	70 7				
Sulphur, % wt	0 035				
Furol viscosity at 122				168	
Flash-point, ° F				277	
B S and W , %				0 8	

In Fig 2 is given the flow diagram of a deFlorez unit It will be observed that the outstanding difference between the Gyro and deFlorez processes lies in the method of

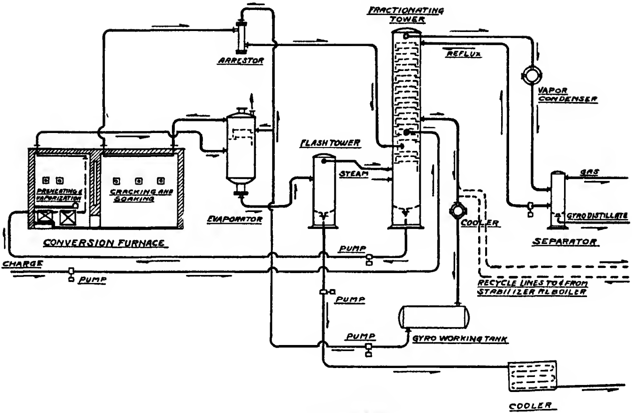

FIG 1 Gyro process flow diagram

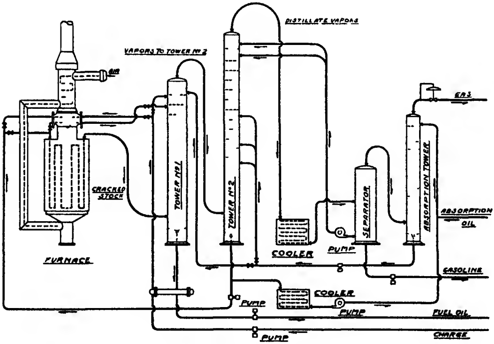

FIG 2 DeFlorez process flow diagram

preparing the vapours to be cracked. DeFlorez vaporizes and cracks in one continuous coil, thus necessitating the use of a very clean, relatively low-boiling charge to the cracking zone. In the case of the Gyro process, dry hydrocarbon vapours are first prepared, and these are submitted to cracking.

In the deFlorez process the arbitrary distinction between the two large classes of cracking processes, namely, liquid and vapour phase, is lost. The operating conditions may be varied so that the type of products approaches more nearly the one or the other. The process permits a wide range of temperatures and pressures, but adheres more nearly to the vapour phase. The unit comprises a vertical tube-still heating element, a primary tower that embodies an expansion chamber, and a secondary tower that completes the separation of the gas and gasoline from the cracking stock. The fresh charge is introduced into the primary tower, coming in contact with the hot vapour from the heater. Fuel oil is drawn off at the bottom. The bottoms from the secondary tower containing the cracking stock in the fresh feed and the recycle stock are charged to the heater. The gasoline is taken overhead from the secondary tower with the gas and condensed. The uncondensable gas is subjected to treatment for recovery of gasoline. Cracking takes place both in the tubular heater and in the expansion chamber, by increasing the pressure, so-called liquid-phase conditions are approached. Yields obtained at low and high pressures on 19.2–20.5 API gravity Venezuela crude are shown in Table II.

TABLE II

Venezuela Crude

	Run 25	*Run 29*	*Run 35*
Stream, hours	400	607	719
Temp., ° F (heater outlet)	1,071	1,046	1,021
Pressure, lb	21	78	78
Charge, bbl	19,422	20,124	19,804
Charge, %	100.0	100.0	100.0
Yield			
Distillate, %	23.71	32.02	26.10
Straight run	7.00	6.00	5.75
Cracked	16.71	26.02	20.35
Residuum, %	69.07	58.64	62.70
Gas, %	6.39	10.16	10.60
Inspections			
Charge, API grav	19.2	20.5	19.0
Distillate, API grav	54.5	56.7	56.6
,, end-point, ° F	393	392	364
,, colour (Saybolt)	yellow	−2	+1
Residuum API grav	11.2	10.0	9.9
Viscosity (Furol) at 122° F	703	297	326

In Fig. 3 is presented a flow diagram of the Knox process, which uses an inert gas as the medium for transmitting heat into the vapours to be cracked. The oil to be processed is first passed through a vaporizer and into a flash drum. The vapours are then superheated to a temperature 40–50° F below that at which they are to be cracked. A relatively large volume of inert gas previously heated to 1,100° F. in a regenerative furnace or stove of the conventional blast-furnace type is mixed with the superheated oil vapour in a chamber, thereby raising the mixture to the required cracking temperature of 980 to 1,020° F. The mixture passes into a reaction chamber in which the pressure is maintained at 50 lb. Cracked vapours and gas are passed into a scrubber, where heavy tar or asphalt is separated. Further separation of the products is effected in a rectifier in the usual manner. The bottoms from the rectifier with the necessary fresh feed are returned to the vaporizer. The gasoline overhead is condensed and the uncondensable gas treated in an oil-absorption system for recovery of gasoline, and the required quantity of dry gas is returned to the stove to start another cycle. The process is characterized by a high conversion of oil in each cycle, which averages 32% for gas oil and is higher for lighter charges. Any charge that can be vaporized can be successfully processed. Yields from a variety of oils are shown in Table III.

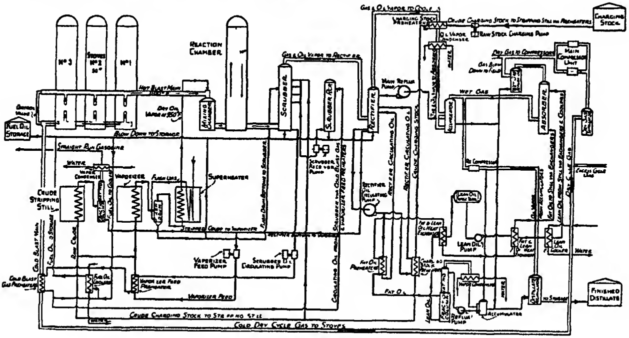

FIG 3. Knox process flow diagram.

TABLE III

Yields

Charging stocks	*Straight-run naphtha*	*Kerosine*	*Gas oil*	*Reduced Mid-Continent crude*
Gasoline, 410° F , E P 73 5	%	%	%	%
Octane Number (A S T M)	87	82	67	60
Fuel oil	4	8	20	30
Gas	9	10	13	10

Chorging stocks crude	*Mid-Continent*	*East Texas*	*Kettleman Hills*	*Signal Hill*	*Seminole*	*Van Zandt*	*Sterlitomak (Russian)*
Gasoline 410° F , E P 74 Octane Number	%	%	%	%	%	%	%
(A S T M)	69	71	73	67	74	71	51
Fuel oil	23	21	20	25	19	22	42
Gas	8	8	7	8	7	7	7

In addition to these better-known processes a number of other vapour-phase processes have been tried out within the last 10 years Leamon [11, 1927] used a catalyst deposited on pumice stone Pratt [15, 1932] employed a slight modification of the deFlorez operation The Clark process [1, 1935] cracks vapours by contacting with freshly generated hot flue gases The Houdry process [13, 1933] uses a catalyst prepared from clay and operates at temperatures below 800° F The gasoline produced appears to consist largely of branched-chain paraffins of high octane number Aromatic nuclei present in the charging stock are concentrated in the recycle stock, which therefore constitutes a better charging stock for a straight thermal process than for return to the Houdry unit

The products obtained by low-pressure, high-temperature treatment of gas oil vary markedly from those produced at lower temperatures and higher pressures The distillate of gasoline boiling range has an iodine number above 200, often as high as 250, and invariably possesses a characteristic yellow colour and marked odour The removal of this colour and the production of a stable motor fuel may be accomplished by re-running through fuller's earth, or by treating with sulphuric acid under controlled conditions followed by re-running The fuel thus produced has an octane number of 80–85 by the C F R research method and 70–73 by the C F R motor method (A S T M D 357–34 T) It therefore resembles the unsaturated hydrocarbons very closely in its behaviour in internal-combustion engines This characteristic is not surprising when it is considered that the finished motor fuel usually contains 45–50% of olefines, less than 10% of combined paraffins and naphthenes, and the remainder is composed of aromatics and partially hydrogenated aromatics

Perhaps the most noticeable difference from other processes is observed in the composition of the gas produced at low pressure and high temperature Gas analyses from a variety of charging stocks are given in Table IV, some figures being from commercial units, others from laboratory scale equipment, and the remainder from semi-commercial size operation

It will be noted that there is a striking uniformity in these analyses, particularly if allowance be made for the presence of gasoline fractions present in some of the samples. Hague and Wheeler [9, 1929, 1934] observed that pyrolysis of the normal paraffins from ethane to hexane inclusive gave gases of uniform composition. The same observation in connexion with small-scale cracking of various gas oils was made by Osterstrom and Wagner [14, 1929] and attributed by them to the production of gas as the result of secondary reactions By a series of experiments using the same charging stock and cracking at the same temperature, but with varying times of reaction, they demonstrated that very little of the light gasoline fraction was produced at

TABLE IV

Gas Analyses

Charging stock	*Corning gas oil*	*Cabin Creek gas oil*	*Mexican gas oil*	*Nujol*	*Seminole topped crude*	*Polymers**
CH_4+H_2+air, &c	35·4	35·0	38·6	45·6	37 5	48 4
C_2H_4	22 8	24 6	22 8	29 8	20 3	14·2
C_2H_6	13 2	11 9	11 9	9 4	12 6	12 3
C_3H_6	18 0	18 0	12 5	11 8	12 3	12 6
C_3H_8		2 5	6 1		8 6	2 8
C_4	6·9	4 7	8 1	3 4	8 6	7 4
C_5 and heavier	2 9	3 1				2 3

* Polymerized products from the fuller's-earth treatment of vapour-phase cracked distillate

Charging stock	*Spindletop topped crude*	*Mt Pleasant topped crude*	*Heavy naphtha*	*Mid-Continent topped crude*	*Mid-Continent topped crude*	*Van Zandt gas oil**
CH_4+H_2+air, &c	38 8	24 4	29 6	33 2	28 5	34·7
C_2H_4	20 3	23 1	23 1	26 7	23 1	22 6
C_2H_6	13 2	12 5	12 8	12 8	11 1	15 3
C_3H_6	13 1	14 9	13 3	16 2	15 7	17·9
C_3H_8	5 7	6 1	4 9	4·0	4 4	
C_4	6 4	10 9	8 3	5 9	10 1	7 9
C_5 and heavier	2 5	8 1†	8 0†	1 2	7 1†	1 6

* This gas sample was taken when cracking at 1,275° F

† Wet gases before extraction of any gasoline fractions

TABLE V

Charging stock	*Cabin Creek gas oil*	*426 E P Dist from Cabin Creek gas oil*
Temperature of cracking, ° F.	1,068	1,070
Gallons charged per hour	93 5	47 2
Per cent steam added by weight	0 6	1 8
Per cent distillate made	63 8	63 7
Per cent dry gas made	29 7	20 8
Per cent fuel (or polymers) made	6 0	15 1
Dry gas made per hour, cu ft	579	781
Gas analysis		
Sp gr of dry gas	1 050	1 041
CO_2+H_2S	0 1	0 2
O_2	0 0	1 5
N_2	0 0	6 6
CO	0 1	0 3
H_2	5 8	6 3
Olefines	52 2	50·4
C_nH_{2n+2}	41 8	34 7
Value of *n*	1 3	1 32
Distillate inspection		
API grav of distillate	54 9	52 0
Iodine number	209 8	213 0
I B P , ° F	100	90
10%	152	138
20%	191	165
30%	224	188
40%	258	212
50%	294	237
60%	328	266
70%	362	302
80%	386	343
90%	410	390
End-point	435	436
Loss, %	2 9	3 7

short reaction times, and also that the ratio of gas to gasoline produced was increased by increasing the time of reaction for a given cracking temperature By processing gasoline boiling-point distillate at the same temperature and at about the same reaction time as the original charging stock, they produced a gas of almost exactly the same composition The significant data are given in Table V

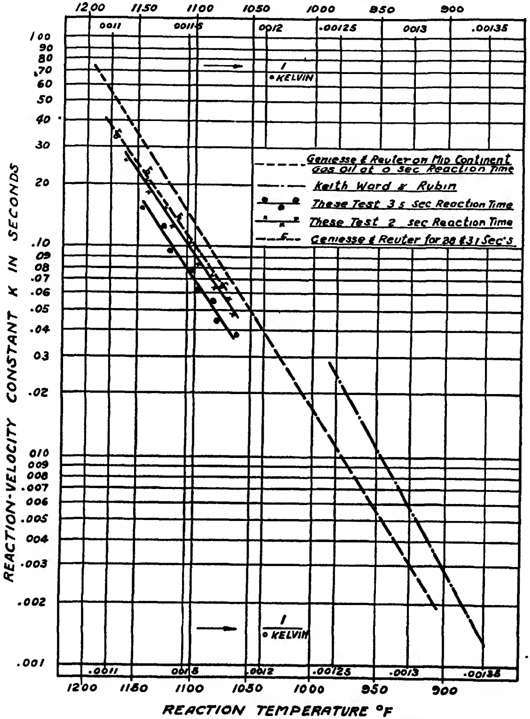

Fig 4 Variation of reaction-velocity constant with reaction temperature

It will be observed that gases produced by cracking Spindletop crude and polymers contain less olefines and more paraffins than gases from other charging stocks listed in Table IV. This is not surprising, since both of these charging stocks contain relatively large percentages of compounds possessing cyclic nuclei When decomposition of these compounds occurs, it is logical to assume that alkyl substituents will split off before rupture of the ring takes place. Where the charging stock is as complex as is the case with gas oil or topped crude charged to cracking units, it is impossible to state definitely what does occur in the cracking reaction. Hague and Wheeler [9, 1929, 1934] have shown that the normal paraffins tend to split close to the centre of the molecule, giving a paraffin and a straight-chain olefine of about equal molecular weights This fact was utilized commercially by Sullivan and his co-workers [18, 1931] in preparing such olefines by the vapour-phase cracking of paraffin wax The almost complete absence of straight-chain paraffins of molecular weight higher than butane in the distillate produced by commercial vapour-phase cracking operations may be due to one or both of the following factors. Except for the paraffin waxes, practically no normal paraffin hydrocarbons are present in commercial charging stocks In 1923 Wagner [20] pointed out that Mid-Continent kerosine contained few, if any, paraffin hydrocarbons Scission of the molecules present, therefore, could scarcely be expected to yield fragments [5, 1930, 1931] that would have the formula, C_nH_{2n+1}, which by picking up atomic hydrogen would become paraffins Where such molecular fragments are produced, as would be the case where a paraffin hydrocarbon is split in the middle, then the formation of paraffin hydrocarbons from those fragments is dependent upon the existence of atomic hydrogen in the immediate neighbourhood Otherwise, the extreme instability of these fragments would cause them to decompose still further In view of the fact that less than 10% of the dry gas produced in commercial vapour-phase cracking is hydrogen, it must be apparent that the hydrogen content of the vapours present in the cracking zone is well under 1% by volume, and the amount of this that is in the atomic state must be very small indeed

It has been shown by Geniesse and Reuter [7, 1930, 1932] that an increase of 17° C (31° F) in reaction temperature is sufficient to double the reaction velocity in vapour-phase cracking Fig 4 is taken from a paper by Schutt [17, 1932], who checked their results very closely The former worked with Mid-Continent gas oil, the latter with an East Texas gas oil Data from a paper by Keith, Ward, and Rubin [10, 1933], who used a 35 A P I gravity virgin Mid-Continent gas oil, are also given The equation involved is

$$\log_e K = -\frac{U}{RT} + C,$$

where K = reaction velocity constant,

U = energy of activation = $-53{,}400$,

T = absolute temperature of reaction,

R = gas constant,

C = a constant = 28 8

Schutt also gives the effect of cracking temperature upon octane number This effect is shown in Fig 5, and it should be noted that, whereas the extent of cracking is affected by both time and temperature (see Geniesse and Reuter), octane number is influenced by temperature, but not appreciably by time of reaction The extent to which commercial motor fuels can be produced having higher octane numbers than those now being marketed is, therefore, dependent upon the ability of technologists to develop a cracking process that will operate efficiently at temperatures well above those now being employed

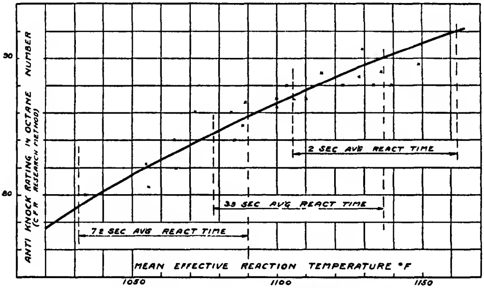

FIG 5 Anti-knock characteristic of gasoline

This problem is occupying the attention of petroleum technologists from both a practical and theoretical point of view, as evidenced by papers presented at the meetings of the Petroleum Division of the American Chemical Society [6] in New York in April 1935, in San Francisco in August 1935, in Kansas City in April 1936, and in Pittsburgh in September 1936 High-temperature pyrolysis of substantially saturated gases and subsequent polymerization of the resulting unsaturated products and also polymerization of cracked gases produced by normal operation of vapour-phase cracking units are indicated as a promising line of future development

The formation of aromatics is the characteristic which distinguishes vapour-phase cracking from liquid phase cracking Theoretical chemical consideration of vapour-phase cracking is naturally concerned chiefly with this phenomenon Valuable contributions have been made to the study of this subject, among which the work of Hague and Wheeler [9, 1929, 1934] and of Groll [8, 1933] may be mentioned Hague and Wheeler explain the formation of aromatics by the polymerization of ethylene and its homologues to butylene. This intermediate product loses hydrogen to form butadiene, which in turn combines with another molecule of ethylene to form cyclohexene. By dehydrogenation benzene is formed as the final product, or, when propylene combines with butadiene, the final product is toluene According to Groll the olefine is demethanized to give methane and an acetylene The acetylene polymerizes to give the aromatic For example, if propylene is the initial olefine, the final product will be benzene

It is interesting to note that both theories presuppose the formation of a low-boiling olefine by rupture of long-chain hydrocarbons, and that polymerization plays an important role in producing the aromatic The reactions involved are of such complexity that no simple theory satisfactorily explains just what happens This is particularly true in the formation of tar in the cracking of high-gravity gas oils at either 750° F. in the liquid phase or 1,000° F. in the vapour phase If formation of aromatics were accomplished by dehydrogenation or demethanization, the cracking of low-temperature coal tar would be a profitable source of aromatics

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CATALYTIC REFORMING

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Introduction

THE modern cracking process is not an ideal means for the production of anti-knock gasoline, although it is at present the most important source of such material The cracking processes in present use are almost without exception non-catalytic and, in the case of the one or two so-called catalytic cracking processes which have been described, no definite evidence of catalytic activity has been forthcoming All the chemical reactions involved in the cracking process are brought about by the action of heat and pressure alone, and apart from these agencies the only other controlling factor is time of reaction Consequently the process lacks adequate control with regard to the chemical nature of the products obtained

The reactions involved in such thermal treatment are very complex, and little is known concerning the mechanism of cracking However, not only does degradation of the molecule occur, but also the frequent synthesis of heavier and more complicated molecules, that is, the desired products are accompanied by those that are definitely undesirable, although the amount of the latter formed is small

One of the greatest disadvantages of the modern cracking or reforming process is the large gas production and the consequent low yield of anti-knock gasoline obtained The average yield of gas in cracking operations in the United States of America during 1935 was 500 cu ft per barrel of oil processed, while the corresponding yield of gas in gasoline reforming operations was 800 cu ft per barrel The grand average gas production corresponding to these two figures was approximately 20% by weight The reforming operation gives, on Mid-Continent naphtha, when producing 72 octane number gasoline, approximate average yields as follows gasoline 70%, residue 5%, gas 25% by weight

During the past few years definite advances have been made in the direction of catalytic conversions, whereby cracking and reforming may be carried out under carefully controlled selective conditions in the presence of suitable active catalysts Such processes are not yet ready for commercial application, and much more development work is necessary before they can become important factors in anti-knock gasoline production On the other hand, rapid strides are being made, and this article indicates the progress already made and the probable direction of future research. An important tendency is the segregation and treatment of substantially pure hydrocarbons and the production of individual chemical entities

Chemistry of the Cracking Process

The desired result of the cracking operation as applied to high molecular weight oils is the production of the highest possible yield of gasoline and the elimination of by-products This involves the break-down of molecules, i.e. the products must necessarily have a lower average molecular weight than the material treated It is, however, not possible to carry out the thermal break-down of heavier oils exclusively to produce gasoline, and there are also formed appreciable quantities of both lighter and heavier products Thus, a reaction such as

$$C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{18}$$

is always accompanied by reactions involving the scission of nearly all the carbon-carbon linkages in the molecule Products of higher molecular weight than the feed are formed by secondary polymerization reactions involving the olefinic products of the primary reactions In addition to these changes various other reactions such as isomerization and cyclization also take place because the gasoline products of cracking contain appreciable quantities of ring compounds, e g naphthenes and paraffins, even when the charge stocks contain none of these substances Such reactions take place after the primary cracking reactions and are entirely uncontrolled, although they have a profound effect on the quality of the gasoline produced

It is because of the lack of chemical control in the cracking process that attention is now being directed to catalytic processes, and it is reasonable to expect a large measure of success in the near future In this new work attempts are being made to separate the various chemical reactions which occur in thermal cracking and to carry out each individual reaction (if it is a desirable one) under its own optimum conditions according to requirements

The chief reactions involved may be summarized as follows

1 Dehydrogenation,
2 Scission of carbon-carbon linkages,
3 Isomerization,
4 Cyclization,
5 Alkylation,

and it is convenient to consider these reactions in this order

Dehydrogenation.

This reaction involves the elimination of one or more molecules of hydrogen from a hydrocarbon with the production of a substance containing the same number of carbon atoms Thus paraffin hydrocarbons may be converted by this reaction into olefines or diolefines, and six-membered ring naphthenes may be converted into aromatics The reactions involved are as follows

$$(1)\ \underset{\text{Paraffin}}{C_nH_{2n+2}} \rightarrow \underset{\text{Olefine}}{C_nH_{2n}} + H_2$$

$$(2)\ C_nH_{2n+2} \rightarrow \underset{\text{Diolefine}}{C_nH_{2n-2}} + 2H_2$$

$$(3)\ \underset{\substack{\text{Six-membered}\\\text{ring naphthene}}}{C_nH_{2n}} \rightarrow \underset{\text{Aromatic}}{C_nH_{2n-6}}$$

and each of these are reversible reactions governed by the laws of reaction equilibria

All simple dehydrogenation reactions of this type are endothermic and are favoured by high temperatures On the other hand, high temperatures also accelerate thermal decomposition reactions and a suitable catalyst must be employed to promote dehydrogenation at a temperature low enough to prevent such decomposition

The use of elevated pressures suppresses the dehydrogenation reaction because it involves an increase in volume

In the case of the gaseous paraffins, ethane, propane, and the butanes, reliable information is available regarding the dehydrogenation-hydrogenation equilibria Thus Frey and Huppke [1, 1933] have studied the dehydrogenation of these gases at 350–500° C in the presence of a chromic oxide catalyst and determined the values of the equilibrium constant over this range These investigators found that side reactions, particularly thermal decomposition, took place readily in the case of propane and butane at 500° C in the presence of the particular catalyst used This decomposition was responsible for the deposition of carbon on the catalyst and consequently caused rapid decrease of catalyst activity It must be concluded, therefore, that the catalyst used by Frey and Huppke was not fully satisfactory, in that it accelerated decomposition reactions as well as dehydrogenation

One important fact observed by Frey and Huppke was the complete absence of isomerization reactions accompanying the dehydrogenation *n*-Butane gave a mixture of *n*-butenes, while isobutane gave isobutylene exclusively

Concerning the simple dehydrogenation of the higher paraffins very little is known As it is possible to hydrogenate the higher olefines such as the hexenes and heptenes, &c , to the corresponding paraffins, it should also be possible to effect the reverse reaction, but such dehydrogenation reactions appear to have been very much neglected The production of olefines by the simple dehydrogenation of C_6—C_{10} paraffins is very attractive because of the high yields theoretically obtainable and because of the high increase in anti-knock value which would result Thus in the production of hexenes from straight-run hexanes the theoretical yield is 97 6% by weight, while the increase in anti-knock value is shown in the following figures taken from the publications of Lovell, Campbell, and Boyd [6, 1931, 1934]

Calculated blending	*Octane number*
n-Hexane	29
Hexene-1	85
Hexene-2	100

However, there are several difficulties in carrying out such reactions effectively The first is concerned with the choice of catalysts, most of which also catalyse decomposition at the same time as dehydrogenation A further difficulty is that the required products (i e olefines) have substantially the same boiling range as the parent paraffins, and hence separation of unreacted paraffins from the product for the purpose of recycling is not feasible On the other hand, a recycle system is necessary because the conversion per pass is limited to a low figure by the low reaction temperatures necessary for the avoidance of cracking reactions

An additional complication is that the allowable range of operating temperatures is very narrow, a change of temperature of as little as 50° C covering both complete decomposition to carbon and hydrogen and also first signs of perceptible change

The dehydrogenation of six-membered ring naphthenes into the corresponding aromatics is much more easily carried out than the conversion of paraffins into olefines In this case also the reaction is reversible, as shown in the classic work of Sabatier and Senderens (1899–1905), and may be performed with equal ease in both directions, although there is always a tendency, in the dehydrogenation reaction, for side chains to be split off and for methane to be formed by other decomposition reactions Thus at 250° C cyclohexane is readily dehydrogenated to benzene, no other liquid products are obtained, and the liberated gas is substantially pure hydrogen At higher temperatures, however, methane appears in the gaseous reaction product, and toluene and dibenzyl are formed in small quantities The mechanism by which these higher aromatics are formed is obscure

Similarly, when the higher homologues of cyclohexane are submitted to dehydrogenation in the presence of suitable catalysts there is an increasing tendency for side chains to be split off at temperatures above 250° C , but in addition small amounts of higher aromatics are also produced Thus the dehydrogenation of ethyl cyclohexane at 350° C yields benzene, toluene, ethyl-benzene, and small quantities of higher aromatics in addition to large quantities of methane Such reactions have been classified by Ipatieff as belonging to the destructive alkylation type, and take place much more readily in the presence of nickel-alumina catalysts than in the presence of platinum or palladium black

The elimination of side chains from the ring structure in the dehydrogenation of six-membered ring naphthenes is to be avoided if at all possible The formation of methane and ethane causes a decrease in the yield of liquid hydrocarbons obtained and is nearly always accompanied by rapid deterioration of catalytic activity brought about by the condensation of high molecular weight products, and also possibly carbon, on the catalyst

Cyclopentane derivatives are not amenable to simple dehydrogenation, and the same is true with respect to cycloheptane homologues Moreover, disubstituted cyclohexanes in which both the substituted groups are attached to the same carbon atom are not convertable to the corresponding aromatics by dehydrogenation

With regard to suitable catalysts for the dehydrogenation of liquid hydrocarbons, it is at once obvious that neither platinum nor palladium may be used because of the ease with which these substances are poisoned by traces of sulphur compounds, which are almost invariably present in petroleum distillates On the other hand, these catalysts have proved very satisfactory in laboratory work in which catalyst life is not very important, and Zelinsky and Shuykin [13, 1935] have used platinum on active carbon as a catalyst in the dehydrogenation of Surakhany light distillates rich in six-membered ring naphthenes

Nickel in the reduced state is also an effective dehydrogenation catalyst, but also has a profound accelerating effect upon decomposition reactions leading to the production of hydrocarbons of lower molecular weight, permanent gas, and carbon These undesirable characteristics are, however, considerably modified by incorporation with alumina in the manner suggested by Zelinsky [12, 1924] or later by Jones and Linstead [3, 1936] Little information is available concerning the active life of nickel catalysts or their susceptibility to poisons in dehydrogenation reactions, likewise little is known concerning the efficacy of cobalt catalysts

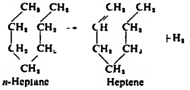
Chromium has been employed as a dehydrogenation catalyst in the form of chromium oxide (Cr_2O_3). In the production of aromatics from naphthene hydrocarbons Karshev, Severjanova, and Sivova [4, 1936] found that, at 500–550° C , four catalysts had activities in the following ascending order Al_2O_3, Cr—Cu—H_3PO_4—Al_2O_3,

Cr_2O_3—H_3PO_4, Cr—Cu, phosphoric acid being incorporated in the second and third presumably to increase their mechanical strength The copper-chromium catalyst was stated not to be adversely affected by sulphur compounds It is not known whether the copper acts as a promoter to chromium, but it is claimed to have valuable dehydrogenating properties when used alone [10, 1930]

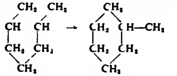
Important work carried out by Moldavski and Kamusher [7, 1936] has indicated that chromic oxide is an effective catalyst for the simultaneous dehydrogenation and cyclization of paraffin hydrocarbons at temperatures of 450–480° C Thus *n*-octane, passed over this catalyst at 460° C, gave a liquid product containing 63% of aromatic hydrocarbons (chiefly *o*-xylene) and 6% of olefines The gas liberated contained 92% of hydrogen and 7% of gaseous paraffins Similarly, *n*-heptane yielded toluene, *n*-hexane gave benzene, and di-isobutyl yielded *p*-xylene

The reactions involved in this transformation are not fully understood, but it is evident that extensive cyclization or ring formation occurs Perhaps the initial reaction is dehydrogenation to the corresponding olefine which is followed by cyclization to a naphthene and then by further dehydrogenation to an aromatic In this case the three steps would be as follows

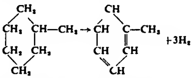
(*a*) Dehydrogenation to corresponding olefine



(*b*) Cyclization of olefine to corresponding naphthene



(*c*) Dehydrogenation of naphthene to corresponding aromatic



The presence of small amounts of methane in the gas liberated is explained by the splitting of side chains from the ring structure

The chromium oxide catalyst quickly lost activity, however Other catalysts were examined, including zinc oxide, aluminium oxide, thorium oxide, nickel chromate, molybdenum sulphide, uranium oxide, and floridin, but of these only molybdenum sulphide possessed any activity The rate of catalytic deterioration was, however, more rapid in this case than in the case of chromium oxide

This type of conversion process, whereby paraffins may be converted in good yield into aromatic hydrocarbons, is of great interest and potential value to the petroleum industry as it will give a valuable supply of gasoline of high anti-knock value which will also constitute a source of pure aromatic hydrocarbons for use in the chemical industries

Scission of Carbon–carbon Linkages.

It has already been mentioned that in conventional non-catalytic cracking carbon–carbon linkages are severed at all points in the molecule The factors controlling the point of attack are very imperfectly understood, and there appears to be no method available whereby the point of scission may be controlled without changing the extent of decomposition Unfortunately, the reactions involved in molecular break-down are, in the main, not reversible, and as a result they are not capable of control, either by the use of catalysts or by the choice of other operating conditions, to such a marked extent as in dehydrogenation Another point of importance is that catalysts found active in promoting cracking reactions also have a greater effect in accelerating decomposition to carbon and hydrogen Up to the present no fully satisfactory cracking catalyst is known

The peculiar catalytic properties of aluminium chloride need special mention here It is not a cracking catalyst in the above sense of the term, but it does effect the scission of carbon-carbon linkages at very low temperatures in reactions of the destructive alkylation type

Isomerization.

The potentialities of isomerization reactions are enormous, especially when it is considered that few of the hydrocarbon molecular configurations really effective in imparting anti-knock value are present in straight-run distillates to any great extent Thus, of the paraffins boiling above 60° C only those of branched-chain structure, preferably those of compact molecular configuration and containing a tertiary carbon atom, are of high anti-knock value The remaining paraffins are of little use as gasoline engine fuel because they lack the molecular form of their isomeric homologues Perhaps the most important potential supply of high octane number motor fuels lies in the satisfactory development of isomerization reactions Important progress in this direction is now being made

As examples of promising isomerization reactions the following may be mentioned

(*a*) The conversion of 1-butene into 2-butene by the action of phosphoric acid-alumina and phosphoric acid catalysts [2, 1934] At 249° C and in the presence of the latter catalyst the conversion is complete Perchloric acid, benzene-sulphonic acid, and zinc chloride are also effective catalysts for this reaction

(*b*) **Isomerization of Hexenes** When tertiary butyl ethylene, *as*-methyl-isopropyl ethylene, or tetramethyl ethylene is passed over phosphorous pentoxide on silica gel at 300° C an equilibrium mixture of all three hexenes is produced [5, 1934]

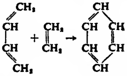
(*c*) **Isomerization of Paraffins** In the presence of zinc chloride for a period of about 6 hours at 300–400° C and under a pressure of nitrogen or hydrogen, *n*-heptane undergoes isomerization and yields 20–25% of isoheptanes Molybdenum sulphide is also an effective catalyst for this reaction at 420° C *n*-Octane reacts in a similar manner [10, 1935] According to Moldavski and his co-workers [9, 1936], however, these changes only take place under conditions involving the production and condensation of unsaturated hydrocarbons Aluminium chloride brings about similar isomerization of the normal paraffins at 20–90° C, the reaction being accelerated by the presence of hydrogen chloride

(*d*) **Isomerization of Naphthene Hydrocarbons.** Numerous isomerizations of naphthene hydrocarbons have been accomplished, for instance, the conversion of cyclohexane into methyl cyclopentane, which is accompanied by destructive alkylation reactions, and the conversion of ethyl cyclohexane into dimethyl cyclohexane

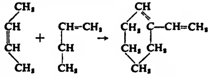
(*e*) **Isomerization of Olefine Hydrocarbons into Naphthenes.** This conversion is also an example of a cyclization reaction and is, according to Francis and Kleinschmidt, thermodynamically possible at all temperatures up to 400° C Direct experimental evidence of the occurrence of this reaction is scarce, but it is probable that in conventional cracking and reforming processes the reaction occurs to a measurable extent On the other hand, experimental evidence is very much in favour of this reaction taking place to an important degree in polymerization processes catalysed by aluminium chloride

Cyclization.

Cyclization, i e ring closure-, reactions are important in all pyrolytic conversions Thus, by suitable heat treatment yields of aromatic hydrocarbons of up to 40% may be obtained from the gaseous aliphatic hydrocarbons The mechanism of such changes is imperfectly understood, but it is postulated by some workers that cyclization occurs by the condensation of ethylene and butadiene in the following way



Similarly, the polymerization of butadiene is known to yield vinyl cyclohexene, thus



The possible isomerization of straight-chain olefines into six-membered ring naphthenes which may be dehydrogenated to aromatics is of considerable importance in view of the large increase in anti-knock value thereby obtainable The possible conversion of cracked spirits into those of naphthenic structure is also of value because of the high gum stability of saturated materials The high anti-knock value and good lead response of naphthenic spirits are also very important points in their favour compared with cracked gasolines from paraffin-base crudes

Alkylation.

Alkylation consists of the combination of unlike hydrocarbon molecules to form one molecule of a hydrocarbon possessing a molecular weight equal to the sum of the molecular weights of the original hydrocarbons Examples of such combinations are as follows

(*a*) Olefines and aromatics,
(*b*) Olefines and paraffins,
(*c*) Olefines and naphthenes,

and in each case the use of a catalyst is beneficial, if not absolutely necessary Satisfactory catalysts are the anhydrous metal halides, some oxides, and phosphoric and sulphuric acids

Alkylation reactions are believed to take place to a small extent in conventional non-catalytic cracking and reforming operations as well as in thermal polymerization Under these conditions, however, the reaction is not controlled in any way and may, depending upon the operating conditions, be either beneficial or harmful with regard to the properties of the gasoline produced Recent work has shown how alkylation reactions may be carried out while avoiding secondary changes, and thus an important step has been made towards the production of synthetic gasolines of very high anti-knock value

Considering first of all the condensation of olefines and aromatic hydrocarbons, which may be accomplished at ordinary temperatures and at normal or increased pressures using sulphuric acid as a catalyst, this general reaction is a means of converting the gaseous olefines into stable high octane number gasoline containing only traces of unsaturated hydrocarbons and which are fully suitable for incorporation in aviation fuels This conversion is also a convenient means for the synthesis of substantially pure aromatic hydrocarbons Thus ethyl benzene, propyl-, and butyl benzenes may be obtained by condensing benzene with the appropriate olefine Such substances are especially valuable in the preparation of low-volatility fuels of high anti-knock value, e g high flash-point safety aviation fuels

The alkylation of naphthene hydrocarbons, although of great academic interest, is not of such great potential value because the higher substituted cyclohexanes and cyclopentanes have, in general, low anti-knock values, with the exception of those containing tertiary carbon atoms in the substituted groups

Perhaps the most important alkylation reaction with regard to the production of premium grade gasolines is the combination of olefines and paraffins Examples of such reactions are the condensations of ethylene with *n*-hexane, isobutylene with isobutane and *n*-butane, and ethylene with isobutane, &c The products obtained contain only traces of olefines and are predominantly fully saturated and paraffinic in nature, they consist largely of isoparaffins of high anti-knock value

Conclusions

It is evident that many synthetic reactions are in course of active study for the production of premium-grade products and that the use of these reactions will create a supply of fuel hitherto not available At present the most pressing need is for a process whereby naphthas and gas oils may be broken down to gasoline hydrocarbons under carefully controlled conditions whereby the production of gaseous aliphatic hydrocarbons may be reduced to a negligible amount or eliminated entirely Such a process is not yet available, but the knowledge now being rapidly accumulated on dehydrogenation, cyclization, isomerization, and alkylation reactions may soon enable such a process to be evolved

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ECONOMIC SIGNIFICANCE OF CRACKING

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THE dominating factor in the oil industry from the economic standpoint, and the strongest force for conservation, is the cracking process This process influences not only the business of producing and refining petroleum, but it is vital to the automobile and aeroplane industry It also affects in very definite ways the industries concerned with gas and coal, road building, organic chemicals, alloy steels, and the manufacture of control instruments

In its early stages the automobile industry gave indications of outrunning the capacity of the refining industry to supply gasoline This threat spurred on chemists and other technical men to develop methods for producing more gasoline from crude oil The cracking process provided the means for meeting the increased demand for motor fuel

Gasoline consumption in the United States has paralleled the increased registration of motor vehicles, as indicated in Table I

TABLE I

Automobile Registration v Motor Fuel Consumption

Year	*Automobiles in use*	*Motor fuel consumption, bbl*
1920	9,232,000	108,945,000
1925	19,937,000	232,182,000
1930	26,524,000	398,075,000
1932	24,150,000	373,770,000
1933	23,849,000	377,003 000
1934	24,751,000	406,269,000

When the cracking process was put into commercial operation about 23 years ago, its motor fuel was looked upon as an inferior product, although, as a matter of fact, it was superior to the straight-run product then standard Because refiners could not meet the demand to make more gasoline they accepted cracking, but at first as a necessary evil For many years it was not believed that the gasoline produced by nature could be equalled by the 'artificial' variety produced by man

However, the situation has changed At present not only does cracked gasoline command a premium over straight-run from most crude oils, but certain straight-run gasolines, notably Pennsylvanian, which were formerly considered premium products, are unable to satisfy the demands of the modern motor, and cannot be readily marketed unless they are cracked or otherwise treated to improve their knock rating So great is the demand for anti-knock gasoline that one-quarter of the 219,583,000 bbl of straight-run gasoline produced (1935) in the United States was cracked or 'reformed'

The most enthusiastic prophet seeing the cracking stills of 20 years ago would not have envisioned the great technological development which has taken place in the cracking art since that time One of the first commercial units processed about 125 bbl of gas oil per day, and yielded 30 to 35% of gasoline of low octane number, while the largest modern unit now treats about 30,000 bbl of crude oil a day and produces 68% of high anti-knock fuel

The cracking process has developed not only in the size of the units, but in its flexibility, particularly since the introduction of multiple heating coils Whereas a run of 2 days was the best expected 23 years ago, continuous cracking runs of more than 90 days, producing as desired gasoline, gas, and coke or gasoline, gas, and fuel oil, are now common The widest conceivable variety of charging stocks are now cracked, producing besides high anti-knock gasoline, gas, coke, and fuel oil, tractor fuel, Diesel oil, and furnace oil when desired An important recent development in cracking is the use of polymerization processes by which gas from cracking stills is converted into gasoline of high anti-knock value As technology has advanced, more and more severe conditions have been employed in cracking, until to-day temperatures reach from 475 to 600° C , and pressures of over 1,000 lb per sq in are sometimes used

The present investment in cracking equipment amounts to over $400,000,000 in the United States, and the extensive research going on in the field of cracking requires a yearly expenditure of over $5,000,000

The tremendous significance of the cracking process as a force for conservation is clear from the fact that to manufacture gasolene without the use of cracking would require about double the production of crude oil over that now required When it is considered that in 1935 the 26,000,000 motor-cars in the United States called for 18,167,000,000 U S gallons of gasoline, the importance of this conservation can scarcely be overestimated

The greater part of the world's cracking industry is located within the United States, which in 1935 produced 8,716,554,000 U S gallons of cracked gasoline, as against an estimated production of 1,900,000,000 by the rest of the world There are cracking units in operation in Russia, Great Britain, Canada, Egypt, Belgium, France, Germany, Italy, Poland, Rumania, India, Russia, Burma, Borneo, Canary Islands, Island of Aruba, Trinidad, Curaçao, Peru, Argentina, and Mexico, and the use of the cracking process outside the United States is rapidly increasing

Modern Gasolines

The trend of the age is towards ever-increasing speed, and to satisfy it the automotive industry has been supplying increasingly powerful and rapid transportation

One way in which automobiles have been improved has been in increased compression ratios The trend in this direction is clearly shown in Table II, which gives the average compression ratio of automobiles in the United States in the last 12 years

Each increase in compression ratio requires improved quality in the gasoline because of the knocking which occurs if gasolines of too low octane number are used This has caused more and more emphasis to be laid on the anti-knock value of gasoline, measured in terms of octane number This property is governed by the type of hydrocarbons present, and can be controlled to some extent when gasoline is made by cracking, but not when distilled directly from the crude.

TABLE II

Year	*Average compression ratio* [1]
1924	4.36
1925	4.40
1926	4.47
1927	4.55
1928	4.86
1929	4.99
1930	5.15
1931	5.23
1932	5.29
1933	5.57
1934	5.72
1935	5.98
1936	6.1

The average octane number of regular-grade gasolines sold in the United States in 1934 is estimated at 69–70 and 1935 at 70–71. Straight-run gasoline (sold as third grade) has an average octane number of 55. About 2% of the total gasoline marketed is a premium grade of 67 octane rating.

The superiority in knock rating of cracked to straight-run gasoline from the same crude is shown by the data in Table III.

TABLE III

Octane Numbers of Straight-run and Cracked Gasolines (Co-operative Fuel Research Steering Committee Research Method) [2]

	Straight-run gasoline	*Cracked gasoline*
California (Kettlemen Hills)	60	80
" (Ellwood-Santa Fe)	52	74
East Texas	57	70
" (Joiner)	56	73
Texas (Yates)	62	81
" (Van Zandt)	43	71
" (Refugio)	58	90
Kansas	45	73
"	40	71
Mitchigan (Mt. Pleasant)	19	64
Mid-Continent	51	77
Montana (Kevin Sunburst)	54	81
New Mexico (Hobbs)	55	76
Oklahoma (Allen)	61	78
" (Oklahoma City)	47	72
Pennsylvania	50	74
"	43	72
Wyoming (Lost Soldier)	71	81

The octane number of the cracked gasolines is due to their higher content of aromatic and olefine hydrocarbons, and lower percentage of straight-chain paraffins. This is evident from the data in Table IV, which compares the hydrocarbon composition of cracked and straight-run gasolines from several typical stocks. The straight-run gasolines have an average paraffin hydrocarbon content of 74% and an octane rating of 57, the paraffin content of the cracked gasoline averages 47% and the octane number 72.

Polymer Gasoline

The cracking process produces in addition to other products over 300,000,000,000 cu. ft. of gas annually in the United States. This gas contains varying percentages of olefines, principally ethylene, propylene, and butenes, and also paraffin hydrocarbons. To date cracked gas has been largely used as fuel. Gasoline of 80–82 octane number is being produced from cracked gas at low temperatures and pressures in the presence of catalysts, and also by various thermal treatments.

TABLE IV

Chemical Analyses of Gasolenes [3]

	Naphthenes %	*Aromatics* %	*Unsaturates* %	*Paraffins* %
Arkansas (Smackover)				
Straight-run	14.5	11.3	7.9	66.3
Cracked	21.2	27.5	14.7	36.3
California				
Straight-run	34.9	2.8	5.1	57.2
Cracked	16.7	22.0	23.0	38.3
Kansas				
Straight-run	20.3	0.4	2.7	76.6
Cracked	12.8	17.8	16.1	53.3
Kentucky (Somerset)				
Straight-run	20.6	5.3	3.8	70.3
Cracked	11.8	14.9	12.5	60.8
Kentucky				
Straight-run	23.1	2.8	5.8	68.3
Cracked	18.8	26.0	12.5	42.7
Michigan (Mt. Pleasant)				
Straight-run	7.4	4.5	2.9	85.2
Cracked	3.1	33.5	25.9	37.5
Oklahoma (Cushing)				
Straight-run	23.7	4.9	1.6	69.8
Cracked	18.0	19.8	10.9	51.3
Pennsylvania				
Straight-run	13.0	6.9	2.2	77.9
Cracked	10.2	23.5	9.7	56.6
Texas (Van Zandt)				
Straight-run	0.0	2.9	1.7	95.4
Cracked	0.0	35.2	22.2	42.6

The heat and pressure methods use temperatures ranging from about 500 to 550° C. and pressures of 1,000 lb. per sq. in. to as high as 3,500 lb. The catalytic method uses temperatures of about 230° C. and pressures of about 200 lb. per sq. in.

These processes are capable of producing 1,000,000,000 gallons of 80–82 octane number motor fuel yearly from the cracked gas available in the United States. The significance of this advance is apparent when one realizes that the total gasoline production in the United States in 1935—cracked, straight-run, and natural gas gasoline, and motor benzol—was 19,552,000,000 gallons, and that its average octane number was about 66.

Refining of Cracked Gasoline and Use of Anti-oxidants

Cracked gasolene brought with it new refining problems because of its high content of unsaturated hydrocarbons.

For a number of years all cracked gasoline was chemically treated before marketing, necessitating expense for equipment, chemicals, and operation of the treating plant, and occasioning loss of gasoline and depreciation of its anti-knock rating. By using anti-oxidants to inhibit gum formation it has been possible to reduce and in some cases entirely eliminate treatment (with possible exception of sweetening) and effect savings of as high as 17 cents per barrel of gasoline. The use of anti-oxidants is rapidly increasing, and less and less cracked gasoline is refined with sulphuric acid or clay. About 85% of the gasoline now marketed in the United States is dyed, thus simplifying the refining process by eliminating treatments to produce water-white colour.

Economic Effect of Cracking upon other Parts of the Oil Industry

Cracking, although primarily a refining process, has a direct effect upon other branches of the oil industry. By increasing the amounts of desirable commercial products obtainable from a given volume of petroleum, the necessary yearly crude-oil requirement is strikingly decreased, as has already been noted. The effect of cracking upon oil production, based on gasoline alone, has been to conserve over 5,000,000,000 bbl. in the last 8 years, i.e. without the cracking process the oil resources of the United States would have been depleted by 5,000,000,000 more barrels of crude in order to meet the motor fuel demand.

Had it been necessary to drill enough wells to produce 600,000,000 bbl. more crude oil each year, the added cost to the producer would have been over $120,000,000 a year.

It would also have been necessary to provide added storage tanks for the crude oil and pipelines for its transportation. The existing pipelines for crude-oil transportation cover a distance of over 100,000 miles, represent an investment of $800,000,000, and have a yearly carrying capacity of about 1,000,000,000 bbl. Without the cracking process, the increased pipeline capacity required would have cost an additional $480,000,000.

Intimately associated with the production of crude oil from known fields is the equally important activity of locating new areas to exploit. This calls for the expense of geologists, palaeontologists, physicists, mathematicians, chemists, engineers, and drillers. The intensity of search for new oil-pools is influenced by the rate of depletion of the known supply. Consequently, by retarding the rate of depletion, the economic effect of cracking is felt by the searchers and producers of oil.

Without cracking, a further serious problem would have developed in the marketing of the other products from crude oil, such as kerosine, gas oil, and fuel oil, which would have been produced in undesirably large amounts.

TABLE V

Principal Petroleum Products from Crude Oil

Year	*U.S. crude refined, 1,000 bbl.*	*Gasoline and naphtha %*	*Kerosine %*	*Gas and fuel oil %*	*Lubricants %*
1880		10.3	75.2		2.1
1889		12.8	65.9		7.7
1899		12.9	57.6	14.0	9.1
1904		10.3	48.3	12.8	11.6
1909		10.7	33.0	33.6	10.7
1914		18.2	24.1	46.5	6.6
1917		21.5	13.1	49.2	5.7
1918	326,025	25.3	13.3	53.5	6.2
1919	361,520	25.2	15.4	50.2	5.6
1920	433,915	26.1	12.7	48.6	5.7
1921	443,363	27.1	10.5	51.9	4.7
1922	434,976	28.8	11.0	50.9	4.7
1923	538,252	30.0	9.6	49.5	4.5
1924	597,954	31.2	9.3	49.8	4.3
1925	698,582	32.4	8.1	49.3	4.2
1926	737,598	34.9	7.9	46.9	4.1
1927	778,729	36.0	6.8	47.4	3.8
1928	835,711	37.4	6.6	46.7	3.8
1929	912,191	39.4	5.8	45.4	3.5
1930	866,615	42.0	5.3	40.2	3.7
1931	894,608	44.3	4.7	37.7	3.0
1932	819,997	44.7	5.3	35.9	2.7
1933	861,254	47.3	4.4	36.7	2.9
1934	893,303	47.4	6.0	37.5	2.8
1935	966,243	48.2	5.7	35.3	2.8

It is of interest to note the changing percentages of products obtained from a barrel of crude petroleum as influenced by the development of cracking, as shown in Table V.

Effect of Cracking on Industries other than Petroleum

A. Gas Industry.

Cracked gases have an average heat content of about 1,400 B.Th.U. per cu. ft., about 300 B.Th.U. higher than natural gas. They are, therefore, useful for blending to raise the heating value of low B.Th.U. gas, or they may be reformed or cracked to lower B.Th.U. gas. The reforming of cracked gases may be either a process of gas-cracking or involve their passage through an incandescent coke bed in the presence of steam, thus producing water gas at the same time. Cracked gas is substituting manufactured gas produced either from gas oil, coal, or both in many consuming areas.

Hydrogen is produced both as an original component of cracked gases and by their reforming. As one of the products of cracking, hydrogen extends the effects of the cracking process to modern synthetic industries, outstanding among these, as a logical market for this hydrogen, being the synthetic ammonia and oil hydrogenation industries.

B. Coal Industry.

An important factor in the competition of fuel oil with coal is the increasing amount of cracked residue included in the yearly supply of fuel oil. The cracking process controls the properties of cracked fuel oil as well as those of cracked gasoline, and may be regulated to yield a product to meet any specification. Sometimes, indeed, the demand for special fuel oils, such as domestic furnace oil, may at times be more profitably filled than that for gasoline, so that at times some cracking units in the United States are operated to produce primarily furnace oil rather than motor fuel.

Natural fuel oil obtained by atmospheric distillation of crude must depend upon the varying constituents of crude oil for its properties. Cracked residual fuels surpass the usual natural fuel oil in heat content per barrel, viscosity, and cold test—three important fuel characteristics. The number of British thermal units per gallon of cracked fuel oil is about 10% higher than that of the natural product.

In 1934, 178,866,000 bbl. of the total 325,000,000 bbl. of fuel oil used in the United States was cracked fuel. This volume of cracked fuel is equivalent to over 46,000,000 tons of bituminous coal.

Another product from petroleum which is in direct competition with coal is petroleum coke, 1,300,000 tons were produced by the cracking process in 1934. Petroleum coke is also in active competition with coal coke for metallurgical purposes.

Petroleum coke is now produced by the cracking process in a continuous operation which is much less expensive and far more efficient than the older batch process used in conjunction with atmospheric distillation.

Proximate analyses and heat contents of representative atmospheric distilled and cracking-process cokes are given in Table VI.

TABLE VI

Properties of Petroleum Coke

Coke	Water %	Volatile matter %	Free carbon %	Ash %	Sulphur %	Heat value, B Th U per lb
Cracked						
Mid-Continent	0·50	8·07	91·81	0·05	0·83	15,645
Texas	0·15	15·02	83·21	1·62	1·96	15,456
Smackover (Ark)	0·11	12·28	87·15	0·46	4·18	15 898
Kentucky	0·39	11·65	87·42	0·54	0·66	16,403
Pennsylvania	0·20	11·39	87·42	0·99	0·22	16,248
California	0·47	18·03	80·49	0·91	1·09	15,295
Atmospheric distilled						
1	0·6	2·1	95·8	1·5	0·5	14 480
2	0·3	3·9	94·1	1·0	0·7	14,900

C. Road-building Industry.

Road oils, the production of which amounted to 5,425,000 bbl in 1930, 5,177,000 in 1931, 6,879,000 in 1932, 7,700,000 in 1934, and in 1935 6,832,000, were produced in part by the cracking process Moreover, road oil may be obtained by cracking some crude oils, such as those from Pennsylvania, which do not yield such oils by atmospheric distillation For example, cracked road oils meeting commercial specifications can be produced by cracking Pennsylvania paraffin-base crudes

Another phase of the road-building industry to which cracking is offering new supplies of a satisfactory product is the utilization of asphalt The amount of asphalt produced from United States petroleum was 3,830,457 tons in 1929, 3,223,888 in 1930, 2,975,690 in 1931, 2,474,919 in 1932, and 2,675,800 in 1934 It is possible to crack a crude petroleum which contains no asphalt so as to obtain both a good yield of high anti-knock gasoline and marketable asphalt

D. Chemical Industry.

The chemical industry is utilizing the olefines present in cracked gases to produce a variety of synthetic products

The amount and nature of the gas produced in the cracking process is governed by several factors, such as the composition of the charging stock and the operating conditions of time, temperature, and pressure used during the processing of the oil

The potential capacity of the oil industry is over 1,000,000,000 gallons a year of alcohols (such as ethyl-, propyl-, butyl-, and amyl-) from cracked gases The present output of ethyl alcohol from cracked gases is over 4,000,000 gallons a year at a price enabling it to compete with ethyl alcohol produced from grain or molasses Any conceivable demand for alcohols could be supplied by the oil industry through the use of the cracking process

Compounds of the following groups have been synthesized and produced commercially from cracked gases alcohols, amines, chlorides, glycols, nitroglycols, chlorohydrins, ethers, ketones, acids, and esters

Some of the outstanding uses for these products are as anti-freeze agents (ethylene glycol), explosives (nitroglycols), agents to remove hydrogen sulphide or carbon dioxide from gases (triethanolamine), solvents for lubricating oil treatment (dichloroethyl ether), medicinals (acetoacetanilide), fumigants (ethylene oxide), solvents for plastics and lacquers, resins, synthetic rubber (alcohols, esters, ketones), and others By the action of aluminium chloride upon cracked distillates, the unsaturated hydrocarbons are polymerized into solid resins of commercial value Varnishes made with this resin dry exceedingly fast and are highly resistant to water, alkali, and acid The resin is thermoplastic and can be moulded when mixed with suitable fillers

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SECTION 32

HYDROGENATION

THE HISTORICAL DEVELOPMENT OF HYDROGENATION

By Dr. FRIEDRICH BERGIUS, Hon. M.Inst.P.T.

RESEARCH and technical work on hydrogenation under high pressure have had my particular attention ever since 1910 Apparatus and equipment of my own construction then installed in my laboratory at Hanover offered every possibility to study chemical reactions under pressures up to 300 atm

At that time, the rapid progress in automobilism with its prospective highly increased demand for gasoline in the near future, suggested the idea of finding new ways to augment the supply of this commodity by way of cracking heavy oils and oil residues into gasoline in the most efficient manner possible

The deficiencies of the cracking processes then in use, leading to an inferior quality of unsaturated gasoline and to heavy losses through the simultaneous formation of coke and methane, could evidently only be overcome by replacing the hydrogen eliminated in the shape of methane during the cracking operation by a fresh supply of hydrogen in order to prevent the separation of unsaturated products which is also the cause of coking Investigations as to high-pressure hydrogenation of petroleum hydrocarbons under temperature conditions favouring the cracking reaction showed that cracking oils readily absorb hydrogen, yielding lighter oils of a more saturated character without giving rise to the formation of coke The possibility of effecting combination of hydrogen under high pressure with the split-up molecular complex of the high-boiling petroleum fraction is limited to a range of temperatures within which the velocity of the hydrogenating action is not surpassed by the speed of the cracking process Furthermore, the hydrogen pressure must be high enough to ensure quick termination of the hydrogenation reaction, and provision must be made that each oil molecule splitting up shall encounter a sufficient supply of hydrogen, which necessitates a thorough mixing of gas and liquid best attained in a rotating autoclave

Prolonged experimental work along these lines convinced us of the technical feasibility of the process and led to our first application for a patent on high-pressure hydrogenation of oils in May 1913

Special experiments carried out with all precautions to prevent the oil to be hydrogenated from getting into contact with the iron walls of the reaction vessel made it evident that the process is in no way influenced by the action of metallic contact substances

Early in 1914 we began with experiments on a somewhat enlarged scale, using a 40-litre bomb of stationary type heated from the outside, the hydrogen passing through the liquid, which was kept in motion by a stirrer As raw material, a heavy gas oil was used, which was hydrogenated at a temperature of 430° C under a pressure of 120 atm We succeeded in transforming about 50% of the gas oil used into gasoline, no coking taking place

All through 1913 and 1914 experimental work was devoted to the splitting of gas oils and heavy distillation residues from Galician and Roumanian crude oils In all cases gasoline of a practically saturated character could be produced, the formation of coke being avoided by proper distribution of the hydrogen. The sulphur content of these oils was eliminated for the largest part in the form of hydrogen sulphide, or it combined with the ferric oxide added for this purpose, the distillation products were practically free from sulphur

The trend of our work changed somewhat when the events of the War called peremptorily for the development of technical apparatus to carry through the hydrogenation of oils as well as of *coal* on a large scale As to the *origin* of coal, and what 'coal' really is, I had already been led to certain hypothetical reflections when, in 1911, I made the observation that peat, when exposed to temperatures of more than 300° C in the presence of liquid water, gives off considerable quantities of carbonic acid and is reduced to a powdery residue of a composition closely resembling that of natural bituminous coal The process of decomposition of vegetable substances in nature and their gradual transition into coal in the course of millions of years might well be considered to be of a similar character Cellulose, the main constituent of vegetable substances, is, from a thermodynamical point of view, an unstable product whose velocity of decomposition at normal temperatures, however, is slow enough to escape observation It has repeatedly been attempted to speed up the decomposition process of vegetable substances, such as cellulose or wood, and their transformation into coal, through application of heat, or, to avoid local superheating of the carbonizing material, more recently, of steam We selected the way of bringing peat, wood-cellulose, and other vegetable substances into closest contact with liquid water at a working temperature of 290–350° C under pressures up to 200 atm Under these working conditions water is not transformed into steam, but, as a good conductor of heat, absorbs and distributes the heat produced during the decomposition process without becoming a reaction participant itself The carbonic acid as well as the water formed could be quantitatively recovered Two parts of cellulose yielded 2 parts of carbonic acid and 5 parts of water, leaving behind a powdery substance corresponding to the composition $C_{10}H_8O$, the hydrogen content varying slightly

Theoretically, this 'synthetic coal', produced through 'Inkohlung', as we called it, of cellulose, could be assumed to be a combination of carbon, hydrogen, and oxygen of a structure akin to certain unsaturated compounds of a terpene-like character and apt to absorb a considerable quantity of hydrogen; through hydrogen absorption this compound would approach the class of heavy petroleum hydrocarbons Experiments, of a character analogous to the hydrogenation of oil, carried through during the summer of 1913 demonstrated from the very start that *coal produced from cellulose by the process of 'Inkohlung', when treated with hydrogen at a pressure of about 150 atm. at temperatures between 400 and 450° C can be transformed to about 80% into gaseous, liquid, and benzol-soluble products.*

These experiments, repeated with natural coal, gave practically the same results They formed the basis for the process of producing liquid and soluble compounds from coal for which a patent application was filed in the autumn of 1913. This process soon became known under the name of **Coal Liquefaction.**

To prevent the injurious decomposing effect of the considerable heat developed during the absorption of hydrogen by the coal, we employed the latter in the form of a suspension with a suitable oil which is liquid at the working temperature The oil in this case has the same effect as the water in the process of 'Inkohlung'

So-called younger coals and lignites proved more or less suitable for liquefaction, wood and lignin especially after previous 'Inkohlung' Coals poor in hydrogen and anthracites, the carbon content of which exceeds 85% in the ash-free substance, cannot be hydrogenated

The gaseous part of the hydrogenation products includes *methane* and *ethane* and, in the case of hydrogenation of young lignites, a considerable amount of *carbon dioxide* The nitrogen of the coal is transformed to about 50% into *ammonia*, while the rest occurs in the distillation products in the form of organic bases Sulphur, for the largest part, escapes as *hydrogen sulphide* About one-half of the oxygen content of the coal reappears as water in the liquid portion of the reaction products, and the main part of the carbon is present in the shape of light, medium, and heavy oils, the rest, which is poor in hydrogen and oxygen, being removed together with the ash as unliquefied substance

When, in 1914, we took up the hydrogenation of heavy oils and coal on a technical scale, we faced the difficult problem of constructing technical high-pressure apparatus into which liquids together with solid substances and gases could be introduced, there to be heated, mixed, and brought to reaction, allowing at the same time the continuous discharge of the reaction products Technical high-pressure apparatus until then had been constructed only for gas reactions in the homogeneous system At that time, cylindrical wrought or pressed steel vessels had been available only up to a very limited diameter, so that we were compelled to make use of a reaction vessel of considerable length, i e 8 metres, in order to obtain sufficient reaction space We decided to arrange the reaction vessel in a horizontal position, the raw material being introduced on one side and the reaction products drawn out on the other, because in a vertically placed vessel, with its comparatively high column of liquid kept in lively agitation by the gas bubbling through, intermixing of freshly added with partly worked-up material is liable to occur at any time

For the originally planned rotating apparatus a stationary vessel, equipped with a stirring arrangement, was substituted.

Constructing an appropriately shaped stirring-rod of 8 metres length and dependable stuffing-boxes for its insertion into the reaction chamber offered no less difficulties than the designing of durable valves to regulate the expansion of the reaction products, consisting of liquid, solid, and gaseous substances, from 150 to 1 atm , or the devising of instruments for the exact measurement of flowing high-pressure gases In fact, not until 1924 had the technical apparatus reached its final perfection

Taking into consideration the fact that the strength of iron is unfavourably affected at the working temperatures of our process, we refrained from heating the high-pressure vessel from the outside to avoid any local overheating We designed instead a special heating arrangement inside the reaction vessel, making use of a heat-transfer medium in the shape of a chemically indifferent compressed gas, such as carbon dioxide or nitrogen, kept in circulation by a pressure-pump Through heat-exchange between the hot reaction product and the circulating gas, the latter is heated to above 300° C. and enters the mantle surrounding the reaction chamber after it has been brought to the required final temperature in a special furnace The gas then returns to the circulating pump without being expanded This economic heating arrangement allows temperature to be maintained for several weeks with a variation of but a few degrees

One of the most difficult problems to be solved consisted in finding a practical way of feeding the coal continuously into the reaction chamber The question was satisfactorily settled in 1920, when we adopted the method of mixing the powdered coal with a viscous oil, such as tar or the heavy part of the coal-hydrogenation product from a previous run, to a pasty mass which is easily forced into the high-pressure vessel with the aid of hydraulically moved pistons

The erection of the large-scale experimental plant at Mannheim-Rheinau was started in 1916 Practical work was taken up in 1919 with the splitting of heavy, sulphur-containing residues from Panuco and Persian oils and other products with a maximum throughput of 30 metric tons per day Depending on the raw material, average yields of 25–35% gasoline and 40–50% gas oil were obtained, the rest, consisting of heavy products, was converted into lubricating oils, while a small percentage of asphalt and methane formed the waste products

After the large-scale apparatus had sufficiently been tried out with oil, it served the working up of *coal* for some time The bulk of the experiments, mainly carried through from 1922 to 1925 and covering several thousand practical tests with some 200 different kinds of coal, was executed in a rotating experimental bomb, more extensive investigations being carried out in a smaller unit of the large-scale apparatus having a daily capacity of about 1 metric ton and a somewhat simpler heating arrangement 100 kg of coal were mixed with 40 kg of oil from a previous operation, some ferric oxide added, and the pasty mass fed into the high-pressure apparatus together with 5 kg of hydrogen The output was represented by 128 kg of liquid and solid products, including 7 kg of water containing about ½ kg of ammonia, and 20 kg of gas from which 2 kg of gasoline could be washed out The oil obtained could be fractioned into 20 kg of oil with a boiling-point up to 230° C, 10 kg of products boiling between 230 and 330° C, 51 kg heavy oils and asphalt, containing the inorganic constituents of the coal and the non-liquid or soluble coal substance, amounting to about 10% of the coal used The accurate working of the experimental apparatus made it possible that with a daily throughput of 1 metric ton of coal, all the materials employed could be accounted for in the final products with a total loss of but 1%

The consumption of hydrogen averaged about 5% of the weight of the coal No difficulties were encountered in adding considerably larger quantities of hydrogen by submitting the primary products to another treatment under high pressure, the result being a noteworthy increase in low-boiling products at the expense of the high-boiling oils

Some difficulties were at first met with in trying to separate the heavy oil portions from the inorganic substances, an item of greatest importance in practical coal liquefaction We finally succeeded in finding the proper way by submitting the hydrogenation products to filtration in cell-filters at suitable temperatures It could be shown that the separation of the two bodies is better accomplished the more completely the products leaving the hydrogenation apparatus have been submitted to the influence of hydrogen

From the heavy parts of the coal oil, lubricating oils of good quality could be produced

To regenerate the hydrogen required for the oil-liquefaction process from the methane and ethane contained in the gaseous products of hydrogenation, we worked out a technical method on the basis of splitting these two gases at high temperature in the presence of steam Methane and steam interact with formation of carbon monoxide and hydrogen

$$CH_4 + H_2O = CO + 3H_2$$

If this carbon monoxide-steam mixture is allowed to pass over a contact substance in the presence of surplus steam, another molecule of hydrogen is split off

$$CO + H_2O \quad CO_2 + H_2$$

Thus every molecule of methane yields 4 molecules of hydrogen, and by converting part of the methane-ethane mixture in this manner all the hydrogen necessary for the liquefaction process can be procured The carbon dioxide accompanying the hydrogen can easily be separated after compression of the gases This method of producing the hydrogen required for the hydrogenation of oil is said to be now in use in the United States

Our own work on the hydrogenation of coal and oil terminated in 1927 after we had demonstrated by large-scale experiments in a technical plant the possibility of practical application of the hydrogenation reaction to the conversion of petroleum residues and coal into distillable oils, gasoline, gas oil, and lubricating oils We made no systematic investigations as to the influence of contact substances in connexion with hydrogenation, though occasional observations made in 1920 and 1921 pointed to a beneficial effect of catalysts upon the consumption of hydrogen by the initial material The Badische Anilin- und Sodafabrik, whose hydrogenation process is founded upon our patents, at that time took up extensive and highly successful experiments in that direction with different catalysts which led to the well-known hydrogenation processes as now practised by the I G Farbenindustrie A G

EARLIER WORK ON HYDROGENATION AT HIGH TEMPERATURES AND PRESSURES

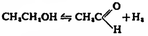
By V. N IPATIEFF, D.Sc.

Chemical Research Director, Universal Oil Products Company

Introduction

EVERY investigator in the field of petroleum technology understands the tremendous part played by the hydrogenation and the dehydrogenation reactions of organic compounds, especially hydrocarbons If we turn to the historical development of chemistry during the last 35 years, we can see that the year 1901 must be looked upon as the beginning of an extensive study of these reactions The French scientists Sabatier and Senderens discovered reduced nickel as a catalyst and studied hydrogenation at atmospheric pressure The author [9, 1901] studied hydrogenation and dehydrogenation under high pressure, and found a number of catalysts, the metals Fe, Zn, Sn, and brass, and their oxides Fe_2O_3, CuO, ZnO, SnO, and NiO These catalysts later came to play an important part in the synthesis of various organic compounds

The study of the hydrogenation reactions of organic compounds, especially hydrocarbons, preceded a discovery of the reverse reaction of dehydrogenation of alcohols and their almost quantitative conversion into aldehydes, ketones, and hydrogen under the influence of the above-mentioned catalysts [9, 1901]



$$CH_3CH_2OH \rightleftharpoons CH_3C\overset{O}{\underset{H}{\lessdot}} + H_2$$

In order to study the reversibility of catalytic reactions and also the kinetics of these processes it was necessary to build an apparatus which would permit the use of high pressures and temperatures In 1901–3 it was impossible to find an autoclave in which reactions at 400–500° C and a pressure of 400 atm could be carried out In 1903, after many attempts, it was possible to construct a simple autoclave bomb, which satisfied the requirements for the study of high-pressure reactions, the main feature of this apparatus being a gasket consisting of a metallic ring into which knife edges were fitted, the latter being placed in the head and the tube of the apparatus For the purpose of mixing the substances inside the bomb the apparatus was rotated in different ways, and various stirrers were introduced

The first experiments on hydrogenation and dehydrogenation of organic compounds gave some very valuable results In the first place it was shown that many catalytic reactions are reversible at high temperatures, and it also appeared possible to observe various phases of the reaction, which, in most cases, cannot be done at ordinary pressures The speed of many reactions is considerably increased when pressure is applied, and it is possible to hydrogenate many substances which decompose at ordinary pressure and at the temperature of hydrogenation Finally, by introducing an excess of hydrogen into the high-pressure apparatus the hydrogenation reaction can be carried to completion From the theoretical point of view, the study of high-pressure reaction of organic compounds is valuable in so far as it is possible to follow the course of the reaction from the kinetic viewpoint

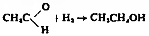
The indicated advantages of carrying out hydrogenation under pressure were soon recognized by the chemical industry, and at the present time practically all hydrogenation reactions are conducted under pressure

Hydrogenation

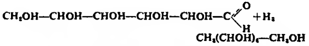
The scheme at the bottom of the page shows various types of hydrogenation of chemical compounds The characteristics of each type will be given later

Normal Hydrogenation

This type of hydrogenation is characteristic of the fact that molecular hydrogen combines, under the influence of various catalysts, with the molecule of a given organic compound, which has double or triple bonds or an aromatic nucleus Similarly, substances containing oxygen, such as aldehydes, ketones, and ethers, can also undergo hydrogenation and change into the corresponding alcohols



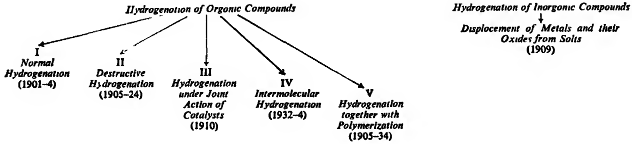
$$CH_3C\overset{O}{\underset{H}{\lessdot}} + H_2 \rightarrow CH_3CH_2OH$$



$$CH_2OH—CHOH—CHOH—CHOH—CHOH—C\overset{O}{\underset{H}{\lessdot}} + H_2$$
$$CH_2(CHOH)_4—CH_2OH$$

Hydrogenation can also go further in replacing the atoms of oxygen by hydrogen, the resulting substances being saturated hydrocarbons Under the influence of catalysts

HYDROGENATION UNDER PRESSURE



it is also possible to hydrogenate nitrogen derivatives [21, 1922, 1927], such as nitriles and oximes, under ordinary as well as under high pressures This indicates the wide application of hydrogenation in organic chemistry

All these hydrogenation reactions can be carried out according to the method of Sabatier and Senderens [23, 1905], but in most cases the reaction does not go to completion, and also not all substances can be hydrogenated because of the possibility of their decomposition Hydrogenation under hydrogen pressure makes it possible to complete the reaction as well as to conduct the reaction in the liquid phase, without fear as to the decomposition of either the starting material or of the product From the very beginning of the investigation of the dehydrogenation and the hydrogenation reactions of organic compounds it became evident that in many cases there is a separation of carbon at ordinary pressure, but in the same reactions carried out under pressure there is absolutely *no separation of carbon* This discovery, made in 1904 [10], undoubtedly had a great significance in the development of the ideas about hydrogenation of organic compounds under pressure and led to the problem of obtaining liquid fuel from tars and various types of coal

The first results of hydrogenation of organic compounds under the influence of an iron catalyst (iron walls of the bomb) were found during the investigation of the dehydrogenation reaction of alcohols The study of the decomposition of alcohols under pressure without any added catalysts, that is, under the influence of the iron walls of the autoclave alone, has shown that at high temperatures and pressures the final products are chiefly paraffin hydrocarbons, a small amount of polymerization products of ethylene, and water The high yield of paraffin hydrocarbons accounts for the fact that this type of decomposition is called *paraffinic* The non-formation of carbon can be explained by the fact that hydrogen, formed during the first phase of decomposition of alcohol, combines with, or hydrogenates, the fragments or radicals formed during further decomposition of the alcohol molecule During the study of pyrolysis of methane it was found that carbon monoxide and dioxide are converted into methane [13, 1913]

$$CO+3H_2 \rightarrow CH_4+H_2O, \quad CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$$

Later, during the study of the synthesis of methane from carbon and hydrogen under pressure and in the presence of a nickel catalyst, the author discovered that the reaction of converting carbon dioxide into methane is a reversible reaction, because under the given conditions water is able to oxidize methane into carbonic acid This reaction later served as the means of obtaining hydrogen from methane

The study of dehydrogenation of methanol has shown that this reaction is also reversible The results suggested that the gases formed in this reaction, i e carbon monoxide and hydrogen, can combine with each other to give formaldehyde, which, in its turn, can be hydrogenated to alcohol In view of the fact that zinc oxide decomposes aldehydes into carbon monoxide and saturated hydrocarbons only to a small degree, Patart suggested this catalyst for the synthesis of methanol from carbon monoxide and hydrogen under pressure

Further experiments on hydrogenation in iron autoclaves without the addition of any other catalysts have shown that hydrogen can combine with organic compounds which contain a double bond For instance, in the polymerization of ethylene in an autoclave in the presence of hydrogen and under the influence of iron, a hydrogenation of the double bond takes place in the case of both ethylene and the products of its polymerization [11, 1906–7]

Hydrogenation under the influence of various catalysts and under a molecular hydrogen pressure not only increased the speed of the reaction with different organic compounds and made the reaction go to completion, but it also made it possible to conduct, by correct choice of catalysts, a systematic and a *selective hydrogenation* Such catalysts as the metals Zn, Cu, Mn, Sn, and others, as well as their oxides, can be used for both hydrogenation and dehydrogenation, but only a few of these can serve for the purpose of hydrogenating mononuclear aromatic hydrocarbons Ordinary double bonds can be hydrogenated, regardless of position, by all the above-mentioned catalysts For example, on hydrogenation of allylbenzene under pressure and in the presence of copper oxide one obtains propylbenzene as the only product, whereas on hydrogenation of the same compound in the presence of nickel or cobalt oxides it is possible to obtain propylcyclohexane The author has used selective hydrogenation, particularly in the case of hydrogenating the terpenes This rule applies also to the hydrogenation of compounds containing oxygen such as eugenol, anethole, and others

In the presence of copper oxide only the double bond is hydrogenated

$$C_6H_3(CH—CH-CH_3)(OCH_3)OH(1,3,4)+H$$
$$\rightarrow C_6H_3(CH_2—CH\,CH_3)(OCH_3)(OH)$$

It is also possible to hydrogenate selectively eugenol and other organic compounds containing a double bond, using nickel oxide as a catalyst, if carried out in a cyclohexane solution and the temperature does not exceed 180–200° C At higher temperatures hydrogenation of the aromatic nucleus takes place This method of hydrogenation of unsaturated hydrocarbons was successfully applied to prove the presence of aromatic hydrocarbons in the products obtained by various processes of cracking, polymerization, and others Selective hydrogenation at a temperature not higher than 200–220° C saturated all the double bonds, and the resulting hydrocarbons did not react with a permanganate solution (the colour of a 2% solution of permanganate did not change for a period of 5–6 min), nor did they dissolve in 96% sulphuric acid, but reacted very energetically with a nitrating mixture forming the nitro-compounds The hydrocarbons obtained by such a method dissolved in fuming sulphuric acid (15% SO_3) and also could be hydrogenated under pressure and under the influence of nickel oxide at 300–320° C, the products being naphthenes These hydrocarbons no longer dissolved in fuming sulphuric acid (15–20% SO_3), nor reacted with a nitrating mixture At the present time, selective hydrogenation is one of the most reliable methods of distinguishing different types of hydrocarbons

For the purpose of hydrogenation nickel oxide [11, 1906–7] can be used very successfully instead of reduced nickel, because very often the reaction proceeds with greater speed, and also an extra operation of preparing reduced nickel is eliminated

As contrasted with hydrogenation under atmospheric pressure, the reaction under high pressure can be conducted in both the liquid and the solid phases Under high pressure the product in most cases remains in the liquid phase and hydrogenation proceeds with greater speed and goes to completion, especially if the liquid is stirred.

It is also possible to conduct the hydrogenation of organic compounds under pressure in water solution Many mono- and poly-saccharides were converted into the corresponding hexites, mannites, sorbites, and dulcites by means of this method In the same way water solutions of aromatic and unsaturated acids were hydrogenated to saturated and naphthenic acids

It is interesting to note that silico-organic compounds containing phenyl radicals, such as triphenyl or tetraphenyl *silicanes*, cannot be hydrogenated by heating with hydrogen under pressure and at temperatures up to 360° C in the presence of reduced nickel, thus showing that these compounds are more stable than the corresponding phenyl substituted methanes

Finally, we must note that hydrogenation under pressure can also take place with the solid salts of aromatic acids, these being converted into salts of naphthenic acids

At the present time, hydrogenation under pressure is used to a great extent for the purpose of hydrogenating aromatic hydrocarbons, such as naphthalene (for the production of tetralin and decalin), various phenols, and aromatic acids

Hydrogenation of various organic compounds using different catalysts was studied by many investigators Some of the most important works on hydrogenation under ordinary pressure were made by P Fokin [4, 1907–8], Skita [25, 1910], Willstatter [27, 1910, 1923], Paal [20, 1905, 1914], Adams [1, 1922], Adkins [2, 1931], and Zelinsky [28, 1911–12] In their investigations particular attention was paid to the catalytic action of platinum and palladium An extensive study of hydrogenation under pressure was made by Brochet and Adkins, the latter paying special attention to the preparation of mixed active catalysts

To give a general theory of catalytic reactions would be just as impossible as to give the same explanation for all ordinary chemical reactions Only a brief discussion of the author s views are given here

A catalytic reaction must be looked upon as a chemical process, and the reasons for the catalysis of a given reaction is to be sought in the chemical properties of the catalysts and those substances which participate in the reaction It is necessary to discover all the intermediate reactions which reproduce the catalyst For this purpose modern physico-chemical methods must be used The early definition of the catalyst, namely, that a catalyst only changes the speed of reactions, was found to be incorrect in many cases, and must be changed A catalyst repeats a chemical reaction many times, being reproduced every time, and therefore it would be better to call it a *multi-actor* or a *polyactor* The accumulated experimental data and perfected methods of studying chemical reactions may make it possible to understand catalytic reactions

For the explanation of hydrogenation and dehydrogenation reactions the author believes that it is possible to accept the most probable hypothesis of formation of metal oxides with the aid of water, during which reaction hydrogen is given off, the oxides oxidize the organic compounds by taking away its hydrogen These reactions can be represented as follows

$$\mathrm{Me+H_2O \rightarrow MeO+H_2}$$
$$\mathrm{MeO+C_2H_5OH \rightarrow Me+C_2H_4O+H_2O}$$

This hypothesis is supported by the fact that metals and their oxides are catalysts for dehydrogenation and hydrogenation reactions, and without the aid of water these reactions do not take place In some cases it can be supposed that the metal takes hydrogen from the organic compounds, with the formation of the unstable metal hydrides These hydrides decompose with the separation of hydrogen, and the metal is regenerated

Destructive Hydrogenation.

When an organic substance decomposes at high temperature in the presence of hydrogen it dissociates into several fragments, or radicals, and hydrogen immediately combines with the latter, resulting in the formation of saturated molecules of smaller molecular weights This type of hydrogenation is called destructive hydrogenation, it can be illustrated by the following reaction

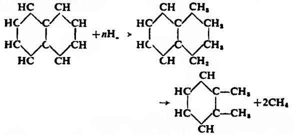
$$\mathrm{C_{12}H_{26} + H_2 \rightarrow C_8H_{14} + C_4H_{10}}$$

The presence of excess hydrogen and pressure prevents the formation of carbon, and saturated hydrocarbons are the product

The investigation of destructive hydrogenation was started by the author in 1904–5 While studying the decomposition of organic compounds under pressure in iron autoclaves in the presence of hydrogen, it was noted that hydrogen also adds to the products of thermal polymerization of ethylene

The above-mentioned investigations were the basis for further study of hydrogenation under pressure of various organic compounds and led Bergius to the patented method of obtaining liquid fuel out of tars, petroleum residuum, and certain kinds of coal This method of obtaining liquid motor fuel is carried out on an industrial scale in Great Britain, Germany, and in the United States In the author's opinion this method is not economical under present conditions, and cannot compete with the gasoline obtained by the cracking process

The works of the author [15, 1925, 1933] and of other investigators on hydrogenation under pressure of unsaturated organic compounds with aromatic rings, such as naphthalene, fluorene, phenanthrene, in the presence of various catalysts, have shown that during the first phase of the reaction hydrogen attaches to the aromatic nucleus, and the resulting hydrocarbon (not completely hydrogenated) decomposes into substituted mononuclear aromatic hydrocarbons



The temperature at which such a reaction takes place is about 425–450° C, and the initial pressure of the hydrogen pumped into the autoclave must be about 70–80 atm This destructive hydrogenation can take place in an iron autoclave under the indicated conditions without the addition of special catalysts

The presence of sulphur compounds does not interfere with destructive hydrogenation, and under these conditions thiophene is completely decomposed.

By means of destructive hydrogenation it is possible, for example, to convert organic compounds containing oxygen into hydrocarbons, phenol and cresol into benzene, toluene, &c

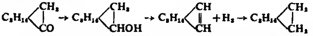
At the indicated conditions of temperature and pressure the aromatic nucleus is not decomposed, but if a catalyst which is able to hydrogenate the nucleus is used, there is more or less formation of naphthenes

During the last 10 years destructive hydrogenation has been the object of extensive study in many countries Some of the most interesting work was carried out in France, by Kling and Florentin [17, 1926], in Germany, by the I G Farbenindustrie [8], in the United States by the Standard Oil Company (Haslam) [7, 1930], in the U S S R , in the Institute of High Pressures and the Petroleum Institute by Klukvin, N Orlov, Belopolski, Nemtzov, and Klimov

Hydrogenation under the Joint Action of Catalysts.

Although it was long known that the addition of the product of a certain chemical reaction to the initial substance considerably facilitated the course of the reaction, increasing the speed and lowering the temperature, these cases were unique and could not be explained The experiments of the author [12, 1910, 1912] in 1909–10 on hydrogenation of amylene under pressure in the presence of copper oxide showed that the walls of the autoclave in which the reaction was carried out had an enormous effect on hydrogenation Thus the hydrogenation of amylene in the presence of copper oxide in an autoclave made of phosphor bronze proceeds very slowly and does not go to completion, while the same catalyst put into an iron autoclave effects the reaction much faster and the hydrogenation goes to completion, the isopentane produced containing no traces of amylene This discovery undoubtedly influenced the study of hydrogenation of organic compounds, and since then many substances have been suggested which may be added to the basic catalyst in order to increase its activity These substances are called *promoters*

The first study of the combined action of catalysts was made using nickel and aluminium oxides (2NiO, $1Al_2O_3$) for the hydrogenation of terpenes [12, 1910, 1912], camphor, borneol, and fenchone It was shown that in the presence of nickel oxide the hydrogenation of the terpenes occurs only at 360–400° C , and the reaction proceeds very slowly and is accompanied by the formation of side products If aluminium oxide is added to nickel oxide, the hydrogenation proceeds energetically at 190–200° C , and an almost quantitative yield of camphane and fenchane is obtained



Thus at 200° C , through the joint action of two catalysts, one of which aids hydrogenation and the other which aids the dehydration, an energetic hydrogenation takes place, and from a cyclic ketone a corresponding cyclic hydrocarbon is readily obtained

If instead of an active hydrogenating catalyst we take a less active one, such as copper oxide or aluminium, then in the presence of hydrogen the hydrogenation of terpenic alcohols will be different In spite of the fact that copper oxide is a hydrogenating catalyst of the double bonds, we cannot, in this case, obtain a saturated dicyclic hydrocarbon, but instead an unsaturated terpenecamphene will be the product The hydrogenation of camphor or borneol into iso-camphane in the indicated example, and also the experiments of Medsforth [18, 1923] on the hydrogenation of carbon monoxide in the presence of reduced nickel and promoters, makes it possible to explain these reactions in the following manner

For camphor first we have the hydrogenation of camphor into borneol, then the dehydration of borneol with the aid of aluminium hydrate, the latter forming with borneol a complex ether hydrate of aluminium oxide

$$AlO(OH)+C_{10}H_{18}O \rightarrow AlO(OC_{10}H_{17})+H_2O$$

During the dissociation of the ether the hydrogenation of the radical $C_{10}H_{17}$ into iso-camphane takes place with great facility under the influence of nickel oxide

$$AlO(OC_{10}H_{17})+H_2 \rightarrow AlO(OH)+C_{10}H_{18}$$

In order to explain the action of promoters in the formation of methane from carbon monoxide and hydrogen the following scheme of reaction is proposed instead of the explanation of Medsforth

If we assume that in the first phase of the reaction formaldehyde and methanol are formed, then during the next phase, under the influence of the dehydrating catalyst, the formation of methyl ether may take place This reaction was confirmed by our experiments

$$2CH_3OH \rightarrow H_2O + CH_3OCH_3$$

Under the influence of a hydrogenating catalyst methane is very easily formed

The use of promoters in the synthesis of methanol from water gas played a very important part We know that a great number of mixed catalysts were proposed for the synthesis of this alcohol, and one of the most active catalysts found is a mixture of the oxides of zinc, chromium, and copper, where the basic catalyst is zinc oxide, which only slightly decomposes aldehydes into carbon monoxide and saturated hydrocarbons

The combined action of catalysts is also illustrated by the interesting synthesis of hydrocarbons from water gas under ordinary pressure and at a temperature not higher than 200° C , discovered by F Fischer [6, 1926] and H Tropsch [26, 1929] The catalysts used for this process consisted of the following nickel oxide, cobalt oxide, aluminium oxide, thorium oxide (with the addition of very small amounts, sometimes traces, of alkali) When water gas is passed through these mixed catalysts the main products of the reaction are paraffins and olefines At the present time this reaction is being studied from the viewpoint of maximum gasoline yield from water gas, and in the near future the process may be used on an industrial scale We cannot, as yet, form any definite conclusions as to the theory of this reaction, but judging from the character of the participating catalysts, we can suppose that two catalytic reactions take place hydrogenation and hydration Under the conditions of the experiment (ordinary pressure and fairly low temperature) it can be supposed that the first product of the action of hydrogen on carbon monoxide is formaldehyde, which, according to the experiments of A. Butlerov and others, very easily undergoes aldol condensation, the products of which are later hydrogenated into alcohols, and from these either paraffins or olefines are formed

It is also possible that carbides are initially formed which are later converted into various hydrocarbons An example of such a reaction is the formation of paraffins and olefines through the decomposition of carbides of iron and manganese by dilute sulphuric acid as was shown by the experiments of Cloez, Hahn, and of the author. Further theoretical investigations must throw light on this interesting process Aside from the chemical properties of promoters, they also aid in increasing the surface of the catalyst, in facilitating absorption, in preventing the formation of large crystals of the basic catalyst, and in preventing the sintering of the latter, thus lengthening the life of the catalyst.

Intermolecular Hydrogenation.

The term 'intermolecular hydrogenation' is used for a double reaction, namely, one molecule of a hydrocarbon loses its hydrogen atoms and this atomic hydrogen combines with a molecule of another hydrocarbon, which can be hydrogenated under the given conditions. Thus intermolecular hydrogenation can take place without the introduction of molecular hydrogen. This type of hydrogenation arouses great interest and was first observed by the author together with H. Pines during the study of polymerization of ethylene under pressure in the presence of phosphoric acid. Experimental work made it possible to clear up the entire mechanism of the latter reaction and to check quantitatively all products derived in the course of this reaction.

The accomplishment of hydrogenation without participation of molecular hydrogen requires conditions favourable to the dehydrogenation of an organic compound formed during the reaction; on the other hand, an acceptor which can combine with the liberated hydrogen must be present. A similar reaction of dehydrogenation and hydrogenation was observed in the action of aluminium chloride on various aromatic compounds, as illustrated in R. Scholl's reactions [24, 1910, 1912]. Interdehydrogenation takes place in the Friedel and Crafts [5, 1883] reactions as well as in the reactions studied by Nenitzescu [19, 1931], where the formation of diphenyl, dicyclohexyl, dinaphthyl, and other hydrocarbons takes place. It must be noted that the above reactions involve complicated transformations which are difficult to explain, and are sometimes followed by complete rupture of the molecule. For example, during the action of benzene on azobenzene [21, 1922, 1927] in the presence of aluminium chloride the product is *p*-amino diphenyl.

$$2C_6H_6 + C_6H_5—N=N—C_6H_5 \rightarrow 2p\text{-}NH_2—C_6H_4—C_6H_5$$

Here, in all probability, we have destructive hydrogenation by means of hydrogen which is liberated during the formation of diphenyl.

The reaction of aluminium chloride and benzene and cyclohexane, studied by V. Komarevsky and the author [16, 1934], proves the complexity of the action of this catalyst on the simple hydrocarbons, for both intermolecular hydrogenation and *destructive alkylation* take place simultaneously.

Similarly, there is reason to believe that during the polymerization of olefines, especially ethylene, in the presence of aluminium chloride, there takes place an intermolecular hydrogenation of the low-boiling polymers by hydrogen, which is liberated on formation of naphthenes following cyclation of higher polymers of ethylene. The preliminary investigations carried out by A. v. Grosse and by the author [14] confirmed these suppositions, but only further experiments will explain both the character of the resulting hydrocarbons and the whole mechanism of this interesting reaction. It must be noted that another explanation of the formation of paraffins during the polymerization of ethylene is possible [14], for the author has recently discovered a reaction of alkylation of paraffins and naphthenes by olefines in the presence of aluminium chloride.

$$C_6H_{14} + C_2H_4 \rightarrow C_6H_{13}C_2H_5$$
$$C_6H_{12} + C_2H_4 \rightarrow C_6H_{11}C_2H_5$$

This reaction can also account for the large formation of paraffins. It is sufficient to add, for instance, some hexane to the products of polymerization of ethylene and it will undergo alkylation by ethylene, resulting in the formation of a number of various paraffin hydrocarbons. If the polymerization of ethylene under the influence of aluminium chloride still represents an unexplained reaction, the reaction of polymerization of ethylene and of other olefines in the presence of phosphoric acid gives a definite proof concerning intermolecular hydrogenation which takes place under the conditions of the experiment, the products being chiefly paraffin hydrocarbons. The normal polymerization of ethylene under pressure in the presence of phosphoric acid at 300–330° C consists in the formation of dimers, trimers, &c., of ethylene (that is, butylenes, hexylenes, and others). Investigations have shown that on the formation of tetramers of ethylene, i.e. octylenes, the latter are able to isomerize into naphthenes. It was proved that in the fraction of ethylene polymers containing octylenes, dimethylcyclohexane was present. As the polymer chain becomes longer the cyclation of these polymers proceeds with greater ease, and the fraction of ethylene polymers which boil above 225° C contains practically no olefines, but only cyclic hydrocarbons. Another reaction is noted, namely, dehydrogenation of naphthenes with the formation of aromatic hydrocarbons. The liberated atomic hydrogen, coming in contact with olefines, such as butylenes, hexylenes, and others, hydrogenates them very easily, and as a result large amounts of paraffins are obtained in the low-boiling fractions of ethylene polymers. Investigations have shown that such an intermolecular hydrogenation actually takes place, and the amount of paraffins which could be formed using hydrogen liberated on dehydrogenation of naphthenes was determined. Analysis and calculations fully confirmed the suggested mechanism of the reaction, and it was shown that the products of the polymerization reaction contains 46% paraffins (18% of these being isobutane), 7% olefines, 21% naphthenes, and 22% aromatic hydrocarbons. Thus, during the polymerization of ethylene in the presence of phosphoric acid intermolecular hydrogenation takes place to such an extent that almost one-half of the product is the product of hydrogenation. The course of the polymerization of ethylene under pressure, but without a catalyst, is entirely different, for the product contains absolutely no aromatic hydrocarbons, and the rest of the hydrocarbons are distributed as follows: 8% saturated hydrocarbons, 24% naphthenes, and 68% unsaturated hydrocarbons. The formation of saturated hydrocarbons can be explained by the hydrogenation of olefines by the atomic hydrogen which was liberated during the formation of either dicyclic compounds or of cyclic olefines containing double bonds.

The study of intermolecular hydrogenation and dehydrogenation of hydrocarbons is very important in the chemistry of petroleum, and it may contribute towards the explanation of the process of petroleum formation in nature. It would be very desirable to correlate the finding of aromatic hydrocarbons in different kinds of petroleum with their paraffin content. At the present time, knowing the conditions necessary for the polymerization of olefines and diolefines and the effect of catalysts on the course of the reaction, and further granting that petroleum was formed by the decomposition of animal and plant organic matter, the author concludes that the formation of several classes of petroleum did not require especially high pressures and temperatures This view is shared by many investigators, and was especially developed by Brooks [3, 1934] The formation of petroleum cannot be proved by chemical reactions alone, and for an understanding of petroleum formation in the depths of the earth it is necessary to look for biological as well as geological processes

Poly-hydrogenation.

Poly-hydrogenation represents a process which is composed of two reactions, one is the polymerization of the unsaturated hydrocarbons and the other consists in the hydrogenation of the polymers formed

The first reaction can proceed thermically without the influence of a catalyst, but the second reaction requires the influence of a catalyst Such a case was investigated by the author [11, 1906–7], for which purpose he used ethylene and hydrogen with iron serving as the hydrogenating catalyst A much more interesting case of poly-hydrogenation is one where two catalysts, one for each reaction, are participating It is then found that the energy of one reaction aids the course of the other reaction, and the process proceeds more favourably in the desired direction with the formation of the hydrogenated polymer

Hydrogenation of Inorganic Compounds.

After the discovery of hydrogenation reactions of organic compounds under pressure it was interesting to study the action of hydrogen under pressure on various inorganic compounds Beginning in 1909, the author and his associates have carried out experiments to determine the action of hydrogen on the salts of inorganic acids, oxides, &c

In 1909, by the action of hydrogen under pressure, metals in crystalline conditions were separated from salts of metals For example, by means of hydrogen under a pressure of 25–30 atm and at a temperature of 125–150° C beautiful, well-developed copper crystals (more than a centimetre in length) are separated from a copper sulphate solution, sulphuric acid being formed,

$$CuSO_4 + H_2 \rightarrow Cu + H_2SO_4$$

At a lower temperature we have first the precipitation of the basic salt, $CuSO_4 2Cu(OH)_2$, followed by the separation of beautiful, magnificently formed, ruby-coloured crystals of cuprous oxide (Cu_2O), and finally at a higher temperature copper crystals separate out

Each metal has its corresponding *critical temperature and pressure* at which the separation of the metal takes place Thus it was possible to separate the following metals from the solution of their salts Cu, Ag, Zn, Cd, Hg, Sn, Pb, Rh, As, Sb, Bi, Co, Ni, Pd, and Pt

On complete hydrogenation of acids the following products were obtained from sulphuric acid—hydrogen sulphide, from nitric acid—ammonia, from arsenic acid—arsenious acid, from chromic acid—chromic oxide, from carbonic acid—formic acid On the oxidation of phosphorus by water, formation of hydrogen takes place, and the latter, being in *statu nascendi*, hydrogenates the phosphorus which has not entered the reaction, giving as the product in the first phase of the reaction phosphine and phosphorous acid, which are later oxidized into phosphoric acid

$$4P + 3H_2O \rightarrow P_2O_3 + 2PH_3$$

Finally, the hydrogenation of salts of inorganic acids leads to the formation of various complex compounds and natural minerals On hydrogenation of complex salts of iron such as $K_4Fe(CN)_6$ magnificent octahedrons of magnetite, Fe_3O_4, are formed On hydrogenation of copper nitrate the natural mineral Gerhardite,

$$\left[Cu\left(\begin{matrix}HO\\HO\end{matrix}Cu\right)_3\right](NO_3)_4,$$

is obtained

The study of hydrogenation and oxidation of inorganic compounds under pressure will undoubtedly furnish much valuable information towards an explanation of the formation of minerals, for many of these processes undoubtedly take place under pressure and at an elevated temperature

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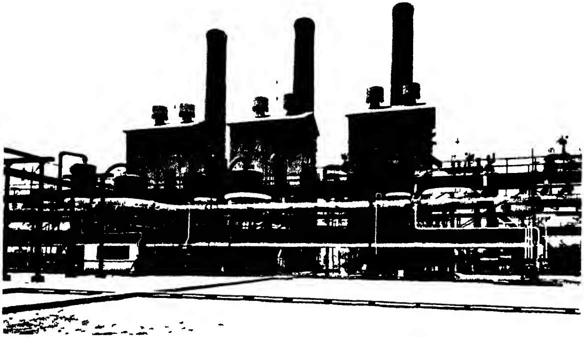

FIG. 1 Hydrogen manufacturing equipment Baton Rouge Hydrogenation Plant

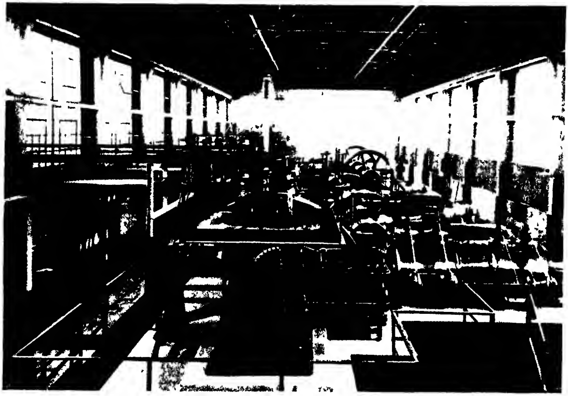

FIG. 2 Hydrogen compressors Baton Rouge Hydrogenation Plant

THE HYDROGENATION OF PETROLEUM

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THE conditions under which commercial hydrogenation has been practised since the time of Sabatier have been restricted until the last few years to the use of (1) hydrogen at substantially normal pressure or 2 or 3 atm above normal, (2) hydrogen of a high degree of purity particularly with respect to such catalyst poisons as sulphur, arsenic, and the like, (3) powerful but sensitive catalysts of the type of reduced nickel, and (4) temperatures safely below those at which thermal decomposition of the stock to be hydrogenated takes place Coal and oil, both always containing sulphur, were not amenable to this type of hydrogenation, and it was therefore restricted to animal and vegetable fats and oils, pure hydrocarbons and also pure organic compounds By eliminating the catalyst and substituting hydrogen pressures one-hundred fold greater than had previously been used, a high degree of liquefaction of coal was obtained, but the oils thus produced contained relatively large percentages of oxygenated bodies of the cresolic type, making the oils hard to crack or refine The research organization of the I G Farbenindustrie, through their experimentation, recognized the need of greater hydrogenation intensity than was obtainable with hydrogen pressures then commercially permissible and developed a line of sulphur-resistant catalysts which materially speeded up hydrogenation and caused the elimination of all the oxygen from the hydrogenated product In addition, their long experience in the field of synthetic ammonia enabled them to devise apparatus and methods for better carrying out this type of hydrogenation in a continuous manner

In 1927 the Standard Oil Company of New Jersey, through its Development Company, joined with the I G in the further development and commercialization of this method of treatment, and erected special laboratories for high-pressure experimentation Previous efforts had been directed largely towards the conversion of coal to gasoline or the conversion of asphaltic crudes and residual fuel oils to distillate naphthas and gas oils Although work along these lines was continued with particular emphasis on the simplification of the process, much of the effort in co-operation with the I G was to broaden the use of the process The results of this work were first reported by Haslam and Russell in 1930 [4]

Description of Process

Hydrogen Production. The hydrogen used in the operation is obtained from natural gas or refinery gas according to the following typical reactions

$$CH_4+H_2O = CO+3H_2$$
$$CO+H_2O = CO_2+H_2$$

If refinery gas or sulphur-containing natural gas is used, provision must be made for removing sulphur prior to reformation to hydrogen The first reaction is carried out in tubes packed with catalyst and heated by direct firing in a radiant-type downflow furnace to a temperature of about 1,600° F at approximately atmospheric pressure Following this, additional steam is added, and the second reaction is carried out using another catalyst at about 850° F. The gas leaving this stage of the operation is composed roughly of 77% hydrogen, 20% carbon dioxide, and 3% unconverted hydrocarbons and other gases The gas is cooled with water and conducted to a holder for temporary storage prior to compression Fig 1 shows a general view of this equipment

From the hydrogen holder the gas passes through a moisture trap to the suction of the compressors where the gas is compressed in several stages to a pressure of about 250 lb per sq in (Fig 2) The gaseous mixture is then conducted to equipment for removal of carbon dioxide (Fig 3) This is effected by scrubbing the gas in a bubble-plate tower with triethanolamine under the pressure mentioned above The dissolved carbon dioxide is subsequently stripped from the scrubbing medium with steam at atmospheric pressure, after which the stripped liquor is cooled and recycled to the absorption tower It is also possible to use water scrubbing for removal of carbon dioxide The scrubbed gas contains more than 95% hydrogen and is returned to the remaining stages of the compressors wherein it is raised to a pressure of approximately 3,500 lb per sq in (Fig 2)

Safety Precautions in Handling Hydrogen. Because of the explosive nature of hydrogen-oxygen mixtures, many precautions have been taken to guard against infiltration of air to the hydrogen stream Each compressor is provided with a recording oxygen alarm on its low-pressure side, which actuates a siren if more than 0 2% oxygen is present The combined discharge of all the machines is provided with a similar instrument In addition, a low-pressure alarm is fitted to the suction of each compressor This device is adjusted to sound should the suction pressure approach atmospheric Pressure is normally maintained at about 10 in of water at this point by the hydrogen holder This holder, which acts as a surge chamber between the hydrogen-producing equipment and the compressors, has been provided with both high- and low-level alarms Special precautions have been taken in all buildings to provide a high degree of ventilation in order to sweep out any hydrogen which might be vented through accidental leakage Similarly, care has been exercised in construction to eliminate pockets beneath which this gas might collect

Flow of Oil in Process The stock to be hydrogenated is raised to operating pressure by steam-driven plunger pumps, the exhaust steam from which is employed in hydrogen manufacture The high-pressure pump house, which also serves as the control room for the carbon dioxide removal system, is shown in Fig 4

The hydrogen from the compressors, together with recycled gas, is now mixed with the oil and delivered to tubular heat exchangers where the mixture is preheated by the hot hydrogenated products coming from the reaction chambers Following this, additional heat is supplied in a fired pipe coil wherein the temperature of the mixture is raised to about 700–850° F, after which it is introduced into the reaction chambers In the present plants these drums are about 40 ft in length and mounted vertically Ordinarily several are connected in series in each unit (see Fig 5) The reaction space is about 3 ft in diameter This free space is lined with a non-corrosive alloy and filled with a sulphur-resistant catalyst Inasmuch as no coke is formed in the process, and since the catalysts are extremely rugged, the process is virtually continuous In the large-scale plants continuous runs of one year in length are usually made, after which shutdown is made to replace the catalyst This catalyst is restored to its original activity by chemical treatment Since the hydrogenation reaction is exothermic, an increase in temperature takes place as the oil and hydrogen pass through the catalyst bed This raises the temperature of the reactants to 750–1,000° F or more, depending on the type of operation employed For this reason the amount of heat added in the fired coil is relatively small

From the reaction chambers the mixture of hydrogenated products and gas pass through the heat exchangers, a cooling coil, and thence to a separator Here the gas and liquid products are separated under full pressure, the liquid being withdrawn to a low-pressure separator from which it passes to storage The gas from the high-pressure separator is conducted to a booster compressor where it is recompressed to full operating pressure for mixing with the fresh hydrogen coming from the compressors Gases which are formed in the process are, in many cases, removed to a sufficient extent by solubility in the liquid product However, high-pressure scrubbing equipment is provided for removal of these gases if necessary By this means the recycle gas coming from the high-pressure separator is scrubbed with oil prior to recompression in the booster compressors

A general view of the Bayway hydrogenation plant is shown in Fig 6 Additional information on the operation of the process may be found by reference to Haslam and Russell [4, 1930] and Byrne, Gohr, and Haslam [1, 1932]

Major Adaptations of Hydrogenation

In each of the major applications of hydrogenation discussed below the equipment and even the arrangement of this equipment is essentially the same, the results obtained being controlled by suitable alteration of operating conditions

There are seven adaptations of hydrogenation which appear to be of most immediate importance in oil refining These are

1 The improvement of low-grade lubricating distillates to obtain high yields of lubricating oils of premium quality with regard to viscosity-temperature relationship, Conradson-carbon content, flash-point, and specific gravity

2. The conversion of paraffinic or aromatic gas oils into colour stable gasolines of low-sulphur and gum contents without production of coke or tar

- (*a*) Using high-temperature operation to produce high anti-knock gasoline
- (*b*) Using highly active catalysts at lower temperatures to obtain high conversions to gasoline of moderate octane number but exceptional lead susceptibility

3 The alteration of off-colour, inferior burning oils, or light gas oils, to produce high A P I gravity, low-sulphur, water-white kerosines of superior burning characteristics

4 The production of Diesel fuels of high Diesel index, excellent colour, and low-sulphur content from low-grade distillates

5 Conversion of heavy, high-sulphur content, asphaltic crude oils and refinery residues into gasoline and distillates low in sulphur content and free from asphalt, without concurrent formation of coke

6 The desulphurization, and colour and gum stabilization of high-sulphur content, badly gumming naphthas

7 Manufacture of new and specialized products, such as high flash-point safety aviation fuel of high anti-knock quality, and high-solvency naphthas for use as varnish and lacquer diluents, &c

Improvement of Low-quality Lubricating Distillates

It has been found that by hydrogenation it is possible markedly to improve inferior lubricating distillates Under the best conditions for this type of hydrogenation there are produced from 100 bbl of lubricating distillate 103 to 108 bbl of hydrogenated product containing from 60 to 85 bbl of lubricating oil, somewhat lower in viscosity but much more paraffinic than the charge, together with about 5 to 10 bbl of gasoline and from 10 to 35 bbl of gas oil

Fig 7 shows results obtained in an operation of this kind upon a heavy Mid-Continent lubricating fraction

Fig 8 shows products obtained by treatment of a West Texas lubricating fraction

The hydrogenated lubricating oils are characterized by high-viscosity index and high flash-points, both of which qualities are found in the Pennsylvania type oils The disadvantage of high Conradson-carbon content possessed by Pennsylvania oils, however, is not found in the hydrogenated products, thus accounting for their low carbon formation in actual service Although not shown in Figs 7 and 8, from 80 to 90% of the sulphur in the feed stock is eliminated by hydrogenation as hydrogen sulphide Other alien elements, such as nitrogen and oxygen, are also removed as gaseous hydrides Colour is greatly improved, thus reflecting the low Conradson carbons characteristic of hydrogenated lubricants These products have accordingly shown application in the manufacture of medicinal oils, white oils, and other products requiring high purity Additional inspections of hydrogenated lubricating oils have been presented elsewhere [1, 1932, 2, 1932]

Numerous engine tests, both in the laboratory and on the road, which have been carried out on hydrogenated motor oils, have demonstrated them to be superior to the highest grade natural lubricants, as regards oil consumption, carbon formation, valve gumming, and engine wear, both for conditions of moderate and severe service A description of some of these motor tests may be found in a paper by Haslam and Bauer [3, 1931] Extensive laboratory and field-test results have been reported by Haslam, Russell, and Asbury [5, 1933]

Production of Gasolines

As indicated above operation for gasoline may be conducted according to two methods Each of these will be described separately below

High Temperature Operation for High Octane Number. The production of anti-knock gasolines by this method of hydrogenation, although carried out in the same equipment as the other adaptations of the process, differs from them, in that the extent of hydrogenation is limited so that stable but non-paraffinic products are formed Sufficient hydrogenation to avoid the formation of coke or tar is permitted to take place A discussion of the thermodynamics involved in this type of operation has been reported by Sweeney and Voorhies [9, 1934] Recycle operation has been largely employed, whereby material not converted to gasoline is recycled to the operation By this means a yield of 85 to 95% gasoline is obtained on the charge, the remainder going to gas

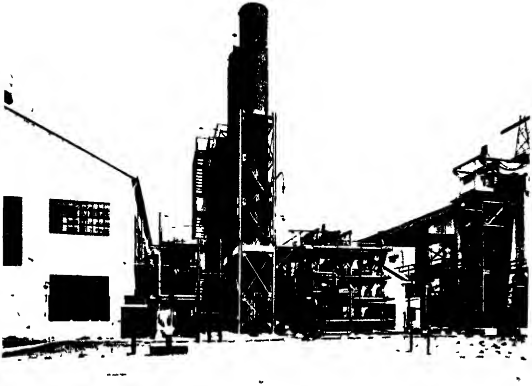
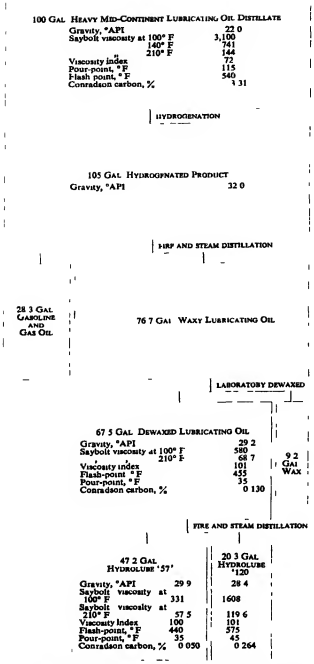


FIG 3 Carbon dioxide removal equipment Baton Rouge Hydrogenation Plant

FIG 4 High-pressure feed pumps Baton Rouge Hydrogenation Plant



100 Gal Heavy Mid-Continent Lubricating Oil Distillate

Gravity, °API	22 0
Saybolt viscosity at 100° F	3,100
140° F	741
210° F	144
Viscosity index	72
Pour-point, ° F	115
Flash point, ° F	540
Conradson carbon, %	1 31

105 Gal Hydrogenated Product

Gravity, °API 32 0

28 3 Gal Gasoline and Gas Oil

76 7 Gal Waxy Lubricating Oil

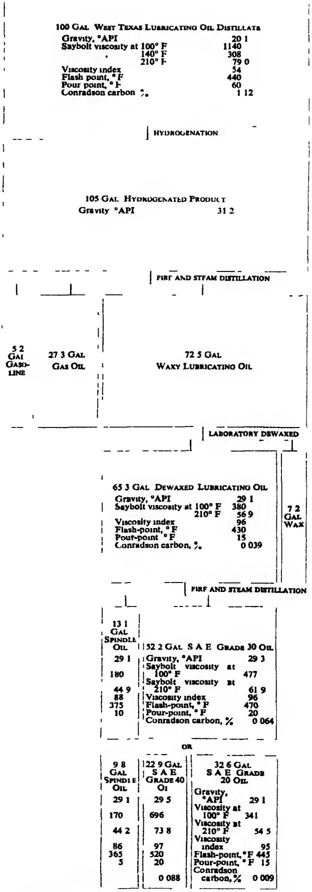
67 5 Gal Dewaxed Lubricating Oil

Gravity, °API	29 2
Saybolt viscosity at 100° F	580
210° F	68 7
Viscosity index	101
Flash-point, ° F	455
Pour-point, ° F	35
Conradson carbon, %	0 130

9 2 Gal Wax

	47 2 Gal Hydrolube '57'	20 3 Gal Hydrolube '120
Gravity, °API	29 9	28 4
Saybolt viscosity at 100° F	331	1608
Saybolt viscosity at 210° F	57 5	119 6
Viscosity Index	100	101
Flash-point, ° F	440	575
Pour-point, ° F	35	45
Conradson carbon, %	0 050	0 264

Fig 7 Products from treatment of Mid-Continent lubricating fraction



100 Gal West Texas Lubricating Oil Distillate

Gravity, °API	20 1
Saybolt viscosity at 100° F	1140
140° F	308
210° F	79 0
Viscosity index	54
Flash point, ° F	440
Pour point, ° F	60
Conradson carbon %	1 12

105 Gal Hydrogenated Product

Gravity °API 31 2

5 2 Gal Gasoline

27 3 Gal Gas Oil

72 5 Gal Waxy Lubricating Oil

65 3 Gal Dewaxed Lubricating Oil

Gravity, °API	29 1
Saybolt viscosity at 100° F	380
210° F	56 9
Viscosity index	96
Flash-point, ° F	430
Pour-point ° F	15
Conradson carbon, %	0 039

7 2 Gal Wax

	13 1 Gal Spindle Oil	52 2 Gal S A E Grade 30 Oil
Gravity, °API	29 1	29 3
Saybolt viscosity at 100° F	180	477
Saybolt viscosity at 210° F	44 9	61 9
Viscosity index	88	96
Flash-point, ° F	375	470
Pour-point, ° F	10	20
Conradson carbon, %		0 064

OR

	9 8 Gal Spindle Oil	22 9 Gal S A E Grade 40 Oil	32 6 Gal S A E Grade 20 Oil
Gravity, °API	29 1	29 5	29 1
Viscosity at 100° F	170	696	341
Viscosity at 210° F	44 2	73 8	54 5
Viscosity index	86	97	95
Flash-point, °F	365	520	445
Pour-point, ° F	5	20	15
Conradson carbon, %		0 088	0 009

Fig 8 Products from treatment of West Texas lubricating fraction

The process has been found to be particularly applicable to aromatic, low aniline-point gas oils Table I shows two stocks together with the results of their hydrogenation

TABLE I

Production of Anti-knock Gasoline from Gas Oils

	Mid-Continent	*California-cracked*
Feed Stock		
Gravity, °API	37 8	25 7
I B P, ° F	435	342
At 460° F, % distillate	3 5	31 0
At 550° F % ,,	90 0	91 0
F B P, ° F	629	602
Sulphur, %	0 179	0 554
Aniline point, ° F	159	79
*Hydrogenated Product**		
Yield, % by volume	86 5	89 0
Gravity, °API	56 4	43 7
I B P, ° F	86	105
At 212° F, % distillate	36 0	19 0
At 284° F, % ,,	61 0	47 5
At 356° F, %	83 0	85 5
At 374° F, % ,,	87 5	90 0
F B P, ° F	433	417
Octane no †	75 1	94
Dissolved gum, mg per 100 c c	3 6	2 8
Sulphur, %	0 022	0 017

* As received from hydrogenation unit

† Series '30 engine at 212° F jacket temperature, 600 r p m, 190–200 lb per sq in compression pressure

The gasolines produced are low in sulphur content and gum content They pass doctor and corrosion tests after soda washing and are quite gum stable, in certain cases some treating has been necessary, but this has been small in amount Higher anti-knock quality is obtained from the more aromatic feed stock, or alternatively with less paraffinic charging stocks it is possible to obtain higher yields of gasoline of a given octane number, or much better octane numbers for a given yield This is brought out in Table II

TABLE II

Influence of Feed Stock on Anti-knock Quality

General character of feed stock	*Highly paraffinic*	*Moderately paraffinic*	*Inter-mediate*	*Moderately aromatic*	*Highly aromatic*
Aniline point of feed stock, ° F	161	139	102	79	t0
Gasoline yield, %	89 9	91 4	88 0	89 0	88 0
Octane no of gasoline at 212° F *	72	75	85	92	Above 100

* See footnote † to Table I

The value of these high anti-knock gasolines as blending agents is apparent In addition, the low-sulphur content of hydrogenated gasolines makes them advantageous for blending with naphthas having sulphur contents difficult to reduce to specification limits Detailed information on high-octane hydrogenated fuel has been reported by Haslam and Bauer [3, 1931]

Operation for Moderate Octane Number and High Conversion In this method more active catalysts are employed than in high-temperature operation By this means lower temperatures are possible together with greater throughputs and higher yields For example, in recycle operation yields of stabilized gasoline of 110 to 120% (by volume) on the feed are obtained Although the gasoline so made is of poorer octane number than the high-temperature product, it has high lead susceptibility and is a stable and refined product except for the necessity of a caustic wash to remove hydrogen sulphide In view of these factors the use of these highly active catalysts is more favourable economically

Results from recycle operation on three stocks are shown in Table III These stocks range from a light highly aromatic cracked gas oil to a heavy fraction from Coastal crude In the runs shown in the table, temperature in the reactor was adjusted to maintain 60% fresh feed in the total feed to the unit It will be noted that in all cases 110 to 120% by volume of finished, stabilized gasoline was obtained All these gasolines are high in colour, have virtually no gum, and are low in sulphur content They have normal distillation characteristics and are highly susceptible to tetraethyl lead, resembling in the latter the most lead-susceptible straight-run gasolines

TABLE III

Production of Gasoline from Gas Oils using Highly Active Catalysts in Recycle Operation

	Cycle gas oil	*Heavy coastal*	*L Texas gas oil*
Feed stock			
Gravity, API	21 5	24 7	35 7
Aniline point, ° F	52	157	163
% sulphur		0 20	0 12
I B P, ° F	388	428	386
10% distillate at	440	493	494
50% ,,	464	640	547
90%	502		598
F B P, ° F	556		640
Yields			
% vol yield raw dist on Feed	122 5	118 2	114 2
Estimated Stabilized Distillate yield	119	117	112
Unstabilized distillate inspection data (Washed with soda and/or doctor solution)			
Gravity, API	57 7	62 2	66 3
Distillate plus loss at 122° F	5 0	5 0	8 0
,, 140° F	8 5	9 5	13 0
% at 212° F	28 0	33 5	35 0
,, 284° F	55 5	61 5	64 0
90% point	370	378	372
F B P, ° F	400	406	407
Dist loss, %	3 0	2 0	3 0
Colour Saybolt	+30	+30	+30
Preformed gum mg per 100 c c	0 0	0 0	0 0
Copper dish gum, mg per 100 c c	1 2	2 4	0 6
Breakdown time, min	240+	240+	240+
Doctor test	pass	pass	pass
Corrosion test	pass	pass	pass
Sulphur %	0 010	0 016	0 018
Octane no, C F R (MM)	61 4	58 2	53 8
Octane no, C F R (MM)+ 1 c c lead	75 0	71 5	69 8

Operation with these highly active catalysts may also be conducted on a once-through basis Results from this method of operation are shown in Table IV It will be observed that approximately 110% of hydrogenated product is obtained, consisting roughly of 70% gasoline and 40% gas oil As with recycle hydrogenation, the gasolines possess normal distillation characteristics and are of good colour and low sulphur content They likewise require no treatment except a caustic wash, and have high lead susceptibilities The gas-oil fraction is water-white, lower boiling than the feed, paraffinic in character, and negligible in sulphur content Because of these characteristics this gas oil is suitable for Diesel fuels (see below) or may be used as a cracking stock of excellent quality

Fig. 5 Interior of enclosure containing reactors and heat exchangers Bayway Hydrogenation Plant

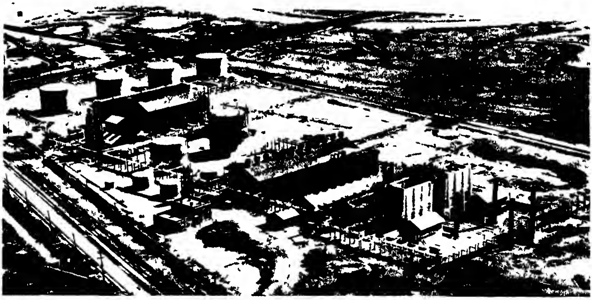


Fig 6 General view of Bayway Hydrogenation Plant

TABLE IV

Production of Gasoline and Paraffinic Gas Oil using Highly Active Catalyst in Once-Through Operation

	Naphtha bottoms	*Virgin Venezuelan gas oil*
Feed Stock		
Gravity, ° API	32 1	29 0
Aniline point ° F	114	136
% sulphur	0 28	0 90
I B P, ° F	395	442
10% distillate at	432	479
50% ,,	470	550
90% ,, ,,	540	625
F B P, ° F	598	652
Yields		
% vol yield hydro product on feed	111 8	109 6
,, , gasoline (unstab) ,,	73 4	56 0
,, ,, gas oil ,,	38 4	53 6
Raw gasoline inspection data (unstab)		
Gravity, ° API	59 8	67 2
Distillate plus loss at 122° F	7 5	8 9
,, ,, , 140° F	10 0	14 6
% distillate at 158° F	11 5	17 0
,, , 212° F	26 0	43 0
,, , 284° F	50 5	87 5
,, 374° F	84 5	
F B P, ° F	401	327
Dist Loss	3 7	4 8
Colour, Saybolt	+30	+30
Sulphur, %	0 019	
Octane no C F R (MM)	54 8	66 6
Gas oil inspection dota		
Gravity, ° API	43 5	43 1
Aniline point, ° F	174	168
Colour, Saybolt	+27	+25
Sulphur, %	0 02	0 03
I B P, ° F	415	335
10% distillate at	434	378
50% ,, ,,	453	436
90% ,, ,,	502	547
F B P, ° F	548	613

Economic studies have indicated that hydrogenation is ordinarily most advantageously applied to gasoline production by operating in conjunction with cracking plants In this method, refractory cycle stock is drawn from the cracking plant and charged once-through to the hydro plant using a highly active catalyst The hydrogenated product is distilled to remove the gasoline and the gas oil returned to the cracking operation The major results of this combined method of operation compared to cracking alone are

(*a*) For a given amount of gasoline less crude is required, owing to the higher yields obtained by hydrogenation and

(*b*) less fuel oil is produced, since no tar is produced in the hydrogenation process Detailed information on an economic study of this kind has been presented by Russell, Gohr, and Voorhies [7, 1935]

Production of High-grade Kerosines

High-sulphur content, low-gravity, off-colour kerosine distillates and poor-quality light gas oils may be hydrogenated to produce water-white distillates and burning oils of high quality In general these products meet specifications as to sulphur, colour, and smoke tendency, with no other treatment than reduction to flash-point and viscosity requirements

In this adaptation of hydrogenation it has been found desirable to start with a stock somewhat more viscous than the desired finished oil, with the result that in many cases the actual yield of finished high-grade burning oil has been greater than the amount of low-grade material of kerosine boiling range and viscosity originally present in the charging stock Liquid yields are from 100 to 105% by volume and the product contains from 65 to 85% of high-grade burning oil, the remainder being a gasoline This is shown for a typical case in Fig 9 In Fig 10 are shown results where operation is conducted to produce a substantial yield of gasoline along with high quality burning oil

TABLE V

Results of Hydrogenating Various Burning Oil Distillates

Feed stock	*Low grade Mid-Continent*		*Alamatos (Calif)*	*Long Beach (Calif)*	*West Texas Light gas oil*	*Cracked plant distillate*	*Colombia*	*Cracked Mid-Continent*	*West Texas Diesel fuel*
Gravity, ° API	40 2	41 1	36 4	36 8	35 3	39 0	36 1	39 7	30 5
Ref oil viscosity*	485	480	750	750	705	335	600	400	595
Sulphur, %	0 221	0 285	0 550	0 240	0 761	0 157	0 202	0 334	0 487
% '400' viscosity oil† in original	58	90	38	40	30	100	30	100	40
Gravity, ° API of '400' viscosity oil	41 2	40 0	40 0	39 9	39 1	39 0	38 9	39 7	35 1
Viscosity of '400' viscosity oil	400	450	380	400	410	335	400	400	400
Results of hydrogenation									
Volumetric recovery ‡	106	100	106	99	102	100	101	103	105
Gravity, ° API of total product	48 9	52 1	46 0	45 6	54 2	45 8	51 6	47 2	51 0
% sulphur of total product	0 006	0 011	0 022	0 025	0 026	0 024	0 029	0 014	0 019
% '400' viscosity oil in total product	83	75	65	60	58	85	73	80	65
Gravity, ° API of '400' viscosity fraction	46 0	46 7	43 0	43 3	45 5	43 8	44 1	44 4	44 0
Viscosity* of '400' viscosity fraction	415	380	410	400	375	335	355	360	360
Sulphur, %	0 007	0 012	0 013	0 012	0 018	0 022	0 013	0 025	0 015
Flash-point, ° F (Abel)	107	100	122	120	109	128	104	106	115
Colour (Saybolt)	22	25	17	25	25	25	18	25	
% sulphur elimination	97	96	96	90	97	85	86	96	96
Improvement in API gravity of '400' viscosity fraction	4 8	6 7	3 0	3 4	6 4	4 8	5 2	4 7	8 9

* Saybolt Thermo viscosity of refined oil at 60° F

† The term '400' viscosity oil is used to denote the fraction of about 400 viscosity and above 100° F Abel flash-point As will be noted, the true viscosity of most of the cuts actually made was slightly above or slightly below 400

‡ Not including a small yield of recovery naphtha produced concurrently

Operation on a number of feed stocks has shown that burning oils at least equal to those obtained from straight-run Mid-Continent or Pennsylvania distillates can be obtained from such stocks as California or Coastal fractions, heavy distillates from cracked Mid-Continent gas oils, and a number of others Table V shows a comparison of the results obtained with various feed stocks

In Table V the quality of the burning oils produced may be judged by the gravity of the '400' refined oil viscosity oil produced, this generalization having been proved by numerous lamp tests Thus a cut of 400 viscosity and 42° API gravity would give a burning test about equivalent to that of a 400-viscosity cut from Mid-Continent crude, and a cut of 400 viscosity of 45° to 46° API gravity would be equivalent to a Pennsylvania fraction of the same viscosity It is interesting to note in this connexion that lamp tests of hydrogenated kerosines have shown them to possess burning characteristics considerably superior to those indicated by their viscosity-gravity relationship

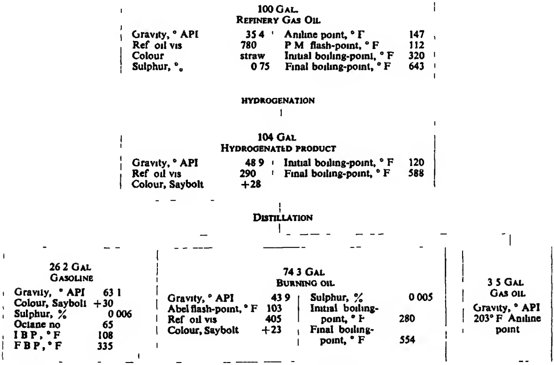


Fig 9 Production of burning oil

All the hydrogenated burning oils have been found to be very stable

The following points are worthy of note in Table V and Figs 9 and 10

1 The sulphur elimination is from 85 to 95% of the total, despite the wide variety of sulphur forms encountered in the different stocks used

2 In contradistinction to other methods of burning-oil improvement now available, none of the charge is degraded The entire hydrogenated product consists of burning oil and gasoline, both of which are more valuable than the charging stock In other words, hydrogenation reconstructs the undesirable constituents present in the feed rather than separating them as in solvent extraction

3 All the stocks, although differing widely in initial chemical characteristics, after hydrogenation equal the highest API gravity natural burning oils in physical characteristics Analysis indicates that by hydrogenation (*a*) olefines are almost completely eliminated, (*b*) the greater portion of the aromatics are converted into naphthenes and paraffins, and (*c*) there is very little apparent effect on the naphthenes, probably since new naphthenes are formed from aromatics in the charge, thus offsetting the improvement brought about as the original naphthenes are changed into more paraffinic compounds

Production of Diesel Fuels

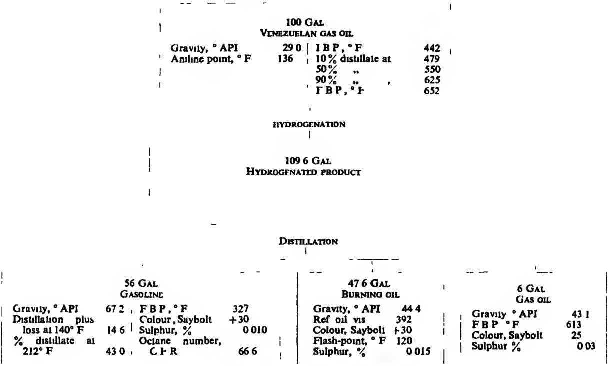
As mentioned above, the gas oils produced in once-through operation for gasoline production meet all requirements for high-quality Diesel fuels, particularly when highly active catalysts are used For example, in Table IV, Naphtha Bottoms yielded a gas oil of 75 Diesel Index As an additional example, operation on a heavy Venezuelan fraction showed the results presented in Table VI when operated primarily for Diesel oil The high-gravity and aniline point indicate that this gas oil is of the paraffinic or paraffinic-naphthenic type with virtually no unsaturation It should be noted that this fraction meets all the requirements of a high-speed Diesel fuel in that it possesses

(*a*) high paraffinicity,
(*b*) low pour-point,
(*c*) low sulphur content,
(*d*) water-white colour

No treatment is required on the hydrogenated product except a caustic wash to remove hydrogen sulphide

Conversion of Refinery Residues into Gasoline and Gas Oil

The conversion of coal or heavy, asphaltic, high-sulphur content products into high yields of gasoline is probably the most widely discussed adaptation of hydrogenation



100 Gal
Venezuelan gas oil

Gravity, ° API	29 0	I B P, ° F	442
Aniline point, ° F	136	10% distillate at	479
		50% ,,	550
		90% ,,	625
		F B P, ° F	652

Hydrogenation

109 6 Gal
Hydrogenated product

Distillation

56 Gal
Gasoline

Gravity, ° API	67 2	F B P, ° F	327
Distillation plus loss at 140° F	14 6	Colour, Saybolt	+30
% distillate at 212° F	43 0	Sulphur, %	0 010
		Octane number, C F R	66 6

47 6 Gal
Burning oil

Gravity, ° API	44 4
Ref oil vis	392
Colour, Saybolt	+30
Flash-point, ° F	120
Sulphur, %	0 015

6 Gal
Gas oil

Gravity ° API	43 1
F B P ° F	613
Colour, Saybolt	25
Sulphur %	0 03

Fig 10 Production of burning oil and gasoline

For the hydrogenation of heavy asphaltic crudes or residues from these crude oils or from cracking processes, once-through liquid-phase operation may be carried out in the liquid phase to convert the heavy charging stock into 100% or more by volume of product of a more highly paraffinic nature The gasoline content may represent from 5% to upwards of 35% of the liquid product from this operation with 80 to 90% boiling below 700° F If a higher yield of gasoline is desired, the heavier part of the product may be recycled in the same unit In general, the application of this adaption of the hydrogenation process would be to process these heavy asphaltic products in the liquid phase to produce small yields of gasoline and the remainder gas oil, with a total volumetric yield of 101 to 104%, the gas oil would then be cracked to produce gasoline in existing cracking equipment or converted into naphtha by hydrogenation as previously described If the gas oil is cracked in conventional apparatus, as much of the cracking-plant tar as is needed for the production of steam and power in the refinery would be used as fuel and the remainder returned to the hydrogenation unit It is believed, however, as pointed out previously, that, in general, gasoline production can be carried out most economically using highly active catalysts operating on cracked cycle stocks to produce gasoline and paraffinic gas oil for subsequent cracking [7, 1935]

During liquid-phase hydrogenation the asphalt content may be completely converted and 65 to 95% of all the sulphur in the charging stock eliminated Even if the product charged is highly asphaltic and of high-sulphur content, the gasoline produced is easily finished to give a low-sulphur content, gum-stable product The anti-knock value of the gasoline produced by this application of hydrogenation is dependent somewhat on conditions, particularly the type of charging stock—crude residues from Smackover, Venezuela, Colombia, and similar crudes giving higher octane number gasolines than residues from Mid-Continent crude The gas oil formed in the liquid-phase operation, in addition to having a relatively low-sulphur content, cracks to give a gasoline which finishes to specification easily even when the gas oil is produced by hydrogenating a crude or residue of high sulphur and asphalt contents

Table VI

Production of Gasoline and High Diesel Index Diesel Fuel from Venezuelan Heavy Gas Oil

Feed stock	
API gravity	18 5
10 mm distillate	
I B P ° F	432
50% distillate at	521
95% ,, ,,	590
% sulphur	1 7
Yields	
% vol yield gasoline on Feed	20 5
% ,, Diesel oil ,,	87 8
Gasoline (raw, unstab)	
I B P ° F	106
Distillate and loss at 140° F	5 5
% distillate at 158° F	7 0
,, ,, 212° F	30 5
F B P ° F	340
Colour, Saybolt	+30
Octane no C F R (M M)	60
Diesel fuel	
API gravity	35 0
Aniline point ° F	188
Diesel index	66
Flash-point (P M) ° F	170
I B P ° F	374
10 % distillate at	433° F
50 % ,, ,	606° F
% at 700° F	77
Colour, Saybolt	+22
% sulphur	0 02
Pour-point, ° F	−40

TABLE VII

Results of Hydrogenating Heavy Residues

	Topped crane Upton crude			*Topped Nacona crude*		*Cracking plant tar*	
		Product					
	Feed	*Expt 1*	*Expt 2*	*Feed*	*Product*	*Feed*	*Product*
Product, % by volume		107 7*	100 5*		101 5*		98 9*
Gravity, ° API	23 4	35 8	35 1	24 9	37 5	12 4	23 5
I B P , ° F	350	138		344	130	340	153
% at 212 F		4 0			4 0		3 0
„ 284° F		8 5			10 0		6 5
„ 374° F		18 0	24 5		21 0		12 5
„ 400° F		22 0	30 0	1 0	25 0	0 5	14 0
„ 460° F	6 5	33 5	41 0	1 5	36 5		20 5
650° F	40 5	77 5	79 0	34 0	76 0	34 5	67 0
„ 700° F	66 0	87 5	86 5	82 0	85 5	49 0	82 0
% sulphur	1 25	0 198	0 530	0 760	0 108	0 702	0 246
% gasoline*		22 0	30 0		25 0		14 0
Gravity ° API of gasoline		57 3	57 6		60 8		56 4
% sulphur in gasoline		0 034	0 056		0 049		0 019

* Does not include a small yield of absorption naphtha produced concurrently

Some typical examples of the once-through liquid-phase operation are given in Table VII, in which a comparison is shown of the properties of three heavy feed stocks before and after hydrogenation All the asphalt present in the charge was converted into more paraffinic type products, about two-thirds of the sulphur eliminated, and the entire product was a yellow distillate oil As another example, it was found, in hydrogenating a 7 2° API gravity cracking coal tar, that the sulphur was reduced from 2 77% in the charge stock to 0 49% in the total hydrogenated product The gasoline in this product contained 0 071 % sulphur without further treatment

Treatment of Naphthas for Elimination of Sulphur and Gumming Tendency

In view of the facility with which catalytic hydrogenation eliminates sulphur, this process has been used for the treatment of natural or cracked naphthas By a mild hydrogenation an unstable gasoline of high sulphur and gum contents may be rendered stable, with about 50% of the sulphur eliminated under such conditions of operation that the anti-knock value is lowered only to about the same extent as would result from a slight chemical treatment This phase of the process is referred to as 'Hydrofining' and may be carried out in such a way that no appreciable change is made in the boiling range of the naphtha Yields of 95 to 99% on the feed are obtained The process may also be so operated as almost entirely to eliminate sulphur from a cracked naphtha, with a small decrease, and in some cases an actual material increase, in octane number Operation may also be conducted to obtain increased volatility Depending upon conditions of operation, this treatment eliminates from 65 to 98% of the sulphur in the feed stock and gives a gum- and colour-stable naphtha Table VIII shows the properties of a cracked distillate before and after hydrofining In Table IX are shown results on the treatment of a 70% bottoms fraction from untreated cracked distillate The light ends from this distillate were not hydrogenated since they met specifications after a light chemical treatment It will be noted that hydrogenation and subsequent re-running materially reduced the high-sulphur and gum contents in the bottoms fraction Colour was raised from 17 Robinson to +30 Saybolt and volatility improved

TABLE VIII

Hydrofining Cracked Distillate

	Feed-cracked dist	*Hydrogenated product*
Gravity, ° API	54 9	56 3
% sulphur	0 097	0 055
Colour, Saybolt	yellow	+23
Octane no at 212° F (S 30 engine)	81 6	82 2
Preformed gum, mg per 100 c c	77 3	3 8
Copper dish „ „ „		1 5
I B P ° F	88	112
% at 140° F		5 0
„ 158° F		12 0
„ 212° F	35 0	38 5
„ 284° F		69 0
„ 356° F		92 0
„ 374° F	82 0	95 5
F B P ° F	432	390

TABLE IX

Elimination of Sulphur and Gum

	Feed-cracked heavy naphtha	*After hydrogenation and redist*
Gravity, ° API	47 2	52 2
% sulphur	0 760	0 024
Colour	17 R	+30 S
Octane no at 212° F (Series 30 engine)	67 5	65 0
Preformed gum, mg per 100 c c	76 1	2 3
Copper dish „ „ „	39 0	2 1
Breakdown time, min	90	240+
I B P ° F	178	130
% at 158° F		2·0
„ 212° F	1 5	20 0
„ 284° F	37 0	63 5
„ 356° F	73 0	88 5
„ 374° F	78 5	91 5
F B P ° F	484	432
% Recovery	98 5	98 5

High Flash-point Safety Fuels

In air and marine transportation the use of gasoline constitutes an important hazard, owing to the tendency of gasoline to flash into flame or explode through accidental ignition Experience in the handling, storing, and utilization of kerosines, cleaners' naphthas, &c , has shown that the danger from this source is negligible if the flash-point is maintained above approximately 105° F.

Obviously, a high flash-point may be met by using close fractionation to raise the initial boiling-point of the fuel. With both natural and cracked products, however, this results in a fuel of octane number below the practical limits for the Otto-cycle engine. The use of tetraethyl lead in such fuels in permissible amounts does not improve detonation sufficiently.

In contrast to this, it has been found that hydrogenated fuels of certain types have the best anti-knock qualities in their heavier fractions. Because of this property, hydrogenation yields a high flash-point safety fuel of extremely good quality. An extended discussion of hydrogenated safety fuels was published by Howard [6, 1922]. Table X shows a comparison of the specifications of commercial gasoline and kerosine with those of hydrogenated safety fuel.

TABLE X

Comparison of Specifications of Various Fuels

	Av. commercial gasoline			*Kerosine*	*Hydrogenated safety fuel*
Gravity, ° API	59.0	to	68.0	46.0	29.8
I.B.P. ° F	90	„	105	380	312
End-point ° F	390	„	435	550	406
Abel flash-point ° F	−40	„	−55	107	106
Octane no.	65	„	75	below 50	87–95*
Copper-dish gum, mg. per 100 c.c.	5	„	7		1.0

* Determined against iso-octane and normal heptane blends on Series 30 engine. 300° F. jacket temperature, 600 r.p.m., 190–200 lb. per sq. in. compression-pressure. Other octane numbers in this table were obtained by the same method and conditions, except at the less severe jacket-temperature of 212° F.

In the production of high flash-point fuel the hydrogenated product from the unit is distilled into two cuts. The bottoms fraction comprises the safety fuel, whereas the overhead cut represents a high-quality light aviation fuel. Table XI shows a typical example of the feed stock and the two products obtained.

The difference between the sum of the yields of the two products in Table XI and 100% is represented by loss of feed to gas during the hydrogenation operation. The two products are characterized by high octane number, low-sulphur and gum contents, and good colour. Their high anti-knock value makes them suitable for blending purposes to replace benzene and tetraethyl lead.

Practical use of any high flash-point fuel requires special attention to ease in starting. There are a number of solutions to this problem, most of which are in use at the present time.

High-solvency Naphthas

As in the production of safety fuel, solvents are obtained under hydrogenating conditions analogous to those in the manufacture of high octane-number gasoline. Low aniline-point straight-run, or cracked light-gas oils serve as the feed stock. The solvent power of naphthas so produced is usually superior to that of ordinary petroleum solvents. Table XII compares a typical hydrogenated solvent with a petroleum solvent and a coal-tar solvent of similar boiling range.

In solvents of the type shown in Table XII, high solvency is indicated by low API gravity, low aniline-point, and high Kauri butanol value. On this basis the hydrogenated solvent naphtha is decidedly superior to the petroleum solvent produced by ordinary refining methods, and in addition can be made better than coal-tar products as shown in Table XII.

TABLE XI

Production of High Flash-point Safety Fuel

Feed stock

Gravity, ° API	25.5	Aniline point, ° F.	10
Sulphur, %	0.89	I.B.P., ° F.	348
Colour, Saybolt	8	F.B.P., ° F.	570

	Hydrogenated products	
	Light aviation fuel	*High-flash aviation fuel*
Yield on feed, %	29.0	55.0
Gravity, ° API	49.5	28.5
Sulphur, %	0.005	0.010
Abel flash-point, ° F.		107
Colour, Saybolt	30	28
Colour hold (1 hr. sunlight)	No drop	No drop
Copper-dish gum, mg. per 100 c.c.	2.5	4.8
Doctor test	Passes	Passes
Corrosion test	Passes	Passes
Aniline point, ° F.		−20
Octane no. at 300° F.*	83	93
I.B.P., ° F.	100	309
F.B.P., ° F.	335	411

* See footnote * to Table X.

TABLE XII

Comparison of Various Solvents

	Solvent naphtha		
	Hydrogenated	*Normal petroleum*	*Coal-tar*
Gravity, ° API	31.6	51.9	33.1
Colour, Saybolt	25	30	22
Aniline point, ° F.	−19*	147	17
Sulphur, %	0.06	0.03	0.06
I.B.P., ° F.	293	311	302
F.B.P. ° F.	412	413	378
Kauri butanol value†	77	30	72

* Extrapolated value.

† Standard testing method in the varnish and lacquer industry, denoting the amount of solvent naphtha which can be added to a standard Kauri gum solution without coagulation.

TABLE XIII

Hydrogenated Solvent Naphthas

Fraction	200–275° F.	275–365° F.	365–419° F.	419–460° F.
Gravity, ° API	50.6	34.0	26.2	19.6
Specific gravity	0.777	0.855	0.897	0.937
Colour, Saybolt	+25	+23	+23	0
Doctor test	pass	pass	pass	pass
Corrosion (Cu)	„	„	„	„
„ (Hg)	„		„	
Sulphur, %	0.038	0.040	0.040	0.042
Flash point, ° F. (closed cup)		61	135	190
Kauri butanol value	55	76	77*	86*
Dimethyl sulphate value	24	62	87	100
Dilution ratio	1.9	2.8	2.6	2.4
Aniline point, ° F.	52	−1†	−10†	−33†
I.B.P., ° F.	168	270	352	410
10% at	198	293	368	423
50% „	228	317	383	434
90% „	279	358	412	458
F.B.P., ° F.	322	397	438	489

* Kauri butanol values calculated from 50/50 blend of solvent in Kahlbaum benzene of 31.5 Kauri butanol value.

† Extrapolated value.

In the production of solvents the hydrogenated product from the unit is fractionated into a number of cuts of desired boiling range In ordinary operation the following four cuts are usually made

Solvent No 1	200–275° F	boiling range
,, ,, 2	275–365° F	,, ,,
,, ,, 3	365–419° F	,, ,,
,, ,, 4	419–460° F	,, ,,

The relative proportions of these fractions, as well as their distillation characteristics, may be controlled by adjustment of feed-stock boiling range Table XIII shows the properties of solvents 1 to 4 obtained by fractionation of the hydrogenated product from a low aniline point, light-gas oil

By the standard tests the hydrogenated solvents show a high degree of refinement The low sulphur content and ability to pass corrosion tests, both with copper strip and mercury, meet the requirements for high-grade solvent naphthas As judged by Kauri-butanol values, dimethyl sulphate values, and aniline points, the solvency powers of hydrogenated solvents increase with boiling-point

These materials find application as lacquer diluents, paint and varnish thinners, rubber solvents, and resin solvents, as well as in a number of special uses where a combination of high-solvent power and controlled evaporation rate is essential Tests have shown these high-solvency naphthas to be equal to toluene and xylene as solvents for most of the resins now on the market [8, 1934]

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THE HYDROGENATION OF COAL

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Since the ratio of hydrogen to carbon is much lower in coal than in hydrocarbon oils, it follows that the conversion of coal into liquid fuel must involve the addition of hydrogen For this reason the term hydrogenation has been applied to the treatment of coal under high hydrogen pressure and high temperatures, although the action of the hydrogen in this case is more comprehensive than true addition The reactions which occur are complicated, and the final result is a compromise between (i) the true hydrogenation of complex hydrocarbons, (ii) the cracking or pyrolysis of these at the high temperatures involved, (iii) the saturation of the unsaturated bodies formed by pyrolysis, and (iv) the reduction of oxygenated groupings to aromatic hydrocarbons The balance of these depends upon the conditions chosen, but the overall result is that the oil product has a higher hydrogen/carbon ratio than the original coal

In comparison with other methods of obtaining supplies of liquid fuel from coal, hydrogenation possesses the advantage of giving by far the greatest yield, the conversion to liquid being complete except for a proportion of gas formation and a small residue of unconverted coal

The first attempt to hydrogenate coal was made by M Berthelot in 1869 [2], who treated coal with hydriodic acid solution at 270 C and obtained a yield of 60% of hydrocarbon oils Similar experiments have been made with other reducing agents, but the first practical advance was not made until 1924, when Bergius reported the successful working of a hydrogenation plant treating about 40 kg of coal per hour This plant was the result of earlier researches by Bergius Starting with the production of spirit by heating petroleum oils to 450° C with hydrogen at 20 atm pressure, he later (1913) applied this treatment to artificial coal made by heating cellulose to 340° C at 100 atm pressure for 8 hours [1, 1933] Using a temperature of 400° C, he converted this product mainly into a material soluble in benzene The first patents of the Bergius process were taken out in 1914 (B P 18,232) Apart from the early papers by Bergius, little information was available of the process and little interest taken in it until the continuous plant at Rheinau came into operation in 1925 After that date interest was stimulated by the formation of many groups of investigators and later by technical applications of the process in Germany by the I G Farbenindustrie and in England by Imperial Chemical Industries Ltd The investigators in England were J I Graham and his co-workers at the University of Birmingham and the Fuel Research Station of the Department of Scientific and Industrial Research The investigations as a whole have given birth to a considerable literature [3] dealing mainly with the reactions involved in the treatment of coal and with patent details The control of the patents relating to hydrogenation is now mainly vested in International Hydrogenation Patents Ltd , a company formed by the Standard-I G (a company promoted by the Standard Oil Company of New Jersey and the I G Farbenindustrie), the Royal Dutch Shell Company, and the Imperial Chemical Industries The exploitation of any hydrogenation process by any concern outside these companies would hardly seem possible except under licence

THE BERGIUS PROCESS

A diagrammatic arrangement of the final form of the Bergius plant is shown in Fig 1 The coal was crushed to pass a 2-mm sieve, mixed with heavy oil or tar in the proportion of about 2 5 to 1, and hydrated iron oxide (5% of the coal), and pumped at a pressure of 200 atm into one end of the first converter consisting of a horizontal steel cylinder closed at both ends by special joints and heated by gas through a lead-filled jacket Each converter was fitted with a paddle stirrer Hydrogen and coal paste entered at the same point of the converter, and the reactions involving liquefaction of the coal proceeded so rapidly that the product was sufficiently fluid to flow through the connecting pipe to the second similar converter Three converters in all were used, the coal being in process for about 2 hours The temperature used varied with the coal from 440 to 490° C

Bergius added the iron oxide ('luxmasse') with the idea of fixing the sulphur of the coal which he considered deleterious, but it has since been shown that the material has a marked catalytic effect on the reactions

THE MODERN COAL HYDROGENATION PROCESS

The reactions in the Bergius process took place essentially in the liquid phase In the modern process the coal is first treated in one, or two, liquid phases, and then a portion of the product of suitable boiling range is further hydrogenated in the vapour phase Even so, the first stage in the liquid phase differs from the Bergius process by permitting the more complex molecules a longer reaction time and by the use of more active catalysts

The complete process is best described in relation to a modern plant One conception of such a plant is shown in diagram in Fig 2

The Liquid-phase Stage

The coal is pulverized, mixed, or 'pasted' with heavy oil and catalyst, the latter being usually less than 0 1% of the coal processed, and pumped with hydrogen at 250 atm pressure through a preheater into the bottom of the liquid-phase converter The temperature may be raised to the working level of 400–480° C in the preheater, or additional heat may be supplied in the converter The reaction products which vaporize are carried with the excess hydrogen, and the gaseous hydrocarbons formed, from the top of the converter and pass through a condenser into a separator, where the condensate collects and whence the 'residual' gas passes to a gas-washing tower, where the heavier hydrocarbon gases are washed out with a hydrocarbon oil and the remaining impure hydrogen is purified and returned to the process.

The average time of treatment in the liquid phase is about 2 hours The heavier molecules exceed this time, and

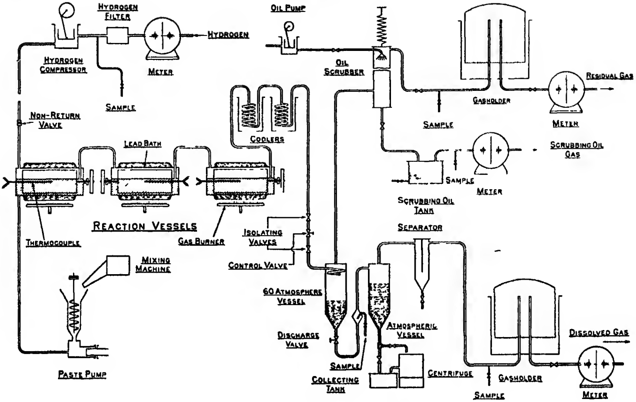

Fig 1

FLOW DIAGRAM OF HYDROGENATION PLANT AND REFINERY

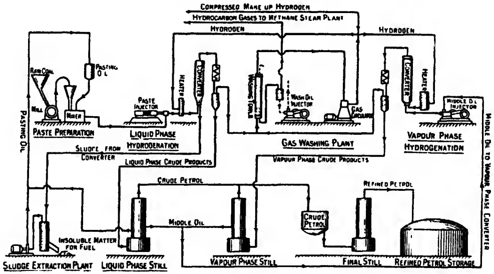

Fig 2

the lighter undergo a shorter time The reactions are exothermic H G Grimm [10, 1931] has given a heat of reaction figure of 450 kg -cal per kg of coal converted into middle oil. The crude condensate from the liquid phase is distilled and separated into three fractions. (i) spirit up to 200° C ; (ii) middle oil 200–300° C.; and (iii) heavy oil over 300° C. Any material which resists conversion into vaporized products, i.e. fusain, coal ash, and catalyst, is run continuously from the converter, together with a proportion of heavy oil, in the form of a sludge This sludge may be treated in various ways, by centrifuging or by carbonization, in order to recover heavy oil and a dry, solid residue The heavy oil is returned, with the oil boiling over 300° C. from the liquid phase, to the beginning of the process, where it is used for pasting fresh coal.

To remove the solids, filtration, centrifuging, or settling methods may be employed, usually after dilution with a lighter oil. The residual oily solids are then carbonized and the oils obtained returned to the process The coke obtained serves as a fuel.

Vapour-phase Stage

The middle oil passes to the second-stage or vapour-phase converter In admixture with hydrogen the oil is preheated almost to reaction temperature and the vapours pass through a bed of catalyst material, the heat of reaction, which is very marked, being utilized to maintain the temperature at the required level of 400–480° C The pressure in this system is the same, 250 atm The vapours leaving the converter are condensed, the oils passing to a distillation plant at atmospheric pressure, and the residual gas and surplus hydrogen to the gas-washing plant for recovery of hydrogen

The average time of treatment in the vapour phase is much shorter than in the liquid phase, and may be of the order of 1 minute only

The process of condensation and separation may be substituted in both stages by a system of partial condensation under pressure, the great advantage of which is that oils which are still in process remain under pressure, and the separated middle oil can be sent forward directly to the vapour-phase stage

The liquid product is freed from water and distilled to give crude spirit to 200° C and oil boiling above 200° The oil is preferably reprocessed in the vapour-phase converter

The overall thermal efficiency of the combined liquid and vapour phase has been given [7, 1931] as 43 % and [14, 1935] as 40 %

Products from the Bergius Process

The crude product from the Bergius process consisted of a black tar containing in suspension in a very stable form water, unconverted coal, coal ash, and luxmasse catalyst Separation of the water and solids was difficult, and centrifuging was the most satisfactory method The solid-free 'oil' cannot be regarded as a true oil Only about 50% distilled up to 360° C The distillate consisted of phenols, bases, and neutral oil representing about 6%, 2 5%, and 22% of the ash-free, dry coal The residue boiling above 360° C consisted of a pitch much of which was insoluble in petroleum ether and was asphaltic in nature Further details of the composition of oils and spirits from the process have been published [6, 1935]

Typical yields from a British coal are given in Table I The coal was treated at 450° C and 200 atm pressure

TABLE I

Yields from the Bergius Process
Yorkshire Coal

	% of ash-free, dry coal
Coal	100 0
Hydrogen	5 7
	105 7
Oil produced	
Spirit to 200° C	11 0
Oil, 200–300° C	17 5
Residue, above 300° C	37 1
	65 6
Gaseous hydrocarbons, &c	20 0
Carbonaceous matter	6 7
Water (including NH_3)	4 8
Loss	8 6
	105 7

In this table the amount of hydrogen shown is that of the hydrogen reacting

Products from the Modern Process

In the liquid-phase stage of the modern process two separate oil products are obtained One of these is a residue heavy oil used as recycle material, and the other is a light oil condensed from the exit hydrogen The latter is light brown in colour and free from suspended solid It consists of phenolic, basic, and neutral substances, and although obtained by condensation from the hydrogen it contains oils boiling up to 360° C Distillation gives a spirit boiling up to 200° C, which after refining is suitable for use as motor spirit A typical spirit, b p up to 170° C before refining, consisted of the following

	%
Aromatics	22
Unsaturateds	4
Saturated	74

The proportion of spirit, middle oil, and heavy oil obtained naturally depends upon the working conditions By employing a high throughput and a low reaction temperature, heavy oils are obtained in quantity These, however, possess no value either as bases for the preparation of Diesel engine fuel or lubricants By further hydrogenation, K Gordon [8, 1933] claims to have produced a Diesel oil from a bituminous coal, but makes no such claim for lubricating oils M Pier [15, 1933] has claimed, however, that similar heavy oil from brown coal will yield on further treatment some 20% of lubricating oil

In the vapour-phase converter conditions are chosen so as to give as high a conversion of oil to spirit as possible in one passage through the catalyst without forming an undue proportion of gaseous hydrocarbons Normally the treatment gives 55% of spirit, 5% of water, and 6% of permanent gas, the remainder being unconverted heavy oil which is recycled

The yields of products from the combined process are most readily considered in terms of complete conversion of the coal to motor spirit boiling below 200° C, it being understood that any less complete conversion giving fuel oil as an additional product would entail a lower consumption of hydrogen and a higher throughput in the vapour-phase converter.

Typical conversion data are given in Table II The upper part of the table shows the liquid-phase reactions, the middle portion the vapour-phase reactions, and the lower portion the combined processes in which the coal has been converted almost completely to spirit These data were obtained on an experimental plant, and the yield of spirit in a plant of industrial size would be rather higher, K Gordon [7, 1931] claims 165 gal per ton of dry, ash-free coal from a plant treating 15 tons of coal per day. In Table II the liquid-phase yield is 110 gal of oil and 60 gal of spirit with the expenditure of 24,000 cu ft of hydrogen In the vapour phase the yield is 110 gal of spirit for a similar expenditure of hydrogen The combined yield is 170 gal of spirit The figures for hydrogen are quoted in terms of hydrogen reacting, i e forming oil, water, and hydrocarbon gases The net amount of hydrogen forming oils and water, and therefore not recoverable, is much less than this, about 22,000 cu ft. The hydrogen which forms gaseous hydrocarbons is recoverable, and in a commercial process will form the major part of the requirements

TABLE II

The Complete Hydrogenation of Coal

Hydrogenation temperature	°C	450
Hydrogenation pressure	Atm	200
First stage in liquid phase		
Hydrogen reacting, cu ft per ton a f d coal		24,000
Yields		
Spirit, b p < 200° C, gal per ton a f d coal		60
Oil, b p > 200° C " " "		110
Total oil " " "		170
Second stage treatment in gas phase, of oil b p 200° C produced in first stage		
Hydrogen reacting, cu ft per ton a f d coal		24,000
Yields		
Spirit, b p < 200° C gal per ton a f d coal		110
Combined figures for the two stages		
Hydrogen reacting, cu ft per ton a f d coal		48 000
Yields		
Spirit, b p < 200° C, gal per ton a f d coal		170
Properties of spirit from combined stages		
Distillation		
Fraction b p < 100° C, % of spirit		20
" b p 100–200° C "		78
Specific gravity at 15° C		0 75
Octane number (motor method)		82
Composition		
Aromatic hydrocarbons, % of spirit		24
Unsaturated " "		7
Naphthene " "		28
Other saturated hydrocarbons % of spirit		41

The refractory nature of the product from the Bergius process has already been emphasized The modern process yields a spirit as the main product The refining of this spirit presents no difficulties The vapour-phase product is entirely free from acidic substances That produced in the liquid phase requires an alkali wash to remove phenolic substances The tendency to gum formation is not pronounced, and washing with sulphuric acid of 60% strength is sufficient to render the spirit sufficiently stable in this respect. When highly active catalysts are employed the vapour-phase spirit requires no refining treatment other than an alkali wash

Effect of Variables on the Liquid-phase Stage

The variables which affect the conversion of coal to heavy oil in the liquid phase are pressure, temperature, nature of coal, time of contact, the catalyst, and the pasting oil Temperature and pressure are connected in their effects to a large extent, since high temperatures are necessary for the reactions and a high pressure is necessary to accelerate the hydrogenation reactions in preference to those of cracking or carbonization Actually the reactions follow more nearly the course of direct hydrogenation, cracking, or pyrolysis of the hydrogenated products with hydrogenation of the molecular fragments produced by cracking

A wide range of coals can be treated by the hydrogenation process, but the ease of treatment and the yield of oil varies with the type of coal The most suitable coals are those containing from 80 to 84% of carbon and from 5 0 to 5 8% of hydrogen Coals of lower carbon content are readily treated, but give lower yields of oil owing to their higher oxygen content Brown coals and lignites differ from bituminous coal in being influenced by different catalysts. Coals of higher carbon content are more difficult to hydrogenate, requiring the use of higher temperatures and a longer time of treatment, both changes tending to a greater degree of cracking to permanent gas and therefore a lower yield of oil Of the macroscopic constituents of coal, the brights—vitrain and clarain—are the most easily hydrogenated, whilst dull coal—durain—is less easily converted Fusain is comparatively inert

The following examples illustrate the wide suitability of British coals

	Yorkshire steam coal	*Lancashire coking coal*	*N Staffs coking coal*	*Kent coking coal*
Composition of coal				
Carbon, %	83 5	82 0	85 1	87 5
Hydrogen %	5 5	5 4	5 6	5 3
Oil produced, %	73 4	72 4	74 6	71 0

One important factor in the choice of coal is freedom from inorganic impurities The average ash content of British coal is about 4 5%, which means that, for every ton of coal treated, 100 lb of residue must be withdrawn from the liquid-phase converter The abrasive action of this ash on release valves would be considerable, and, in addition, it would greatly reduce the value as a fuel of the solid fuel produced by carbonizing the sludge after extraction of the heavy oil which it contains Since the carbonaceous residue from the coal is from 5 to 8% of the coal, the solid fuel from a coal containing 4 5% of ash would contain 30–40% of ash For both these reasons, it seems certain that the choice of coal for hydrogenation purposes will fall upon coals which can readily be cleaned to an ash content of the order of 1%

The use of a coal containing little sulphur is not necessary, since the catalysts employed are sulphur resistant Indeed, sulphur appears to be beneficial in small amounts

Similarly, chlorine is not harmful in small amounts, since the hydrogen chloride formed is beneficial in overcoming the possible harmful effects of alkaline inorganic constituents In large amounts, however, it may be the cause of corrosion troubles

It follows from the Law of Mass Action that the rate of a reaction involving hydrogen is increased by raising the pressure and therefore the concentration of hydrogen Also, since hydrogen absorption means a decrease of volume, increase of pressure must favour hydrogenation The general effect of this can be seen in autoclave experiments, where the initial pressure is varied J G King [13, 1936] quotes results for Beamshaw (Yorkshire) coal at 445° C in the absence of an added catalyst

TABLE III

Effect of Pressure on the Hydrogenation of Coal

Pressure atm		*Products*		
Initial	*Maximum*	*Solids*	*Water*	*Oil*
80	203	41 2		37 2
100	245	26 1	6 1	50 2
120	283	21 6	6 4	56 7

At the lowest pressure the product was still solid The considerable increase in the amount of oil produced by increasing the pressure is shown by starting at higher initial pressures of 100 and 120 atm respectively

The general effect of increase of temperature is that both hydrogenation and cracking reactions are accelerated, but since increase of temperature reduces the degree of hydrogenation possible, there is an upper limit beyond which it is not practicable to go In the case of pure substances the limitations of temperature can be determined, but with a complex material such as coal only the overall effect can be observed Since the object of the process is to produce oils and the formation of permanent gas is to be avoided, it follows that there must be some temperature at which there is the best compromise between cracking and hydrogenating reactions This temperature is partly defined by the amount of hydrocarbon gas formed which is necessary to supply the hydrogen required

The effect of temperature in a continuous system has been defined by K Gordon [7, 1931] for a fixed reaction time of 2 hours His results are expressed graphically in Fig 3 As the temperature rises the residue of carbonaceous matter decreases, the total yield of oil decreases owing to the formation of more gas and a little more water, and the nature of the oil changes At 420° C the proportion of spirit is 22, while at 460° C it has risen to 48% of the coal The high-boiling oil has decreased proportionately, but the amount of middle oil has not greatly changed It will be obvious from this Figure how the temperature in the liquid phase will affect the process Too high a temperature will give more spirit without affecting the amount of middle oil passing to the vapour phase, but there may be a deficiency of heavy oil for 'pasting' Too low a temperature will have the opposite effect

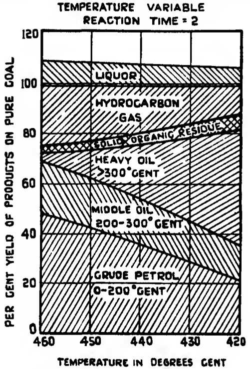

FIG 3 Effect of temperature on the hydrogenation of coal

These observations define the effect of temperature within the working range for the production of oil The reactions which occur in the heating-up stages are of importance in other directions It has been shown [12, 1933] that the action of hydrogen upon coal first begins at about 320° C in the presence of a catalyst, oxygen being eliminated as water, and hydrogen combining with the coal, these processes leading to the formation of increased amounts of resinous compounds The effect is so marked with some non-coking coals [5, 1931] that if the reactions be interrupted at this stage a solid product is obtained of high coking power, less than 0 5% of hydrogen reacting to bring about the change It is possible that this reaction may become of technical importance in connexion with coke manufacture

Time of contact is also important in this connexion, and Gordon also shows [7, 1931] that increase of reaction time has the same effect as increase of temperature At 440° C, as shewn in Fig 3, an increase of reaction time from 2 to 4 hours is equivalent to raising the temperature 20° C

Catalysts The catalyst to be used in the liquid-phase hydrogenation of coal has been the subject of a large number of patent applications for both simple and promoted catalysts and variations in the method of application The most suitable catalysts for bituminous coals are certain elements of the fourth group of the Periodic Classification These are titanium, germanium, tin, and lead, the most active of these being tin Titanium is active only in association with iron Zinc also has some activity, while iodine is a particularly active catalyst, and it is unfortunate that its action upon the containing vessels cannot be prevented in order that this activity can be explored and made use of The failure of nickel, a well-known hydrogenating catalyst, is probably caused by the action of sulphur compounds, but some nickel compounds, e g nickel oleate, are active despite the fact that they are not stable substances under the conditions used

Elements of the sixth group, molybdenum, tungsten, are less suitable for the liquid phase than for the vapour phase, but under chosen conditions, and particularly for brown coals and lignites, give good results They are not, however, active in small quantities like the elements of the fourth group The latter need be used only to the extent of less than 0 1% of the coal

It has been suggested that certain coals may contain active elements such as germanium, and that such coals might be particularly suited to the process It is unlikely, however that the amount present in very clean coal would be sufficient, or that the use of less clean coal would be justified, simply to avoid the addition of catalyst

The object of using a catalyst is to accelerate the rate of the hydrogenation reactions so that they may proceed at least as rapidly as those of cracking There is no reason, however, why the cracking reactions should not also be accelerated in the presence of a good hydrogenating catalyst A measure of the value of a catalyst is therefore obtained by observing the ability to reduce the temperature at which rapid combination with hydrogen takes place This may be done be measuring the rate of production of liquid products from coal L Horton, J G King, and F A Williams [12, 1933] have heated coal to reaction temperature in a stream of hydrogen and measured the rate of production of oil The curves shown in Fig 4 illustrate the comparative rates Curve 1 gives the rate in the absence of a catalyst or a vehicle, the coal yielding 24% of oil up to reaction temperature and 38% altogether In the presence of a stannous hydroxide catalyst (curve 2) the corresponding yields are 30 and 69% respectively

An effect which is of the greatest importance is revealed by curves 4 and 5 These represent experiments in which the coal was treated in admixture with a heavy oil as in the full-scale process In the absence of a catalyst a curve is obtained which shows a much greater conversion to oil than in the case of dry coal, and in the presence of a catalyst the conversion is still further improved Since in this experiment the oils produced are continuously removed from the system, it follows that the action of the liquid medium takes effect in the early stages For this reason it can be deduced that the dispersive action of a heavy-oil vehicle is a most important factor in coal hydrogenation, quite apart from the practical value of the oil in forming a pumpable paste This conclusion suggests that fine grinding of the coal in admixture with the oil, in order to assist the dispersive effect of heat in the presence of the oil, would repay any additional cost it might incur, by accelerating the rate of hydrogenation

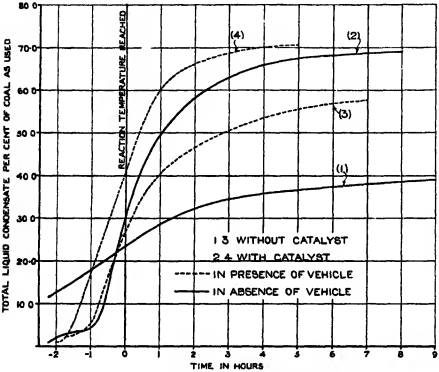

FIG 4 Rate of production of liquid product from coal

Effect of Variables on the Vapour-phase Stage

The conversion of the middle oil from the distillation or fractional condensation of the liquid-phase product is chemically the same in principle as the treatment of the coal paste The conditions chosen for pressure and temperature are those which give the best compromise between cracking and hydrogenation as regards yields and throughput From a study of the behaviour of pure compounds it can be deduced that the first action is that of hydrogenation, and that this is followed by cracking of the hydrogenation products with simultaneous hydrogenation of the unsaturated products

The optimum temperature in the vapour-phase converter varies from 400 to 500° C., depending upon the catalyst used and the type of product required Variations can lead to either an aromatic or a naphthenic spirit. Reaction begins about 360°C , both as regards decrease of molecular weight and reduction of oxygenated compounds Too high a temperature means that too high a proportion of the oil is cracked to permanent gas, and also that the rate of deterioration of the catalyst is increased

Catalysts. As in the case of the liquid-phase process, a very large number of substances have been patented for application in various ways In this case the catalyst must be applied in a granular porous form so that a large surface is exposed to the reacting vapour without freedom of passage being impeded The expedients adopted to overcome this difficulty have been mainly deposition on a porous granular support such as alumina gel [14, 1934] or the pelleting of the finely powdered materials The most promising catalysts are compounds of molybdenum and tungsten, although the halogens, particularly iodine, are as active, but their application in practice is difficult Alkalis and alkaline earths are deleterious in that they accelerate coke formation as in the liquid phase Molybdenum and tungsten are particularly active in the form of sulphides They are normally applied in the form of their ammonium salts, converted to the trioxides by heating in air and to sulphides in use, either by the addition of sulphur or by the action of sulphur compounds in the raw material, this sulphur being converted to hydrogen sulphide Attempts to produce metallic catalysts of sufficiently high thermal conductivity do not appear to have been successful

The reactions of hydrogenation-cracking are strongly exothermic, and difficulties arise in practice owing to local overheating in the catalyst bed This may be overcome by flooding with a less reactive oil such as a portion of the reaction product Metallic alloy catalysts of high thermal conductivity would be useful in this connexion

Vapour-phase catalysts deteriorate during use owing to the cloaking of their surface with solid matter, polymers of high molecular weight or even carbon resulting from cracking The rate of deterioration is, however, extremely slow when the reaction conditions are carefully controlled In the case of molybdenum and tungsten catalysts the catalyst may be revivified by oxidation with air at about 500° C , its full activity being recovered

Further details relating to the vapour-phase conversion will be found in the article upon hydrogenation of tars, the treatment of low-temperature tar and tar distillates is conducted upon exactly similar lines

Hydrogen

The supply of hydrogen is an important factor in the hydrogenation process It is shown in Table II that approximately 50,000 cu ft of hydrogen are required per ton of coal treated This hydrogen can be supplied by the interaction with steam of the gaseous hydrocarbons produced in the process, but may be prepared direct from coke or by the separation of hydrogen from coke-oven or other gases

It can be calculated that the entire process can become self-contained as regards hydrogen if about 15% of the carbon content of the coal treated is converted to gaseous hydrocarbons Under these conditions the yield of spirit and oil would be about 72%

COMMERCIAL DEVELOPMENTS

The operation of the hydrogenation process on a commercial scale was first achieved in Germany at Leuna. The raw material used was first brown coal in 1927, but this was later replaced by brown-coal low-temperature tar in 1929 For the last few years both coal and tar and crude German petroleum have been treated, and the output of motor-spirit has been about 250,000 tons per annum The costs of production have been high and the continuance of manufacture has been achieved only by the institution of a protective tariff of 1*s* per gallon An association has been formed by the Reich Minister for Economic Affairs for the further development of spirit from brown coal The process adopted will probably be that of the I G Farbenindustrie, and efforts will be made to increase the output at Leuna to 350,000 tons and to build additional plant in the Ruhr to produce 500,000 tons Since present German consumption amounts to about two million tons per annum, the above aims cover a large proportion of the requirements

Commercial developments in Great Britain have been solely in the hands of Imperial Chemical Industries, Ltd, who are partners in International Hydrogenation Patents, Ltd

Following experimental work upon a 15-ton per day plant Imperial Chemical Industries have erected a large plant which is intended to treat 400 tons of coal per day Owing to the low cost of imported petroleum spirit it is necessary for this plant also to have the benefit of a protective tariff if it is to achieve commercial success For this purpose the British Hydrocarbon Oil Production Bill was passed in 1934, guaranteeing the continuance of a tariff on imported spirit of at least 4*d* per gallon for nine years from April 1935 The tariff is now 8*d*

K Gordon [9, 1935] has stated that the cost of the new plant amounted to £5,500,000 including existing plant brought into service He estimates the output as 150,000 tons of motor spirit per annum, of which 100,000 tons are derived from coal and the remainder from creosote oil and low-temperature tar The cost of production has been given as about 7*d* per gallon of spirit obtained Gordon estimates that the thermal efficiency of the process would be 40% if the hydrocarbon gas produced were reconverted to hydrogen

The total production of spirit from the plant should be about 3 6% of the total consumption of spirit in Great Britain

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THE HYDROGENATION-CRACKING OF TARS

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THE advances which have been made in the application of hydrogenation technique to coal and bituminous materials generally open up a promising market for tars and tar products for which existing markets may become from time to time uncertain In this country approximately 1 5 million tons of tar are produced annually, and this finds a market after treatment mainly as road tar, creosote, pitch, benzole, toluole, xylole, naphthas, tar acids, tar bases, and naphthalene It is impossible to indicate the relative amounts of these products, since as markets vary from year to year first one and then another shows serious over-production During the years 1931–3 the creosote market dropped and large quantities were sold at low prices, while in 1934–5 the difficulty was to dispose of pitch In Great Britain at present (1934–5) approximately half of the tar produced is distilled to give pitch, while the other half is treated to give road tar, light creosote, and benzoles only The figures for 1934 were

	Tar distilled	*Pitch produced*
Gas works	980,200	208,400 tons
Coke ovens	462,800	156 000 ,,
Others	38,280	15,900 ,,
	1 481,280	380 300 ,
Road tar	770,000	

Conversion to motor spirit by hydrogenation-cracking offers a remedy for these troubles, since the market for spirit is sufficiently large to absorb all that is likely to be made in this way On a commercial scale the application of this technique in Great Britain would not be economic at the prices at present (1936–7) prevailing for petroleum motor spirit, but, in the event of the protective tariff continuing, the producer of tar would be certain of a profitable market for the products he is unable to dispose of through normal channels

In view of the variation in normal tar markets it will be apparent that the hydrogenation process must be capable eventually of dealing with high-temperature tars or even pitch as well as the more amenable materials such as low-temperature tar and tar distillates In view of the greater difficulty which attends the treatment of tars produced by the carbonization of coal at high temperatures, much more attention has been given so far to low-temperature tar and tar distillates In this country the amount of low-temperature tar produced is small, but in Germany large quantities of brown-coal tar have been produced and successfully converted into motor spirit and fuel oils

The technique used for the hydrogenation of low-temperature tar and tar distillates is the same as that used for the second stage in the hydrogenation of coal, i e the vapour-phase treatment of the 'middle oil' obtained by the distillation of the crude coal oil from the first or liquid-phase stage It consists in passing the vaporized tar with hydrogen under pressure through a catalyst bed maintained at the correct temperature

At present the chief aim of the process is the production of low-boiling oils, and for this purpose the temperature employed varies from 440 to 500° C , the pressure of hydrogen is 200 atm or more, and a hydrogenating catalyst is used to prevent the undue preponderance of cracking Under these conditions, in once-through operation, a normal low-temperature tar absorbs about 5 % by weight of hydrogen and yields a product which is completely soluble in petroleum ether (b p 40–60° C), and contains only traces of tar acids The pitch, tar acids, and bases are completely converted to liquid hydrocarbons, sulphur is eliminated as hydrogen sulphide, and nitrogen as ammonia The amount of spirit (b p up to 200° C) is increased from 7 to 50 % or more

The main reactions are the absorption of hydrogen (hydrogenation) and the production of low-boiling oils (cracking) It is apparent that a powerful hydrogenating catalyst is required Compounds of molybdenum and tungsten, especially the sulphides, are the most promising, and, since it is not possible to deal with all the catalysts described in the literature, it is proposed to discuss the subject mainly in relation to the use of molybdenum catalysts

Although tars are complicated mixtures of organic compounds, the nature of these is known to a considerable extent, and light has been thrown upon the behaviour of tar by studying pure compounds under the same conditions of treatment By this means C M Cawley and C C Hall [2, 1934] have recognized three main types of reaction in the hydrogenation-cracking process

(i) De-oxygenation reactions involving the removal of oxygen as water Those involving the elimination of nitrogen and sulphur as ammonia and hydrogen sulphide respectively may be included in this section

(ii) Reactions in which hydrogenation precedes cracking

(iii) Cracking reactions

The de-oxygenation reactions may be typified by the reactions of the phenols In the absence of a hydrogenation catalyst, phenol and the cresols are fairly stable at 450° C , but dihydric phenols and pyrogallol are relatively unstable, and are decomposed to pitch, carbon, and water In the presence of a catalyst phenol begins to react with hydrogen at about 350° C , and at 450° is converted completely to hydrocarbons Cawley and Hall recognize three reactions

(*a*) De-oxygenation $C_6H_5OH \rightarrow C_6H_6$ followed by some hydrogenation $C_6H_6 \rightarrow C_6H_{12}$

(*b*) Hydrogenation followed by dehydration

$$C_6H_5OH \rightarrow C_6H_{11}OH \rightarrow C_6H_{12}$$

(*c*) Condensation $C_6H_5OH \rightarrow C_6H_5\ C_6H_5$

The extent of each of these reactions depends upon the temperature, the pressure, and the catalyst Condensation (*c*) is a side-reaction and does not occur in the presence of a hydrogenating catalyst such as molybdenum sulphide The other reactions (*a*) and (*b*) proceed at approximately equal rates, e g with a molybdenum catalyst at 450° C the proportions of benzene and cyclohexane in the product are 45 35

The cresols behave similarly to phenol, giving mainly toluene, by reaction (*a*), and methyl cyclohexane, by reaction (*b*) In the presence of a strong hydrogenating catalyst the dihydric phenols are hydrogenated readily, and benzene and cyclohexane result

If these results are applied to tar, it is realized that reaction (*a*) should be favoured (by raising the temperature as much as possible) in order to produce a spirit of high anti-knock value and to save hydrogen, cyclohexane requires for its formation four times as much hydrogen as benzene

Reaction (ii), in which hydrogenation precedes cracking, is typified by the behaviour of the condensed nuclear hydrocarbons, of which naphthalene may be taken as an example

Naphthalene is stable at 450° C, but in the presence of a hydrogenating catalyst the tetrahydro derivative is formed at 350–400° C Above this temperature decomposition occurs by the opening of the hydrogenated ring and benzene and its homologues are formed At 450° C tetrahydronaphthalene gives about 30% of such derivatives, and at 500° C 90% The homologues of naphthalene behave similarly

In applying this result to tar it is apparent that since low temperatures (*c* 400° C) favour hydrogenation while high temperatures favour cracking, it might be preferable to treat the tar in a two-phase process, consisting of (1) a low-temperature or liquid phase, and (2) a high-temperature or vapour phase The effect of temperature is, however, twofold, for while low temperatures favour a larger degree of conversion, higher temperatures give higher rates of hydrogenation It is thus possible and convenient to treat tar in a mixed-phase process at some temperature intermediate between the optimum temperatures for hydrogenation and cracking

Finally, the cracking reactions (iii) can be considered as of special importance in view of their action in reducing the molecular weight and boiling-point of the components of the tar. Cracking is taken to mean the scission of carbon to carbon linkages in chains or saturated rings, it occurs mainly under the influence of high temperatures, although its rate may be accelerated in the presence of certain catalysts Thus ethyl benzene in the absence of a catalyst yields 32% of benzene at 480° C, but in the presence of active carbon yields 49%

The value of cracking reactions in reducing the molecular weight of the complex substances in tar is obvious By varying the temperature of reaction it is possible to alter the boiling range of the product within wide limits There are in the tar, however, substances which crack so readily that a hydrogenating catalyst must be employed to ensure that the rate of hydrogenation is at least equal to that of cracking in order to prevent the cracking reactions from proceeding too far A higher limit is thus set to the temperature at which the hydrogenation-cracking of tar may be carried out

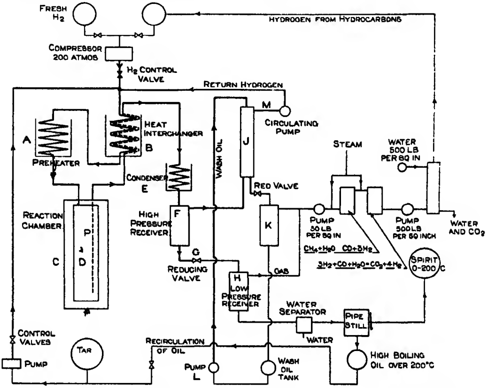


FIG 1

Technical Methods

The course of the reactions described above decides to some extent the method adopted in the technical treatment of tars Factors which have an important influence are temperature, pressure, ratio of tar to hydrogen, and time of contact with the catalyst, but before considering these it is desirable to describe the technique adopted in the practical treatment of tar and the results which can be attained

Although so much work has been done in Germany on brown-coal tar, an authentic description of the plant used is not available For that reason it is proposed to describe the process in terms of a hypothetical plant, Fig 1, containing the essential features and to quote mainly the results obtained in experimental work on a semi-technical scale at the Fuel Research Station In Fig 1 the tar is pumped with hydrogen at 200 atm pressure into the heat exchanger

B, thence to the preheater *A*, where the mixture is further raised in temperature by external heat. The heated tar and hydrogen then enter the converter *C*, which is conveniently a tall cylindrical vessel containing an enclosed catalyst chamber of smaller diameter, the annular space being filled with thermal insulation material. The tar vapours and hydrogen flow downwards through the catalyst bed and the products leave by the pipe *P*, passing through the heat exchanger to the condenser *E*. The condensate is collected in the high-pressure receiver *F*, and the hydrocarbon gases and surplus hydrogen pass to the scrubber *J*, where the former are washed out by hydrocarbon oil under pressure. The liquid product in *F* flows steadily through a reducing valve *G* to a receiver *H* at atmospheric pressure. A small proportion of hydrocarbon gas is liberated by the reduction of pressure. The purified hydrogen is returned to the beginning of the process. The hydrocarbon gases are recovered by releasing the pressure in *K*, the wash-oil being recirculated. These gases may be converted into hydrogen by methods described elsewhere in this volume.

The reason for having a separate catalyst chamber inside the converter is to allow of the introduction of sufficient lagging to keep the temperature of the pressure wall below 180° C. If this is done, attack by hydrogen is prevented and the vessel may be made of mild steel. In other parts of the plant, e.g. the preheater, where the metal has to withstand the full working temperature and pressure, alloy steels are necessary.

The reaction chamber need not be made of great strength since a pressure-equalizing line controls the pressure difference between the chamber and the annular space, keeping the difference within from 1 to 2 atm.

The process is started by applying heat to the preheater and circulating tar until the temperature rises sufficiently in the reaction chamber for the exothermic heat of reaction to bring it to the working level. A very important factor in obtaining steady conditions of operation is the maintenance of an even flow of raw material through the catalyst. This is normally achieved by regulating the rate of passage of the hydrogen and the withdrawal of the residual gas, the input of tar, and the rate of withdrawal of the liquid reaction product from the high-pressure vessel *F*.

At a working temperature of 480° C. the heat of reaction with low-temperature tar is of the order of 300 kg.-cal. per kg., and it can be calculated that, with a full-scale converter, very little preheating of the raw material might be necessary, heat-interchange between this and the products being almost sufficient to carry on the reaction.

A semi-technical plant used in the Fuel Research Station experiments is shown in Fig. 2. In this case, owing to the small scale (throughput 1.2 to 2·0 kg. of tar per hour) it is necessary to heat the reaction chamber externally. This is done by a suitably lagged electrical winding arranged in the annular space surrounding the chamber. In this plant the hydrogen is not recovered from the residual gas.

The plant is arranged for accurate control and the measurement of raw materials and products. The results of experiments upon low-temperature tar, low-temperature tar oil, and high-temperature tar creosote are given in Table I. The catalyst material used was ignited granular alumina gel, impregnated with ammonium molybdate and dried, the dry material containing 25% of this substance. In use the ammonium molybdate is converted to molybdenum sulphide (MoS_2) by the hydrogen sulphide formed from the sulphur compounds in the tar.

TABLE I

Hydrogenation-cracking of Low-temperature Tar and Tar Oil, and Creosote

	L.-t. tar	*L.-t. tar oil*	*Creosote*
Temperature, ° C.	480	480	480
Pressure, atm.	200	200	200
Weight Balance			
Raw material	100.0	100.0	100.0
Hydrogen absorbed	5.5	5.0	6.4
	105.5	105.0	106.4
Spirit to 200° C.	42.3	68.6	55.9
Oil above 200° C.	46.8	16.9	35.7
Total oil	89.1	85.5	91.6
Water	7.5	9.8	4.6
Hydrocarbon gas	7.4	7.8	8.4
Loss	1.5	1.9	1.8
	105.5	105.0	106.4
Sp. gr. of raw material	1.058	0.965	1.065
Sp. gr. of total oil	0.870	0.808	0.861
Volume Data			
One Treatment			
Spirit to 200° C.	55	83	72
Oil above 200° C.	53	19	41
Hydrogen absorbed, cu. ft. per 100 gal. raw material	10,000	8,500	12,000
Complete Conversion to Spirit			
Spirit to 200° C.	101	99	106
Hydrogen absorbed, cu. ft. per 100 gal. raw material	18,000	10,000	16,000
Properties of the Spirit			
Sp. gr. at 15° C.	0.810	0.800	0.830
Analysis, % by weight			
Aromatic hydrocarbons	33	33	29
Unsaturated hydrocarbons	2	2	2
Saturated hydrocarbons and naphthenes	65	65	69
Amount below 100° C., % by volume	17	18	18
Octane number	75	75	80

The first half of the table shows the yields as percentages by weight when tar only is the raw material fed to the plant. The data given in the second part of the table show the same yields on a volume basis and also the yields, &c., which are obtainable when the crude liquid product of hydrogenation is distilled and the oil boiling above 200° C. is continuously recycled.

In the case of low-temperature tar the product after one treatment is a clear, amber-coloured oil, completely soluble in petroleum ether (b.p. 40–60° C.) and containing about 50% of spirit boiling below 200° C. In order to achieve this conversion 5.5 parts of hydrogen by weight of the tar reacts to form oil, 89 parts, water, 7.5 parts, and hydrocarbon gas 7.4 parts. The tar has therefore been converted into approximately equal parts of spirit and oil. Re-treatment of the oil increases the overall yield of spirit to 101 gal. of spirit per 100 gal. of tar treated. The consumption of hydrogen is 180 cu. ft. per gallon of tar, but, if the hydrocarbon gas formed were cracked with steam, 120–40 cu. ft. of hydrogen would be recoverable from it, and the process would be partly self-contained in regard to hydrogen requirements.

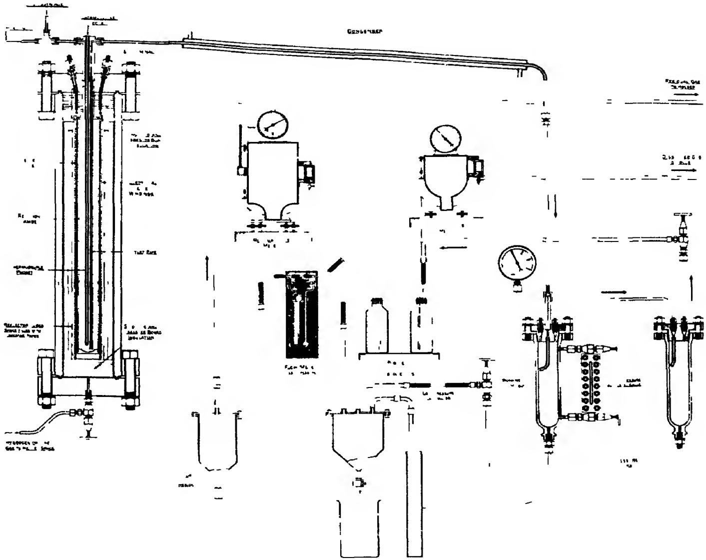


Fig. 2

The temperature of treatment is 480° C., and at this temperature the catalyst slowly deteriorates owing to the cloaking of its surface with carbon and pitchy material. The only preparation to which the tar is subjected before treatment is filtration to remove dirt. The tar then contains up to 2% of water, some finely divided dirt ('free carbon'), and iron salts in solution. It has been ascertained that the catalyst will retain a sufficiently high activity for 30 days. Reactivation is achieved by oxidation with air at a temperature of 500° C. when the initial activity is regained. This periodic life is equivalent to 300 vol. of tar per unit volume of catalyst or 400 lb. of tar per lb. of MoS_2. Deterioration is measured by observing the specific gravity of the crude oil product, a decrease of specific gravity of 0.004 corresponding roughly to a diminution in the weight yield of spirit of 1.0.

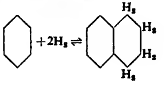
In the treatment of low-temperature tar oil and creosote the same phenomena occur, except that with the former the rate of deterioration is smaller; data for these raw materials are given later. Low-temperature tar oil is therefore a particularly suitable raw material for the process; the crude product is a water-clear oil and the spirit produced by complete recycling requires very little refining to give a motor fuel which is stable on storage.

The compositions of the final spirits from these three raw materials do not differ greatly. They each contain about 30% of aromatic hydrocarbons, 65–70% of saturated hydrocarbons and naphthenes, and only about 2% of unsaturated hydrocarbons. As motor spirit they have sufficient volatility, a reasonable octane number (75–80), and a gum content of only a few mg. per 100 ml. after 6 months' storage in a steel drum.

The above yields of hydrogenation products were obtained under more or less standard conditions, but in a commercial process the choice of optimum conditions would be influenced by considerations of throughput and the nature of the product required. These are, in turn, influenced by a number of variables which affect working conditions. The most important of these variables are temperature, pressure, ratio of hydrogen to tar, time of contact of reactants, and the nature of the catalyst. The effect of these variables upon the treatment of the above three raw materials is described below briefly, it being understood that the choice of conditions in any plant would be made only after careful consideration of the effect of each variable so as to find the optimum conditions for the type of raw material treated. In certain cases it will be apparent that the rate of deterioration of the catalyst will frequently be the deciding factor since it will most affect the total output. For this reason it imposes a definite limitation on the temperature of operation.

Effect of Variables in Vapour-phase Hydrogenation

Pressure. It follows from the Law of Mass Action that the rate of any reaction involving hydrogen will be increased by an increase of the pressure and therefore the concentration of hydrogen. Also, when hydrogenation involves a reduction of volume, the reactions must be favoured by increase of pressure. For example, in the hydrogenation of naphthalene



the point of equilibrium will shift to the right as the pressure is raised. At atmospheric pressure naphthalene is stable up to a high temperature in the absence of hydrogen, whereas at a high pressure of hydrogen it is converted at 400° C. to tetrahydronaphthalene, which in turn decomposes to benzene and its homologues at higher temperatures. The general effect of increase of pressure in the hydrogenation of tars and tar products is therefore a greater absorption of hydrogen and an increase in the proportion of low-boiling material in the product. The greater absorption of hydrogen means also a higher proportion of naphthenes.

Below 400° C. and at pressures of about 200 atm. the effect of any further increase of pressure is small; above 400° C. the proportion of low-boiling oils increases up to about 350 atm., at which pressure it appears to reach a maximum value. At 480° C., for example, low-temperature tar gives the following:

Pressure, atm.	100	150	200	300	400
Spirit yield, % of tar	35.4	36.3	41.0	41.8	42.2

In this comparison the amounts of tar and hydrogen are proportional to the pressure, e.g. the throughput of tar at 400 atm. is double that at 200 atm.

If the pressure falls, or the temperature rises, so that cracking proceeds more rapidly than hydrogenation, a point is reached where the yield of spirit begins to diminish rapidly. In the above example (480° C.) this point is about 200 atm.; at higher temperatures it is higher, i.e. at 510° C. it is probably about 400 atm.

The important effect of pressure in reducing the rate of deterioration of the catalyst is dealt with later.

Effect of Temperature. The general effect of increase of temperature is that the rates of both hydrogenation and cracking reactions are accelerated, but the extent to which hydrogenation can proceed decreases. Thus in the hydrogenation of naphthalene referred to above the equilibrium shifts to the left as the temperature is raised. At a high temperature the effect may be considerable, so that an upper limit is imposed upon the reaction temperature. The rate of reaction increases with temperature; thus tetrahydronaphthalene, for example, is decomposed by temperature as follows:

Temperature, ° C.	400	450	500
Substance decomposed, %	3	30	90

Phenol, similarly, is stable at 300° and is converted to benzene and cyclohexane at 400° at three times the rate obtaining at 350° C.

Temperature, ° C.	300	350	400	450
Degree of conversion, %	nil	24	78	100

In the case of complex materials such as tar, only the overall effect of temperature can be assessed, and a compromise must be made between hydrogenation and cracking so that the best conversion to liquids of low boiling-point is achieved without undue absorption of hydrogen or undue cracking to permanent gas. At a pressure of 200 atm. the action of hydrogen on low-temperature tar begins at about 300° C. The complex molecules which form pitch on distillation are attacked first to form oils which are soluble in petroleum ether (b.p. 40–60°). At this temperature the amount of cracking is negligible, but, as the temperature increases, cracking gradually increases until an excessive amount of permanent gas is formed. With increase of cracking the amount of spirit rises to a maximum and then decreases.

The specific gravity of the oil produced forms a measure of the reactions, and is found to decrease linearly with increase of temperature within certain limits Since decrease of specific gravity means an increase in the proportion of low-boiling oils, the latter also increase linearly up to a point F S Sinnatt and J G King [4, 1935] give the following data for Fuel Research low-temperature tar treated in a continuous plant in the presence of a molybdenum sulphide catalyst

TABLE II

Effect of Temperature in the Hydrogenation-cracking of Low-temperature Tar

Percentages by weight of tar treated

Press., atm		*Temperature C* 300	350	390	430	450	480	510
200	Specific gravity		0 970	0 930	0 902	0 887	0 867	0 847
	Spirit	7 2	13 4	19 7	30 4	34 2	41 0	46 0
	Acids	18 8	19 0	7 5	1 1			
400	Specific gravity		0 970	0 930	0 893	0 875	0 847	0 815
	Spirit			20 7	30 6	35 5	42 2	56 0
	Acids			8 5	1 2			

Although the data in Table II refer only to one throughput, the same general relations hold over as wide a range as 0 25 to 4 0 vol of tar per volume of catalyst space per hour

The effect of pressure in reducing cracking is seen markedly in this table, at 510° the difference in spirit yield between 200 and 400 atm is much more marked than at lower temperatures The change in the appearance of the product from low-temperature tar is interesting At 370° it is brown, at 410° dark orange and transparent, at 430° orange, and at 450° lemon coloured The effect of temperature upon the tar acids in the tar is similar to its effect on phenol, reduction begins about 350° C and is complete about 440° C

Similar relationships hold with creosote (C M Cawley, C C Hall, and J G King [3, 1935])

Temperature, ° C	480	495	510
Specific gravity of product	0 852	0 832	0 815
Spirit to 200° C, %	64 7	69 6	69 8

but at 510° and 200 atm the degree of cracking is so high that the spirit yield was little better than at 495°

The important effect of temperature upon the life of the catalyst is dealt with below

Ratio of Hydrogen to Raw Material In the case of low-temperature tar it is found that the yield of low-boiling oils is sensitive to the molecular ratio of hydrogen to tar up to a ratio of 40 to 1 (taking the mol wt of tar as 250) Above this ratio an increase seems to have little effect The optimum ratio increases with increasing temperature

Table III illustrates these conclusions

TABLE III

Effect of Hydrogen-tar Ratio

Hydrogen/tar, molecular ratio	13	16	19	22	37	52	97	158
Sp gr of liquid product	0·867	0 859	0 858	0 854	0 847	0 848	0·847	0·849
Spirit to 200° C, % by weight	40·5	42 9	44 0	44 2	44 5	45 8	45 2	44 9

Time of Contact of Tar and Catalyst. The degree of conversion of tar to spirit decreases only slightly as the throughput of tar per unit volume of catalyst is raised, the decrease being less at lower temperatures, this is true between very wide limits The comparatively small effect of the time of contact is shown by the results in Table IV, obtained by treating low-temperature tar at 480° C and 400 atm at various times of contact

TABLE IV

Effect of Time of Contact of Tar and Catalyst

Time of contact, min	20	10	5	2 5	1 25
Sp gr of liquid product	0 811	0 832	0 847	0 859	0 882
Spirit to 200° C, % by wt	56 3	47 5	42 2	41 3	36 5

The relatively large change in time from 20 to 5 min causes a reduction in spirit yield of from 56 3 to 42 2 only

Effect of Catalyst. The effect of the catalyst upon the different variables has already been discussed The following example illustrates the large part which the catalyst plays in the treatment of low-temperature tar

TABLE V

Effect of Catalyst in the Hydrogenation of Low-temperature Tar

Pressure 200 atm Temperature 450° C

	Original tar	*Expt without catalyst*	*Expt with* MoS_2 *catalyst*
Sp gr 15° C	1 060	1 002	0 890
Tar acids, %	19	18	1
Yield of crude product, %		95	95
Yield of spirit to 200° C, %	7	13	34

The effect of the catalyst is seen in the complete reduction of the tar acids to aromatic hydrocarbons and in the greater production of spirit

The important features in the preparation of a vapour-phase catalyst are that the active agent should present a large surface to the reactants, should be in a robust form, should not offer undue resistance to the passage of vapours, and should not deteriorate rapidly during use The results of deterioration may be less serious if the deteriorated catalyst is easily reactivated Catalysts prepared in a pelleted form or absorbed on porous granules of inorganic material fulfil these requirements and many methods of preparation are possible Metallic catalysts of high thermal conductivity would be valuable, but are not yet available in a sufficiently active form

The effect of physical and chemical variables upon the catalysts used in the treatment of tars may be explained with reference to molybdenum A molybdenum catalyst can conveniently be prepared from ammonium molybdate by impregnation on a porous support such as alumina gel or bauxite, followed by ignition to MoO_3 and conversion *in situ* to molybdenum disulphide The behaviour of the catalyst in use is best explained by reference to the specific gravity of the product When a fresh batch of catalyst is used, the specific gravity of the product decreases at first owing to the conversion of the molybdenum oxide to molybdenum sulphide, which is a more active catalyst, and then increases steadily, as the catalyst deteriorates, at a rate depending upon the working conditions and the raw material In the case of tar products containing 0 5 to 1 0% of sulphur the molybdenum is maintained in the form of the disulphide MoS_2

The effect of the different physical variables can be explained in relation to low-temperature tar Under optimum conditions in the neighbourhood of 480° C and 200 atm a molybdenum sulphide catalyst deteriorates at a rate given by an increase of 0 006 in the specific gravity of the product per day, this corresponds to 1 5% on the spirit yield Increase of pressure decreases the rate of deterioration by speeding up hydrogenation, and increase of temperature increases the rate by tending to cause the deposition of carbon or polymers on the surface of the catalyst From a practical point of view the great effect of pressure in reducing the rate of deterioration is most important This is demonstrated by the results of the treatment of low-temperature tar, shown in Table VI

TABLE VI

The Effect of Pressure on the Rate of Deterioration of a Molybdenum Catalyst

Pressure atm	Temperature ° C	Increase of sp gr product	Decrease of spirit yield
		per 10 vol tar per 1 vol catalyst	
200	480	0 002	0 25
400	480	0 0004	0 07

In this case the rate of deterioration at 400 atm is less than half that at 200 atm

Similarly, temperature has an important effect on the rate of deterioration At 200 atm pressure the rates of deterioration are as follows, in the same units as for Table VI

	Increase of sp gr	Decrease of spirit yield
400° C	0 0008	0 30
480° C	0 002	0 25
510° C	0 003	0 70

The rate of deterioration of the catalyst does not increase proportionally to the tar throughput, the rate, per unit of tar treated, decreases as the throughput is raised, i e as the time of contact decreases A measure of this is given by the data in Table VII

TABLE VII

Effect of Time of Contact on the Rate of Deterioration of a Molybdenum Catalyst

Time of contact min	Increase in sp gr of liquid product	Decrease in spirit yield
	per 10 vol tar per 1 vol catalyst	
10	0 004	0 5
5	0 002	0 25
2 5	0 0013	0 4

The rate of deterioration increases very slightly, as the ratio of hydrogen to tar increases, up to a maximum at the point at which the maximum activity of the catalyst is reached, and thereafter diminishes

The rates of deterioration of the catalyst when used with different raw materials are shown in Table VIII In this case the catalyst is in a more active form.

TABLE VIII

Effect of Raw Material on the Rate of Deterioration of a Molybdenum Catalyst

	Increase in sp gr of liquid product	Decrease in spirit yield
	per 10 vol tar per 1 vol catalyst	
Low-temperature tar	0 006	1 5
Low-temperature tar oil	0 0016	0 8
Creosote	0 007	2 9

Compared with low-temperature tar, low-temperature tar oil gives a much lower, and creosote a rather higher, rate of deterioration Such rates are sometimes compared in terms of the volume or weight of raw material which 1 vol of prepared catalyst will treat before its activity falls so low that it is not economical to use it further without reactivation By reference to the above data and to Table I the effects upon a sulphide catalyst of the above three raw materials can be compared

One volume of supported catalyst will treat

(i) 80 vol of low-temperature tar while the spirit yield decreases from 42 to 30%

(ii) 480 vol of low-temperature tar oil while the spirit yield drops from 69 to 30%

(iii) 90 vol of creosote while the spirit yield drops from 56 to 30%

In each case the minimum activity has been taken as that equivalent to a spirit yield of 30%, the starting yield being that normal to the raw material Comparison in this way is rather against the low-temperature tar, a further decrease in the yield of spirit to 25% would permit the catalyst to be used for the treatment of 150 vol of tar

High-temperature Tar

Tars produced by the carbonization of coal at high temperatures, as in the manufacture of coal gas and metallurgical coke, are not amenable to hydrogenation in a mixed phase as in the case of low-temperature carbonization tars These tars normally contain a proportion of refractory high-boiling materials which do not yield readily to hydrogenation and which may become adsorbed on the surface of the catalyst, thereby causing a rapid deterioration of its activity In addition the tars contain a high proportion of free carbon which may in part be deposited in the catalyst bed, thus acting as a filter This general statement is modified to some extent by the inherent differences in high-temperature tars Those which are prepared by the carbonization of coal in horizontal gas retorts or coke ovens are the most difficult, containing 10 to 20% of free carbon and having a pitch content of over 55% Tars produced in continuous vertical retorts, however, are less refractory, in that the coal is heated more gradually and the tars are removed at a lower temperature and even protected by steam Such tars contain only 2 to 5% of free carbon and about 40 to 50% of pitch They represent an intermediate stage between true high-temperature tar and the low-temperature tar described above Although they cause a vapour-phase catalyst to deteriorate rapidly, they may be readily treated in a process comprising both liquid and vapour-phase treatment

Little work has been done on the hydrogenation-cracking of high-temperature tars, attention being given rather to the treatment of their distillates That the creosote from these tars is a satisfactory raw material has been shown above The examination of high-temperature tars is now in progress Tar and hydrogen are pumped at 200 atm pressure into a reaction vessel maintained at 450° C, the catalyst being supplied in the finely divided state The greater proportion of the products is vaporized and leaves the converter in the stream of hydrogen while the remainder is withdrawn in the liquid state The products are then distilled and the middle fraction treated in the vapour phase The low-boiling fraction can be prepared for sale without further hydrogenation treatment The high-boiling fraction can be prepared for the pitch or road-tar market

TABLE IX

Pressure Distillation of High-temperature Tar in Hydrogen
(Chemical Reactions Ltd)

Converter 5 litres capacity, throughput = 600 ml per hr temperature 430–440° C, pressure = 200 atm

Tar	Topped coke oven tar		Topped v r tar		Topped h r tar		Topped chamber-oven tar	
	Original	*Hydrog*	*Original*	*Hydrog*	*Original*	*Hydrog*	*Original*	*Hydrog*
Sp gr of tar	1 167	1 085	1 075	1 015	1 195	1 122	1 143	1 054
Yield, % by vol		98		96		94		98
Constit insol in petroleum spirit* but sol in benzene, %	57	19 5	35 0	8 1	42 5	29 0	53 0	8 8
Constit insol in petroleum spirit and insol in benzene, %	8 0	2 5	8 8	1 7	13 5	9 4	17 5	0 9
Ash, %	0 07							
Distillation, % by vol								
Oil to 360° C	38	54	69	78	25	54	48	73
Pitch	60	41	28	19	73	44	50	26
Characteristics of oil to 360° C								
Sp gr		1 005		0 981		1 030		1 028
Phenols, %		10 2		17 5		11 0		16 9
Distillation (Engler), %								
up to 180° C		4 0		4 5		1 0		0
200		14 5		16 5		9 0		7 0
250		51 0		50 5		56 0		36 0
300		75 5		70 0		79 5		
360		96 0		94 0		96 0		91 0

* b p 100–110° C

TABLE X

Results of Liquid-phase Hydrogenation

Material	Low-temperature tar (brick retort)		High-temperature tar (horizontal retort)			
	Original tar	*Hydrogenation product*	*Original tar*	*Hydrogenation product*		
Catalyst (0 5%)		MoO$_3$		none	MoO$_3$	SnCl$_2$
Sp gr 15° C of liquid product	1 06	0 95	1 20	1 11	1 12	1 09
Yields per cent. by weight of original tar						
Free carbon	1	nil	13	9	8	9
Material insoluble in petroleum ether (b p 40–60° C)	25	trace	59	27	24	21
Material boiling above 360° C (pitch)	42	20	64	48	49	38
,, ,, below ,,	58	74	36	51	50	61
,, ,, above 300° C	53	28	82	63	63	59
,, ,, 200–300° C	40	46	17	31	31	33
,, ,, below 200° C	7	20	1	1	5	7
Tar acids	19	14	3	3	3	3

By the courtesy of Messrs Chemical Reactions, Ltd, it is permitted to quote certain of their results obtained by the liquid-phase hydrogenation of high-temperature tars These results are given in Table IX, and show that the hydrogenated tars contain a very much higher proportion of distillable oils than the original tar A topped coke-oven tar, for example, which gave only 38% of distillate, yielded after treatment at 200 atm 98% of a product which gave 54% of distillate The profound change in this product is shown by the fact that it contained only 22% of material insoluble in light petroleum as against 65% in the original tar. Horizontal-retort and chamber-oven tars behave similarly Vertical-retort tar gives appreciably higher yields of oil boiling below 360° C, the original tar gave on distillation an oil yield of 69%, and on treatment a yield of 78% The material insoluble in petroleum spirit in the tar was 43 8 and in the product only 9 8% There is a clear indication that the free carbon in these tars is converted partially into liquid products In the case of the vertical-retort tar the free carbon is reduced from 8 8% of the tar to 1 7% of the product

Some results for the liquid-phase hydrogenation of low-temperature and high-temperature tars are given by Cawley [1, 1936] and are reproduced here in Table X

The unsaturated and highly condensed compounds in tar are insoluble in petroleum ether (b p 40–60° C), the amount of material insoluble in this solvent is, therefore, a useful measure of the degree of hydrogenation of a tar When low-temperature tar is treated in the presence of 0 5% of a molybdenum catalyst at a temperature of 450° C and under a pressure of 200 atm. of hydrogen, this insoluble material (25%) is completely hydrogenated to oil. At the same time the boiling range of the tar is considerably lowered and the tar acids are partially converted to hydrocarbons The hydrogenation product contains no pitch in the usual sense of the word, the material boiling above 360° C is a distillable oil In effecting these changes, the amount of hydrogen consumed is 3%

When high-temperature (horizontal retort) tar is treated under similar conditions the change is not so pronounced, as shown by the results in Table X, the extent of the change is dependent to some extent upon the catalyst used The molybdenum catalyst appears to have very little influence upon the reaction, but in the presence of a tin catalyst the material insoluble in petroleum ether is reduced from 59 to 21%, and the free carbon from 13 to 9% The pitch (by distillation) is reduced from 64 to 38% and appears to be unchanged in quality The H/C ratio of the tar is raised from 0 66 to 1 The net results of the hydrogenation are thus an increase of 25% in the amount of distillable oils and a hydrogen consumption of 3%

These results are not complete, the pitch could probably be further converted to oil by recycling or by employing a more active catalyst It is almost certain, however, that horizontal retort and coke-oven tars contain a proportion of refractory material which will not yield to hydrogenation

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THE PRODUCTION OF WATER GAS FROM METHANE AND OTHER HYDROCARBONS

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WATER gas, or blue water gas, is the name employed to designate the gaseous product obtained by the interaction of steam and coke, or other form of carbon, at elevated temperatures As carried out industrially at temperatures in the neighbourhood of 1,000° C, this reaction follows the course indicated by the equation

$$H_2O + C \rightarrow CO + H_2$$

The ideal water gas should, therefore, consist of hydrogen and carbon monoxide in equimolecular proportions In actual practice, however, small amounts of carbon dioxide and methane as well as nitrogen (introduced during the air-blow period) are also present, but the hydrogen and carbon monoxide are present in nearly equal proportions, and constitute the major part of the gas mixture

The reaction between carbon and steam can also be effected at lower temperatures in the presence of certain active catalysts Under these conditions the above reaction is suppressed in favour of another reaction which yields hydrogen and carbon dioxide in accordance with the equation

$$2H_2O + C \rightarrow CO_2 + 2H_2$$

The extent to which these competing reactions take place depends mainly upon the temperature In the presence of an active catalyst the relative proportions of hydrogen and oxides of carbon in the reaction mixture at any temperature are controlled by the equilibrium constant of the well-known water-gas reaction

$$H_2O + CO \rightleftharpoons CO_2 + H_2,$$

this equilibrium is fundamental in all considerations of water-gas production, and will be discussed later in greater detail

It will be seen, therefore, that the manufacture of water gas at elevated temperatures as carried out industrially furnishes a gas containing approximately 50% each of hydrogen and carbon monoxide Nevertheless, the composition of such water gas can be varied so as to contain carbon dioxide as well as carbon monoxide In the following discussion, therefore, the term water gas is used in its wider sense to denote any gas mixture containing hydrogen and oxides of carbon in which the proportion of hydrogen to oxides of carbon may be varied within wide limits

Utilization of Water Gas

Water gas is used extensively as a gaseous fuel both for industrial and domestic purposes The main technical advantages in the use of water gas in admixture with coal gas are that its production represents a more or less complete gasification of the carbon content of coal, and that water-gas plants are very flexible in operation and can rapidly be started up Water gas can therefore be used, either carburetted or uncarburetted, to mix with coal gas in proportions suitable for controlling the heating value of the resulting mixture, or for supplementing coal-gas supplies during periods of peak load In modern gas manufacturing practice, water-gas plants are provided with suitable carburetting devices so that an additional control of calorific value is obtainable One serious objection to the employment of water gas in admixture with coal gas for domestic purposes is that its high content of carbon monoxide renders such mixtures highly poisonous

In addition to its value as a gaseous fuel, water gas is used extensively as a raw material for the large-scale production of hydrogen Enormous quantities of hydrogen for the synthesis of ammonia, for the hydrogenation of coal and hydrocarbons, and for the production of synthetic products by hydrogenation are now being prepared from water gas Technical methods for the manufacture of hydrogen from water gas are discussed later The manufacture of methanol and also of mixtures of methanol and higher aliphatic alcohols from mixtures of hydrogen and carbon monoxide constitutes one of the most remarkable developments of modern technical chemistry and shows clearly the potentialities of water gas as a raw material in large-scale organic synthesis The work of F Fischer and others on the catalytic production of liquid hydrocarbons from water gas is also of the most profound scientific and technical interest, although the large-scale application of this process is beset with difficulties

Raw Materials for Water-gas Manufacture

The simplest and most abundant source of carbon for the production of water gas is obviously coal, lignite, and similar natural carbonaceous substances The production of water gas from such sources is carried out on an enormous scale in many parts of the world An intermittent process is employed in which the fuel bed is raised to incandescence by blowing with air, after which the endothermic steam reaction is allowed to take place until the temperature has fallen to a lower limit, and the sequence of operations is again repeated

From the point of view of the petroleum industry the cheapest raw material for the production of water gas is clearly methane, a hydrocarbon which constitutes by far the largest constituent of practically all natural gases, and which is also present in large amounts in refinery gases and gases from cracking plants For these reasons, and also because of the ease of conversion of methane into water gas, this hydrocarbon may be regarded as by far the most suitable raw material The lower homologues of methane, which are also present in petroleum gases, may also be used as raw materials for the production of water gas, but they are more expensive and less abundant than methane and, moreover, are finding increasing application in other directions On this account the methods for the conversion of methane into water gas have been extensively studied and applied in large-scale operations, whereas little data is available in regard to the use of other hydrocarbons for this purpose

Conversion of Methane into Water Gas by Partial Oxidation

The direct combustion of methane with oxygen, or oxygen-containing gases, gives rise to a variety of products depending upon the reaction conditions Neglecting the transitory intermediate products of oxidation, such as formaldehyde, which are only formed under special conditions, the direct oxidation of methane can proceed in two different ways as represented by the equations

$$2CH_4+O_2 \rightarrow 2CO+4H_2+18\ \text{kg -cal} \qquad (1)$$

$$CH_4+2O_2 \rightarrow CO_2+2H_2O+214\ \text{kg -cal} \qquad (2)$$

A calculation of the equilibrium constants of these two reactions from available free-energy data indicates that, except at high temperatures, the values of K_p for reaction (1) are always smaller than those for reaction (2) It follows, therefore, that under conditions unfavourable for the occurrence of side reactions, such as short contact times and absence of catalysts for such side reactions, the combustion of methane with only sufficient oxygen for equation (1) will proceed very largely according to reaction (2), i e mixtures of carbon dioxide, steam, and unreacted methane will be formed At longer times of contact, and more especially in the presence of certain catalysts, the composition of the reacting mixture will be influenced by the simultaneous occurrence of the following reactions between methane and the initial combustion products

$$CH_4+CO_2 \rightarrow 2CO+2H_2$$

$$CH_4+H_2O \rightarrow CO+3H_2$$

and

$$CH_4+2H_2O \rightarrow CO_2+4H_2$$

At temperatures of 800° C and over, these reactions are all well over to the decomposition sides From a theoretical standpoint, therefore, the incomplete combustion of methane at these temperatures in the presence of active catalysts should proceed in such a way as to produce hydrogen and carbon monoxide mainly, so that the overall effect will be represented under these circumstances by equation (1) Under conditions of equilibrium the relative proportions of carbon monoxide and carbon dioxide in the reaction mixture will be governed by the well-known water-gas equilibrium

$$H_2O+CO \rightleftharpoons CO_2+H_2$$

These theoretical conclusions are substantiated by the work of Liander [26, 1929], who studied the reaction of 2 volumes of methane and 1 volume of oxygen at various temperatures both in the presence and absence of catalysts In the absence of catalysts and at temperatures of 700–850° C, carbon dioxide and water were the sole products, whereas, in the presence of a supported nickel catalyst, carbon monoxide and hydrogen with small amounts of carbon dioxide were formed It appears certain, therefore, that the primary reaction occurring in the partial combustion of methane is that yielding carbon dioxide and steam, but these initial products are able to react further with unchanged methane, provided that the gas is exposed to the action of suitable catalysts for a sufficient length of time Under the latter circumstances the net result is the formation of carbon monoxide and hydrogen in proportions indicated by equation (1)

The partial oxidation of methane, and of gases containing methane, by means of oxygen or air has been studied by Padovani and Franchetti [31, 1933], who employed catalysts of nickel on a porous refractory material and catalyst volumes up to 10 litres A few of the experimental results of these workers are summarized in the appended table

These results show clearly that the partial oxidation of methane to yield hydrogen and carbon monoxide can be carried out by using air or oxygen at temperatures of 850–950° C in the presence of a nickel catalyst with satisfactory velocity and practically complete conversion The reaction rate is higher when using oxygen than in the presence of steam or carbon dioxide

Composition of reaction mixture			*Temp ° C*	*Contact time Seconds*	*Composition of reaction products*				
CH_4	O_2	N_2			CO_2	CO	H_2	CH_4	N_2
65 4	34 6		850	4 33	2 8	31 0	63 4	2 8	
65 7	34 3		850	2 16	1 2	31 8	64 0	3 0	
65 7	34 3		850	1 23	trace	32 6	65 0	2 4	
67 5	32 0		850	2 27	0 2	29 7	61 0	1 8	7 3
27 4	15 1	57 4	900	1 02	0 5	18 9	36 9	0 9	42 9

(All gaseous compositions in volume per cent)

By the incomplete combustion of methane with oxygen in the manner described above, a gas mixture is obtained containing hydrogen and carbon monoxide in a volume ratio of 2 to 1 Such a gas mixture is quite suitable for direct application in the methanol synthesis, and may also be used as a source of hydrogen by removing the carbon monoxide in the form of carbon dioxide after applying reaction with steam at 500° C The incomplete combustion of methane with oxygen for the production of water-gas mixtures suffers from the disadvantage that pure oxygen is relatively expensive and the reaction mixture violently explosive When combined with the endothermic steam-methane, or methane-carbon dioxide reactions, the incomplete combustion process can be more economically effected and serves to supply internal heat If air is employed in place of oxygen, the gas resulting from the incomplete combustion of methane will contain roughly 20% of carbon monoxide and 40% each of nitrogen and hydrogen Subjection of such a mixture to the water-gas reaction and removal of the carbon dioxide formed would yield a gas containing 60% of hydrogen and 40% of nitrogen by volume, this ratio of nitrogen to hydrogen being too high for direct conversion into ammonia In order to obtain by this sequence of reactions a gas mixture containing nitrogen and hydrogen in proportions suitable for the ammonia synthesis, the incomplete combustion of methane would need to be effected by means of an air-oxygen mixture containing 33% of oxygen

As far as is known, the incomplete oxidation of methane and similar hydrocarbons to produce water gas has not been applied on a technical scale, though it has been used in conjunction with the steam-methane reaction In general, it has been proposed to subject mixtures of methane and the requisite amount of oxygen or air to elevated temperatures either in the presence of coke or refractory materials or, alternatively, to the action of certain specific catalysts. The latter mode of operation is advocated by the Badische Co [2, 1927], the catalysts specified including nickel on magnesia, and molten iron alloys For example, a coke-oven gas, previously freed from benzene, and consisting of 2% carbon dioxide, 2% heavy hydrocarbons, 7% carbon monoxide, 52 5% hydrogen, 29 5% methane, and 7% nitrogen, is mixed with 23% of oxygen and partially combusted at about 1,000° C in the presence of nickel-impregnated magnesia The resulting gas mixture contains 1 5% carbon dioxide, 26% carbon monoxide, 64% hydrogen, 3 5% methane, and 5% nitrogen, and, after purification from sulphur compounds, it may be used directly for the methanol synthesis

The Reaction of Methane with Steam

Methane reacts with steam in the presence of suitable catalysts or contact materials according to the following equations.

$$CH_4+H_2O \rightleftharpoons CO+3H_2-51 \text{ kg.-cal} \quad (3)$$

$$CH_4+2H_2O \rightleftharpoons CO_2+4H_2-40 \text{ kg.-cal} \quad (4)$$

In general, both reactions take place simultaneously to an extent dependent upon the reaction conditions, particularly the temperature. Both reactions are strictly reversible, low temperatures favouring the formation of methane and high temperatures promoting decomposition into hydrogen and oxides of carbon. The equilibria involved have been investigated experimentally by a number of workers, whose results are in good agreement with the following equations, deduced from the available free energy data.

For equation (3)

$$\log K_3 = \frac{-10308}{T} + 4.87 \log T + 0.000066T - 0.0000000081T^2 - 3.04,$$

where
$$K_3 = \frac{P_{CO} \times P^3_{H_2}}{P_{CH_4} \times P_{H_2O}}$$

For equation (4)

$$\log K_4 = \frac{-8100}{T} + 3.96 \log T + 0.00104T - 0.00000023T^2 - 3.15,$$

where
$$K_4 = \frac{P_{CO_2} \times P^4_{H_2}}{P_{CH_4} \times P^2_{H_2O}}$$

The numerical values of K_3 and K_4 increase rapidly with rising temperature, the actual figures for K_3 at 800°, 900°, and 1,000° C. being 1.51×10^2, 1.30×10^3, and 7.94×10^3 respectively.

The equilibria constants for these two reactions may also be calculated by combining the known equilibrium constants of the three reactions

$$CH_4 \rightleftharpoons C+2H_2$$

$$C+CO_2 \rightleftharpoons 2CO$$

and
$$CO+H_2O \rightleftharpoons CO_2+H_2$$

This method has been adopted by Gluud [14, 1930], whose calculated results are given in the appended table, the equilibrium concentrations of reactants at different temperatures being expressed in per cent. by volume.

Reaction $CH_4+H_2O \rightleftharpoons CO+3H_2$ (3)

Temp. °C.	CH_4	H_2O	CO	H_2
500	33.3	33.3	8.33	25.0
580	21.4	21.4	14.3	42.9
635	12.5	12.5	18.8	56.3
710	5.6	5.6	21.2	66.7
835	2.7	2.7	23.7	71.0
940	0.5	0.5	24.8	74.1

Reaction $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$ (4)

Temp. °C.	CH_4	H_2O	CO_2	H_2
420	23.6	47.1	5.9	23.4
535	15.8	31.6	10.5	42.1
635	9.5	19.0	14.3	57.2
765	4.4	8.8	17.3	69.5
890	2.1	4.1	18.7	75.1
1,160	0.4	0.8	19.7	79.1

These results indicate that both the reactions concerned should proceed practically to completion at temperatures in the neighbourhood of 1,000° C. Actually, while reaction (3) can readily be carried to completion with theoretical steam ratio in the presence of suitable catalysts, reaction (4) can only be partly realized because, with rising reaction temperature, the carbon dioxide formed reacts with hydrogen to yield carbon monoxide and steam according to the water-gas equation. In the presence of catalysts favouring the water-gas equilibrium, the relative proportions of carbon monoxide and dioxide in the reaction mixture will be controlled by the water-gas equilibrium. Since at high temperatures this equilibrium is almost completely over to the carbon monoxide side, reaction (3) will predominate at higher temperatures. When the catalyst used for promoting the methane-steam reaction does not catalyse the water-gas reaction, considerable proportions of carbon dioxide may be produced even at high temperatures. The work of Matignon and Séon [27, 1932] would appear to indicate that the reaction of methane with an excess of steam at 1,050° C. in the presence of catalysts of thoria and zirconia yields much carbon dioxide.

The equilibrium between methane and steam has been investigated experimentally by Neumann and Jacob [29, 1924] in the presence of a nickel-magnesia catalyst. Their observed values of K_p for reaction (3) in the temperature range 860–1,050° C. are in good agreement with those calculated from thermodynamic data. In the region 450–780° C., the reactions producing hydrogen and oxides of carbon were complicated by the simultaneous occurrence of a secondary reaction, namely, the decomposition of carbon monoxide into carbon and carbon dioxide according to the equation $2CO \rightarrow CO_2+C$. Even with excess of steam the composition of the gas produced by reaction at temperatures in the region of 1,000° C. agreed closely with that required by equation (3). The following table shows the composition of gases produced by passage of a mixture of 47% of methane and 53% of steam over a nickel-magnesia catalyst at various temperatures and at a gas rate of approximately 3 litres per hour per 50 g. of catalyst.

	Per cent. by volume			
Temp. °C.	CH_4	CO	CO_2	H_2
330	100.0			
470	75.5	2.0	2.6	19.9
544	48.1	4.1	3.9	43.9
600	29.7	4.6	5.1	60.6
700	11.5	15.0	2.7	70.8
860	2.0	23.4		74.6
940	0.9	24.3		74.8
1,034	0.3	24.8		74.9

Neumann and Jacob concluded that, although both reactions take place simultaneously at moderate temperatures, at high temperatures reaction (4) is suppressed in favour of reaction (3) because of the interaction of carbon dioxide with methane according to the reaction

$$CH_4+CO_2 \rightarrow 2CO+2H_2$$

Several important studies have been conducted on the influence of various catalysts on the reaction of methane with steam, one of the most comprehensive being that of Fischer and Tropsch [12, 1928], who obtained high conversions in the presence of various metallic catalysts at 860–1,000° C. in a small externally heated tube. Nickel and cobalt were found to be the best catalysts and were preferably supported on clay fragments, while the addition of alumina increased the activity of these materials. On the other hand, iron, copper, molybdenum, and tungsten were poor catalysts, and coke was also unsatisfactory. In contrast to these results, Klyukvin and Klyukvina [23, 1930] find that the activity of a reduced nickel-oxide catalyst is retarded by the addition of alumina at 850° C, while semi-coke prepared from brown coal as well as coke from hard coal are catalysts of the same order of activity as nickel In view of the activating action of numerous difficultly reducible oxides on the catalytic reduction of oxides of carbon in the presence of nickel, it is to be expected the reverse processes will also show evidence of promoter action According to Kubota and Yamanaka [24, 1929], the decomposition of methane by steam at 1,000° C in the presence of nickel is promoted by the addition of alumina, zirconia, thoria, beryllia, chromium oxide, ferric oxide, ceria, and magnesia, and the effect is noticeable even with a ratio of 1 mol of promoter to 100 atoms of nickel As might be expected, promoter action is very noticeable when working at moderate temperatures, and Takenaka [38, 1933] has reported that the formation of hydrogen and carbon dioxide from methane and excess of steam at 650° C is effectively catalysed by a catalyst consisting of nickel promoted by alumina and potassium carbonate

The results of Patryn and Ziolkowski [33, 1932] shed considerable light on the catalysis of the methane-steam reaction, and indicate that the activity of various metallic catalysts for this process is a function of their resistance to oxidation by steam, those metals which are readily oxidized by steam being inactive Among the catalysts tried were reduced iron, nickel, and cobalt deposited on asbestos cloth as well as mixtures of these elements At temperatures of 350–550° C, best results were obtained with a reduced nickel catalyst and employing an excess of steam, i e 10 mols of steam per mol of methane Under similar conditions iron and cobalt gave entirely negative results, being oxidized by the steam At above 800° C the oxides of iron and cobalt exerted a pronounced catalytic action, probably because of their reduction to the metallic form Mixtures of iron, nickel, and cobalt were not in any way superior to nickel alone Nickel is most resistant to the oxidizing action of steam, and its resistance is increased by the addition of activators, such as alumina, manganese oxide, chromium oxide, zinc oxide, and potassium oxide, a fact which may explain the promoter action of these substances For the reaction of methane and steam at low temperatures best results were obtained by Patryn and Ziolkowski with a catalyst containing 80% of nickel and 20% of alumina with a methane/steam molar ratio of 1 to 5

The inactivation of the catalytic activity of some metals as a result of oxidation with steam can be correlated with the mechanism of the methane-steam reaction proposed by Padovani and Franchetti [32, 1934], who suggest that the first stage of the process consists in a decomposition of methane into its elements, followed by interaction of steam with the carbon formed This is supported by the fact that those metals which are active for the methane-steam reaction are, under similar temperature conditions, also active for the decomposition of that hydrocarbon into its elements. Oxidation of metallic catalysts by steam would suppress the activity of such materials in catalysing the decomposition of methane into carbon and hydrogen, and would, therefore, inhibit the methane-steam reaction if the above mechanism be assumed

The influence of various impurities on the activity of catalysts for the reaction between methane and steam, according to both equations (3) and (4), is of considerable technical importance Catalysts which are used to accelerate reaction (4) must be highly active at comparatively low temperatures (500–600° C), and must, moreover, be resistant to oxidation by the large excess of steam necessary for this operation As might be expected, these active catalysts for use in the lower temperature range are more susceptible to catalyst poisoning than the more robust catalysts which can be employed at higher temperatures for effecting reaction according to equation (3) The influence of oxygen on catalytic activity is of significance, since it has been proposed to combine the endothermic steam reaction with the exothermic partial combustion of methane with air or oxygen As might be expected from the experimental results of Patryn and Ziolkowski, difficulty has actually been experienced in carrying out the methane-steam reaction, particularly at lower temperatures, in the presence of nickel catalysts owing to the inactivation of such catalysts resulting from the formation of a protective film of oxide This has been specially noted in the reaction of methane with excess of steam in the presence of a nickel catalyst at a temperature below 700° C, and Beekley [4, 1929] overcomes this difficulty by introducing certain proportions of hydrogen and carbon monoxide into the reaction mixture of methane, steam, and air (or oxygen) under these circumstances, the reducing action of the hydrogen-carbon monoxide mixture is sufficiently powerful to prevent poisoning of the catalyst surface through formation of a film of oxide At high temperatures poisoning of nickel catalysts by oxygen does not appear to occur to any appreciable degree Thus, the catalysts used by Hawk, Golden, Storch, and Fieldner [17, 1932] were quite uninjured by exposure to direct heating with a blast of natural gas and air, even when a moderate excess of oxygen was present in the flame during the heating period The best catalysts found by these workers for the high temperature reaction of steam with methane to yield hydrogen and carbon monoxide consisted of pieces of refractory material, such as alundum or corundite, impregnated with nickel nitrate, then ignited at 250–300° C and finally reduced up to about 1,100° C in the presence of natural gas

As regards the influence of small amounts of sulphur compounds, such as hydrogen sulphide, on the activity of catalysts for reactions (3) and (4), the evidence is rather conflicting Fischer and Tropsch reported that their best metallic catalysts, consisting of cobalt or nickel promoted with alumina and dispersed on a refractory carrier, were not seriously injured by the presence of sulphur compounds in the gas employed After a short period of very high activity, the catalysts declined somewhat in activity, but this deterioration soon ceased and was succeeded by an apparently indefinite period of constant activity On the other hand, Gluud [14, 1930] reports that a nickel catalyst, supported on refractory material, used for the methane-steam reaction at 1,000° C, was gradually poisoned by sulphur compounds in the gas and that nickel sulphide was formed However, the activity of the catalyst could be restored by oxidation with air or steam Organically combined sulphur, as well as inorganic sulphur, is said to be prejudicial to the life of the catalyst, and it has been proposed to remove the former by passage over a suitable metallic mass, capable of fixing sulphur compounds or converting them into hydrogen sulphide In this connexion it is interesting to note that Goodfellow and Spencer [15, 1932] claim that the catalytic activity of a chromium catalyst for the decomposition of hydrocarbons by steam is actually increased by the addition of at least 1% of hydrogen sulphide, or other gaseous sulphur compound, to the reacting gases

Carbon formation has been reported by several investigators as a by-product in the interaction of methane with steam at high temperatures, and its formation is objectionable as it may cause inactivation of the catalyst In the case of methane, the formation of carbon at high temperatures can be suppressed by the use of a slight excess of steam over that required by equation (3), though the use of too much steam is objectionable According to Neumann and Jacob, the deposition of free carbon on the catalyst is very liable to occur when appreciable proportions of methane homologues are present along with the methane treated Here again, however, the employment of a sufficient excess of steam should help to obviate this difficulty Deposition of carbon is also liable to occur when the methane-steam reaction is carried out at below 700° C (according to equation (4)) in the presence of unsaturated hydrocarbons Williams [40, 1928] proposes to overcome this difficulty by hydrogenating the unsaturated hydrocarbons in the gas mixture prior to the application of the steam reaction

The main characteristics of the reaction between methane and steam may be briefly summarized as follows At high temperatures, reaction (3), producing hydrogen and carbon monoxide, can be carried practically to completion by using the theoretical amount of steam, while the reaction mixture produced in these circumstances will contain only traces of carbon dioxide Increasing the proportion of steam at high temperatures tends to increase the carbon-dioxide content of the reaction products, but even with a large excess of steam the major portion of the methane transformed is converted into carbon monoxide and hydrogen At lower temperatures in the presence of suitable catalysts, both reactions (3) and (4) take place simultaneously, but can never be carried to completion By using a large excess of steam at 500–600° C reaction (4) can be made the predominant mode of decomposition, though it is difficult to decompose more than 80–90% of the methane present

The Reaction between Methane and Carbon Dioxide

In the presence of active catalysts and at elevated temperatures, methane reacts with carbon dioxide according to the equation

$$CH_4+CO_2 \rightarrow 2CO+2H_2-61\ \text{kg -cal} \qquad (5)$$

The equilibrium constants of this reaction may be calculated from available free energy data as

$$\log K_5 = \frac{-12450}{T} + 7\ 59 \log T - 0\ 00236T + \\ +0\ 000000068T^2 - 6\ 64,$$

where

$$K_5 = \frac{P^2_{CO} \times P^2_{H_2}}{P_{CH_4} \times P_{CO_2}}$$

The value of K_5 increases with rising temperature of reaction, the figure for 900° C corresponding to a conversion of about 96%, which is of the same order as that obtained in the reaction of methane and steam at the same temperature The values of the constant K_5 are $1\ 95\times10^2$, $2\ 35\times10^3$, and $1\ 90\times10^4$ at 800°, 900°, and 1,000° C respectively

The equilibrium constant of reaction (5) may also be calculated by combining the known constants of the two reactions

$$CH_4 \rightleftharpoons C+2H_2 \text{ and } C+CO_2 \rightleftharpoons 2CO$$

This computation gives the following values for the equilibrium concentrations of reactants at atmospheric pressure and at a series of temperatures

Reaction $CH_4+CO_2 \rightleftharpoons 2CO+2H_2$

Temp °C	*Volumetric composition of reactants*			
	CH_4	CO_2	CO	H_2
450	43 5	43 5	6 5	6 5
550	28 7	28 7	21 3	21 3
650	15 5	15 5	34 5	34 5
750	3 0	3 0	47 0	47 0
850	0 8	0 8	49 2	49 2
900	0 1	0 1	49 9	49 9

The equilibrium has been investigated experimentally by Schmidt and Neumann [35, 1932] in the region 500–800° C, using a catalyst of silica gel impregnated with nickel Above 600° C the experimental results were in agreement with those calculated from the free energy data, but below that temperature the observed conversion of the methane is larger than that calculated, probably on account of the simultaneous occurrence of the side reactions

$$H_2+CO_2 \rightarrow CO+H_2O$$

and

$$H_2O+CH_4 \rightarrow CO+3H_2$$

As catalysts for the reaction between methane and carbon dioxide at temperatures of 800° C and over, Fischer and Tropsch [12, 1928] found that nickel-alumina supported on clay fragments was most efficacious Cobalt proved as active as nickel, but copper, iron, and molybdenum were feeble catalysts In general, those catalysts which are active for the methane-steam reaction at high temperatures are also active for the reaction between methane and carbon dioxide Klyukvin and Klyukvina [23, 1930] have shown that the passage of an equimolecular mixture of methane and carbon dioxide over an active reduced nickel catalyst at 1,000° C gives a practically complete conversion into hydrogen and carbon monoxide Satisfactory results were obtained by Hawk and his collaborators [17, 1932] by passing a mixture of carbon dioxide and natural gas (containing 11% of ethane and a residue of methane) over catalysts of nickel on alundum or corundite and employing a system in which the heat of reaction was supplied by intermittently blasting the contact mass with an air-gas flame In this way, and employing a gas containing 52% of carbon dioxide at temperatures of 790–1,100° C (this wide temperature range being due to the cycle of operations employed), the content of methane in the gaseous reaction products could be reduced to 2–3%, the remainder being hydrogen and carbon monoxide with only a small amount of carbon dioxide Typical results of Padovani and Franchetti [32, 1934], who employed an equimolecular mixture of methane and carbon dioxide in the presence of a catalyst of 12 5% nickel and 25 5% of alumina on clay at 850° C, are as follows

Time of contact, seconds	*Volumetric composition of reaction gas*			
	CO_2	CH_4	H_2	CO
7 2	1 7	1 2	48 9	48 2
9 8	1 1	0 7	50 9	47 6

Interesting details of the industrial application of this reaction have been supplied by the I G Farbenindustrie A -G [18, 1926] Residual gases from the destructive hydrogenation process are mixed with carbon dioxide and passed over a catalyst of nickel supported on refractory filling in a shaft furnace, or, alternatively, the furnace may be filled with coke and worked as a producer, the mixture of hydrocarbon gas and carbon dioxide being introduced at the cold blowing part of the cycle For example, a mixture of 23 6% carbon dioxide, 52% hydrogen, 22 5% methane, 1 3% nitrogen, and 0 6% carbon monoxide yields, on passage through a catalyst bed in a shaft furnace heated to 1,100° C, a gas mixture of the composition 31 4% carbon monoxide, 66 2% hydrogen, 1 1% carbon dioxide, and a residue of 1 3% nitrogen and unchanged methane

The reaction between methane and carbon dioxide takes place with an increase in the number of molecules, so that decomposition should be favoured by working at reduced pressures This has been substantiated by the work of Fischer and Pichler [11, 1931], who showed that practically complete conversion could be attained at 500–600° C. under 0 01 atm pressure, whereas under an absolute pressure of 1 atm the same degree of conversion could only be reached by raising the temperature to 900° C

Industrial Application of the High Temperature Reaction of Methane with Steam or Carbon Dioxide

The reactions of methane with steam or carbon dioxide at elevated temperatures have been the subject of industrial exploitation Most of the industrial processes which have been developed have for their object the production of mixtures of hydrogen and carbon monoxide, from which either pure hydrogen or hydrogen-nitrogen mixtures suitable for the ammonia synthesis can readily be prepared

The high temperature reactions between methane and steam and methane and carbon dioxide can be carried practically to completion at high temperatures with very high space velocity, and are, therefore, well adapted for large-scale application Moreover, unlike the reaction between methane and steam to produce carbon dioxide and hydrogen, the high temperature reactions are accelerated by catalysts which are not unduly sensitive to catalyst poisons, and can thus be employed for prolonged periods without substantial diminution of activity Unfortunately, the high temperature reactions are highly endothermic, and it is necessary, in order to carry them to completion, to supply to the reacting gas mixture very large quantities of heat at a high temperature level This fact undoubtedly constitutes the main difficulty encountered in the large-scale application of such reactions In addition, the selection of suitable materials for the construction of plant to be used at high temperatures is rendered more difficult by the highly corrosive action of steam under such conditions

In order to minimize the necessity for external heating of the catalyst chamber, part of the heat necessary for the methane-steam reaction may be produced *in situ* by partial combustion of some of the methane with oxygen, or air-oxygen mixtures However, in order to make this combined process thermally self-supporting, about 6 volumes of methane would need to be partially combusted for each volume decomposed by steam Thus, in general, even when the partial combustion of methane is employed to produce internal heating, it will be necessary to supply additional heat by external heating The disadvantages of using oxygen to effect the partial combustion are obvious, and when air is used the resulting gas mixture will contain nitrogen By suitably adjusting the proportions of methane, steam (or carbon dioxide), and air in the reaction mixture, a gas suitable for the synthesis of ammonia can be obtained

An alternative method of internal heating consists in carrying out the endothermic methane-steam reaction in the presence of a contact mass, which is used as a heat accumulator by intermittently blasting such contact material by a suitable air-hydrocarbon flame so as to raise it to a high temperature

The high temperature reaction between methane and steam to produce carbon monoxide and hydrogen is carried out on a large scale by the Standard Oil Company of New Jersey for the production of pure hydrogen at their hydrogenation plants at Bayway, N J, and at Baton Rouge, La The process is carried out at approximately atmospheric pressure in tubes packed with catalyst and heated by direct firing in a radiant type downflow furnace to a temperature of about 870° C Methane, or refinery gas, is first washed in caustic scrubbers to remove hydrogen sulphide prior to admixture with steam After reaction, the resulting mixture of hydrogen and carbon monoxide contains only about 2% of unconverted methane By a further treatment with steam in the presence of a catalyst at about 460° C, the carbon monoxide is converted into hydrogen and carbon dioxide and, after removal of the latter, there is obtained hydrogen of sufficient purity for use in the hydrogenation process Three units having a combined capacity of 9,000,000 cu ft per day of hydrogen are described by Byrne, Gohr, and Haslam [7, 1932] Details of the design and construction of the catalyst chambers for the methane-steam reaction have not so far been divulged It appears, however, that the difficulties associated with the operation of this endothermic reaction at the high temperature necessary may be greatly minimized by the use of specially designed regenerative heat exchangers

It is interesting to note that, in order to minimize deterioration of plant employed for the high temperature steam reaction, it has been proposed [19, 1928] to employ somewhat lower temperatures so that the reaction is incomplete and the resulting gas still contains up to 15% of methane, which is subsequently removed by washing with a suitable solvent under pressure The lower temperature employed is naturally less deleterious to the apparatus, which under these conditions may be constructed of special heat-resisting alloys, such as 'Nicrotherm', 'WT2', or 'V2A' steels A somewhat novel procedure is advocated by Schulz and Eisenstecken [37, 1928], who proposed to react hydrocarbon gases with steam at about 1,000° C in the presence of catalysts, such as iron, nickel, cobalt, chromium, &c, in a channel of carborundum which is heated by means of a high-frequency electric current

Combination of the endothermic steam reaction with the exothermic partial combustion of methane using oxygen, or gases containing oxygen, has been employed in a number of technical processes Thus, in the process of Casale [8, 1927], mixtures of methane, oxygen, and excess of steam are passed through a reaction chamber at temperatures of 1,100–1,300° C and under sub-atmospheric pressures In connexion with the use of such a method, the semi-technical investigations of Gluud and his collaborators [14, 1930] are of great interest The object of these experiments was the production of nitrogen-hydrogen mixtures from methane, or coke-oven gas, by the use of the high temperature steam reaction in conjunction with the exothermic partial oxidation The converter used in these experiments was an externally heated tube composed of a special heat-resisting alloy of 20% nickel, 25% chromium, and 55% iron This material was found to be satisfactory at the temperatures employed The converter, which was 94 cm long and 12 cm in internal diameter, was packed with a catalyst of nickel supported on refractory material. The results obtained are exemplified by the treatment of a coal distillation gas of the composition 6% carbon monoxide, 26% methane, 55% hydrogen, and 8% nitrogen. Passage of a mixture of 6 cu. m. of this gas with 3 kg. of steam and 3 cu. m. of air per hour over 10 litres of the above catalyst at about 1,050° C. resulted in the production of a gas mixture containing 2% carbon dioxide, 17% carbon monoxide, 56.5% hydrogen, and 24.5% of nitrogen, with only traces of methane. In the absence of air or oxygen, the output of the apparatus was materially reduced and only about 3.5 cu. m. of coal gas could be converted per hour to obtain a product of low methane content. However, by the introduction of air into the reaction gases at definite points in the catalyst bed, the methane content of the gaseous products could be reduced to below 0.1%.

Intermittent internal heating of the catalyst mass, carried out in alternation with the endothermic methane-steam reaction, has been advocated by a number of workers. In some processes catalysts are not employed and reliance is placed on refractory material, or coke, of large surface and heated to temperatures substantially higher than those necessary in the presence of catalysts. Thus, in the process of Kuhlmann [25, 1928] the reaction with steam and/or air is carried out in a chamber packed with coke and maintained to at least 1,200° C. by alternate blowing with preheated air. After passing the gas through the apparatus in one direction for some time, a current of air is introduced in order to burn deposited carbon, after which the steam reaction is again allowed to take place. An inert gas is used to sweep out the apparatus between these operations. A similar non-catalytic process, in which the decomposition of hydrocarbons with steam is carried out alternately with a direct heating of the contact mass by an air-hydrocarbon flame, has been used by the Union Chimique Belge S.A. [39, 1931], regenerators are employed for preheating the air used for combustion and also for preheating the mixture of methane and steam.

It appears from the work of Hawk and his co-workers [17, 1932] that intermittent heating of the catalyst bed by means of an air-gas flame can be successfully applied to the reaction of methane with steam at high temperatures. The converter used by these investigators consisted of an alundum tube, 3 in. in internal diameter and 20.5 in. long, incased in a 4-in. iron tube. The cycle of operations consisted of blasting the catalyst bed with an air-gas flame until the mass had attained a sufficiently high and uniform temperature, then purging the products of combustion, and finally passing through the mass a mixture of about equal volumes of steam and natural gas until the temperature had fallen too low for efficient operation. Using slightly more than 1 volume of steam per unit volume of natural gas, no trouble was experienced with carbon deposition, while an increase in the proportion of steam merely increased the amount of carbon dioxide in the reaction products without materially affecting the fraction of methane converted. The temperature in the catalyst bed varied from a maximum of about 1,150° C. to a minimum of 750° C. Under these very exacting conditions, catalysts of nickel on alundum or corundite were entirely satisfactory, whereas nickel-alumina and cobalt catalysts were of less value on account of mechanical disintegration. Inactivation of nickel catalysts by the oxygen present during the blow period was not noticed in this investigation.

Besides the catalysts previously mentioned, certain special catalysts for the reaction between methane and steam, or carbon dioxide, at high temperatures have been claimed in various patents. These include nickel on ignited magnesia, a special iron-chromium alloy, a metal of the iron group together with a difficultly reducible oxide, &c. Nickel, cobalt, or iron mixed with an aluminium compound containing oxygen, and at least one of the elements silicon, carbon, boron, phosphorus, and sulphur together with magnesium or an alkaline-earth oxide have also been claimed as catalysts for this reaction.

It is of interest to note that the production of water-gas mixtures from hydrocarbons may be accomplished in two stages, in the first of which methane is decomposed into its elements at high temperatures, and then the carbon formed in the first stage is subsequently submitted to the action of steam also at elevated temperatures. The decomposition of methane into its elements according to the equation,

$$CH_4 \rightleftharpoons C+2H_2-23 \text{ kg.-cal.},$$

is more or less complete at 1,200° C. in the presence of incandescent coke or refractory materials of large surface. Thus, it is actually possible to produce almost pure hydrogen, and also, by subsequent reaction of the carbon with steam, a mixture of hydrogen and oxides of carbon. Though the decomposition of methane into its elements is catalysed by iron, nickel, and other substances, it is difficult to employ such catalysts in actual practice on account of fouling of the catalyst surface. Molten baths of iron have, however, been suggested for this purpose. A three-stage process is proposed by Harrison [16, 1929] in which hydrogen is produced in one period of the cycle and water gas in a subsequent stage. Methane is passed into a coke-filled reactor, previously heated to 1,500° C. by an air blow. The decomposition of methane into carbon and hydrogen is allowed to proceed until the temperature has fallen to 1,100° C. Between this temperature and 900° C. steam is added to produce water gas, after which the cycle is restarted by an air blow. It is said that the different stages can be balanced so that no coke, but only deposited carbon, is consumed.

From an industrial standpoint, it seems certain that, except in special circumstances, the true vapour-phase combination of methane and steam is to be preferred, on grounds of simplicity of operation, to a process in which the methane is decomposed in two distinct stages.

Industrial Possibilities of the Reaction between Methane and Steam to form Hydrogen and Carbon Dioxide

The reaction

$$CH_4+2H_2O \rightarrow CO_2+4H_2$$

appears at first sight to be exceptionally promising for the manufacture of hydrogen, since carbon dioxide can readily be removed from such gas mixtures by suitable washing operations. In addition, the fact that the reaction, though never complete, is realizable at moderate temperatures of 500–600° C. would seem also greatly in its favour. In actual practice, however, this reaction possesses a number of objectionable characteristics which render its utilization somewhat problematical. For example, the catalysts employed in this reaction must necessarily be of the highest possible activity in order to attain sufficient reaction velocity at the lower temperature of operation. The high activity of catalysts for this reaction renders them more liable to inactivation by catalyst poisons than the catalysts employed at higher temperatures. As a result, a more careful control of this low temperature reaction, both as regards purity of reactants and also reaction conditions, is necessary than in the high temperature process. Perhaps a more serious objection is to be found in the fact that, at moderate temperatures, the equilibrium is by no means completely over to the decomposition side of the equation, so that it is not possible to attain anything approaching complete conversion of the methane Thus, at 500° C the equilibrium conversion of methane into carbon dioxide and hydrogen is only about 30% when using the theoretical proportion of steam Two methods are available to obtain a more complete conversion of the methane The first mode of operation consists in carrying out the reaction in a number of stages with removal of carbon dioxide between each of these stages, as proposed by the I G Farbenindustrie A -G [20, 1927] Another, and possibly better, method of forcing the reaction more nearly to completion consists in using a large excess of steam over that theoretically required This procedure has been elaborated by Blake [5, 1929], who used steam/methane ratios of 3 5 1 to 44 1 at temperatures of 400–700° C in the presence of active catalysts, such as nickel-ceria-alumina From the data furnished by Blake, it appears that a 90% conversion of methane can be obtained at 500–550° C by using 15 volumes of steam per unit volume of methane, under these circumstances the reaction gas will contain only about 1% of carbon monoxide Working at 550° C with a steam/methane ratio of 10 1, a similar conversion is obtained, but the carbon monoxide content of the gas mixture is then 2% Even when using a large excess of steam, therefore, the gaseous reaction products will always contain considerable proportions of unchanged methane in addition to hydrogen, carbon dioxide, and small amounts of carbon monoxide Since the removal of methane from such a gas mixture can only be accomplished by washing with absorbent liquids under pressure, the employment of this reaction as a source of relatively pure hydrogen is beset with difficulty

The tendency of the catalysts used in the low temperature methane-steam reaction to undergo inactivation by poisoning by traces of oxygen, sulphur compounds, and unsaturated hydrocarbons has already been mentioned The catalysts proposed for this reaction consist essentially of nickel promoted with various metallic oxides, such as the oxides of titanium, cerium, zinc, molybdenum, chromium, beryllium, uranium, zirconium, manganese, cadmium, and calcium The catalyst prepared by precipitation of a solution of nickel, manganese and aluminium nitrates by means of potassium carbonate solution followed by a washing with a solution of potassium nitrate is said to be particularly active [21, 1927] The value of salts of the rare earths, particularly those of the cerium group, as promoters is emphasized by Chaffette [9, 1932], while Al [1, 1932] obtains an active nickel catalyst by precipitation of nickel-nitrate solution with less than the theoretical amount of caustic soda, followed by reduction with hydrogen Nickel, cobalt, or iron, activated by difficultly reducible oxides of chromium, vanadium, potassium, magnesium, aluminium, or alkaline-earth metals, are claimed as catalysts for this reaction by Schmidt and Niemann [36, 1932]

Production of Water Gas by Reaction of Higher Hydrocarbons with Steam

Little information is available regarding the reaction of hydrocarbons higher than methane with steam to produce hydrogen and oxides of carbon There is no reason to doubt that reactions of the type,

$$C_2H_6+2H_2O \rightarrow 2CO+5H_2,$$
$$C_3H_8+3H_2O \rightarrow 3CO+7H_2,$$

and generally,

$$C_nH_{2n+2}+nH_2O \rightarrow nCO+(2n+1)H_2,$$

should be realizable at high temperatures in the presence of suitable catalysts The main difficulty in carrying out these reactions would appear to reside in the tendency of higher hydrocarbons to deposit carbonaceous material on the catalyst surface with resultant rapid inactivation For this reason it would be difficult to apply the low temperature reaction with steam, yielding carbon dioxide and hydrogen, to hydrocarbons higher than methane At higher temperatures the reaction with steam is probably preceded by a thermal decomposition in which lower molecular weight hydrocarbons, both saturated and unsaturated, are first formed Unless a considerable excess of steam is present, and a sufficiently long period of contact employed, the reaction with steam will be incomplete and lower saturated and unsaturated hydrocarbons will appear in the products

Very few scientific investigations on the reactions between higher hydrocarbons and steam, or carbon dioxide, have been reported in the literature Bahr [3, 1928] was unable to obtain any reaction between benzene and carbon dioxide, even at 750° C in the presence of various metallic oxide catalysts However, Matignon and Seon [28, 1933] were able to carry the decomposition of hexane practically to completion by using a large excess of steam in the presence of a zirconia catalyst at 1,050° C Under these conditions carbon dioxide and hydrogen were the main reaction products, but at shorter times of contact various amounts of methane and ethylene appeared in the resulting gas The decomposition of benzene with an excess of steam under similar conditions gave the same results

From a technical point of view, refinery gases consisting mainly of methane, but containing also considerable proportions of methane homologues as well as unsaturated hydrocarbons, constitute readily available raw materials for the manufacture of hydrogen In applying the high temperature steam reaction to such gases, Williams [40, 1928] prefers to remove unsaturated hydrocarbons by catalytic hydrogenation prior to treatment with steam If no preliminary removal of olefines is employed, it is necessary to subject the nickel or nickel-alumina catalysts used to frequent reactivation This is effected by passing steam over the catalyst at 650° C for 6–24 hours or, alternatively, by passing a mixture of oxygen, nitrogen, carbon dioxide, and steam over the heated catalyst for several hours [13, 1930]

In subjecting hydrocarbons higher than methane to reaction with steam at elevated temperatures, it is said to be advantageous to employ several layers of catalyst, each layer being more active and maintained at a somewhat lower temperature than the preceding layer [22, 1931] Mixtures of a metal of the iron group with a difficultly reducible metallic oxide are suitable catalysts

The Partial Reaction of Hydrocarbons with Steam

An interesting application of the reaction of steam with gaseous hydrocarbons higher than methane is in the re-forming of such hydrocarbons to produce gaseous fuels containing hydrogen, hydrocarbons, and oxides of carbon In the process described by Oberfell and Guyer [30, 1932], the hydrocarbon gas is subjected to a combination of pyrolysis and reaction with steam, both processes being effected simultaneously in one reaction chamber By suitable control of the reaction conditions the process can be made to produce gas with a range of density and calorific value sufficiently wide to simulate the properties of most of the manufactured or natural gases The gas produced by this method can thus be used to supplement supplies of natural or manufactured gases at periods of peak load The process is continuous, a mixture of hydrocarbon vapour (propane or butane) and steam being passed through a heated coil containing a catalyst The equipment necessary consists solely of a tube-type furnace with heat-resisting alloy heating coils For example, by using commercial butane in this process and controlling the steam/hydrocarbon ratio, the reaction temperature, and the time of contact, gases having calorific values ranging from 260 to 1,800 B Th U per cu ft can be readily produced The great flexibility of this type of re-forming process is shown by the following table, giving the analysis of various gases produced from butane

Gas no	*1*	*2*	*3*	*4*	*5*
B Th U (gross) per cu ft	453	609	666	809	1,266
Sp gr (air = 1)	0 45	0 52	0 55	0 62	0 86
% CO_2	7 2	3 6	6 4	5 0	4 6
% CO	18 2	13 3	15 0	15 0	10 4
% H_2	55 4	47 7	44 9	43 6	38 1
% Unsaturateds	4 3	8 3	9 5	12 9	13 3
% Paraffins	14 9	27 1	24 2	23 4	33 6

Re-forming of cracking and natural gases by a combination of cracking, partial combustion with air, and reaction with steam has been described by Perry [34, 1933]

Production of Hydrogen from Water Gas

A cheap and abundant source of hydrogen is essential, not only for the large-scale synthesis of ammonia, but also for the more recent industrial developments based on the destructive hydrogenation of coal and petroleum hydrocarbons In Germany, and also in Great Britain, water gas is used extensively as a raw material for the manufacture of hydrogen, but dilution with nitrogen during the blow period renders the resulting material somewhat unsuitable for hydrogenation purposes The use of oxygen in the blow period has, however, solved the difficulty of producing water gas free from nitrogen and lignite Bosch [6, 1934] reports that this process is being operated in Winkler generators by the I G Farbenindustrie A -G

When methane is employed as a source of hydrogen by application of the reaction with steam, it is possible to produce 4 volumes of hydrogen per volume of methane decomposed Pure hydrogen may, of course, be produced by the complete thermal decomposition of hydrocarbons, but this process yields considerably less hydrogen than the steam reaction In locations where cheap supplies of methane and water are available, the methane-steam reaction is likely to prove the most convenient method of producing hydrogen

The reaction

$$CH_4+2H_2O \rightarrow CO_2+4H_2$$

is best realized in two stages, in the first of which methane and steam are allowed to react at high temperatures so as to effect complete conversion to hydrogen and carbon monoxide By subjecting the resulting mixture to a further reaction with steam in the presence of a suitable catalyst at lower temperatures, the carbon monoxide may be converted into carbon dioxide and hydrogen This two-stage process may be summarized in the equations

$$CH_4+H_2O \rightarrow CO+3H_2,$$

and $$CO+H_2O \rightarrow CO_2+H_2,$$

the overall effect being

$$CH_4+2H_2O \rightarrow CO_2+4H_2$$

The gas resulting from this two-stage system, and consisting of approximately 80% hydrogen and 20% carbon dioxide, can be readily freed from the latter so as to yield relatively pure hydrogen

The reaction between carbon monoxide and steam

$$CO+H_2O \rightleftharpoons CO_2+H_2+10\ \text{kg -cal} \qquad (6)$$

is the well-known water-gas equilibrium, the constant of which is related to temperature by the equation

$$\log K_6 = \frac{2210}{T} - 0\ 9103 \log T +$$
$$+0\ 000974T - 0\ 000000149T^2 - 0\ 118,$$

where $$K_6 = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}}$$

The values of K_6 diminish with rising temperature, showing that carbon-dioxide formation is favoured by the use of low temperatures and vice versa At 400° C and 500° C, K_6 has the numerical values 15 2 and 5 9 respectively, showing that these temperatures are suitable for the conversion of carbon monoxide into hydrogen and carbon dioxide under the action of steam With a ratio of steam to water gas of 3 volumes to 1, the concentrations of unchanged carbon monoxide in the equilibrium mixture after removal of water are about 2% at 550° C, 1% at 445° C, and 0 5% at 380° C Even more favourable conversions may be attained at lower temperatures, but this necessitates the use of highly active catalysts, which are less resistant to poisoning than those which can be employed at somewhat higher temperatures For this reason, and because high reaction velocities are necessary in practice, temperatures of 450–500° C are commonly employed in large-scale operations In the absence of a catalyst, the reaction between steam and carbon monoxide is very slow, and accordingly the success of the process is dependent on the employment of a catalyst sufficiently active to allow of operation at temperatures below 500° C, and, at the same time, rugged enough to withstand prolonged treatment Many catalysts have been suggested, in most of which the oxides of metals of the iron group are the main constituents Evans and Newton [10, 1926] have examined numerous catalysts for this reaction, and their work indicates that iron oxide is the best single-component catalyst The activity of iron oxide and cobalt oxide can be promoted by the addition of aluminium and potassium oxides, but cobalt-oxide catalysts are readily poisoned by sulphur compounds, whereas iron-oxide catalysts merely suffer a reduction in activity in the presence of sulphur compounds

In order to attain as complete a conversion of carbon monoxide as possible, large excess of steam is commonly employed Even with a very large excess of steam it is not possible to reduce the content of carbon monoxide to a sufficiently low figure to permit the use of the resulting hydrogen, without special purification, in the ammonia synthesis However, by employing a material which freely absorbs carbon dioxide at the reaction temperature, the equilibrium may be disturbed and practically complete conversion attained Gluud [14, 1930] proposed to employ dolomite at 480–500° C in order to remove the carbon dioxide as formed, and in this way was able to reduce the carbon-monoxide content of the final gas to 0 05–0·07% by volume The regeneration of the dolomite was carried out at temperatures not exceeding 1,050° C, and it was found that samples of dolomite containing calcium and magnesium in equal atomic proportions were most resistant to disintegration under the influence of repeated regenerations

The reaction between carbon monoxide and steam is exothermic and may be made almost thermally self-supporting In order to increase reaction velocity, the process may very conveniently be carried out in two stages in the presence of suitable catalysts In the first stage the catalyst is maintained at a higher temperature than normal so that a high velocity is obtained, but the reaction gas contains a certain amount of unchanged carbon monoxide Passage of the gases through a second catalyst bed at a lower temperature serves to reduce the carbon-monoxide content to a figure of 1–2%

In the two-stage process used by the Standard Oil Company of New Jersey, the gases from the first stage, consisting of hydrogen, carbon monoxide, and small amounts of unconverted methane, are mixed with additional steam and subjected to the action of a second catalyst at about 450° C The gases leaving this second stage contain, in round numbers, 78% hydrogen, 20% carbon dioxide, 2% of unchanged methane, together with small amounts of carbon monoxide After removal of the carbon dioxide by scrubbing with water or triethanolamine under pressure, the gas is of sufficient purity for use in the hydrogenation of carbonaceous materials In this case the presence of small amounts of unchanged methane and carbon monoxide is not deleterious, but hydrogen intended for use in the synthesis of ammonia must be further purified from methane and carbon monoxide The complete removal of carbon monoxide is effected on a large scale by washing under high pressure with aqueous solutions of cuprous ammonium formate or carbonate, whereby the last traces of carbon dioxide and small amounts of oxygen in the gas are also eliminated

Where the low temperature reaction of methane with steam is used to produce a gas containing hydrogen and carbon dioxide, appreciable amounts (5–15%) of unchanged methane as well as 1–2% of carbon monoxide will also be present in the products The methane concentration of such gases can be reduced to a figure which would render the gas suitable for hydrogenation purposes, by subjecting them to a counter-current washing under high pressure with suitable solvents, such as mineral oils

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SECTION 33

ENGINEERING AND CHEMICAL ENGINEERING AS APPLIED TO REFINING

The Principles of Heat Transfer	H M WEIR
The Thermal Conductivity of Solids	H M WEIR
The Emissivity of Surfaces	E S L BEALE
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Condenser, Heat Exchange, and Tube-Heater Equipment	
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Heaters	L A MEKLER
Insulation	
Heat Transfer through Insulation	E C RACK
Insulation of Oil Industry Equipment	E RINEHART

THE PRINCIPLES OF HEAT TRANSFER

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THERE are three ways in which heat may be conveyed from one region to another by conduction, by convection, and by radiation Convection alone involves the motion of discrete masses of materials Conduction and radiation are due to changes in molecular or electronic motion, but neither phenomena primarily requires the motion of any larger material masses

In many cases of practical interest heat is conveyed by all three modes of transfer Since conduction, convection, and radiation are subject to very different laws, rigorous calculations would often be too involved for practical work It is usual, therefore, to work out each of these effects independently, and the subject is treated in this way in the present article, the subject being grouped under these three heads in the order conduction, radiation, and, lastly, convection

Very few fundamental studies of heat transfer have been made in which petroleum materials or apparatus closely paralleling refinery equipment have been the focus of attention It is therefore usually necessary to adapt the principles and data from other branches of engineering

The published literature on the subject is very large and the bibliography must necessarily be selective, but it is hoped that most of the important references have been cited

Particular reference should be made to the following works, to which special acknowledgement is due

BADGER *Heat Transfer and Evaporation*	[2, 1926]
Dictionary of Applied Physics, Vol I	[14, 1922]
FISHENDEN and SAUNDERS *The Calculation of Heat Transmission*	[22, 1932]
MCADAMS *Heat Transmission*	[59, 1932]

In so far as possible the recommendations on terminology of the Committee on Heat Transmission of the National Research Council have been adopted Accordingly, terms ending in 'ivity', such as conductivity, resistivity, &c , express properties of matter which are independent of size and shape Terms ending in 'ance', as conductance, resistance, &c , refer to properties which depend both on the substance and its size and shape Finally, terms ending in 'ion' denote the rate of heat transfer and are accordingly influenced by all the conditions of a particular case, examples are conduction and transmission

A uniform nomenclature has been used as far as possible, and it is to be noted that, unless particular units are given for an equation, any self-consistent set of units may be used, such as c g s °C or ft lb hr °F Tables of physical data applicable to heat transfer will be found in another article As many of these data are usually given in c g s units, it is often more convenient to evaluate dimensionless groups, such as the Reynolds number, using c g s data even when working with British Thermal Units

Conduction of Heat

The necessary and sufficient condition for heat flow by conduction is that a difference in temperature exists at two points not separated by a region devoid of matter Consequently, heat conductivity is a property of all matter whether solid, liquid, or gaseous

Two types of conduction can be distinguished for simplicity in discussion

1 The temperatures and the differences in temperature of the source and receiver are constant with reference to time The form of the system does not change with the time A system of this character is said to exhibit conduction in the steady state The terms source and receiver, or source and sink, are employed here and elsewhere to distinguish elements of a system in which heat is passing from the source to the receiver or sink In the absence of an agency in the path which performs work at the expense of outside energy, the source is always at a higher temperature than the receiver

2 The temperature of either, or both, source and receiver changes with time—and the form of the system may also change Such a system exhibits conduction in the unsteady state

Elementary Mathematical Theory of Conduction.

The basis of all mathematical treatment of problems of heat flow by conduction is the monumental work of Fourier [23, 1822] The assumption originally made, and which has been amply justified by experiment, is that in an isotropic body the flux of heat across a plane element, drawn in any direction through a point within the body, is in the direction of decreasing temperature Furthermore, it is proportional to the space rate at which the temperature falls in the direction of the normal to the plane Accordingly, if

δA = the area of the elemental plane,

δx = an elementary length of the normal to it,

δQ = the differential amount of heat,

δt = the differential time interval,

$\delta\theta$ the differential change in temperature,

then the positive or negative amount of heat which flows across the elemental plane is

$$\delta Q = -k\frac{\delta\theta}{\delta x}\delta A\,\delta t, \tag{1}$$

k being a coefficient called the *thermal conductivity*

The simplest problems are those of linear flow in which the isothermal surfaces are parallel planes Where the faces of a large slab are parallel and are subjected to changes in temperature which are uniform over each face, this condition is fulfilled If the x-axis be taken normal to these planes, the amount of heat entering a volume element of unit area and thickness δx in time δt is

$$-k\frac{\delta\theta}{\delta x}\delta t$$

The amount of heat which is leaving through the other face of the element is

$$-k\left(\frac{\delta\theta}{\delta x}+\frac{\delta^2\theta}{\delta x^2}\delta x\right)\delta t$$

Accordingly, there is a (positive or negative) gain of heat stored by the element equal to

$$k\frac{\delta^2\theta}{\delta x^2}\,\delta x\,\delta t$$

To find the change of temperature of the element it is necessary to divide this quantity by the heat required to raise it one degree on the temperature scale chosen. This is, of course, the product of the specific heat, c, and the weight of the element $\rho\delta x$, where ρ is the density. Hence

$$\frac{\delta\theta}{\delta t}\,\delta t = \frac{k}{\rho c}\left(\frac{\delta^2\theta}{\delta x^2}\right)\delta t,$$

or

$$\frac{\delta\theta}{\delta t} = a\left(\frac{\delta^2\theta}{\delta x^2}\right), \tag{2}$$

where $a = k/\rho c$. This is called the 'diffusivity'. Since all the factors in this expression are properties, the diffusivity is also a property, and its value for various substances is given in the tables of physical properties. The general Fourier equation for heat flow in any direction can be derived in a similar manner or can be inferred from the above to be

$$\frac{\delta\theta}{\delta t} = a\left(\frac{\delta^2\theta}{\delta x^2} + \frac{\delta^2\theta}{\delta y^2} + \frac{\delta^2\theta}{\delta z^2}\right) \tag{3}$$

The Steady State of Conduction

(*a*) **Single Conductors.** Under this condition the temperature at any specified point in the body does not vary with time. Accordingly, the temperature gradient, written as $-\delta\theta/\delta x$ in equation (1), is independent of time, as is also the rate of heat flow, $\delta Q/\delta t$, i.e.

$$\frac{\delta Q}{\delta t} = q$$

It is convenient, furthermore, to choose the fixed location of the area δA at right angles to the temperature gradient, writing distances in the direction of the gradient with the symbol x. With these changes equation (1) becomes, for the case of steady conduction,

$$q = -kA\frac{d\theta}{dx} \tag{4}$$

The coefficient of thermal conductivity, k, is expressed in the units

$$\frac{(\text{Heat quantity})\times(\text{Length})}{(\text{Area})\times(\text{Temperature difference})\times(\text{Time})}$$

It is a unique property of a given material which, however, varies to a certain extent with temperature. This variation can usually be expressed with sufficient accuracy by an equation of the form

$$k = k_0(1+\alpha\theta) \tag{5}$$

(*b*) **Multiple Conductors.** The flow of heat successively or simultaneously through several solids is usually of more interest than through a single one. Two cases need to be considered: (1) several solids are joined together to form a single or series path for the flow of heat, and (2) the different solids present parallel paths for the flow of heat.

It is helpful to notice that heat flow under either condition is entirely analogous to the flow of electricity in corresponding circuits, temperature difference and voltage drop being the respective measures of tendency to flow.

In the first case, that of series conduction, the heat flux under steady conditions is the same through each material, and the temperature gradient in each solid is the primary cause of flow. Consequently, for steady conditions of heat flow through conductors in series

$$q = \frac{k_1A_1\Delta\theta_1}{x_1} = \frac{k_2A_2\Delta\theta_2}{x_2} = \frac{k_3A_3\Delta\theta_3}{x_3} = \dots = \frac{k_nA_n\Delta\theta_n}{x_n}$$

The convenience of introducing the concept of *resistance* to heat flow is obvious. Resistance $= R = (x/kA)$. Using this nomenclature, equation (1) becomes

$$q = \frac{\Delta\theta_1}{R_1} = \frac{\Delta\theta_2}{R_2} = \frac{\Delta\theta_3}{R_3} = \dots = \frac{\Delta\theta_n}{R_n},$$

from which

$$qR_1 = \Delta\theta_1,\quad qR_2 = \Delta\theta_2,\quad qR_3 = \Delta\theta_3,\quad \&c.$$

Since the total temperature difference, or gradient, from the beginning to the end of the series path is the sum of all separate gradients,

$$q(R_1+R_2+R_3+\dots+R_n) = \sum_1^n \Delta\theta_n \tag{6}$$

In the second case in which the paths for heat flow are in parallel, the temperature gradient is the same for each solid and the total heat flux is the sum of the separate flows through each of the n paths

$$\begin{aligned}\sum q &= \frac{\Delta\theta}{R_1}+\frac{\Delta\theta}{R_2}+\frac{\Delta\theta}{R_3}+\dots+\frac{\Delta\theta}{R_n}\\ &= \Delta\theta\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}+\dots+\frac{1}{R_n}\right)\end{aligned}$$

If *conductance* is defined as the reciprocal of resistance, we have

$$\text{Conductance} = C = \frac{1}{R} = \frac{kA}{x},$$

$$\sum q = \Delta\theta(C_1+C_2+C_3+\dots+C_n) = \Delta\theta\sum_1^n C_n \tag{7}$$

In complete correspondence to the rule for electrical circuits the findings of this section can be summarized. *For the flow of heat in a system of conductors in series, resistances are additive, while for a system of conductors in parallel, the conductances are additive.*

Equations (6) and (7) are exact. Applications of them, particularly in the case of conductors in series, may result in error due to failure to take into account all of the resistances actually in the path. For instance, there is usually considerable thermal resistance at the junction between two metal surfaces due to imperfect contact or the inclusion of a film of oxide or oil or air.

When all the principal elements of a conducting system have high thermal resistance, the percentage errors which may arise in calculating conductances are apt to be smaller than in the case of good conductors. Van Dusen and Finck [94, 1931] have studied the thermal resistance of single and composite wall-materials, masonry, &c. Their observations on the differences in values attributable to chance factors, to differences in workmanship, &c., are interesting and show that on the average the calculated heat transfer values are not far from the values determined by experiment.

Conduction in Solids.

For practical purposes solids may be divided into two classes: metals and insulators. As a class metals are distinguished for their high values of thermal conductivity.

For pure metals the coefficient α in equation (5) is in general small and negative, while for alloys it is positive.

Solids which have exceptionally low values of thermal conductivity are of special industrial interest since they are extensively used as heat insulators The natural low conductivity of such materials is usually enhanced by using them in more or less finely divided form A relatively large volume of air is thus trapped with the loose fibrous, cellular, or unoriented aggregate Well-known examples of these materials are abestos wool, granulated cork, hair felt, magnesia flour In addition to heat conduction through point-to-point contact of the solids which form the mass of the substance, heat transfer occurs by convection of the air in the tiny cells and by radiation from wall to wall of these air spaces

The three modes of transfer are not easily, or for most purposes conveniently, separated, so that the values of thermal conductivity k, reported in the literature for non-homogeneous solids are ordinarily *apparent values* only Nevertheless, these data can be used in the same way as true k values, providing the conditions of application do not depart widely from the circumstances under which the value of k was measured This limitation is important especially as regards the temperature and the bulk density of the material Among the many determinations which might be cited to illustrate the controlling effect of bulk density, those of Petavel [73, 1915–16, 74, 1930] with slag wool are typical Petavel found a minimum value of heat transfer with a bulk density of 10 lb per cu ft At a density of 5 lb per cu ft the heat transfer was 130%, and at 15 lb per cu ft it was 110% of the minimum value More recently Griffiths [26, 1932] has obtained results of the same general character

Heterogeneous materials of the type under discussion may approach the low conductivity value for air, but with one possible exception never equal it On reducing the size of the interstices of the composite material by finer subdivision, or by closer packing, the contributions of radiation and convection to the total heat transfer can be materially reduced But true conduction inevitably increases by the very circumstance of greater bulk density The better heat insulation materials incorporate a nice (natural or artificial) balance between these opposing factors tending to alter the flow of heat

The exception mentioned in the previous paragraph was noted by S S Kistler [50, 1931, 51, 1932], who has produced a gel structure with silica in which the fluid phase is a gas, e g air, instead of a liquid Together with Caldwell [6, 1934] he measured the heat conductivity of some of these 'aerogels' and reported in 1934 that, on the average, they exhibited about 10% less conductivity than air at atmospheric pressure

Conduction in Liquids.

The thermal conductivities of nearly all non-metallic liquids lie between 0 0002 and 0 0006 c g s units, being therefore of a much lower order than the conductivities of most solids However, under engineering conditions heat transfer in liquids always involves important convection effects, so that low conductivity is by no means synonomous with low total transfer rate

For liquids the value of the coefficient α in equation (5) is usually negative Water is an exception from two standpoints its conductivity increases with temperature [42, 1920] and its absolute value is unusually high

The effect of pressure change on the heat conductivities of liquids is negligible for most engineering purposes, but presumably the rate of change would become much greater in the region just below the critical point

Conduction in Gases.

According to the kinetic theory originally developed by Clark Maxwell, the thermal conductivity of gases should be independent of pressure This is found to be true experimentally down to very low pressures when the mean free path of the molecules becomes comparable with the dimensions of the containing vessel At these low pressures the conductivity is nearly proportional to the pressure

There is a useful relationship derived from the kinetic theory between the conductivity k and the absolute viscosity η of gases, namely,

$$k = f\frac{C_v}{M}\eta, \tag{8}$$

where C_v is the specific heat at constant volume and M is the molecular weight If the values of the variables are expressed in c g s units, the constant f should theoretically be equal to 2 5 However, this is approximately true only for monatomic gases For diatomic gases the constant has a value about 1 75, and for triatomic gases about 1 4 This relation may be used to calculate the conductivity of gases when the specific heat and viscosity only are known

Calculation of Steady Conduction. Mathematically Simple Forms.

Equation (1) is the basis for calculation of all problems of conduction in the steady state It is convenient to operate on the derived equation (4), modifying it to take account of the variations of k with temperature which becomes important where source and receiver are widely different in temperature By rearrangement of equation (4) and integrating we get

$$-\int_{\theta_1}^{\theta_2} k\,d\theta = q\int_{x_1}^{x_2}\frac{dx}{A}$$

Substituting the value of k from equation (5) and integrating,

$$k_0\left[1+\alpha\left(\frac{\theta_1+\theta_2}{2}\right)\right](\theta_1-\theta_2) = q\int_{x_1}^{x_2}\frac{dx}{A}$$

Since the product of the first two factors on the left side of the equation is the arithmetic mean of the upper and lower values of the conductivity, it may be written k_{mean}, and we get

$$k_{\text{mean}}(\theta_1-\theta_2) = q\int_{x_1}^{x_2}\frac{dx}{A} \tag{9}$$

The application of this equation to specific problems simply involves the expression of the area, A, as a function of the length, L, after which the indicated integration can be performed

A flat wall offers the most elementary example of the use of the equation, since in this case A is independent of L, i e the heat flow is perpendicular to the sides of the wall, providing these are at two different uniform temperatures Equation (9) becomes

$$k_{\text{mean}}(\theta_1-\theta_2) = q\frac{x}{A}, \tag{10}$$

or

$$q = k_{\text{mean}}\frac{A(\theta_1-\theta_2)}{x}.$$

The equation holds accurately for all portions of the wall area where the temperature gradient is actually perpendicular to the faces of the wall. If the ends and top surfaces of the wall are unprotected, heat loss occurs there, the temperature gradient lines are curved, and the equation fails to describe the heat transfer in this locality. However, if the wall is relatively large in area, so that the 'edge and adjacent' area is small in proportion to the whole, it serves as an entirely satisfactory approximation.

Another common and simple case is that of conduction through a cylindrical shell surrounded by a central-heated or cooled core. A lagged steam pipe is a good example. If the length of the shell of lagging is very great in comparison to its thickness, the edge losses at the ends will be trivial in comparison to the total losses, so that the calculation can be made of heat loss/unit length and the result multiplied by actual length.

In this case the temperature gradient is radial and the problem reduces to one of expressing the area at right angles to this gradient in terms of the radius r.

Writing r_1 = the inside radius
r_2 = the outside radius,
l = length of shell.

Then equation (9) becomes

$$k_{\text{mean}}(\theta_1-\theta_2) = q\int_{r_1}^{r_2}\frac{dr}{2\pi rl}$$

Integrating and rearranging, we get

$$q = \frac{2\pi l(\theta_1-\theta_2)k_{\text{mean}}}{\log_e\frac{r_2}{r_1}} \qquad (11)$$

$$= \frac{2.73l(\theta_1-\theta_2)k_{\text{mean}}}{\log_{10}\frac{r_2}{r_1}} \qquad (11a)$$

Calculation of Steady Conduction. The Shape Factor.

It is often very convenient to make use of the idea of the 'shape factor' which was probably originated by Langmuir and Adams [55, 1913].

For this purpose we can rewrite equation (9) in the form

$$q = k_{\text{mean}}(\theta_1-\theta_2)S, \qquad (12)$$

where

$$S = \frac{1}{\int_{x_1}^{x_2}\frac{dx}{A}},$$

and is called the 'shape factor'.

The shape factor may be regarded as the mean area of the conducting path divided by its length. It will also readily be seen that $k_{\text{mean}}\times S$ is a thermal conductance. The shape factor for a flat plate (thickness small compared to other dimensions) is then simply A/L. The shape factors for two other simple cases are as follows.

Hollow Cylinder. Diameter small compared to length. Uniform temperature at inner and outer surfaces.

$$S = \frac{2\pi l}{\log_e\frac{r_2}{r_1}} \qquad (13)$$

Hollow Sphere. Uniform temperature at inner and outer surfaces.

$$S = \frac{2\pi r_1 r_2}{(r_2-r_1)} \qquad (14)$$

If equation (13) is compared with equation (11) it will be seen that the 'mean area' in this particular case is given by

$$A_{\text{mean}} = \frac{(A_2-A_1)}{\log_e\frac{A_2}{A_1}}$$

This is the same form as the 'logarithmic mean' used for the temperature difference of heat exchangers. When the ratio of the radii is less than 2.0, the arithmetic mean of the areas is within 4% of the true value and it is therefore often used for simplicity.

Langmuir and Adams [55, 1913] calculated the flow of heat from cubical and rectangular volumes enclosed by walls of uniform thickness and checked their theoretical deductions by measuring electrical conductance of volumes of electrolyte having the same shape as the walls of the various enclosures. In this way they found what allowance for a square edge, a square corner, &c., had to be added to the shape factor for the slabs of insulation opposite the inner rectangular faces. For instance, they found that a square edge was equivalent to an addition of 0.54 times the length of the edge.

Their conclusions as to the shape factor S for cubical and rectangular boxes can be summarized by equations in which

A = area of the interior surface,
B = area of the outer surface,
X = thickness of walls,
$\sum l$ = total length of edges of internal surface.

The equations differ for individual cases, depending on the relationship of wall thickness to other dimensions, and are as follows.

All interior dimensions > $X/5$

$$S = \frac{A}{X}+0.54\sum l+1.2X \qquad (15)$$

One dimension < $X/5$

$$S = \frac{A}{X}+0.465\sum l+0.35X \qquad (16)$$

Two dimensions < $X/5$ (e.g. rod, square in cross-section, covered with thick insulation)

$$S = \frac{2.73l}{\log_{10}\frac{B}{A}} \qquad (17)$$

Three dimensions < $X/5$ (e.g. small cube with thick insulation on all sides)

$$S = 0.79\sqrt{\left(\frac{AB}{X}\right)} \qquad (18)$$

These formulae apply strictly only if the inner and outer surfaces are at uniform and constant temperature, a condition which does not hold exactly in many practical cases. Nevertheless, they are very useful in estimating approximate heat losses.

Illustration. An electrically heated muffle furnace is 8×12×20 in. inside and has a 6-in. layer of insulation on all sides. Calculate the shape factor S for application in equation (12). Since all interior dimensions are greater than $X/5$, equation (15) applies.

$$A = 2[(8\times12)+(8\times20)+(12\times20)] = 992 \text{ sq. in.}$$

$$X = 6 \text{ in.}$$

$$\sum l = 4(8+12+20) = 160 \text{ in.}$$

$$S = \frac{992}{6}+0.54(160)+1.2(6) = 259 \text{ in.}$$

For this particular case the use of the arithmetic mean area would give a result greatly in error The value of S calculated using the arithmetic, the geometric, and the 'logarithmic' mean areas are given below for comparison

Arithmetic mean $S = 397$
Geometric mean S 322
Logarithmic mean $S = 347$

Graphical Solution of Complicated Shapes.

An approximate solution for the more complicated shapes can often be obtained by reducing the problem to an equivalent simpler case, the exact solution of which is known There are, however, many cases where this is difficult, and some method of dealing with these is required

There is a useful graphical method which depends for its application on the problem being capable of being treated as a two-dimensional one This method consists in drawing in the lines of flow of heat and the isothermal lines over the conducting area according to a simple set of rules These are as follows and they are illustrated by an example shown in Fig 1

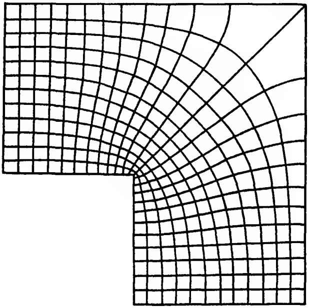


FIG 1

1 The two boundaries must be taken to be isotherms
2 The points of intersection of a line of flow and an isotherm must be at right angles
3 The spacing of the lines is chosen so that the areas enclosed by them approximate to squares Where these areas become much distorted it is only necessary to take the lines of flow and the isotherms proportionately closer together

The example shown in Fig 1 represents one quarter-section of a square bar 9 in square covered with 6 in of insulation Twelve equal temperature steps have been chosen which is found to lead to 12 lines of flow up to the corner, or 24 altogether for the quarter-section When the isotherms and the lines of flow are drawn according to the above rules, this gives a shape factor of $\frac{24}{12} = 2{\cdot}0$ for the quarter-section for unit length of bar This result may be compared with the case of the heat flow being confined to the slabs of insulation opposite the inner faces, that is, not being allowed to spread into the corner The number of lines of flow would then clearly be 9 to the corner or 18 for the quarter-section, giving a shape factor of $\frac{18}{12} = 1\ 5$ per unit length for the quarter-section

The difference between these shape factors is 0 5 which represents the added conductance due to the square edge which agrees quite closely with the value 0 54 given above

Unsteady Conduction.

The majority of processes in the petroleum industry are of the 'continuous' type, and consequently temperatures are steady except for the starting-up and shutting-down periods Although accurate calculation of heat transfer during these periods is not often required, a means of estimating this as well as the temperature gradients in the furnace walls is of value

Certain other processes essentially involve changing temperatures, for instance, batch distillations and regenerators, and there are many cases of a general character where the equations for unsteady flow must be applied

Fourier's general equation (3) can be adapted to the solution of any problem in unsteady heat conduction in an isotropic medium For the most part, however, the equation for heat flow in one direction can be made to cover practical cases This equation may be written

$$\frac{d\theta}{dt} = \left(\frac{k}{\rho c}\right)\frac{d^2\theta}{dx^2}, \tag{19}$$

or, writing a in place of $(k/\rho c)$, the diffusivity, for the sake of brevity as in equation (2), we have

$$\frac{d\theta}{dt} = a\frac{d^2\theta}{dx^2} \tag{20}$$

The diffusivity is that property of a substance which decides the rate at which a change of *temperature* is transmitted by conduction of heat This process bears a very close resemblance to that of molecular diffusion from which it derives its name

The dimensions of diffusivity are $\frac{(\text{length})^2}{\text{time}}$, from which it can be deduced at once that the time required for a given temperature rise in geometrically similar bodies under otherwise identical conditions is proportional to the square of the linear dimensions This is a very important point because, if a numerical example of a particular case is worked out, the temperature distribution, &c , for any other diffusivity or size of body can be readily obtained, since the temperature distribution will be the same throughout the body for corresponding values of at/x^2 Thus, if the outside surface of a certain wall is raised to 150° F in 1 hour after a constant high temperature is suddenly applied to the inner surface, doubling the thickness of the wall will extend the time to reach 150° F to 4 hours

Special Cases of Unsteady Conduction. Analytical Method.

In practised hands equations (3) and (20) are powerful tools, though it often happens that comparatively simple practical conditions lead to mathematical boundary conditions which make the solution extremely tedious or impossible unless simplifying assumptions are introduced

The literature contains many exact solutions of special cases which have close counterparts in practical conditions There are so many different cases that a useful proportion cannot be included in this article and the reader must refer to the text-books on the subject [41, 1913, 7, 1921, 8, 1934] and to the original articles [for example, 31, 1923, and 65, 1936].

These cover cases of slabs, semi-infinite solids bounded by a plane, square beams, cubes, cylinders, spheres, &c., the surfaces of which are heated either periodically, at a given rate of heat input, suddenly to a fixed temperature, or through a heat-exchange medium from a fixed temperature, &c., and solutions are required for the temperature distribution over the surface, at the centre and throughout the volume, and also for the rate of heat absorption and the total heat absorbed.

The most useful form of solution for these cases is graphical, in which curves are given for particular values of (at/x^2) for the reason mentioned above, and many such solutions have been published

Gurney and Lurie [31, 1923] reduced the integrated equations for a number of shapes to functions of four dimensionless groups and have plotted these functions in such a way as to simplify numerical calculations Only three cases can be mentioned in this article, but these will serve to indicate the nature of the analytical problems involving unsteady conduction

(*a*) The simplest case mathematically is that of a solid bounded by a plane, the surface of which is subject to a simple sinoidal variation of temperature with time The plane surface is situated at $x = 0$ and the solid is semi-infinite in extent (in the positive direction of x) Any other periodic variations of temperature can be represented as closely as required by a Fourier series For instance, Pugh [76, 1936] gives one to represent the typical changes in surface temperature of thick walls exposed to the sun

Assume the surface temperature variation to be given by

$$\theta = \theta_0\left(\sin\frac{2\pi t}{T}\right),$$

where

θ = temperature at time t,

θ_0 = amplitude of the temperature oscillation (= half-range),

T = periodic time of oscillation

It can be shown that the solution of equation (20) which satisfies these boundary conditions is

$$\theta = \theta_0 e^{-\sqrt{\left(\frac{\pi x^2}{aT}\right)}}\sin\left\{\frac{2\pi t}{T}-\sqrt{\left(\frac{\pi x^2}{aT}\right)}\right\}$$

Obviously heat will flow in and out of the surface during alternate half-periods of the cycle From the form of the equation it will be seen that the amplitude diminishes as the depth x below the surface increases The following characteristics of the temperature wave may be deduced

Wave-length $= \sqrt{(4\pi aT)}$,

Velocity of propagation $= \sqrt{\left(\frac{4\pi a}{T}\right)}$,

Amplitude at any depth $x = \theta_0 e^{-\sqrt{\left(\frac{\pi x^2}{aT}\right)}}$,

Time lag at depth x $= \sqrt{\left(\frac{Tx^2}{4\pi a}\right)}$.

It can also be shown that the total heat flow Q through the surface during a half-period is given by

$$Q = \theta_0\sqrt{\left(\frac{2k^2T}{\pi a}\right)}$$

(*b*) Another useful and comparatively simple case is that of a wall of finite thickness initially at a uniform temperature θ_1, the front surface of which is suddenly raised to a new and constant temperature θ_2.

If the back surface is protected from heat loss, it is clear that the whole wall will finally be raised to θ_2 At any intermediate time t the temperature distribution is given by

$$\frac{\theta-\theta_1}{\theta_2-\theta_1} = 1-\frac{4}{\pi}\sum_{n=1}^{n=\infty}\frac{e^{-(2n-1)^2a\pi^2t/4X^2}}{(2n-1)}\sin\frac{(2n-1)\pi x}{2X},$$

where X is the total thickness of the wall.

The total amount of heat absorbed by the wall up to time t expressed as a fraction of the total heat when the uniform temperature θ_2 has been reached is given by

$$\frac{Q_t}{Q_\infty} = 1-\frac{8}{\pi^2}\sum_{n=1}^{n=\infty}\frac{e^{-(2n-1)^2a\pi^2t/4X^2}}{(2n-1)^2}$$

Up to the time when the temperature of the back surface starts altering appreciably, this equation may be simplified to

$$\frac{Q_t}{Q_\infty} \approx \sqrt{\left(\frac{4at}{\pi X^2}\right)},$$

and when the back surface has nearly reached the final temperature, all except the first term may be neglected and

$$\frac{Q_t}{Q_\infty} \approx 1-\frac{8}{\pi^2}e^{-a\pi^2t/4X^2}.$$

These equations have been made use of by Lacey [53, 1933] in his work on molecular diffusion of gas in oil, to which the equations for unsteady heat flow are applicable with hardly any modification

(*c*) Another important case is exactly similar to the previous one, with the exception that the back surface is maintained at the initial temperature θ_1 It is clear that, in this case, a constant temperature distribution will finally be set up throughout the slab, and this fact can be deduced directly from the equation (20) By definition,

$$\frac{d\theta}{dt} = 0,$$

and since the diffusivity a is not zero

$$\frac{d^2\theta}{dx^2} = 0$$

The solution of this equation is in the form $\theta = A+Bx$, which represents a straight line, and therefore the temperature at any point between the faces is given by

$$\theta = \theta_1+(\theta_2-\theta_1)\frac{x}{X},$$

where x is the distance measured from the front face at θ_1.

A complete solution for this case has been given in graphical form by Hinton [35, 1935], his chart being shown on Fig 2 The expression $t\frac{a}{d^2}$ being dimensionless, its value is unaltered provided self-consistent units are used. Ingersoll and Zobel [41, 1913] have shown that an allowance can be made for the condition, which is usually the case in practice, that the surfaces are in contact with a heat-transfer medium instead of having constant temperature as assumed, by adding a suitable thickness to the wall and choosing a slightly different temperature in place of θ_2 This point is referred to again later in the next section

Graphical Method.

E. Schmidt [83, 1924] has developed a method by which the heating and cooling of slabs such as furnace walls can be calculated graphically.

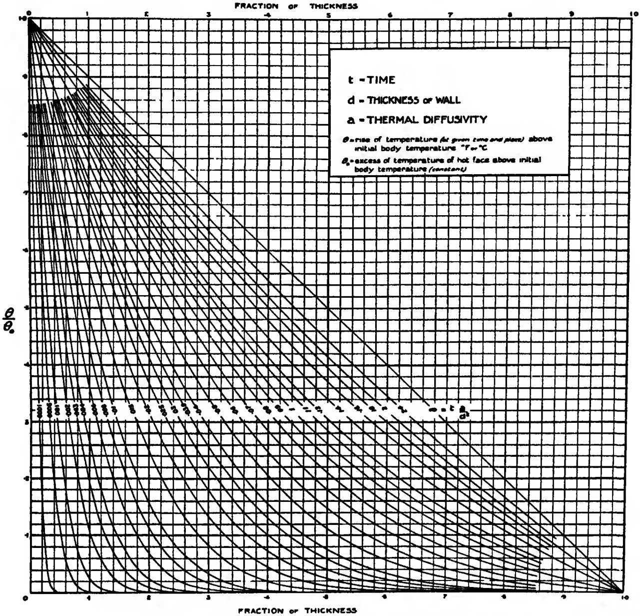


FIG 2 Temperature distribution in unsteady heat flow through walls (*Technical Data on Fuel*)

Fig 3 illustrates the principle of the method

Let Δx = a small but finite element of thickness of the wall,

Δt = a finite time interval,

$\theta_1, \theta_2, \theta_3,$ = temperatures on any convenient scale,

k = the conductivity,

ρ = the density,

c = the specific heat of the material in the wall

The broken solid line on Fig 3 represents the trace of temperature through the wall at a given time, t_n say

Then the heat transmitted in the time Δt, after t_n, through unit area of an element, e g the (2)–(3) element, is

$$(\theta_2-\theta_3)k\frac{\Delta t}{\Delta x},$$

and likewise, through the (3)–(4) element,

$$(\theta_3-\theta_4)k\frac{\Delta t}{\Delta x}$$

The difference in these two quantities is the heat stored during Δt in an element Δx in thickness, located symmetrically on both sides of plane (3) as shown by dot-dash verticals on Fig 3 This stored heat is given by

$$k\frac{\Delta t}{\Delta x}(\theta_2-2\theta_3+\theta_4)$$

This stored heat may also be expressed by the term $(\theta_3'-\theta_3)\rho c\Delta x$, where θ_3' and θ_3 are temperatures in plane (3) at the end and at the beginning of the time interval Δt respectively

Equating the two expressions

$$(\theta_3'-\theta_3)=\frac{k}{\rho c}\left(\frac{\Delta t}{\Delta x^2}\right)(\theta_2-2\theta_3+\theta_4). \qquad (21)$$

Since the time interval Δt and the element of thickness Δx are independent and finite quantities, their values can be selected according to the dictates of convenience

For the purpose of graphical solution it is simplest to choose Δt and Δx such that

$$\frac{2k}{\rho c}\left(\frac{\Delta t}{\Delta x^2}\right) = 1 \tag{22}$$

In this case equation (21) reduces to

$$(\theta_2' - \theta_2) = \tfrac{1}{2}(\theta_2 - 2\theta_3 + \theta_4) = \tfrac{1}{2}(\theta_2 + \theta_4) - \theta_3$$

A straight line, shown dotted in Fig 3, which connects the plotted points θ_2 and θ_4, intersects the vertical line (3) in a point which is seen to be the terminus of a vertical of length $\tfrac{1}{2}(\theta_2 + \theta_4)$ In other words, by choosing Δt and Δx to make equation (22) true, it is possible to determine by a simple graphical procedure the rises in temperature over the time interval Δt This is the fundamental feature of the method for arriving at graphical solutions of heat flow in the unsteady state

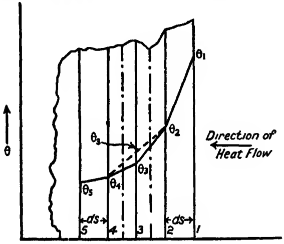


FIG 3

An example may be of assistance in visualizing the implications of equation (22) with reference to the graphical work In studying the heat transfer through a concrete wall of diffusivity 0 0056 c g s unit we should arrange matters so that

$$\frac{\Delta t}{\Delta x^2} \quad \frac{1}{2(0\ 0056)} = 89\ 5$$

If Δx were chosen as 1 cm , we would have ten sections in a 10-cm wall and the time interval would be 89 5 sec A better selection might be $\Delta x = 2$ cm , in which case Δt would be 358 sec

The heat transfer coefficient h_m between the surrounding medium and the surface of the slab or plate is usually assumed to be independent of the temperature-level and directly proportional to the difference between the temperature of the surface θ_s and the temperature of the surrounding medium θ_m At this stage in the discussion of the general subject of heat transfer it is not possible to discuss factors entering into the value of the coefficient h_m, but we can write

$$h_m(\theta_m - \theta_s) = k\frac{\Delta\theta}{\Delta x}, \tag{23}$$

where the left-hand member is the heat transmitted to unit area of the wall surface in unit time, and the right-hand side is the heat conducted through the unit surface in unit time

In terms of a graph the equation means that the tangent to the temperature curve at the surface of the wall goes through a point θ_m located k/h_m units from the surface of the wall

An equation similar to (23) holds for the heat transfer from the other surface of the wall to the medium which surrounds it The temperature of the second medium, which we may designate as θ_M, and the value of the heat transfer coefficient h_M will in general be different from θ_m and h_m Nevertheless, the tangent to the temperature curve at this surface of the wall will pass through a point having coordinates and spaced a distance of k/h_M

If θ_m or h_m or if θ_M or h_M change with the lapse of time during a period under consideration, an appropriate shift of the point or points through which the tangents to the temperature curve pass can readily be made An equivalent change to take care of altered conditions in the environment cannot be made in the course of an algebraic solution of unsteady state conduction This flexibility of solution constitutes one of the great advantages of the graphical method, particularly since many practical problems fall in this class

Radiation of Heat

As is well known, heat in the form of radiant energy can be transmitted across space devoid of matter

It is important to realize that radiation from flames and hot bodies consists of a wide range of wave-lengths conveying different fractions of the total radiant energy

When radiant energy falls on matter it may be absorbed, reflected, or transmitted Expressed in terms of wave-lengths visible to the eye, a body which absorbs the radiation is said to be black, one which reflects it is white, and one which transmits it is transparent Actual bodies have properties intermediate between these extremes

No plane surface is a perfect reflector, nor is there one which is a perfect absorber—even lamp-black reflects about 5% However, a perfect 'black body' is needed both as an idea for theoretical treatment and also in practice for the measurement of temperature, &c This ideal 'black body' can be realized as closely as required by constructing a hollow enclosure opaque to radiation pierced by a relatively small hole In this way any radiation entering the hole is absorbed by multiple reflection on the inside surface of the enclosure and only an infinitesimal fraction escapes from the hole again if this is small enough

The imaginary surface which may be substituted for this hole is termed a perfect black body since it absorbs 100% of all incident radiation Actual solid surfaces possess absorbing properties or 'absorbtivity' in varying degrees, which is expressed as a percentage of the absorption which a black body would show under the same conditions

It is a matter of common experience that hot bodies radiate heat, and that as the temperature is raised not only does the total energy radiated per unit area increase but the quality or 'colour' of the radiation also changes This latter effect is, of course, due to change in the relative amounts of energy in the wave-lengths short enough to affect the eye, and is the basis of the useful colour scale, due to Pouillet, for hot objects which can be approximately regarded as black bodies.

Pouillet's Colour Scale

	°F	°C
First visible red	977	525
Dull red	1,292	700
Turning to cherry	1,472	800
Cherry	1,652	900
Bright cherry	1,832	1,000
Dull orange	2,012	1,100
Bright orange	2,192	1,200
White	2,372	1,300
Brilliant white	2,552	1,400
Dazzling white	2,732	1,500
Sunlight	11,000	5,600

Kirchhoff first pointed out, in 1860, that there is a fixed relationship between the amount of radiant energy which any body will emit, and that which it will absorb The ratio of energy emitted from a surface to that emitted by a black body at the same temperature is defined as the emissivity of the surface The ratio of the radiant energy absorbed by the surface to that which a black body will absorb is termed the absorptivity of the surface In symbols Kirchhoff's law may be written

$$\frac{E_1}{E_B} = e, \qquad \frac{A_1}{A_B} = a, \qquad \frac{E_1}{E_B} = \frac{A_1}{A_B} \tag{24}$$

E_1 and E_B are the radiant energies of any or all wave-lengths emitted from the surface and by a black body respectively for the same area and the same temperature A_1 and A_B are the radiant energies of the same wave-length range absorbed by the surface and the black body respectively Since the emissivity e and the absorptivity a are identical in value, only one symbol, e, will be employed hereafter This coefficient e is less than 1 for all actual surfaces, which is, of course, only a restatement of the fact that the black body is both the most efficient radiator and absorber

The following general statements can be deduced directly from Kirchhoff's law (*a*) If a body absorbs radiant energy of any wave-length, it must also emit the same wave-lengths at the same temperature If a body is placed in a uniform temperature enclosure, the emission equals the absorption after temperature equilibrium is established (*b*) A body at a given temperature cannot emit more of a given kind of radiation than exists in the full radiation for that temperature

Most actual surfaces absorb and emit energy of different wave-lengths selectively In other words, the coefficient of emissivity or absorptivity varies with wave-length of the energy under consideration and also with the temperature of the surface, but whatever the amount of energy emitted in a given narrow band of wave-lengths, it is never greater than the radiant energy of the same wave-length range emitted by a black body at the same temperature The term 'grey body' is used to designate a surface which shows a constant value of e for all wave-lengths and for all temperatures

The coefficient of emissivity (or absorptivity), e, for actual surfaces depends not only on the wave-lengths but also to a certain extent on the angle at which radiation falls on or leaves the surface The normal emissivity for polished metals may be as much as 20% less than the hemispherical emissivity, but for non-metals or metals with a matt surface the two values are very nearly the same Since the latter types of surfaces are most frequently met under conditions of large-scale heat transfer, it is allowable in most engineering calculations to ignore the differences in emissivity as a function of direction.

Black-body Radiation.

The most important relationship from the standpoint of heat transmission is the Stefan-Boltzmann [92, 1879, 4, 1884] law which states that the total rate of heat radiation per unit area, E, of all wave-lengths passing from one black body to another black body is proportional to the difference of the fourth powers of their absolute temperatures, thus

$$E = \sigma(T_2^4 - T_1^4) \tag{25}$$

The constant σ has been experimentally determined and the accepted mean value is

$$5\ 72 \text{ erg (cm)}^{-2} \text{ sec}^{-1} (^\circ\text{K})^{-4},$$

or $$1\ 72 \times 10^{-10} \text{ B Th U (ft)}^{-2} \text{ hr}^{-1} (^\circ\text{F abs})^{-4}.$$

The formula expressing the energy of any specified wave-length λ emitted by a black body, derived theoretically by Planck [75, 1900], is

$$E_\lambda = \frac{C_1 \lambda^5}{(e^{C_2/\lambda T} - 1)} \tag{26}$$

The accepted values of the constants are as follows

$$C_1 = 3\ 703 \times 10^{-5} \text{ erg cm}^2 \text{ sec}^{-1},$$
$$C_2 = 1\ 433 \text{ cm},$$

where λ is expressed in centimetres and T in ° Kelvin, and E_λ is the total hemispherical radiation in erg cm^{-2} sec^{-1}

Fig 4 shows this relation plotted for 1,000° and 1,100° K The dotted line is a trace of the maxima of these curves

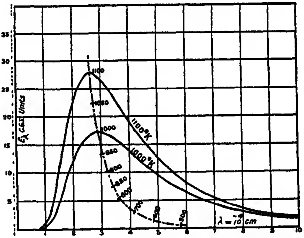


Fig 4

In the present connexion a more important relationship is that between the wave-length of maximum energy λ and the absolute temperature T deduced by Wien [96, 1896], known as Wien's displacement law

$$\lambda_{\max} = bT^{-1} \tag{27}$$

The mean experimental value of the constant b = 0 2885 for λ expressed in cm and T in ° Kelvin

This relationship is useful in showing the predominant wave-length at any temperature for which emissivity data is required in any particular case The following table gives this for a few selected temperatures

Table I

Temperature in °C	$\lambda_{\max}$ *in* μ *(10^{-4} cm)*
15	10
100	8
500	3 7
1,000	2 3
1,500	1 6
Sunlight	approx. 0 5

These relations help to explain Pouillet's colour scale mentioned above, but it will be seen from the above table that the description 'white' given to temperatures between 1,300° and 1,500° C must be attributed to the brightness of large areas at these temperatures rather than to their colour.

Solar Radiation.

The most fundamental single datum in radiation phenomena is, of course, the energy radiated by the sun It has been found by experiment that this is substantially constant The best value of the 'Solar Constant', defined as the radiation falling in unit time on unit area situated just outside the earth's atmosphere, appears to be 425 B Th U $(\text{ft})^{-2}$ hr^{-1} This corresponds to a sun temperature (surface) of 5,600° C if the distance is assumed to be 92,000,000 miles

The fraction of the solar energy which penetrates to the earth's surface is, of course, variable, depending on the weather and other local factors such as smoke and dust in the air Although on exceptional occasions it appears that the radiation may be as high as 300 B Th U $(\text{ft})^{-2}$ hr^{-1} for average clear weather at sea-level, a figure of 250 B Th U $(\text{ft})^{-2}$ hr^{-1} is perhaps more representative [46, 1928]

At night, when the effective radiation is only that small quantity received from the stars, it is calculated that a black surface outside the earth's atmosphere would fall to about −441° F The atmosphere protects the earth from the large radiation to outer space which would otherwise occur by reason of this low temperature Dines [15, 1921] and others have concluded that the equivalent sky temperatures are between −40° and −50° F on clear evenings after sundown The cooling of bodies at night under a clear sky due to radiation to outer space can be calculated approximately on this basis

The selective character of the absorption and emission characteristics of many surfaces is often of controlling importance in their behaviour W W Coblentz [9, 1905] performed some instructive experiments which have a direct bearing on the temperatures attained by surfaces, e g petroleum tankage, exposed to sunlight Coblentz exposed polished sheets of aluminium to the direct rays of the sun and found that they attained a temperature of 111° F Sheets covered with three coats of white lead or zinc oxide paints showed a temperature of 105° F when exposed simultaneously with the others Thus, while the painted surfaces were better absorbers of visible radiation, which includes the maximum radiation in sunlight, they were also better absorbers and hence emitters of energy in the region of 8 to 9μ, which is the region of maximum radiation for temperatures around 100° F, consequently the equilibrium temperature of the painted surfaces was lower than that of the bright aluminium, which does not radiate equally well in this relatively low-temperature region

The Effect of Absorbers in the Path of Radiation.

In discussing conduction the quantitative effect of conductors in parallel and in series was considered There is no exact analogy to parallel conductors in radiation phenomena. However, if two sources of radiation, shielded from one another, radiate to a single absorber, the effects are additive When the sources of radiation are not shielded from each other the treatment is more complicated and will be reserved for later discussion

A partial analogy to a *series* of conductors occurs when a *series* of absorbing surfaces are placed in the path of radiant energy. This is a simplification of an important practical condition met with in insulating against radiation losses, and will be briefly discussed here

Consider an evacuated enclosure bounded by two planes If, for simplicity, these two planes be assumed to have an emissivity value of 1, then the simple Stefan-Boltzmann equation (25) will give the radiation effect, i e

$$E = \sigma(T_2^4 - T_1^4).$$

If the evacuated space be divided into two parts by interposing absorbing planes (emissivity and absorptivity = 1), then the quantity of heat transmitted through each of the two spaces must be equal

$$E_1 = \sigma(T_2^4 - T_3^4) = \sigma(T_3^4 - T_1^4),$$

or

$$T_3^4 = \frac{T_2^4 + T_1^4}{2}$$

Substituting this value in the previous equation,

$$E_1 = \frac{\sigma}{2}(T_2^4 - T_1^4)$$

By similar reasoning it can be shown that in general for *n* planes

$$E_n = \frac{\sigma}{(n+1)}(T_2^4 - T_1^4)$$

Thus the interposition of absorbing planes in the path of radiation reduces radiant heat transfer by the fraction

$$\frac{1}{1 + \text{the number of planes}}$$

A similar argument applies if emissivity factors other than 1 are introduced, as, for instance, with polished metal surfaces which have low emissivities and reduce the radiation still further Direct application of this relationship is made in the interposition of polished metal cylinders in the silvered vacuum jackets of Dewar flasks or of laboratory fractioning columns, and in the use of aluminium foil as a form of insulation

The loss of heat through insulators by radiation has been mentioned When these materials are composite and contain many tiny air cells, the radiation is much less than otherwise due to the circumstance that, in effect, many walls are interposed in the path of radiant energy Notwithstanding the fact that large reduction of loss by radiation is secured in this way, it is by no means true that in all instances this source of loss is unimportant in comparison to losses by convection and by conduction

Calculation of Radiation.

It is now feasible to discuss the engineering applications of the Stefan-Boltzmann relationship (equation (25)) It will be recalled that the equation relates the exchange of radiant energy from one black body to another For practical conditions where this ideal situation does not apply, either the constant must be modified or (preferably) other factors must be introduced to take account of (*a*) the departure of the emissivity and absorptivity of the two bodies from that of black bodies, and (*b*) the geometrical disposition of the radiating surfaces which may or may not prevent the total emission from each of the two surfaces being intercepted by the other

Equation (25) can be modified for convenience in engineering application, first by the substitution of English units, and second by the introduction of the factors just mentioned, to give a basic equation for engineering calculations

$$q = 0.172A\left[\left(\frac{T_2}{100}\right)^4 - \left(\frac{T_1}{100}\right)^4\right]F_eF_s, \qquad (25a)$$

where q = net exchange of radiant energy (B Th U per hr),
A = area of one of the two surfaces (sq ft),
T_1 and T_2 = absolute temperature of the two surfaces (° F),
F_e = a factor of emissivities—in general a function of the emissivities e_1 and e_2 of the surfaces,
F_s = a factor of situation or geometrical arrangement of the surfaces with respect to each other

A few remarks are required before the application of equation (25*a*) to practical problems is illustrated

(*a*) Division of each temperature by 100 before raising to the fourth power is only an artifice to avoid very large figures within the bracket and a very small constant in the equation

(*b*) The emissivity of non-black bodies is influenced somewhat by direction, so that factors F_e and F_s are not strictly independent, but this effect is usually small and will be ignored

(*c*) The method of evaluation of factor F_e for specific cases will be indicated below The derivation assumes that the total emissivity and absorptivity of each surface are numerically equal In general the emissivity of a surface at T_1 is not identical with its absorptivity for radiation from a body at T_2 However, the degree of inequality is not large enough to introduce great error in most cases of engineering interest

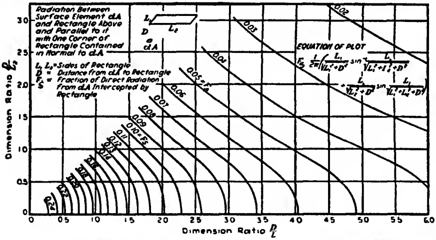


FIG 5 Radiation between surface element and rectangle above and parallel to it (*Chem Eng Handbook*)

(*d*) Since surface temperatures appear as fourth powers in the equation, it is obvious that they must be known with considerable accuracy if large errors in heat transfer calculations are to be avoided

The approximations inherent in equation (25*a*), its sensitivity to small differences in temperature, and other factors such as gas radiation, which will be discussed later, combine to make its application rather inaccurate However, the application of first principles is frequently of material assistance in interpreting furnace behaviour and in predicting the probable effect of modifications of design, even though complete and accurate calculations cannot be made

The evaluation of the factors F_e and F_s in equation (25*a*) has been studied in detail by Hottel [37, 1930] and the results have been presented in a convenient tabular form and in curves Table II and Figs 5, 6, 7 are taken directly from this work Many problems can be solved by the application of the data in the table with more or less obvious modifications thereof

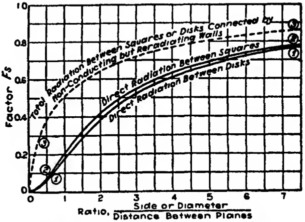


FIG 6 Radiation between equal squares or equal disks in parallel planes, directly apposed (*Chem Eng Handbook*)

Reference to the original article must be made for details as to the method of calculation of the factors F_e and F_s, but the general nature of the argument in evaluating factor F_e can be indicated for two cases Equality of emissivity, *e*, and absorptivity, *a*, is assumed, even though this holds strictly only when equilibrium temperature conditions exist

Case 1 Dimensions of one surface small compared with distance to the other If E = the emission of a black-body surface at the given temperature, surface ΔA_1 emits e_1E Surface A_2 absorbs e_2 of the emission from A_1 and reflects $1-e_2$ Because area ΔA_1 is small, a negligible fraction of this reflected radiant energy will be intercepted by it to undergo a second reflection to A_2 Hence $F_e = e_1$ without great error

Case 2 Infinite parallel planes Radiant energy leaving A_1 undergoes an infinite number of alternate partial absorptions at A_2, and, after alternate reflections, at A_1 The sum of the alternate members of the two infinite series, which give the absorption at each surface, is the expression

$$\frac{1}{\frac{1}{e_1}+\frac{1}{e_2}-1},$$

so that this is the factor to allow for the emission of two infinite parallel planes

Radiation from Non-luminous Gases.

Paschen [72, 1894] published the results of his investigation into the emission and absorption spectra of water vapour and carbon dioxide from which he concluded that

TABLE II

Radiation between Solids, Factors for use in Equation (25*a*)

	Surfaces between which radiation is being interchanged	*Area* A	*Area factor* F_a	*Emissivity factor* F_e
1	Infinite parallel planes	Either	1	$\dfrac{1}{\dfrac{1}{e_1}+\dfrac{1}{e_2}-1}$
2	Completely enclosed body, small compared with enclosing body (Let subscripts 1 refer to enclosed body)	A_1*	1	e_1
3	Completely enclosed body, large compared with enclosing body (Subscripts 1 refer to enclosed body)	A_1	1	$\dfrac{1}{\dfrac{1}{e_1}+\dfrac{1}{e_2}-1}$
4	Concentric spheres of infinite cylinders	A_1	1	$\dfrac{1}{\dfrac{1}{e_1}+\dfrac{A_1}{A_2}\left(\dfrac{1}{e_2}-1\right)}$ or $\dfrac{1}{\dfrac{1}{e_1}+\dfrac{1}{e_2}-1}$ †
5	Element dA and rectangular surface above and parallel to it, with one corner of rectangle contained in normal to dA	dA	Given in Fig 5	$e_1 e_2$
6	Two parallel circular disks of same diameter with centres on same normal to their planes	Either	Given in Fig 6, line 1	Exact treatment dependent on kind of reflection F_e lies between $e_1 e_2$ and $\dfrac{1}{\dfrac{1}{e_1}+\dfrac{1}{e_2}-1}$ for all cases
7	Two equal rectangles in parallel planes and directly opposite one another	Either	Approximate formula‡ $F_a = \sqrt{(F_s F_s')}$	
8	Two equal squares in parallel planes and directly opposite one another Special case of 7	Either	Given in Fig 6, line 2	
9	Two rectangles with common side, in perpendicular planes	Either	Given in Fig 7	Approximately $e_1 e_2$
10	Parallel squares or disks, connected by non-conducting but re-radiating black walls	Either	Given in Fig 6 line 3 (approximate)	Approximately $e_1 e_2$

* Enclosed body must contain no negative curvature if A_1 is used Replace any 'dimples' in surface by equivalent planes in evaluating A_1, and raise 'effective' emissivity from e_1 towards unity in proportion to depth of dimple

† First form results from assumption of completely diffuse reflection, second if reflection is completely specular True value will be very much nearer first than second

‡ F_s — Factor obtained for Case 8, for squares equivalent to smaller side of rectangle
F_s' — Factor obtained for Case 8, for squares equivalent to larger side of rectangle The approximation $F_a = \sqrt{(F_s F_s')}$ introduces less than 1 % error

(Taken by permission of *Mech Eng*)

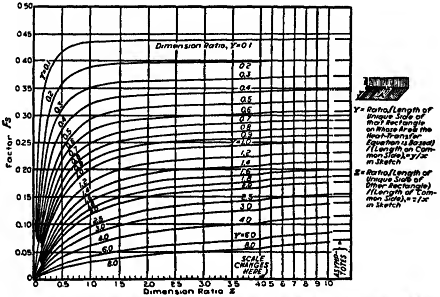


FIG 7 Radiation between adjacent rectangles in perpendicular planes (*Chem Eng Handbook*)

these two gases were entirely responsible for the radiation of heat from non-luminous gases

Since that time further investigations into the absorption of radiation by these gases have been made by H Schmidt [85, 1909], von Bahr [3, 1912], and Hettner [34, 1918], and Schack [81, 1924] calculated from this data the intensity of radiation to be expected from layers of water vapour and carbon dioxide of this radiation in the operation of furnaces

Some direct measurements of direct heat radiated from steam jets were made by E Schmidt [82, 1932] which disagreed with Schack's calculations by 200 or 300%, which shows that this type of calculation could only be regarded as very rough

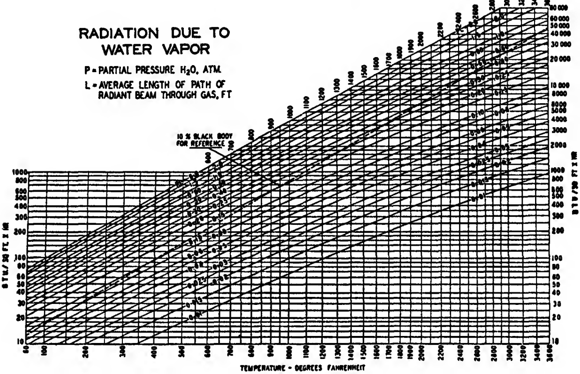


Fig 8

(*Trans Amer Inst Chem Eng* 31, 517 (1935))

The first complete set of measurements of total energy emission from both of these gases at high temperature was published in 1935 by Hottel and Mangelsdorf [39, 1935] The data are set out in the form of energy-emission curves convenient for engineering calculations Figs 8 and 9 are copies of the published data, which should completely supplant the tentative curves of the same general character which had been calculated in 1924 by Schack from infra-red absorption data

The results of a similar investigation which agree with those of Hottel were published by Fishenden [21, 1936], whose paper contains a useful review of the accuracy to be expected from such measurements

Two factors play a part in the net radiation of energy by a hot gas to a surface which enter uniquely because of the nature of gases These factors are the concentration of the constituent which is responsible for the radiation (in case a mixture of gas is involved), and second, the form or shape of the gas volume which 'sees' the surface In addition to these factors, the temperature of both the gas and the surface enter as well as the emissivity of the surface

The two unique factors for gas radiation are grouped together to form a product PL, where P is the partial pressure of the single constituent in a gas (mixture) which is radiating energy at the temperature in question, and L is a function of length which is specific for each of the several forms of gas volume which are ordinarily met in practice All the data refer to a total pressure of 1 atm and for partial pressures up to 1 atm Qualitatively it is known that the total pressure on a gas mixture as well as the partial pressure of the radiating or absorbing constituent influences the character of emission or absorption so that application of these data to superatmospheric pressure involves error, though the magnitude of the error is not yet known

In the literature on gas emission the term 'shape factor' has been employed, but Hottel [36, 1927] has shown that this factor can be taken equal to unity with a good approximation provided values of a characteristic dimension L are taken from the following table

TABLE III

Values of L which yield Shape Factors = 1 0 (approximately)

Shape of gas enclosures		*Value for L*
Sphere		2/3 × diameter
Cube		2/3 × side
Infinite cylinder		1 0 × diameter
Space between infinite parallel planes		1 8 × (distance apart)
Space in between tubes in an infinite bank with centres at apexes of equilateral triangles	Clearance = 2 0 (tube diameter)	3 8 × (clearance)
	Clearance = 1 0 (tube diameter)	2 8 × (clearance)
Rectangular parallelepiped 1 × 2 × 6 radiating to large face		1 3 × (smallest dimension)

In the case of non-luminous gas radiation, as in all others, the net exchange of energy between the source and receiver of the system may be considered to be the difference between energy output and input to either element For the system consisting of a hot gas and a surface it is convenient to consider the net exchange as the difference between the energy *emitted by* the gas at temperature t_1, and that *absorbed by* the gas from the energy beam emitted by the surface at t_s If the temperature of the gas and surface were identical, then the quality and the intensity of the energy absorbed by the gas from the surface radiation would equal that which it would emit at the same temperature, i e Kirchhoff's law would apply, and charts of energy emission *v* temperature such as Figs 8 and 9 would supply all necessary data Since the temperatures are not identical in any practical case, it is only possible at first to write a formal equation such as

$$\frac{q}{A} = e(E_{t_g\,PL} - A_{t_g t_s\,PL}), \qquad (28)$$

where, using the English system of units,

q = heat transferred from gas to surface (B Th U (hr)$^{-1}$),

A = area of surface (ft ^{2}),

e = absorptivity of surface for gas radiation, which may be taken as the normal emissivity of the surface at its temperature t_s (pure number),

$E_{t_g\,PL}$ = energy emitted by gas, temperature t_g, when conditions are denoted by partial pressure P and factor L from Table III (B Th U (ft)$^{-2}$ (hr)$^{-1}$),

$A_{t_g t_s\,PL}$ = energy absorbed by gas at temperature t_g and conditions denoted by PL, as above, when the surface emitting the energy is at temperature t_s (B Th U (ft)$^{-2}$ (hr)$^{-1}$)

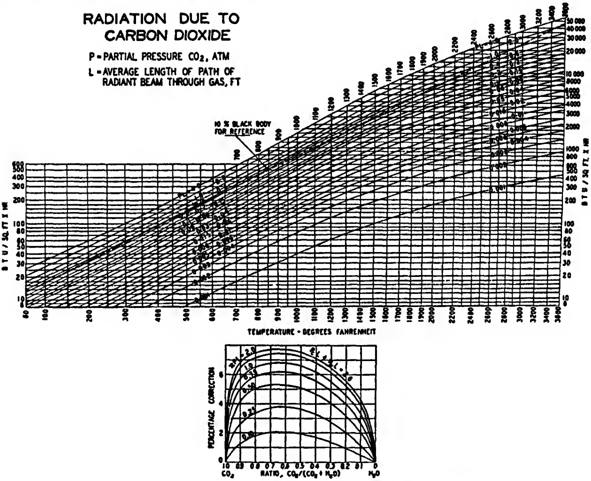


Fig 9

(*Trans Amer Inst Chem Eng* **31**, 517 (1935))

Fig 8 permits the evaluation of $E_{t_g\,PL}$ for cases in which carbon dioxide is present with other non-radiating gases, and Fig 9 can be used likewise for gases containing water vapour as the sole radiating constituent The procedure consists in the erection of a vertical from t_g as abscissa to the appropriate value of PL on the curves and reading the corresponding ordinate

The relation between the quantities $A_{t_g t_s\,PL}$ and $E_{t_s\,PL}$ which can be read from the figures depends on the change in effectiveness of individual molecules as absorbers and also on the change in their number in a given volume with temperature

Hottel's measurements of absorption show that the two factors substantially balance out in the case of water vapour, and therefore in this instance $A_{t_g t_s\,PL} = E_{t_s\,PL}$ The finding is different for carbon dioxide, however The measurements show that

$$A_{t_g t_s\,PL} = E_{t_s\,PL}\left(\frac{T_g}{T_s}\right)^{0.65},$$

in which $$P' = P\left(\frac{T_s}{T_g}\right)$$

P' is the element which takes account of the change in the number of molecules in any given shape as the temperature of the gas differs from that of the surface, whereas the absolute temperature ratio function $(T_g/T_s)^{0\ 65}$ reflects the change of inherent effectiveness of each molecule to absorb radiation

The practical interpretations of equation (28) for use in conjunction with Fig 8 or 9 are therefore as follows

For water vapour use Fig 9 and equation (29)

$$\frac{q}{A} = e(E_{t_g,PL} - E_{t_s,PI}) \tag{29}$$

For carbon dioxide use Fig 8 and equation (30)

$$\frac{q}{A} = e\left[E_{t_g,PL} - E_{t_s,P'L}\left(\frac{T_g}{T_s}\right)^{0\ 65}\right] \tag{30}$$

The method of evaluating the terms $E_{t_g,PL}$ in either equation has already been mentioned The term $E_{t_s,IP}$ in equation (29) is determined in the same way, using the temperature of the surface t_s as abscissa for Fig 9 To determine $E_{t_s,P'L}(T_g/T_s)^{0\ 65}$, first multiply the partial pressure of carbon dioxide in the gas under consideration by the quotient T_s/T_g to get P' and then calculate $P'L$ This quantity determines the intersection of the vertical at t_s against which the ordinate of energy is read on Fig 8 Multiply the value so obtained by $(T_g/T_s)^{0\ 65}$

When both carbon dioxide and water vapour are present together in a gas mixture, as is the case in the combustion of fuels containing both hydrogen and oxygen, the net radiation from the mixture is not equal to the sum of the radiations which would be calculated from equation (29) plus equation (30) This is due to the fact that in certain spectral regions, notably within the band of 2 65–2 85μ and also 13–17μ, both gases radiate energy Consequently each gas affects the behaviour of the other and a correction factor to reduce the sum of the separate energy radiations is necessary The insert at the upper left-hand corner of Fig. 9 supplies this factor K for use in the equation for gas mixtures containing both carbon dioxide and water vapour, namely,

$$\frac{q}{A} = e\left[\left(E_{t_g,PL} - E_{t_s,P'L}\left(\frac{T_g}{T_s}\right)^{0\ 65}\right)_{CO_2} + (E_{t_g,PL} - E_{t_s,PL})_{H_2O}\right]\left(1 - \frac{K}{100}\right) \tag{31}$$

It is necessary to emphasize that equations (29), (30), and (31) tend to give higher heat transfer by radiation than may be expected in actual practice when there is always a layer of gas near the surface which is cooler than the main body of gas In the experiments on which Figs 8 and 9 were based no surfaces were in the path of radiation, and hence the circumstances just mentioned did not arise A means for accurately allowing for this situation is unknown, but Hottel has suggested that the value of L may be taken as 90% of its geometrical value

Finally, it must be stated that while equations (29), (30), and (31) and Figs 8 and 9 should be mathematically applicable to the problem of calculating the heat transfer on *heating* a gas by a surface, as is the case of gas inside a conduit, actually the absorption data obtained was of a much lower order of accuracy than the emission data Consequently, when the terms expressing the absorption of energy of the gases are of controlling importance in obtaining q/A, the results are not likely to be of a high order of accuracy

Radiation from Gases other than Carbon Dioxide and Water Vapour.

In addition to nitrogen and oxygen, which appear to be almost completely transparent to heat radiations, in fuel-fired furnaces the flue gases contain hydrocarbons, sulphur dioxide, and carbon monoxide These are ordinarily present in too small concentrations to affect the total radiation significantly, but, in special instances, as in the case of the combustion of very high sulphur content fuel gas or oil, and particularly with elemental sulphur burners, the sulphur dioxide content may be high enough to warrant special consideration The radiation from sulphur dioxide has been calculated by S A Guerrieri [30] by Schack's method, using the data of Coblentz [9, 1905] These results are well enough represented by the data given for water vapour, Fig 9, multiplied by the factors shown in the following Table 1V The use of these factors appears justifiable between 500° and 2,000° F

TABLE IV

Radiation from Sulphur Dioxide

Value of PL	*Factor*
0 01	1 55
0 10	1 2
1 0	1 0
3 0	0 9

Radiation from Luminous Flames.

Haslam and Boyer [32, 1927] found that an acetylene flame when luminous radiated about 4 times as much heat as when non-luminous The radiant heat transfer from a flame could be calculated from equation (25*a*) if enough data were available 1f T_f and T_w are taken as the absolute temperature (° F) of flame and the surroundings which receive radiant energy respectively, and if e_f and e_w are the emissivities of the flame envelope and the surroundings, then we may rewrite equation (25*a*) thus

$$q = 0\ 172A\left[\left(\frac{T_f}{100}\right)^4 - \left(\frac{T_w}{100}\right)^4\right]e_f e_w, \tag{32}$$

where A is the area of the flame envelope The emissivities enter as a product for the same reason which applied to a small radiating solid surface enclosed within a large one Both T_f and e_f alter as a flame changes from the non-luminous condition, and the fundamental problem in estimating heat transmission is to evaluate both of these factors simultaneously, which is very difficult Probably the most nearly practical method of measuring these two factors under furnace conditions is that proposed by Hottel [38, 1932], using a special optical pyrometer fitted with two colour screens, and he gives working graphs for determining the value of e_f

Radiation from powdered coal flames has been investigated by Wohlenburg [97, 1926] and his collaborators and also by Haslam and Hottel [33, 1928] The latter have worked out an expression for e_f of the form $1-e^{-x}$, where x is a function of the flame thickness and temperature, the coal quality, particle diameter, &c The numerical results are given [8, 1934] for three types of coal investigated.

In the present state of knowledge the chief application of luminous flame calculations is in estimating the effect of minor changes in shape and arrangement of existing furnaces

Heat Transfer by Convection

It is usual to distinguish two types of convection, namely, 'natural' and 'forced' convection Natural convection occurs when parts of a fluid mass are set in motion by local differences in density, due to localized temperature differences Forced convection occurs when the motion of the fluid is due to outside agencies having no direct relation to the existence of temperature differences

The subject is very complicated due to the fact that it involves both the characteristics of fluid flow under conditions difficult to analyse, due, for instance, to viscosity changes, and also the mechanism of heat conduction to the moving fluid under different degrees of turbulence

Neither the highly mathematical nor the purely empirical method of approach to this problem has been very successful The middle course in which the phenomena are expressed in terms of dimensionless groups which have some fundamental basis has proved the most fruitful, even though empirical constants and correction terms may have to be added

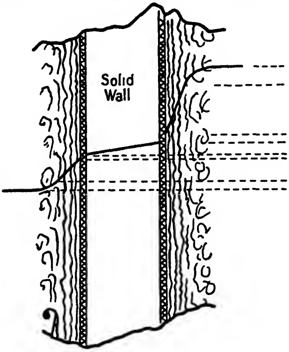


FIG 10

In most practical problems of heat transfer the heat has to be transmitted from one fluid to another through a solid partition, and it is very important to have a clear conception of the several distinct steps in this process The heat may be transferred from a gas to a gas or from liquid to liquid, or between gas and liquid or mixtures of both, but the general character of each case is the same

Fig 10 is a diagrammatic representation of the temperature gradients during steady heat transfer from one fluid to another through a solid partition The total temperature difference $\theta_1 - \theta_8$ is made up of separate steps which may be indicated as follows

$\theta_1 - \theta_2$ = combined convection and conduction in the main body of the hotter fluid, presumed to be in turbulent motion The eddies carry hot fluid from the centre up to the fluid film at the partition

$\theta_2 - \theta_3$ = conduction through the more or less stagnant film in contact with the solid partition Most of the heat transfer through the film is due to conduction, but as the thickness of this film is not well defined, convection must also be considered to play a part

$\theta_3 - \theta_4$ = conduction through the solid scale of oxide or other deposit which usually coats the walls of any commercial equipment

$\theta_4 - \theta_5$ = conduction through the metal of the solid partition

$\theta_5 - \theta_6$ = conduction through scale on cooler fluid side

$\theta_6 - \theta_7$ = conduction through cooler fluid film in streamline flow

$\theta_7 - \theta_8$ = convection and conduction into the main body of the cooler fluid

These various temperature steps represent series resistances to heat flow, and, as discussed under Conduction, we can apply equation (6), thus

$$q(R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7) = \sum_1^n \Delta\theta, \qquad (33)$$

where the subscripts for each local resistance correspond to that of the higher of the two temperatures which together form each of the temperature gradients

In the case of series resistances in pure conduction phenomena, each resistance was equivalent to a (length of path) divided by (area of path) × (conductivity) However, in those cases where convection strongly influences the heat transfer, there is no particular length to the path of heat flow, and it is therefore better to use a coefficient of heat transfer h in place of the conductivity divided by the length of path, since these have the same dimensions We may then write

$$q = \frac{\sum \Delta\theta}{\sum R}$$
$$= \frac{\theta_1 - \theta_8}{\frac{1}{h_1 A_1} + \frac{1}{h_2 A_2} + \frac{L_3}{k_3 A_3} + \frac{L_4}{k_4 A_4} + \frac{L_5}{k_5 A_5} + \frac{1}{h_6 A_6} + \frac{1}{h_7 A_7}} \qquad (34)$$

In many cases the areas of the various sections may be regarded as equal to A, say, when this equation may be written in terms of an overall heat-transfer coefficient U, thus

$$q = UA(\theta_1 - \theta_8) \qquad (35)$$

Mean Temperature Difference.

The remarks in the previous section refer, of course, to one element only of the whole heat-transfer surface, and the total heat transfer will be due to the sum of all such elements

The overall temperature difference $(\theta_1 - \theta_8)$ will, in general, vary from element to element, and so will the overall heat-transfer coefficient U, but the problem is greatly simplified if the overall heat-transfer coefficient U can be regarded as constant for all elements, and this is often a fair approximation to the truth

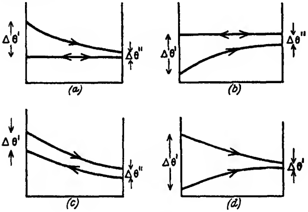
In such cases it is necessary to determine the true or effective mean temperature difference for all the elements of the surface to use in place of $(\theta_1 - \theta_8)$ in equation (35), and writing the total area for A we have the equation for the total rate of heat flow q

All continuous heat-transfer operations are characterized by constant temperature differences with respect to time, and variable differences with respect to surface extension in the exchanger Four of the most usual are indicated by Fig 11 *a*, *b*, *c*, and *d*

In all of these cases it can be shown that, if U is constant, and if the specific heats of the fluids (or fluid) does not alter greatly over the temperature range in question, then the proper temperature difference to use in equation (35) is that known as the 'Logarithmic Mean Temperature Difference', given by the expression

$$\frac{\Delta\theta'-\Delta\theta''}{\log_e\frac{\Delta\theta'}{\Delta\theta''}}, \qquad (36)$$

where $\Delta\theta'$ is the overall temperature difference at one end of the system and $\Delta\theta''$ the temperature difference at the other end



(a) (b) (c) (d)

FIG 11

In batch operations the temperature difference between the two fluids changes with time An illustration is furnished by a tank of liquid which is being heated from one temperature to another by means of a steam coil If the entire length of the inner wall of the coil is exposed to condensing steam at all times, a constant temperature is maintained in the heating fluid throughout the operation In this case, the log mean temperature difference given by equation (32) applies directly, where, however, θ' is the temperature difference at the start of the operation and θ'' is the temperature difference at the end of the operation

In the case of batch heating, if the tank contents are heated by the sensible heat of a fluid passing through the pipe coil, the temperature difference changes with the position in the coil as well as with time

In such cases the system must be subdivided and each section, for which these conditions may be considered constant, worked out separately and combined by trial and error Alternatively, a graphical method of calculation may be used [35, 1935, 24, 1928]

Heat exchangers of the multiple path type do not conform with any of the conditions indicated in Fig 11, and therefore the log mean temperature difference does not apply Nagle [64, 1933] has derived correction factors for exchangers having a single pass and two passes of fluid on the outside of the tubes, and two, four, and six passes within the tubes Bowman [5, 1936] has extended these results to include any number of shell passes, and several of these results are given in the form of curves to save calculation Nusselt [70, 1930] has derived similar factors for the exchange of heat between fluids flowing at right angles to each other Another condition often prevents the accurate application of the log. mean temperature difference, namely, when there is not enough mixing over the cross-sections to produce a reasonably uniform temperature The case of cooling a gas containing condensible vapour is discussed by Lewis [57, 1927] But such cases are obviously very difficult to deal with in any case This applies also, of course, to exchangers in which the path of one of the fluids is not adequately guided and may be very indefinite

Overall Heat-transfer Coefficient.

As indicated above, the overall heat-transfer coefficient is determined by a number of separate resistances, and while the overall coefficient is the figure finally required it is essential to treat the various resistances separately if proper regard is to be paid to the basic principles

The seven separate resistances of equation (33) can be grouped in the following way R_3, R_4, R_5 represent pure conduction through the solid partition and may be discussed together R_1 and R_2 together determine the coefficient of heat transfer from the solid surface through the stagnant film and into the body of the fluid itself It is usually impossible and indeed unnecessary to determine these two resistances separately They are only capable of being separated theoretically as in Taylor's [93] method of approach to the problem In a similar way R_6 and R_7 together determine the coefficient on the cooled side of the partition

In the following treatment the factors governing the coefficient of heat transfer on each side of the partition will be treated as single coefficients in the same way as the conduction through the composite solid partition

These three individual coefficients vary widely in practice, but a general indication of the overall coefficients in commercial equipment may be given in the following table to show the order of magnitude to be expected More extensive tables of overall coefficients to cover practical cases will be found in the various books of reference such as [2, 1926] and [60, 1932]

TABLE V

Overall Heat-transfer Coefficient

	B Th U per sq ft hr °F
Gas to gas	5
Gas to water	10
Kerosine to water	60
Water to water	200
Condensing (gasoline) vapour to water	60
Condensing steam to water	500
Condensing steam to oil	60
Condensing steam to boiling oil	100

Conduction through Partition.

The partition usually takes the form of the walls of metal tubes, and the conductivity of the metal wall itself is usually high enough for its exact value to have little effect on the overall coefficient The resistance of the metal itself can easily be calculated, but that of the scale and any other solid deposits on the surfaces is very much more uncertain This is, unfortunately, often quite an important factor in the overall coefficient

The metal of the tube wall by its resistance to corrosion may greatly reduce the quantity of solid scale The conductance of boiler scales has been measured by numerous workers, among whom are Kamp [44, 1931] and Zarnite [99, 1931]. The conditions in petroleum refinery equipment are so varied that generalized data is of little value. Cooling water containing much dissolved mineral matter or suspended silt may cause a reduction of the overall coefficient of 50% in the first 24 to 48 hours of service, but thereafter the decrease would usually be slowed up The deposit of solids is often greatly reduced if the temperature is kept below a definite value When solid deposits cannot be avoided in this way it is often more economical to install much larger heat-transfer surfaces than to treat the cooling water

Trouble due to deposits of tarry matter, wax, &c, on the oil side can often be avoided by careful operation or the use of generous heat-transfer surfaces, but in all cases the fouling of the surfaces and the need for cleaning should be considered when designing the equipment

Heat Transfer by Convection—Inside Pipes.

Much of the experimental information on heat transfer by convection has been collected from studies of heating of fluids flowing inside pipes It has long been recognized, ever since Reynolds first pointed it out [78, 1874], that there was a very close analogy between the transfer of heat from the body of a fluid in turbulent motion to the walls of a pipe, and the transfer of material in the form of eddies from the centre to the walls This transfer of material clearly involves a transfer of momentum since the fluid near the walls is moving at a lower velocity than at the centre, and this accounts for the pressure-drop due to flow in the pipe and its close connexion with the heat-transfer coefficient This connexion is referred to again later, but for the present it is important to note the fact that the higher the degree of turbulence, that is, the higher the Reynolds number, the more rapidly is the heat carried up to the walls and therefore the higher is the heat-transfer coefficient

There is, however, another factor to be considered, namely, the more or less stagnant film of fluid close to the wall of the tube There is no slip between the fluid and the solid wall, so that the velocity of the fluid immediately in contact with the wall is zero For a short distance from the wall the successive layers of fluid move along parallel with the wall in laminar or stream-line flow, dragged along by the moving body of fluid at the centre This constitutes the stagnant layer through which the heat has to be transmitted to the wall by conduction Clearly the resistance to heat flow through this film will decrease as its thickness decreases The higher the degree of turbulence in the main body the thinner does the stagnant film become, due to the increased violence of the eddies tearing off the top layers of the film For this reason also the heat-transfer coefficient increases with the degree of turbulence

There is actually no sharp division between the turbulent core and the stream-line film at the wall, and this probably accounts for the discrepancies in the application of those theories, such as that of G I Taylor [93], already referred to, which assume such a film It probably gives a more accurate picture to speak of the radial velocity of the eddies becoming smaller and smaller as the wall is approached According to this view, the film merges into the turbulent core, and at no particular distance from the wall can the motion of the film be said to be strictly laminar, but within a certain distance of the wall the heat transferred by these radial velocities (convection) is small compared with the heat transferred by conduction

Reynolds's theory on the correspondence between the transfer of the heat and the transfer of momentum outlined above leads to the conclusion that if the frictional resistance to flow varies as v^n, then the heat-transfer coefficient should vary as v^{n-1}, and this was verified by Stanton [91, 1895].

This has an important bearing on the effect of surface roughness on heat transfer In the same way that roughness increases the friction factor—particularly at high velocities—so does it increase the heat-transfer coefficient Reference to the friction-factor curves (Fig 1 in the article on The Laws of Fluid Flow in Pipelines, p 798) shows that increasing the surface roughness has the effect of increasing the exponent of v^n towards a limiting value of 2 0, and therefore the value of $(n-1)$ also increases towards 1 0 This shows that roughening a surface will cause the heat-transfer coefficient to depend to a greater extent on the velocity, and, conversely, that at low velocities there will be little change due to roughening the surface.

When the flow in the pipe is not turbulent the conditions are entirely different In stream-line flow under isothermal conditions the flow consists of concentric shells of fluid moving with increasing velocity as their radius decreases, the outermost in contact with the wall being stationary In this case heat would be simply conducted through the successive shells to or from the wall and the conditions would be similar to radial conduction in a solid rod However, in practical cases the heat flow causes changes of viscosity in the fluid which produce radial velocities due to a change from the parabolic distribution of velocity, and also the heat flow causes changes of density which produce a circulation of material due to 'natural' convection Thus the velocity profile is distorted even in the case of fluids which are flowing upwards within a vertical pipe, an arrangement which offers the least disturbance to the velocity distribution With horizontal pipes the distortion is still greater It might be expected, when the fluid flow is turbulent, that the non-isothermal velocity profile would not differ greatly from that of isothermal flow In 1916 Pannell [71, 1916–17] found that this was true when air flowed vertically upwards in turbulent motion in an electrically heated pipe, but for water being heated in a long horizontal pipe the experiments of Woolfenden [98] showed that the temperature profile was not symmetrical about the axis of the tube

Clearly the heat-transfer conditions in both turbulent and viscous flow are complicated, and equations developed from simple concepts are not likely to correspond very closely to experimental findings T B Drew [19, 1931] made a valuable contribution in 1931 to the general study of heat transfer from the standpoint of the mathematical attacks on forced convection problems His paper summarizes all the strictly mathematical approaches to these problems which have been made, and clearly sets forth the assumptions which have made solutions possible in certain cases

Turbulent Flow in Pipes. Most experimenters in the field of convection have found it possible to express their findings in terms of one or the other of several relationships based on dimensional analysis This usually takes the form of one or more dimensionless groups raised to some power chosen so as best to fit the experimental data In this way the exponents may have any value without affecting the dimensional correctness of the equation Furthermore, the equation will apply equally well to any set of units provided they are self-consistent The equation of this type which has perhaps had the greatest application is that developed for turbulent flow by Nusselt [66, 1909/10], consisting only of non-dimensional groups As at first proposed it did not include the ratio of the diameter to the length, but later this was added, to give the equation

$$\frac{hD}{k} = a\left(\frac{vD\rho}{\eta_a}\right)^n \left(\frac{\eta_a c_p}{k}\right)^m \left(\frac{D}{L}\right)^b. \qquad (37)$$

In this equation η_a is the viscosity at the mean temperature of the fluid. The first non-dimensional group on the right of this equation is, of course, the Reynolds number, and the second is called the Prandtl number. As it happens, the Prandtl number has a very nearly constant value, approximately 0.76, for any particular gas and does not vary greatly from one gas to another. This allows a considerable simplification to be made in many equations dealing with heat transfer in gases.

The concept of weight velocity, G, is helpful in studies on gases because both v and ρ are functions of temperature and pressure. Since $G = v\rho$, equation (37) may be written

$$\frac{hD}{k} = a\left(\frac{DG}{\eta_a}\right)^n\left(\frac{\eta_a c_p}{k}\right)^m\left(\frac{D}{L}\right)^b \tag{38}$$

The dimensionless group (hD/k) is sometimes called the Nusselt number.

Equation (37) (38) is dimensionally sound, and, in the course of years since it was first proposed, the experimental findings of many investigators taken together show that all of the factors involved probably do play some part in influencing h. At least one factor is not included which almost certainly has an effect on heat transfer, namely, a function for the roughness of the conduit surface. Since practically all of the experimental work on convection heat transfer has been done with smooth pipes, no basis for evaluating the roughness factor is at hand.

There is some question, however, whether the dimensionless ratio (D/L) should be included in the equation. Nusselt [67, 1917] assigned a value of 0.054 to the exponent b. Grober [29, 1921] used 0.05, but numerous workers since then have assumed a zero value. This reflects the lack of experimentation over a wide range of this quotient rather than definite findings that this ratio has no effect.

Dittus and Boelter [16, 1930] proposed two equations of the Nusselt type as the best representation of the data of numerous investigators of the heat transfer to gases and liquids. The two equations, expressed in terms of weight velocity, are

for heating

$$\frac{hD}{k} = 0.024\left(\frac{DG}{\eta_a}\right)^{0.8}\left(\frac{\eta_a c_p}{k}\right)^{0.4}, \tag{39}$$

for cooling

$$\frac{hD}{k} = 0.026\left(\frac{DG}{\eta_a}\right)^{0.8}\left(\frac{\eta_a c_p}{k}\right)^{0.3} \tag{40}$$

The basis for the selection of different exponents for the Prandtl number during heating and cooling were the findings of Morris and Whitman [63, 1928] with oils. This was almost the only data then available on liquids other than water where the Prandtl number exceeded 10. Sherwood and Petrie [87, 1932] found that their experiments on heating water, kerosine, acetone, benzene, and n-butyl alcohol could be very well correlated by equation (39).

Viscous Flow in Pipes. One of the first attempts to express the heat transfer to fluids in viscous flow in pipes was that of Graetz [25, 1885], who, assuming that the distribution of velocity is parabolic, derived an equation in terms of a complex function of the dimensionless group,

$$\frac{Wc_p}{kL} = \frac{\pi}{4}\left(\frac{DG}{\eta_a}\right)\left(\frac{\eta_a c_p}{k}\right)\left(\frac{D}{L}\right),$$

which is known as the Graetz number, in which W = mass rate of flow in mass per unit time.

Drew [19, 1931] has tabulated this function of the Graetz number, but Drew, Hogan, and McAdams [18, 1931] and Kirkbride and McCabe [49, 1931] have pointed out that the heat transfer in *heating* petroleum is higher than corresponds to Graetz's theory, and McAdams [60, 1932] has provisionally recommended the empirical equations given below for heating in pipes in stream-line flow [$(DG/\eta_a) < 2{,}100$]

$$\frac{h_{am}D}{k} = 6.2\left(\frac{Wc_p}{kL}\right)^{0.2} \quad \text{when} \quad \frac{Wc_p}{kL} > 30, \tag{41}$$

$$\frac{h_{am}D}{k} = \frac{2}{\pi}\left(\frac{Wc_p}{kL}\right) \quad \text{when} \quad \frac{Wc_p}{kL} < 30, \tag{42}$$

where h_{am} is the heat-transfer coefficient based on the arithmetic mean between pipe and inlet fluid temperature difference and pipe and outlet fluid temperature difference.

Kirkbride and McCabe [49, 1931] give the following empirical equation in terms of the dimensionless group $k/(Wc_p D)$ known as the Peclet number

$$\frac{hD}{k} = 3.65 + \frac{0.0065}{X} + \frac{0.513}{X^{0.484}},$$

where
$$X = \frac{L}{D}\left(\frac{k}{Gc_p D}\right)$$

Other workers [69, 1929, 12, 1922, 79, 1929, 52, 1927] have correlated their data in terms of the dimensionless group

$$\left(\frac{D^3\rho^2\beta g\,\Delta\theta}{\eta^2}\right),$$

known as the Grashof number, with some success. This group contains the coefficient of thermal expansion of the fluid which is the cause of natural convection inside the pipe, and this point will be referred to again later. Enough will have been said to show that use has been made of most of the more likely dimensionless groups in correlating the data on heat transfer by convection.

Convection in Fluids—Outside Pipes.

This section covers convection for single pipes and also for pipes arranged in regular banks as in tube banks of the convection section of combustion furnaces and in commercial tubular heat exchangers. The fluid may flow either parallel or at right angles to the pipe, but the latter arrangement is the more usual.

Natural convection can in most cases be ignored, as in practical conditions this has small effect compared with the heat transfer due to forced convection. An exception must be made in the case of single pipes represented by steam pipes or the external surfaces of refinery equipment where the heat loss from the surface is important.

Natural Convection. The heat loss from surfaces by natural convection depends on the changes in density of the fluid due to change of temperature causing convection currents to flow past the heated surface. This has been the subject of much investigation, starting with the experimental work of Dulong and Petit [20, 1817] and the theoretical work of Lorenz [58, 1881]. The experiments of Dulong and Petit and those of many of the more recent workers closely confirm the theoretical deduction of Lorenz that the heat loss from relatively large surfaces in still air is proportional to $\theta^{\frac{5}{4}}$, where θ is the temperature difference between the surface and the ambient air.

As would be expected, the heat loss is also very nearly proportional to the surface area, but there is a certain amount of uncertainty on this point. It can be shown from the principle of similarity that if the heat loss is proportional to $\theta^{\frac{5}{4}}$, then the heat loss per unit area instead of being constant should be proportional to $l^{-\frac{1}{4}}$, where l represents the height of the body, whereas if the heat loss is independent of *l* it should then be proportional to $\theta^{5/4}$. This last condition was found to occur with very large bodies by Griffiths and others at the National Physical Laboratory [28, 1921], who measured the heat loss from vertical surfaces of different heights and from different sections of a large vertical surface. The heat loss from a surface 8 ft. high was found to be greater at the bottom, rapidly decreasing to about half-value at about 18 in. from the bottom and then slowly rising to a value about 20% higher than the minimum at about 3 ft. from the bottom. The heat loss per unit area was found to be independent of the height when greater than about 3 ft., and for heights of about 8 ft. the loss was very nearly proportional to $\theta^{5/4}$.

In the case of horizontal cylindrical surfaces, such as pipes and wires, the heat loss per unit area is nearly independent of the diameter when this is greater than about 1 ft., but for smaller diameters such as fine wires the heat loss per unit area increases greatly, and for a wire 0.001 in. diameter it is over 50 times the value for a large pipe. The work of Langmuir [54, 1913] is of assistance in explaining this effect.

For practical purposes the heat loss per unit area from a large vertical surface by natural convection in still air may be taken to be equal to

$$\frac{q}{A} = 0.0000046\theta^{5/4}\ \text{g. cal. (cm.)}^{-2}\,(\text{sec.})^{-1}, \tag{43}$$

where θ is the temperature difference in degrees centigrade,

or $$\frac{q}{A} = 0.3\theta^{5/4}\ \text{B.Th.U. (ft.)}^{-2}\,\text{hr.}^{-1}, \tag{43a}$$

where θ is the temperature difference in degrees Fahrenheit.

For other types of surface the constant should be multiplied by the factors given in the following table, which shows the variation with pipe diameter mentioned above.

TABLE VI

Surface		*Multiplying factor*
Horizontal surface facing upwards and hotter than the air*		1.3
Horizontal surface facing downwards and hotter than the air*		0.65
Horizontal cylinders	$D = 0.1$ ft. (= 3.05 cm.)	1.5
	$D = 0.5$ ft. (= 15.2 cm.)	1.3
	$D = 1.0$ ft. (= 30.5 cm.)	1.25
Large bodies of irregular shape		1.0

* And vice versa.

The heat loss in air is also found to be proportional to $p^{0.45}$, where p is the absolute pressure. This and the other relationships given above will apply equally to other gases with a suitable change of constant.

Although the rate of heat loss is not proportional to the temperature difference, it is often useful to express the heat loss by natural convection in terms of a heat-transfer coefficient h for particular values of the temperature difference so as to bring it into line with other coefficients which do not vary with the temperature difference. According to equation (43*a*), it will be seen that h is proportional to $\theta^{1/4}$. For example, when

$\theta = 1°$ F., $h = 0.30$ B.Th.U. $(\text{ft.})^{-2}\,\text{hr.}^{-1}\,(°\text{F.})^{-1}$,
$\theta = 10°$ F., $h = 0.535$,, ,, ,,
$\theta = 200°$ F., $h = 1.12$,, ,, ,,

The last case corresponds to a bare steam pipe, and, as will be seen later, a coefficient of this magnitude is obtained with very low air velocities in forced convection (of the order of 1 ft. per sec.), and therefore the effects of natural convection are only of importance in air practically free from draughts.

Forced Convection. Heat transfer by forced convection on the outside of pipes when the flow is at right angles to the axis has been investigated by many workers both for single pipes and for banks of pipes in various formations, spacings, and numbers of rows. Although most of this work has been done with air as the fluid, there are so many variables that only a few can be dealt with here.

There have been several investigations of the type of flow at right angles to cylindrical surfaces which show the formation of eddies behind the cylinder. Drew and Ryan [17, 1931] investigated the variation of heat transfer round the circumference of a pipe and found that there was a minimum value at the sides approximately at 90° from the direction of air flow, the heat transfer at this point being only about one-third that at the front or back. These experiments were carried out at a Reynolds number of about 40,000, and the heat transferred from the leading half was about equal to that from the trailing half. There is reason to believe that high Reynolds numbers increase the relative heat transfer from the trailing half and vice versa. King [47, 1914] very thoroughly investigated the heat loss in air from wires of different diameters, and experimentally verified his theoretical formula which showed that the heat loss was proportional to $\{\sqrt{(vD)}+\text{constant}\}$. Hughes [40, 1916] obtained results on pipes with a wide range of diameters and air velocities. Davis [13, 1920] correlated these and other data on pipes and found them to agree very closely with the extrapolation of King's formula. However, when other fluids have to be considered it is better to express the results in terms of the Reynolds number. A Nusselt type of equation similar to (38) can be used, but not enough data is available to determine the coefficient of the ratio D/L. This type of equation has been used by many investigators, but frequently the Prandtl number $(\eta C_p/k)$ is also omitted because nearly all the data refers to air and this number is practically constant for all gases.

McAdams [59, 1932] has plotted the data of numerous investigators in terms of (hD/k_w) and the Reynolds number, finding that a good approximation formula is

$$\frac{hD}{k_w} = 0.45+0.33\left(\frac{DG}{\eta_w}\right)^{0.56}, \tag{44}$$

where k_w and η_w are the thermal conductivity and viscosity of the gas at the pipe-wall temperature, which is assumed to be that of the fluid film. This equation closely represents Hughes's data and also those of Reitschel and Reiher [77, 1926] for a single smooth pipe.

Heat transfer to or from banks of pipes has been thoroughly investigated in the case of air, notably by Reitschel and Reiher for a great variety of pipe arrangements, and by Griffiths and Awberry [27, 1933], who also measured the heat loss when the flow is parallel to the pipes and also when the air is cooled below its dew-point and below the freezing-point of water.

It might be expected that the heat transfer in banks of pipes would deviate largely from that for single pipes, and that eddies in the flow in succeeding rows would cause very large differences from the first row, but it is found that the coefficients are not so very different for all these cases.

The heat loss from the first row of pipes in a bank is smaller than from succeeding rows owing to the turbulence in the air set up in passing the first row. This increase is about 20% in the case of square packing where pipes in succeeding rows come immediately behind those in the front row With staggered packing this increase is about 20% for the second row and about 65% for the third and succeeding rows

The heat loss from the first row is approximately the same as for a single pipe as given by equation (43) Owing to the greater turbulence in the air at succeeding rows of a tube bank the exponent of the Reynolds number is higher than in equation (43) and is given as 0 69 by Reiher for staggered packing, which agrees closely with Griffiths and Awberry's equations

Reference must be made to the original papers for the exact equations covering the details of heat transfer in tube banks, but it may be mentioned that Reitschel and Reiher's equations are quoted in detail by Schack [80, 1933], and Griffiths and Awberry's work by Spiers [89, 1935]

The equations given for air will apply equally well to other gases, but they cannot be assumed to apply to liquids for which the Prandtl number may be very different Unfortunately there is very little data available for this case It is usually assumed that the exponent of the Prandtl number in the Nusselt type of equation (37) is approximately 0 36 as used in the equations (39) and (40) for heat transfer from fluids inside pipes, however, Colburn (see below) uses a value of 0 67 for this exponent, so that it is clearly a matter of some doubt

The equations for forced convection *inside* pipes are also usually applied directly to the case of flow parallel to the axis in a tube bank In this case the dimension D is interpreted as the diameter of a circular pipe having the same hydraulic mean radius as the space between the tubes

Fluid Friction and Heat Transfer.

Nusselt's [66, 1909–10] successful correlation of the dimensionless group (hD/k) with the Reynolds number apparently diverted attention for a number of years from the possibility that the use of the dimensionless group (h/cG) used by Stanton [90, 1914] might be even more advantageous. In an unusually comprehensive paper Colburn [10, 1933] showed that it is possible to obtain excellent correlations of almost all of the existing data on heat transfer of fluids inside of pipes, outside of pipes, and across flat plates, providing the Stanton number (h/cG) is multiplied by the ⅔ power of the Prandtl number $\left(\frac{\eta c}{k}\right)^{\frac{2}{3}}$ and referred to the Reynolds number Colburn defines a heat-transfer factor, j, as follows

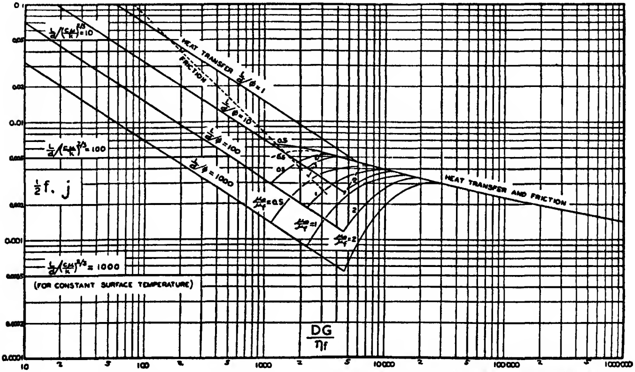


Fig 12 (Colburn, *Trans Amer Inst Chem Eng* 29 (1933))

$$j = \frac{(\theta_2-\theta_1)}{\Delta\theta_m} \times \frac{S}{A}\left(\frac{\eta c}{k}\right)^{\frac{2}{3}}, \tag{45}$$

where θ_1, θ_2 = fluid temperature at inlet and outlet respectively,
$\Delta\theta_m$ = mean temperature difference between fluid and wall,
S, A = cross sectional area and surface area of pipe respectively

He also writes the friction factor for fluid flow in a common form (see article on Law of Fluid Flow in Pipelines)

$$\frac{f}{2} = \frac{R}{\rho v^2} = \frac{P_g S}{\rho v^2 A}$$

Curves showing j and $f/2$ plotted against the Reynolds number are given for fluids flowing inside pipes on Fig 12; for fluids flowing across tubes on Fig 13, for various values of ds/dp, the ratio of the clearance to the tube diameter; and for fluids flowing along plane surfaces on Fig 14 All of these figures are reproduced directly from the original paper.

Fig 12 refers to flow and heat-transfer characteristics of fluids being heated or cooled inside pipes. The heat-transfer factor or 'j lines' are solid over the entire chart; the friction factor line $f/2$ is dotted in the region of viscous flow and in the critical region It will be noted that both $f/2$ and j can be represented by the same line in the region of definite turbulent flow, i e for all cases above

$$Re = 30{,}000$$

The friction factor in the viscous flow region follows Poiseuille's law, which can be written

$$\frac{f}{2} = 8 - \left(\frac{DG}{\eta}\right)$$

The film temperature is calculated by means of the formulae used by Keevil and McAdams [45, 1929] in correlating data on fluid friction, namely

For viscous flow

$$\theta_{vf} = \theta_a + \tfrac{1}{4}(\theta_w - \theta_a) \tag{47}$$

For turbulent flow

$$\theta_f = \theta_a + \tfrac{1}{2}(\theta_w - \theta_a), \tag{48}$$

where θ_a = average temperature of fluid,
θ_w = temperature of wall

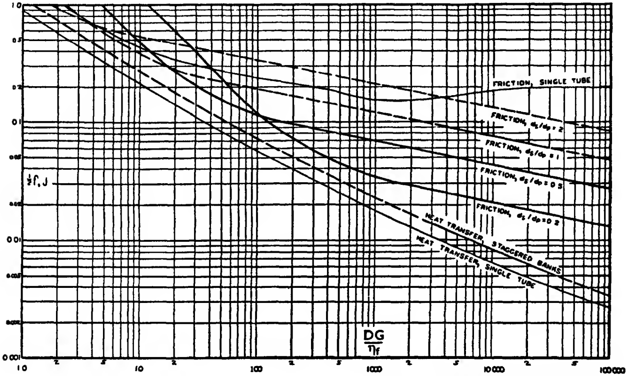


FIG 13 (Colburn, *Trans Amer Inst Chem Eng* **29** (1933))

However, the heat transfer j has not a unique value in this region and is a function of the quantity $\left(\frac{L}{D}\Big/\phi\right)$ also, where L is the heated or cooled length of the tube of inside diameter D, and ϕ is a function of the Grashof number, namely,

$$\phi = \left(\frac{\eta_a}{\eta_f}\right)[1 + 0\,015\ \mathrm{Gr}^{\frac{1}{3}}], \tag{46}$$

where Gr stands for Grashof number $D^3\rho^2\beta g\,\Delta\theta/\eta_f^2$

The Grashof number includes the coefficient of thermal expansion β which is an essential factor in the production of natural convection currents However, this number does not differ greatly between heating and cooling conditions The factor (η_a/η_f) is introduced to allow for the change in the velocity distribution over the cross-section due to changes in viscosity consequent on the heat flow The suffix a refers to the average temperature of the fluid, while the suffix f refers to the 'film temperature' as defined below

It is to be noted that Colburn makes use of the viscosity at the 'film temperature' in calculating the Reynolds number also, and the abscissae on Figs 12, 13, and 14 are therefore given in terms of (DG/η_f)

Colburn concludes that

For heating

viscous flow is maintained up to $Re_{vf} = 2{,}300\dfrac{\eta_a}{\eta_{vf}}$

For cooling

viscous flow is maintained up to $Re_f = 2{,}300\dfrac{\eta_a}{\eta_f}$

Since for heating $\dfrac{\eta_a}{\eta_{vf}} > 1$, while for cooling $\dfrac{\eta_a}{\eta_f} < 1$, the viscous flow-line will extend to values of Re_f larger than 2,300 for heating, and less than 2,300 for cooling Consequently the increase in the friction factor in the transition, or critical region, will be greater and more abrupt for heating than for cooling conditions

The dotted friction-factor line of Fig 12 is carried through the transition or critical region by three branches, for viscosity ratios η_a/η_f of 0 5, 1·0, and 2 0 While the agreement between data and prediction from these curves is in some cases far less satisfactory than could be desired, it is doubtful if any better correlations over extended ranges of the variables have been proposed

Procedure for the use of Fig 12 is as follows

1 Calculate mean fluid temperature, θ_a

2 Calculate average film temperatures, θ_f and θ_{wf}, from equations (47) and (48)

3 Determine η_a and η_f for these temperatures and calculate the corresponding Re_a and Re_f Also determine the ratio η_a/η_f

(a) If $Re_a > 2{,}300$, the flow is turbulent and $\Delta\theta_m$, equation (45) should be calculated as a log mean temperature

(b) If $Re_a < 2{,}300$, the flow is viscous, and $\Delta\theta_m$ should be calculated as an arithmetic mean

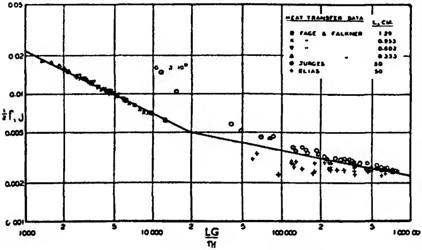


FIG 14 (Colburn, *Trans Amer Inst Chem Eng* 29 (1933))

In case 3 (a) the heat-transfer factor j and the friction factor f will read from Fig 12 either on the main turbulent line or on an interpolated η_a/η_f line in the transition region

In case 3 (b), to determine the friction factor $f/2$ the film temperature θ_{wf} should be used in determining Re_{wf} In order to determine the heat-transfer factor j, it will be necessary to calculate the value $\left(\frac{L}{D}\right)\Big/\phi$ Equation (46) serves to calculate ϕ In estimating L, it should be noted that this is the heated or cooled length before the character of flow is disturbed and abnormal mixing occurs This introduces an element of uncertainty where a number of tube lengths are in series and connected by stream-line fittings With connexions which offer obvious disturbance to flow, a single tube length should be employed for L With the value of $\left(\frac{L}{D}\right)\Big/\phi$ in hand, the appropriate j factor can be read from the chart by interpolation

It should be noted that for a constant surface temperature, in which case it is known that the exit fluid is practically at the pipe-wall temperature, the maximum values obtainable for the heat-transfer factor are those given by $(L/D)(\eta c/k)^{\frac{2}{3}}$ Horizontal lines for certain values of this factor are given on Fig 12

Heat transfer and friction for flow across tubes are correlated in a similar manner in Fig 13, for further details of which the original paper should be referred to, but it should be noted that all the work previously mentioned refers to circular pipes

In an interesting paper summarizing many data on the relationship of fluid friction to heat transfer, White [95, 1932] shows that an aerofoil section (Model R.A.F. 26) will transfer 80% more heat than a circular section when the heating surface and energy expenditure are the same It seems not improbable that future advances in design of heat-exchange equipment may include much more attention to the ratio of pressure drop and heat transfer than has been paid in the past

Smith [88, 1931] reported on friction factors and heat transfer obtained with a single oil of viscosity 2 62 centipoises at 210° C using an unusually complete equipment The heat-transfer data obtained on heating and cooling were correlated with Colburn's method in a moderately satisfactory fashion Friction factors were also calculated according to Colburn's recommendations, and excellent agreement was obtained in the region of turbulent flow, but in the viscous-flow region both heating and cooling friction factors were consistently about 25% higher than predicted values

Sieder and Tate [86, 1936] have criticized the use of the 'film temperature' as used by Colburn on the grounds that the formula for the film temperature is different for viscous and turbulent flow and because the Reynolds number has in any case first to be calculated for the mean fluid temperature in order to determine which type of flow exists Furthermore, the calculation of the tube-wall temperature by successive approximations involves successive recalculations of the abscissae (Reynolds number) as well as the ordinates

They have found that a satisfactory correlation of heating and cooling data for flow inside pipes can equally well be obtained, using the viscosity at the mean fluid temperature for calculating the Reynolds number, and the viscosity at the wall temperature in a much simpler expression than equation (46) to allow for the difference between heating and cooling with oils, namely

$$\phi = 1\ 86\left(\frac{\eta_a}{\eta_w}\right)^{0\ 14} \qquad (49)$$

The smaller exponent to the ratio of viscosities is smaller than that given by Colburn chiefly because $(\eta_w-\eta_a)$ is larger than $(\eta_f-\eta_a)$

Other differences from Colburn's method include the use of the Nusselt group (hD/k) instead of the Stanton number (h/cG), an exponent of $\frac{1}{3}$ instead of $\frac{2}{3}$ for the Prandtl number, and the introduction of the ratio $(L/D)^{\frac{1}{3}}$ The equation for viscous flow is then

$$\left(\frac{hD}{k}\right)\left(\frac{\eta c}{k}\right)^{-\frac{1}{3}}\left(\frac{L}{D}\right)^{\frac{1}{3}}\left(\frac{\eta_a}{\eta_w}\right)^{-0\ 14} = 1\ 86\left(\frac{DG}{\eta_a}\right)^{\frac{1}{3}}. \qquad (50)$$

For turbulent flow and the critical region the heat-transfer data are correlated by plotting

$$\left(\frac{hD}{k}\right)\left(\frac{\eta c}{k}\right)^{-\frac{1}{3}}\left(\frac{\eta_a}{\eta_w}\right)^{-0\ 14}$$

for various values of (L/D) against the Reynolds number (DG/η_a) as shown on Fig 15, from which it appears that viscous flow persists up to $Re = 2{,}100$ The correlation of friction data is made by plotting $(f\times\phi)$ against Re, as shown on Fig 16, where $(f\times\phi)$ is equal to

$$\text{Friction factor}\times 1\ 1\left(\frac{\eta_a}{\eta_w}\right)^{0\ 25}$$

when $\left(\frac{DG}{\eta_a}\right)$ is less than 2,100,

$$\text{Friction factor} \times 1.02\left(\frac{\eta_a}{\eta_w}\right)^{0.14}$$

when $\left(\frac{DG}{\eta_a}\right)$ is greater than 2,100.

In cases where the Grashof number is greater than 25,000, as, for instance, with water, it is suggested that better correlation would be obtained by using an expression more nearly like that of Colburn instead of equation (49), namely,

$$\phi = 1.5\left(\frac{\eta_a}{\eta_w}\right)^{0.14}(1+0.015\,\mathrm{Gr}^{\frac{1}{3}}),$$

but here the Grashof number is to be calculated, using the viscosity at the mean fluid temperature instead of at the film temperature.

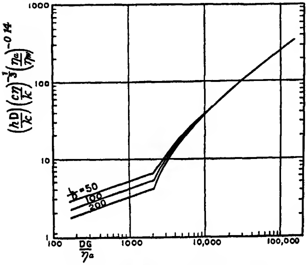


Fig. 15 (Sieder and Tate, *Ind. Eng. Chem.* **28** (1936))

Heat Transfer from Vapours Condensing at a Partition Wall

With few exceptions the experimental studies have been carried out on the condensation of pure saturated vapours, steam, of course, having received the most attention. Nusselt [67, 1913, 1917, 68, 1916] derived theoretical equations which furnish guides to the effects of the various physical properties of the vapour and liquid, the velocity of the vapour, and the shape and position of the condensing surface.

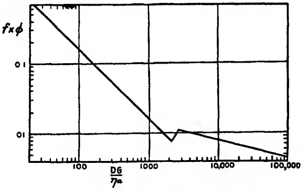


Fig. 16 (Sieder and Tate, *Ind. Eng. Chem.* **28** (1936))

Nusselt dealt with five different cases, always assuming that there is a thin film of liquid on the condensing surface, that the temperature gradient through the film is a straight line, and that the film moves in viscous flow. The cases which received attention were:

(1) Pure saturated vapour without appreciable velocity condensing on a plane surface at an angle with the horizontal.
(2) Conditions as above, except that vapour has appreciable velocity.
(3) Vapour condensing at horizontal tube, conditions otherwise as under case (1).
(4) Superheated vapour condensing on any surface.
(5) Impure vapour condensing on any surface.

Nusselt's equations for case (3) only will be given, namely, for the condensation of a pure saturated vapour on a single horizontal tube. In this case, due to the divided flow of condensate round the outer surface of the tube, the value of the heat-transfer coefficient shown by an elementary area of the tube varies, depending on its position as defined by the angle w which is made by a radial line through the element and the horizontal. The equation for the local coefficient is as follows:

$$\frac{hD}{k} = 0.693\left(\frac{D^3\rho^2 g \sin w}{w\eta}\right)^{\frac{1}{4}}, \tag{51}$$

where w is the mass condensed per unit time per unit perimeter. The average coefficient for the entire perimeter is given by

$$\frac{hD}{k} = 0.725\left(\frac{D^3\rho^2 g\lambda}{k\eta\,\Delta\theta}\right)^{\frac{1}{4}}, \tag{52}$$

where λ is the latent heat of condensation.

These equations are dimensionally correct and apply therefore to any set of self-consistent units. Equation (51) indicates that the upper half of a single condenser tube accounts for about 60% of the total condensate. If a number of tubes are placed one above the other, the drip on to the top surface of the lower tubes decreases the coefficient until, with much flooding, upper and lower halves of the tubes transfer approximately the same total quantity of heat.

For the case for a bank of horizontal tubes Merkel [61, 1927] proposes to include in equation (52) in the denominator under the exponent $\frac{1}{4}$ the number of tubes in a vertical row, thus allowing for the reduced coefficient in the lower rows due to flooding.

Nusselt derived an equation similar to (52) for vertical and inclined condenser tubes but with the right-hand side multiplied by $\left(\frac{D\sin\psi}{L}\right)^{\frac{1}{4}}$, where ψ is the angle of the axis to the horizontal. However, it has been found that for a vertical surface this equation gives coefficients far too low.

Kirkbride [48, 1929] has studied the condensation of pure hydrocarbons and mixtures on horizontal tubes, and he recommends the use of Merkel's modification to equation (52) including in the term λ, the sensible heat of the vapour cooled through the range $\Delta\theta$ as well as the latent heat. He also discusses the effect of two immiscible liquids condensing simultaneously and the effect of the presence of permanent gas.

There appear to be no experimental results on the local coefficients for the condensation of mixtures, and it is to be expected that these would be extremely complicated.

For further discussion of the Nusselt equations the reader is referred to text-books such as that by McAdams [59, 1932] or to the review of the derivation of Nusselt's equations, and a summary of the experimental data bearing on the subject by Monrad and Badger [62, 1930], who also investigated the effects of vapour velocity, superheat, and non-condensable gases

It should, however, be mentioned that there is an entirely different form of condensation in which droplets form and grow in size without fusing with other droplets to any great extent Schmidt, Schurig, and Sellschopp [84, 1930] appear to have published the first quantitive study of heat transfer under this condition They found that the coefficient for this dropwise condensation might rise to as high as 7 or 8 times the coefficient for the normal type of condensation under similar wall-temperature conditions A tendency to dropwise condensation may be expected to arise whenever the conditions are such that the condensate does not wet the solid condensing surface, but it is not at present possible to predict its occurrence Owing to the great variety of circumstances in which condensation occurs in practice, most of the useful data is given in the form of coefficients to suit specific conditions and of limited range of application only

Heat Transfer to Boiling Liquids.

When a liquid is heated by a submerged surface it vaporizes at its own surface continuously and smoothly up to the boiling-point, when vapour bubbles suddenly begin to form at the heating surface There they grow in size until they are finally detached from the surface by a combination of the forces of buoyancy and of natural (or forced) convection of liquid past the anchored bubble If a liquid, such as water, is freed of dissolved air, bubbles form with almost explosive violence and the liquid is said to boil with bumping Moreover, if water is carefully freed of air, and is suspended as a large globule in an oil of the same density, its temperature can be raised to 130–140° C without boiling at atmospheric pressure

These facts can be explained in terms of the surface tension of the liquid in contact with its vapour and the forces of cohesion between liquid molecules and the solid surface and between the liquid molecules themselves

It is not difficult to show that the pressure within a bubble exceeds the pressure on the outside by the quantity $2\gamma/r$, where γ is the surface tension between vapour and liquid, and r is the radius of the bubble When the bubble is very small this excess pressure is very large and may raise the boiling-point very considerably For instance, in the case of water, a radius of 0 001 mm corresponds with an excess pressure of about 2 atm and a boiling-point of about 135° C

Water and most other liquids usually contain gases in solution, and the heated surface is usually somewhat rough, enabling minute bubbles of gas to cling and form the nucleus from which bubbles of vapour can grow The solid surface may also have a comparatively small force of attraction for the liquid molecules or localized areas which behave in this way, thus enabling bubbles to be formed without much excess pressure

Jakob and Fritz [43, 1931] have studied the influence of interfacial tension on bubble formation, and some of the essential differences in the nature of bubble attachment to a solid surface can be observed in two beakers, one of water and one of benzol, both adjusted over a source of heat so that boiling is very slow This is depicted diagrammatically in Fig 17 When the interfacial tension between boiling liquid and solid is high there is a tendency for the bubble of vapour to be pinched off by the reluctant retreat of liquid from the solid surface With small tendency of the hot liquid to wet the surface, a condition such as Fig 17 (*b* or *c*) prevails Jakob and Fritz observed water boiling over a clean copper plate, later covering it with a thin layer of oil to observe that the steam bubbles were then much larger when other conditions were approximately the same

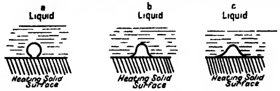


FIG 17

If a liquid wets the surface, high coefficients are usually obtained with clean surfaces, but a small amount of oxide or other scale may decrease the coefficient very markedly When a bubble has been formed at a spot on the heated surface, that spot tends to become overheated owing to the relatively poor heat transfer from solid to vapour As the liquid flows back over this spot the conditions are obviously favourable for the formation of another bubble at the same place, and this effect is often observed McAdams [59, 1932] reports that when liquids are boiling with high transfer rates the heated surfaces sometimes show as much as 10° F variation from point to point as measured by thermocouples

Another very important factor influencing the heat-transfer coefficient with boiling liquids is the velocity of the liquid past the heated surface due to mechanical agitation of convection due to the boiling itself

More than 50 years ago Lord Kelvin seems to have been conversant with the fact that artificial stirring of a boiling liquid would increase the rate of evaporation, and more than 30 years ago Austin [1, 1903] demonstrated the fact by measurements with an evaporator With rapid agitation of water past a vertical heating plate, Austin obtained a substantially constant value of *h* of about 1,400 B Th U per sq ft (° F) hr irrespective of the temperature difference between the plate and the water boiling at atmospheric pressure Without agitation other than natural convection reinforced by the stirring effect due to bubbles, a rate of some 500 B Th U per sq ft (° F) hr was noted with a temperature difference of about 2° F, whereas double this rate was secured when a temperature difference of about 15° F prevailed These data are cited not so much for their intrinsic value as for the side-light which they throw on a peculiar difficulty in formulating coefficients of heat transfer when convection, augmented by the rise of bubbles, is the sole cause of fluid velocity past the surface In this case the transfer coefficient is not only a function of the average temperature difference between surface and liquid, but is also conditioned by the geometrical arrangement of the confining walls and the relative depth of fluid. Arrangements which facilitate circulation will give better coefficients than others where circulation is impeded

The absolute depth of liquid over the heating surface is also important, especially when the hydrostatic head is a large fraction of the total pressure at the surface in question. When liquids are boiled under greatly reduced ambient pressure the rate of change of total pressure with depth of liquid is relatively large, rising bubbles expand rapidly, and entirely different stirring effects result from those which would otherwise occur

There have been very few studies in which the same apparatus has been used for the evaporation of a number of different liquids under conditions which made it possible to determine the heat-transfer coefficient on the boiling liquid side Among the most recent is that of Cryder and Gilliland [11, 1932], who found that their results could be represented well with the empirical equation $h = a\Delta\theta^{2.4}$, having failed to find a satisfactory dimensionless relationship Fig 18 is taken directly from their paper

Fig 19 has been taken directly from McAdams' summary of experimental work on this subject and includes the data of Austin [1, 1903], curve 1, and Jakob and Fritz [43, 1931], curve 5, and Linden and Montillon [56, 1930], curve 6, together with the results of certain thesis investigations not published in journals (curves 2, 3, 4)

As will be apparent from Figs 18 and 19, these heat-transfer coefficients are often so high that the corresponding resistance is not the controlling factor in the overall heat-transfer coefficient, more particularly in the case of water and the more volatile liquids boiling at clean surfaces With petroleum liquids of high boiling-point the coefficient is not very high and may lead to the formation of tars or 'coke', which may reduce the heat-transfer coefficient so that it constitutes the major resistance An aggravated example of this is in the horizontal shell type of coking stills Another factor which differentiates the evaporation of petroleum liquids from that of many others is the formation of metal sulphide corrosion scales which usually offer very large resistance to heat flow

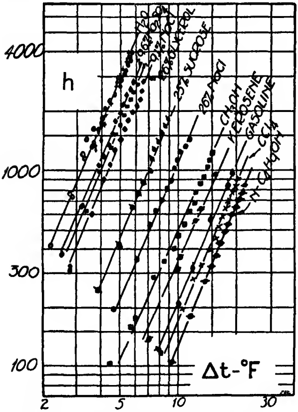


FIG 18 Heat transmission coefficients for various boiling liquids (Cryder and Gilliland, *Ind Eng Chem* **24** (1932))

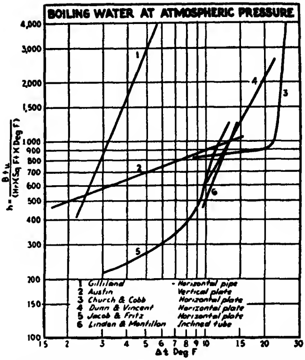


FIG 19 Summary of individual coefficients of heat transfer from metal to boiling water (McAdams, *Heat Transmission* (McGraw-Hill Book Co))

As in the case of surface condensation, most of the useful data refers to specific conditions, and the coefficient can only be applied in similar circumstances

LIST OF SYMBOLS

Symbol		Units	
		ft lb hr °F	*c g s °C*
A	area, surface area	ft²	cm²
a	diffusivity $= \left(\frac{k}{\rho c}\right)$	ft² per hr	cm² per sec
C	conductance	B Th U per hr °F	g -cal per sec °C
c	specific heat	B Th U per lb °F	g -cal per g °C
c_p	specific heat at constant pressure		
c_v	specific heat at constant volume		
D	diameter	ft	cm
E	radiant heat flow per unit area	B Th U per hr ft²	g -cal per sec cm²
e	emissivity		
F_e F_s	radiation factors		
f	friction factor $= 2\left(\frac{R}{\rho v^2}\right)$		
G	mass velocity	lb per hr ft²	g per sec cm²
g	acceleration due to gravity	ft per hr²	cm per sec²
h	film heat transfer coefficient	B Th U per hr ft² °F	g -cal per sec cm² °C
j	heat transfer factor		
k	thermal conductivity	B Th U per hr ft °F	g -cal per sec cm °C
L	length	ft	cm.
P	partial pressure (atm)		
Q	quantity of heat	B Th U	g -cal
q	rate of heat flow	B Th U per hr	g -cal per sec

Symbol		*Units*	
		ft lb hr °F	*c g s °C*
R	thermal resistance	°F hr per B Th U	°C sec per g-cal
	also surface friction	poundals per ft^2	dynes per cm^2
r	radius	ft	cm
S	shape factor	ft	cm
	also sectional area	ft^2	cm^2
T	absolute temperature	° Rankine	° Kelvin
	also periodic time	hr	sec
t	time	hr	sec
U	overall heat transfer coefficient	B Th U per hr ft^2 °F	g-cal per sec cm^2 °C
v	linear velocity (u is also used)	ft per hr	cm per sec
W	weight flow rate	lb per hr	g per sec
X x y z	lengths	ft	cm
β	coefficient of thermal expansion	°F^{-1}	°C^{-1}
η	absolute viscosity (μ is also used)	lb per hr ft	g per sec cm
θ	temperature, temperature difference	°F	°C
λ	latent heat	B Th U per lb	g-cal per g
	also wave-length		
ρ	density	lb per ft^3	g per cm^3

Dimensionless Groups

Reynolds number (Re) $= \left(\frac{vD\rho}{\eta}\right) = \left(\frac{DG}{\eta}\right)$

Nusselt number $= \left(\frac{hD}{k}\right)$

Prandtl number $= \left(\frac{\eta c}{k}\right)$

Peclet number $= \left(\frac{DcG}{k}\right)$

Graetz number $= \left(\frac{Wc}{kL}\right)$

Grashof number $= \left(\frac{D^3\rho^2\beta\,\Delta\theta\,g}{v^2}\right)$

Stanton number $= \left(\frac{h}{cG}\right)$

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THE THERMAL CONDUCTIVITY OF SOLIDS

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The following tables have been taken from the published literature, a selection of the materials given in the various references having been made to cover those more usually occurring in petroleum technology.

TABLE I

*Thermal Conductivity of Metals and Alloys**

k = B.Th.U. per (hr.) (sq. ft.) (°F. per ft.)
For c.g.s. units multiply by 0.004134 (reciprocal 241.9)

Temp., °F	32	212	392	572	752	932	1,112
„ °C	0	100	200	300	400	500	600
Aluminium	117	119	124	133	144	155	
Brass (70–30)	56	60	63	66	67		
Cast iron	29	28					
Cast iron, high silica	30						
Copper (pure)	224	218	215	212	210	207	204
Ferralloy (86% Fe, 14% Al)	7.3						
Invar (65% Fe, 35% Ni)	6.2						
Lead,	20	20	19	18			
Nickel	36	34	33	32			
Nickel-chrome (80% Ni, 20% Cr)	9.2						
Silver	242	238					
Steel (mild)		26	26	25	23	22	21
Stainless steel (18% Cr, 8% Ni)	8.0						
Tin	36	34	33				
Wrought iron (Swedish)		32	30	28	26	23	
Zinc	65	64	62	59	54		

* From *International Critical Tables* and other sources

TABLE II

*Thermal Conductivities of Some Building and Insulating Materials**

Apparent density ρ = lb. per cu. ft. at room temperature
Conductivity k = B.Th.U. per (hr.) (sq. ft.) (°F. per ft.)
For c.g.s. units multiply by 0.00413 (reciprocal 241.9)

Material	ρ	t, °C	k
Asbestos boards	120	20	0.43
Asbestos slate	112	0	0.087
„ „	112	60	0.114
Asbestos	29.3	−200	0.048
„	29.3	0	0.090
„	43.5	−200	0.090
„	43.5	0	0.135
„	36	0	0.087
„	36	50	0.098
„	36	100	0.111
„	36	150	0.117
„	36	200	0.120
„	36	250	0.122
„	36	300	0.124
„	36	400	0.129
Bricks			
Alumina (92–99% Al_2O_3 by wt.), fused		927	2.0
Alumina (82% Al_2O_3 by wt.)	170	500	1.29
Building brickwork		20	0.4
Fire-clay brick (burnt 1,450° C.)		500	0.74
Kaolin insulating brick	27	500	0.15
Silicon carbide brick recrystallized	129	600	10.7
Zirconia (64% ZrO_2 by wt.)	236	500	1.45
„ „ „	236	800	1.23
„	236	1,100	1.10
Calcium carbonate (natural)	162	30	1.3
„ white marble			1.7
chalk	96		0.4
Cardboard, corrugated			0.037
Celluloid	87.3	30	0.12
Coke, petroleum		100	3.4
„ „		500	2.9
Coke, powdered		0–100	0.11
Cotton wool	5	30	0.024
Cork board	10	30	0.25
Cork (regranulated)	8.1	30	0.026
„ (ground)	9.4	30	0.025
Diatomaceous earth powder			
Molded pipe covering	26.0	204	0.051
„ „	26.0	871	0.088
4 vol. calcined earth and 1 vol. cement poured and fired	61.8	204	0.16
Felt, wool	20.6	30	0.03
Fibre insulating board	14.8	21	0.028
Glass			0.2–0.73
„ boro-silicate type	139	30–75	0.63
„ window glass			0.3–0.61
„ soda glass			0.3–0.44
Gypsum (moulded and dry)	78	20	0.25
Hair felt (perpendicular to fibres)	17	30	0.021
Kapok	0.88	30	0.020
Leather, sole	62.4		0.092
Limestone (15.3 vol. % H_2O)	103	24	0.54
Magnesium oxide (compressed)	49.9	20	0.32
Magnesia (powdered)	49.7	47	0.35
„ (light carbonate)	19	21	0.04
Mineral wool	9.4	30	0.0225
„ „	19.7	30	0.024
Paper			0.075
Petroleum coke		100	3.4
„ „		500	2.9
Porcelain			0.6
Rubber hard)	74.8	0	0.092
„ (Para)		21	0.109
„ (soft)		21	0.075–0.092
Sand (dry)	94.6	20	0.19
Sandstone	140	40	1.06
Sawdust	12	21	0.03
Slag, blast furnace		24–127	0.064
Slag wool	12	30	0.022
Snow	34.7		0.27
Sulphur (monoclinic)		100	0.09–0.097
„ (rhombic)		21	0.16
Wall board, insulating type	14.8	21	0.028
„ stiff paste board	43	30	0.04
Wood (across grain)			
Oak	51.5		0.12
Maple	44.7	50	0.11
Pine, white	34.0	15	0.087
Teak	40.0	15	0.10
White fir	28.1	60	0.062
Wood (parallel to grain)			
Pine	34.4	21	0.20
Wool, animal	6.9	30	0.021

* From Marks, *Mechanical Engineers' Handbook*, *International Critical Tables*, and other sources

TABLE III

*Thermal Conductivities of Insulating Materials at High Temperatures**

k = B.Th.U. per (hr.) (sq. ft.) (°F. per ft.)
For c.g.s. units multiply by 0.004134 (reciprocal 241.9)

Material	*For temperatures °F. up to*	*Mean temperature, °F.* 100	200	300	400	500	600	800	1,000	1,500	2,000
Laminated asbestos felt (approx. 40 laminations per in.)	700	0.033	0.037	0.040	0.044	0.048					
Laminated asbestos felt (approx. 20 laminations per in.)	500	0.045	0.050	0.055	0.060	0.065					
Corrugated asbestos (4 plies per in.)	300	0.050	0.058	0.069							
85% magnesia	600	0.039	0.041	0.043	0.046						
Diatomaceous earth, asbestos, and bonding material	1,600	0.045	0.047	0.049	0.050	0.053	0.055	0.060	0.065		
Diatomaceous earth brick	1,600	0.054	0.056	0.058	0.060	0.063	0.065	0.069	0.073		
,, ,,	2,000	0.127	0.130	0.133	0.137	0.140	0.143	0.150	0.158	0.176	
,, ,,	2,500	0.128	0.131	0.135	0.139	0.143	0.148	0.155	0.163	0.183	0.203
Diatomaceous earth powder (density 18 lb. per cu. ft.)		0.039	0.042	0.044	0.048	0.051	0.054	0.061	0.068		
Rock wool		0.030	0.034	0.039	0.044	0.050	0.057				

Asbestos cement 1.2, 85% magnesia cement, 0.6, asbestos and rock-wool cement, 0.9 approx.

* From Marks, *Mechanical Engineers' Handbook*.

TABLE IV

*Thermal Conductivities of Insulating Materials at Low Temperatures (Grober)**

k = B.Th.U. per (hr.) (sq. ft.) (° F. per ft.)
For c.g.s. units multiply by 0.004134 (reciprocal 241.9)

Material	*Density, lb. per cu. ft.*	*Temperatures, ° F.* 32	−50	100	−200	−300
Asbestos	44.0	0.1350	0.1320	0.1300	0.1250	0.1000
	29.0	0.0894	0.0860	0.0820	0.0720	0.0545
Cotton	5.0	0.0325	0.0302	0.0276	0.0235	0.0198
Silk	6.3	0.0290	0.0256	0.0235	0.0196	0.0155

* From Marks, *Mechanical Engineers' Handbook*.

TABLE V

*Diffusivities of Metals and Other Substances**

(Diffusivity = $k/\rho c$)
Values given in c.g.s. units, cm.^{2} per sec.

Metals	*Diffusivity, cm.^{2} per sec.*	*Other substances*	*Diffusivity, cm.^{2} per sec.*
Aluminium	0.826	Air	0.179
Brass	0.339	Asbestos wool	0.0035
Copper	1.133	Brick, fire	0.0074
Ferralloy (86% Fe,		,, building	0.0050
14% Al)	0.036	Coal	0.002
Gold	1.182	Concrete	0.0056
Invar (65% Fe, 35%		Cork (granulated)	0.002–0.003
Ni)	0.027	Glass	0.0057
Iron (wrought)	0.173	Granite	0.0155
,, (cast)	0.121	Ice	0.0112
Lead	0.237	Kieselguhr	0.002–0.003
Magnesium	0.883	Limestone	0.0092
Mercury	0.033	Slag wool	0.002–0.003
Nickel	0.152	Snow (fresh dry)	0.0033
Nickel chrome		Soil,† sand	0.0036–0.0087
(80% Ni, 20% Cr)	0.044	,, gravel	0.0074–0.0125
Platinum	0.243	,, clay	0.0057–0.0136
Silver	1.737	Water	0.00143
Stainless steel			
(18% Cr, 8% Ni)	0.036		
Tin	0.407		
Zinc	0.402		

* From *Dictionary of Applied Physics*, vol. i, p. 466.
† See article on 'Heat Loss from Buried Pipes'.

THE EMISSIVITY OF SURFACES

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THE emissivity of a surface may vary greatly with the wave-length of the radiation. It is, therefore, necessary to define the quality of the radiation, and this is usually done on a temperature basis by assuming the radiation is that of a black body at that temperature.

The emissivity of a surface also may depend greatly on the exact condition of the surface, i.e. whether clean or dirty, polished or matt, and whether there is a film of oxide or not. These variations are particularly marked when the emissivity is low, and in such cases the values found in the tables of this property must usually be regarded as approximate only unless the conditions are very accurately reproducible.

The following tables of emissivities have been compiled from data given by the *International Critical Tables*, Schmidt (Stahl und Eisen (1927) 133, 6), Fishenden and Saunders, *Calculation of Heat Transmission*. More extensive tables are given in the last reference and also in the *Chemical Engineers' Handbook* which may be consulted for further details and for variations in surface conditions.

The values shown in italics have been estimated from similar materials or from neighbouring temperatures and in some cases are not very reliable.

TABLE I

Emissivities of Constructional and Miscellaneous Materials

Material	Normal emissivity	
	50° C	*Solar*
Bricks		
Fletton light portion	*(0·90)*	0·45
,, dark ,,	*(0·90)*	0·65
Red	0·94	0·70–0·77
Purple-blue	*(0·95)*	0·80–0·90
Concrete	*(0·85)*	0·65
Roofing materials		
Red tiles		0·65–0·70
Dark-purple tiles	*(0·95)*	0·82
Slates	0·70–0·80	0·80–0·90
Galvanized iron whitewashed	*(0·95)*	0·21
Asbestos cement, white	*(0·93)*	0·60
Galvanized iron, new	0·23	0·66
,, ,, dirty	*(0·75)*	0·90
Asphalt	*(0·95)*	0·90
Bituminous felt	*(0·95)*	0·90
Paints, pigments, &c		
Paints and varnishes*	0·85–0·95	
Oil in thick layers > 0·2 mm	0·83	
Aluminium paint	0·45–0·65	*(0·40–0·50)*
Bronze paint	0·55–0·70	
Lampblack, acetylene soot	0·95–0·97	0·99
Pigments, red Fe_2O_3	0·96	0·74
,, light yellow $PbCrO_4$	0·95	0·30
,, white ZnO	0·97	0·18
,, white $PbCo_3$	0·89	0·12
Miscellaneous materials		
White paper	0·95	0·28
Glazed porcelain	0·90–0·95	
White marble (polished)	0·90	0·47
Glass	0·90	
Gravel and soil	0·90–1·0	
Plaster of Paris	0·915	
Quartz (rough fused)	0·94	

* Varnish and paints (cellulose or linseed oil base and any pigment), when applied to any surface, give it an emissivity of 0·9–1·0 for radiation corresponding to low temperatures.

TABLE II

Emissivities of Metals

	Radiation	*Normal emissivity*					
	Temp	*50° C*	*200° C*	*400° C*	*600° C*	*800° C*	*Solar*
Metal	*Wave-length*	*9·1μ*	*6·2μ*	*4·4μ*	*3·4μ*	*2·7μ*	*0·60μ*
Aluminium, polished		0·04	0·06	0·07	0·08	0·12	(0·25)
,, oxidized		0·11	0·11	0·15	0·19		
Brass, polished		0·05					
,, dull plate			0·22				
,, oxidized		0·61					
Chromium, polished		0·08	0·15	0·21	0·26	0·31	0·49
Copper, polished		0·04	0·05	0·11	0·18	0·17	(0·40)
,, rough, oxidized		0·74					
Gold, polished		0·02	0·02	0·03	0·03	0·03	
Iron and steel							
Cast iron, clean		0·21–0·44	0·21–0·44				
Steel, rusted		0·65	0·66	0·71	0·78	(0·75)	0·74
,, oxidized		0·79–0·85	0·79–0·85	0·79–0·85	0·79–0·85		
,, calorized		0·50	0·52	0·55	0·57		
Lead, oxidized		0·28	0·63				
Nickel, polished		0·05–0·07	0·08–0·10				
Silver, polished		0·01	0·02	0·03	0·03	0·03	0·11
Tinned iron sheet, bright		0·05					
Zinc, polished		0·02	0·03	0·04		0·06	0·46
,, galvanized iron sheet (fairly bright)		0·25	0·63				

THE CALCULATION OF THE FLOW OF LIQUIDS AND GASES ACROSS BANKS OF PIPES AND IN PACKED COLUMNS

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Flow across Banks of Pipes

THE flow of fluids outside of pipes as, for example, in the shell side of tubular heat exchangers is obviously dependent not only on the arrangement of the tubes, but primarily on the direction of flow relative to the tube bank. If the flow is essentially parallel to the axis of the tubes, the flow can be calculated—for the turbulent flow region—by substituting the usual concept of hydraulic radius or equivalent diameter in the appropriate friction formula. It should be noted that these do not apply in the viscous region with any degree of exactitude.

In the flow across tubes, however, where the area of the flow passage varies from point to point, a simple calculation based on friction alone is not admissible, since there will be losses due to eddies following the expansion and contraction of the fluid stream.

For flow of liquids and gases directly normal to banks of *staggered* tubes, a correlation by Chilton and Genereaux [4, 1933] leads to the following recommended equations

$$\Delta P = \frac{4 f \rho u_{\max}^2 N_R}{2g} \tag{1}$$

For viscous flow, where

$$\frac{D_e u_{\max} \rho}{\mu_f} < 150,$$

$$f = 26.5\left(\frac{D_e u_{\max} \rho}{\mu_f}\right)^{-1} \tag{2}$$

For turbulent flow, where

$$\frac{D_e u_{\max} \rho}{\mu_f} > 50,$$

$$f = 0.75\left(\frac{D_e u_{\max} \rho}{\mu_f}\right)^{-0.2} \tag{3}$$

For tubes on rectangular spacing, *not staggered*, in the turbulent flow region,

$$f = 0.33\left(\frac{D_e u_{\max} \rho}{\mu_f}\right)^{-0.2} \tag{4}$$

The experimental data on which this correlation was based covered a range of tube pitch/tube diameter ratios varying from 1.25 to 7.35, and of free cross-section in first row to free passage between successive rows varying from 0.40 to 0.795. Most of the data, however, were for tubes arranged on equilateral triangular spacing.

These equations may not be strictly applicable to flow of fluids in baffled heat exchangers, not only on account of the fact that the flow is not uniformly at right angles to the tube bank, but also on account of leakage through the clearances between the baffle and the tubes and shell. If applied, the equations will yield conservative results (i.e. high values of pressure loss for a given velocity). Bowman [2, 1934, 1936] obtained approximate agreement with the above equations for pressure drop in a line of similar exchangers, with circular tube bundles baffled to give cross flow, by the introduction of a 'leakage factor' in the calculation of the mass velocity, as follows

$$u_{\max} = \frac{Q}{L_B[D_S - D_P(1.27 N_t)^{0.5}] + 1.25 K D_P N_t}. \tag{5}$$

When the other dimensions are measured in feet, K had the value 0.01.

Short [9, 1934, 1936] has reported extensive tests on models of baffled exchangers, but no generally satisfactory method of calculation has been given.

To allow for the pressure drop around the baffles, if these are segmental, it is suggested that the following simple equation, again yielding conservative results, be employed

$$\Delta P = N_B\left(\frac{Q}{S_B}\right)^2 \frac{\rho}{g} \tag{6}$$

It will be seen that this equation is equivalent to treating the opening as an orifice with a discharge coefficient of 0.71.

Nomenclature for Equations relating to Calculation of Flow across Banks of Pipes.

Any self-consistent set of units may be used, those involving pounds, feet, and seconds are given as examples.

D_o = clearance between adjacent tubes in row, ft.
D_e = equivalent diameter of fluid passage = 4 (free volume/total tube surface), ft.
D_P = diameter of tube, ft.
D_S = diameter of shell, ft.
f = friction factor, defined by equation (1), dimensionless.
g = acceleration due to gravity, 32.2 ft./(sec.)^2
K = clearance factor in equation (5), ft.
L_B = distance between baffles, ft.
N_B = number of baffles.
N_t = number of tubes in exchanger.
N_R = number of rows passed across by fluid.
ΔP = pressure loss, lb. per sq. ft.
Q = volume of fluid, cu. ft. per sec.
S_B = area of free opening in baffle segment, sq. ft.
$u_{\max}$ = velocity through minimum free cross-section of fluid passage (in an average row), ft. per sec.
μ_f = viscosity of fluid, lb./(sec.) (ft.) (equal to 0.00672 × viscosity in centipoises), measured, unless the flow is isothermal, at a temperature obtained by adding (algebraically) one-fourth of the logarithmic mean temperature difference to the arithmetic average fluid temperature.
ρ = density of fluid, lb. per cu. ft.

Flow in Packed Columns

The flow of fluids through beds of packed granular solids or other porous structures cannot be treated directly by the methods used for flow through pipes or other uniform channels, since the diameter factor, or ratio of frictional surface to flow section, cannot be easily evaluated, and since the direction as well as the cross-section of the flow channels changes continuously.

For the flow of a single fluid, gas or liquid, through beds of uniform granular solid particles, a correlation by Chilton and Colburn [3, 1931] of available data leads to the following equations

$$\Delta P = \frac{2f'A_f L\rho u_0^2}{g D_P} \tag{7}$$

For viscous flow,

$$\frac{D_P u_0 \rho}{\mu} < 40$$

$$f' = 850\left(\frac{D_P u_0 \rho}{\mu}\right)^{-1} \tag{8}$$

For turbulent flow,

$$\frac{D_P u_0 \rho}{\mu} > 40$$

$$f' = 38\left(\frac{D_P u_0 \rho}{\mu}\right)^{-0.15} \tag{9}$$

Data in approximate agreement with these equations have been reported by Fancher and Lewis [5, 1933] and Uchida and Fujita [10, 1934], though the latter's results (on spheres) can be more accurately expressed by the equation

$$f' = 5+500\left(\frac{D_P u_0 \rho}{\mu}\right)^{-0.8} \tag{10}$$

over the range of 3 to 1,000 for $(D_P u_0 \rho/\mu)$

An allowance for the variation from the normal void content of a bed of irregular solid particles is offered by Meyer and Work [8, 1936–7], in terms of a modified diameter, D_V defined by the equation

$$D_V = D_P \frac{V_a}{V_n}$$

For the friction factor defined by the equation

$$\Delta P = \frac{2f'' A f L \rho u_0^2}{g D_V} \tag{11}$$

The friction factor, for viscous flow,

$$\frac{D_V u_0 \rho}{\mu} < 10$$

was found to be

$$f'' = 23.6(67-V_a)\left(\frac{D_V u_0 \rho}{\mu}\right)^{-1} \tag{12}$$

The use of these last equations requires, however, a knowledge of the normal void content (loosest packing) and of the actual voids, as well as the average particle diameter These authors were not able to find a satisfactory correlation for data on blends of different sizes

Values of the wall-effect factor, A_f, as computed by Furnas [6, 1929] are given in Fig 1

If the packing is not solid, but formed of hollow shapes, such as Raschig and Lessing rings, Berl saddles, &c, the pressure drop will obviously be less than that computed for solid particles of the same nominal size Factors by which to multiply the calculated pressure drop to take account of this effect for hollow packings are given by Chilton and Colburn [3, 1931] More extensive data considered by White [11, 1935] may be represented by the following expressions

For Raschig or Lessing rings

$$F_h = 0.24(D_P'')^{-0.5} \tag{13}$$

For Berl saddles

$$F_h = 0.13(D_P'')^{-0.5} \tag{14}$$

These equations cover a range of (nominal) packing sizes, D_P'', from about 0.25 in to 2 in They are to be used without allowance for wall-effect factor, referred to above, but apply only when D_P/D_t is less than $\frac{1}{8}$, they appear, however, to apply for viscous as well as turbulent flow

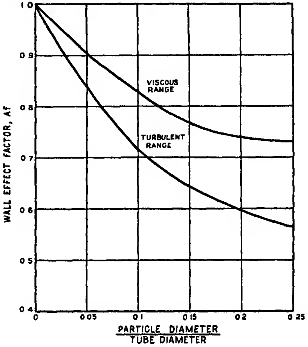

Fig 1

The discussion up to this point covers only flow of gases through dry packing, or flow of single liquid phases through beds of packed solids The effect of wetting a packing is to increase the pressure loss for a given flow of gas, since the effective free volume is thereby diminished, and more and more of the smaller passages are closed off as the liquid flow increases

Factors to allow for wetting of solid packings (wet and drained) and for the effect of circulating liquid (water, at a rate of 0.18 lb /(sec) (sq ft tower cross-section)) are tentatively proposed by Chilton and Colburn [3, 1931] based on data of Zeisberg [12, 1919], as follows

Packing wet and drained

$$F_w = 1+0.22(D_P'')^{-1} \tag{15}$$

Water circulating at rate of 0.18 lb /(sec) (sq ft)

$$F_l = 1+0.47(D_P'')^{-1} \tag{16}$$

The pressure drop calculated for dry packing is to be multiplied by the factors given

The effect of water circulation on pressure loss in gas flow through hollow packings is also considered by White [11, 1935], who gives curves showing the relative increase due to liquor circulation over that for the wet and drained Raschig rings, see Fig 2 The increase of pressure drop for the wet and drained packing over the dry, while not summarized by White, was well enough represented by equation (15), above

Not enough data are available to generalize as to the effect of other liquids than water It seems likely, however, that more viscous liquids would cause a greater increase in pressure drop, at the same rate of flow

Data on the pressure loss in the larger sized fabricated stoneware packing shapes often used in large-scale absorption towers are given by Zeisberg [12, 1919] In the original, values of pressure loss in inches of water per ft of packing are given for an air velocity of 1 ft per min

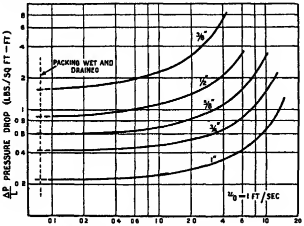

FIG 2

These have been converted to dimensionless friction factors for use in equation (7), assuming that the air density was 0.075 lb per cu ft, and taking for D_P (in ft) the values shown These values may be assumed constant without serious error for the usual range of velocities employed with these packings, that is, a few feet per second See Table below

but in general referring to the maximum velocity for satisfactory operation Data on the flooding and loading velocities for air flow (at a density of 0.075 lb per cu ft) in towers packed with Raschig rings with water circulation

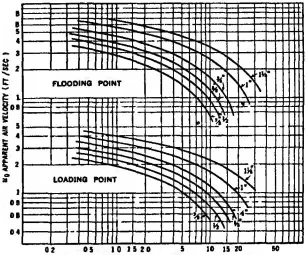

FIG 3

have been collected by White [11, 1935] White's curves are reproduced in Fig 3 The loading-point is taken by White as the gas velocity at which the logarithmic pressure-drop velocity curve first deviates from a slope of approximately 2.0 The flooding-point is the velocity at which the same curve turns abruptly almost vertically upward

For other gases, it is suggested that values of (ρu_0^2) will be the same at the flooding-point as for air ($\rho = 0.075$)

Loading velocities for a few other packings, at a single water rate, are given by Baker, Chilton, and Vernon [1, 1935] Conservative practice dictates operation at not over 50 or 75% of the loading velocity

Friction Factors for Fabricated Packings, for Use with Equation (7)

Data of Zeisberg [12 1919]

		Dumped			Stacked			Packed		
Packing	D_P, *ft*	*Dry*	*Wet*	*Circ*	*Dry*	*Wet*	*Circ*	*Dry*	*Wet*	*Circ*
4×3 in smooth diaphragm rings	0.33	6.1	6.7	7.6	3.0	4.1	4.6		3.9	4.1
3×3 in corrugated diaphragm rings	0.25	4.7	5.1	5.8	2.8	3.8	5.4	2.4	2.6	2.6
3×3 in corrugated spiral rings	0.25	4.1	4.9	5.8	4.9	4.9	5.6			
6×6 in corrugated spiral rings	0.50				6.9	8.6	9.1	4.1	5.7	6.4
6 in corrugated Hechenbleikner blocks	0.50	2.9	6.6	6.6	6.4	6.9	6.9	4.7	5.1	5.1

'Dumped' signifies packing dumped at random

'Stacked' signifies packing arranged regularly in layers, but with no attempt to have pieces in one layer in any way related to those in adjacent layers

'Packed' signifies packing arranged regularly in layers, with axes of pieces in adjacent layers coinciding

'Circ' signifies water circulation at rate of 0.18 lb/(sec) (sq ft)

For grid packings, Johnstone and Singh [7, 1936–7] propose the equation

$$f = 0.08\left(\frac{D_e u\rho}{\mu}\right)^{-0.2} + 0.52\left(\frac{D_b}{D_e}\right)^{1.5}\left(\frac{D_e}{D_g}\right)^{0.75} \tag{17}$$

for use in the customary Fanning equation

$$\Delta P = \frac{2fL\rho u^2}{g D_e} \tag{18}$$

The velocity term in these equations is the actual velocity through the grid passages, that is, the velocity through the tower corrected for the fractional free cross-section, D_e is the equivalent diameter of the passages, defined as usual in terms of the surface area parallel to the flow and the total free volume

One of the most important characteristics of packings for countercurrent flow of liquid and gas is the loading or flooding velocity, or carry-over point, variously defined

Nomenclature for Equations relating to Calculation of Flow in Packed Columns.

Any self-consistent set of units may be used, except where noted, those involving pounds, feet, and seconds are given as examples

A_f = wall-effect factor, see Fig 1, dimensionless
D_b = thickness of grid members, ft

D_e = equivalent diameter of fluid path, ft = 4 (free volume/surface of fluid passage)

D_g = height of individual grid member, ft

D_s = clearance between grid members

D_p = nominal particle diameter, ft

D''_p = nominal packing diameter, *inches* [equations (13)–(16)]

D_t = diameter of tower, ft

D_r - modified particle diameter, ft [equation (11)]

F_c = multiplication factor for effect of liquor circulation, dimensionless, but depends on dimensions of D''_p [equation (16)]

F_h = multiplication factor for hollow particles, dimensionless, but depends on dimensions of D''_p [equations (13)–(14)]

F_w = multiplication factor for effect of wetness of packing, dimensionless, but depends on dimensions of D''_p [equation (15)]

f = friction factor, dimensionless [equation (18)]

f' = ,, ,, ,, [,, (7)]

f'' ,, ,, ,, [,, (11)]

g = acceleration due to gravity, 32 2 ft /(sec)^2

L = height of packing, ft

ΔP = pressure loss, lb per sq ft

u = velocity (actual through fluid passage), ft per sec

u_0 = velocity based on cross-section of empty tower, ft per sec

V_a = actual void content of bed, percentage

V_n = normal (loosest) void content, percentage

μ = viscosity of fluid, lb /(sec) (ft) (equal to 0 000672 × viscosity in centipoises)

ρ = density of fluid, lb per cu ft

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CONDENSER, HEAT EXCHANGE, AND TUBE-HEATER EQUIPMENT

HEAT EXCHANGERS AND CONDENSERS

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IT will be the object of this article to provide methods and data for the design of heat-transfer equipment other than direct-fired units The features of design treated, however, will be limited chiefly to the calculation of the economical heat-transfer surface and its arrangement, the mechanical details, such as methods of securing tubes in tube sheets, joint closures, allowance for differential expansion, &c, will be left largely for the equipment manufacturer to specify

Heat-transfer equipment for the petroleum industry, other than direct-fired types, can be roughly classified as follows heaters, in which a liquid is warmed, generally by condensing steam, heat exchangers, in which one liquid is warmed by another at a higher temperature, condensers, in which a vapour is reduced to liquid, usually by cooling water, and reboilers, in which a liquid is boiled, generally by means of steam The controlling resistances to heat flow in these classes of equipment are different, and will therefore be discussed separately under the appropriate classification

A. Heaters

As just stated, heaters are typically required to raise the temperature of a liquid by means of latent heat available in condensing steam The overall heat-transfer coefficient is not materially affected by the velocity of the steam, consequently no baffles are necessary when the steam is supplied to the shell side of the heater The liquid to be heated is generally sent through the tubes, not only because its velocity can thereby be brought up to a point which will increase the heat-transfer coefficient to a desirably high value, but also because the tube passages can be cleaned readily by flushing, swabbing, or by rotary tube cleaners, while the external surface is not so easily freed from accumulation of material which interferes with heat transmission If for any reason, such as unwillingness to expose the headers to the fluid heated, it is advantageous to send the cold fluid through the shell, the design should be treated as for a heat exchanger, under Section B, below

Typical designs of heaters are given in Figs 1 and 2 It will be noted that in Fig 1 the difference in thermal expansion between the tubes and the shell has been allowed for by a corrugation in the shell, while in Fig 2 one of the tube sheets is free to move longitudinally in the shell (In Fig 2 one baffle has been shown just inside the tube inlet to prevent cutting of the tubes by water carried in the steam) Tubes are generally chosen to conform to some standard dimensions, as, for example, those in Table I Single lengths are ordinarily limited to less than 20 ft, or less if space requirements make it necessary to keep the exchanger length short As pointed out below, the performance of a heater, expressed as the ratio of the temperature rise of the fluid to the available (mean) temperature difference, is nearly proportional to the ratio of length to diameter of the tubes Obviously, therefore, it is desirable to use tubes as small as practicable, so as to keep down the length, and of these the minimum number that will accommodate the specified hourly quantity of fluid to be handled without excessive pressure loss If provision must be made for cleaning the tubes, as is generally the case, the internal diameter should not be less than ½ in, or even ¾ in The thickness should be chosen not only with due consideration of the stress due to any bursting pressure, but equally often with consideration of possible collapse in case the external pressure exceeds that within the tubes, and also with regard to methods of securing the tubes in the tube plates, and to possible corrosion and wear in cleaning Up to the limit set by the possibility of rolling the tubes into tube sheets, thick-walled tubes are more desirable, therefore, than thin A greater thickness will cause an increase in the total installed cost of the equipment of only a small percentage, except in the most expensive alloys, and the influence on the heat-transfer coefficient will seldom be felt with any ordinary metals

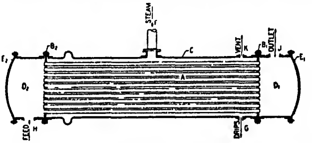


FIG 1 Single-pass tubular heater A Tubes B_1, B_2 Tube sheets C Shell D_1 D_2 Liquor-distribution chambers E_1, E_2 Covers F Steam inlet G Condensate outlet H Liquor inlet. J Liquor outlet K Non-condensed gas vent (*Reproduced by permission of Badger and McCabe, 'Elements of Chemical Engineering'* (McGraw-Hill, 2nd ed) p 162)

As a result of these considerations, tubes smaller than ¾ in or 1 in O D will be used under only unusual conditions, and wall thickness will be seldom less than 0 065 in (16 B W G)

If this practical minimum diameter of tube is still found to require an excessive length, greater effective lengths can be utilized in a single shell by multipass construction, as illustrated in Fig 2, which may be increased to four or eight passes by suitable arrangements, or separate heaters may be connected in series The latter scheme is usually to be preferred when a liquid is to be heated through a very wide temperature interval, since mechanical difficulties may arise because of unequal expansion of the different passes

The spacing between tubes is of no particular consequence as regards heat transfer in a heater utilizing steam, and therefore may be kept at a practicable minimum so as to keep down the diameter of the shell Cleaning of the exterior of the tube bundle is also not often to be provided for. The practicable minimum clearance between tubes, with regard to strength remaining in the tube sheet, may be set at about ¼ in. The minimum diameter of shell will be obtained when equilateral triangular arrangement of the tubes is followed. The shell diameter is best obtained by an actual lay-out, but the ratio, r, of the (internal) shell diameter to the centre-to-centre tube spacing can be approximated for any number of tubes, N_t, by the equation

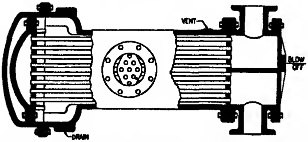


FIG. 2. Two-pass floating-head heater. (*Reproduced by permission of Badger and McCabe, 'Elements of Chemical Engineering'* (McGraw-Hill, 2nd ed.), p. 165.)

$$r = 0.94+\sqrt{\left(\frac{N_t-3.7}{0.907}\right)} \tag{1}$$

The calculation of the heat-transfer surface is now arrived at by the use of the logarithmic mean temperature difference, where this is applicable, and an estimate of the heat-transfer coefficient, with allowance for the series of resistances to transfer of heat from the heating medium to the fluid being heated, in conformity with the usual equation

$$\frac{1}{U}=\frac{1}{h_s}+\frac{1}{h_w}+\frac{1}{h_d}+\frac{1}{h_f} \tag{2}$$

(In this equation, it is assumed that the areas for heat-flow are all equal; if they are not, the individual coefficients must be adjusted to some common basis.)

For the logarithmic mean to be valid, it is sufficient that the water equivalent, WC, of the fluid being heated and the coefficient U be the same for all points of the heating surface. In a heater, provided no vaporization takes place, the first condition is ordinarily approximately satisfied, since for many liquids the variation of the specific heat with temperature is moderate. Serious errors may arise, however, through failure to allow properly for variations in U, which are sometimes considerable. Fortunately, it fre-

TABLE I. *Standard Condenser-tube Data*

Outside diam., in	*Size no. B.W.G.*	*Weight per foot, lb.**	*Thickness, in*	*Inside diam., in*	*Surface, sq. ft. per ft. of length*		*Inside sectional area, sq. in*	*Velocity, ft. per sec. per U.S. gal. per min*	*Capacity at 1 ft. per sec. velocity*	
					Outside	*Inside*			*U.S. gal. per min*	*lb. water per hr*
½	12	0.493	0.109	0.282	0.1309	0.0748	0.0624	5.142	0.1945	97.25
	14	0.403	0.083	0.334	0.1309	0.0874	0.0876	3.662	0.2730	136.5
	16	0.329	0.065	0.370	0.1309	0.0969	0.1076	2.981	0.3352	167.5
	18	0.258	0.049	0.402	0.1309	0.1052	0.1269	2.530	0.3952	197.6
	20	0.190	0.035	0.430	0.1309	0.1125	0.1452	2.209	0.4528	226.4
⅝	12	0.656	0.109	0.407	0.1636	0.1066	0.1301	2.468	0.4053	202.7
	14	0.526	0.083	0.459	0.1636	0.1202	0.1655	1.939	0.5157	258.9
	16	0.424	0.065	0.495	0.1636	0.1296	0.1925	1.667	0.5999	300.0
	18	0.329	0.049	0.527	0.1636	0.1380	0.2181	1.472	0.6793	339.7
	20	0.241	0.035	0.555	0.1636	0.1453	0.2420	1.326	0.7542	377.1
¾	10	0.962	0.134	0.482	0.1963	0.1262	0.1825	1.758	0.5688	284.4
	12	0.812	0.109	0.532	0.1963	0.1393	0.2223	1.442	0.6935	346.8
	14	0.644	0.083	0.584	0.1963	0.1528	0.2678	1.198	0.8347	417.4
	16	0.518	0.065	0.620	0.1963	0.1613	0.3019	1.063	0.9407	470.4
	18	0.400	0.049	0.652	0.1963	0.1706	0.3339	0.9611	1.041	520.5
⅞	10	1.16	0.134	0.607	0.2291	0.1589	0.2893	1.108	0.9025	451.3
	12	0.992	0.109	0.657	0.2291	0.1720	0.3390	0.9465	1.057	528.5
	14	0.769	0.083	0.709	0.2291	0.1856	0.3949	0.8126	1.230	615.0
	16	0.613	0.065	0.745	0.2291	0.1951	0.4360	0.7360	1.358	679.0
	18	0.472	0.049	0.777	0.2291	0.2034	0.4740	0.6770	1.477	738.5
1	10	1.35	0.134	0.732	0.2618	0.1916	0.4208	0.7626	1.311	655.5
	12	1.14	0.109	0.782	0.2618	0.2048	0.4803	0.6681	1.497	748.5
	14	0.887	0.083	0.834	0.2618	0.2183	0.5463	0.5874	1.702	851.0
	16	0.708	0.065	0.870	0.2618	0.2277	0.5945	0.5398	1.852	926.0
	18	0.535	0.049	0.902	0.2618	0.2361	0.6390	0.5022	1.991	995.5
1¼	10	1.74	0.134	0.982	0.3271	0.2572	0.7575	0.4236	2.362	1,181
	12	1.45	0.109	1.032	0.3271	0.2701	0.8369	0.3834	2.608	1,304
	14	1.13	0.083	1.084	0.3271	0.2839	0.9229	0.3477	2.877	1,439
	16	0.898	0.065	1.120	0.3271	0.2932	0.9852	0.3257	3.070	1,535
	18	0.675	0.049	1.152	0.3271	0.3015	1.043	0.3075	3.253	1,627
1½	10	2.12	0.134	1.232	0.3925	0.3227	1.193	0.2688	3.720	1,860
	12	1.76	0.109	1.282	0.3925	0.3355	1.292	0.2482	4.030	2,015
	14	1.36	0.083	1.334	0.3925	0.3491	1.398	0.2292	4.362	2,181
	16	1.09	0.065	1.370	0.3925	0.3585	1.473	0.2180	4.587	2,294
2	10	2.94	0.134	1.732	0.5233	0.4534	2.355	0.1362	7.342	3,671
	12	2.40	0.109	1.782	0.5233	0.4665	2.494	0.1287	7.770	3,885
	14	1.85	0.083	1.834	0.5233	0.4803	2.643	0.1213	8.244	4,122
	16	1.47	0.065	1.870	0.5233	0.4896	2.747	0.1168	8.562	4,281

* In brass, sp. gr. = 8.56.

quently happens that U may be approximated by a linear function of the temperature, and for this circumstance it has been shown [9, 1933, 19, 1929] that the correct heating surface is given by the formula

$$\frac{q}{A} = \frac{U_2\Delta t_1 - U_1\Delta t_2}{2.3\log_{10}\frac{U_2\Delta t_1}{U_1\Delta t_2}}, \tag{3}$$

where Δt_1, Δt_2 = the terminal temperature differences, U_1, U_2 the local overall coefficients at the respective terminals to which Δt_1 and Δt_2 refer

When the fluid being heated moves in a stream-line flow, the overall coefficient varies from point to point along the heating surface and attention must be given to the manner in which experimental results have been computed from the original data in order to determine the correct mode of use In the correlations of stream-line flow data given below, the coefficients are those appropriate for use with an *arithmetic* mean temperature difference

The heat-transfer coefficient, h_s, for condensing steam, if this is employed, is generally so high as to make its reciprocal negligible in the above summation, in comparison with the film coefficient for heating oils In case of doubt, its value may be estimated by the methods in Section C, below The conductance of the tube wall, h_w, is likewise high in comparison, it can be calculated from the conductivity of the metal and the wall thickness

An allowance for the conductance, h_d, of films of material deposited on the surface of the tube from the fluid being heated is, however, of real importance It is here that the experience and judgement of the designer will be called for, since fouling factors vary with the nature of the material handled and the characteristics of the tube metal [20, 1936] For even relatively clean and non-corroding liquids, it is probably desirable never to use a dirt film conductance greater than 1,000 B Th U /(hr) (sq ft) (° F), and perhaps much less if sludge or coke is likely to be deposited, even as low as 50 A value of 200 for heating crude oil or topped crude has been suggested [17, 1933]

The oil film heat-transfer coefficient, h_f, can be estimated fairly closely, on the basis of available correlations, provided the physical properties of the oil are known The correlations here cited involve these properties in sets of dimensionless groups, so that it is essential to substitute numerical values in some set of self-consistent units, as, for example, those in the table of nomenclature at the end of this article

With the diameter of tubes chosen, at least tentatively, the number is then calculated which will probably accommodate the flow without excessive pressure loss, this will ordinarily call for a linear velocity (of liquids of not too high a viscosity) of, say, 1–5 ft per sec The values in Table I will facilitate the calculation of the velocity The formulae of this section generally call for the mass (i e weight) velocity, G, expressed in lb /(hr) (sq ft) This is equal to $3{,}600\rho u$, if u is in ft per sec

For the general case, and especially for large tubes, long tubes, or for fluids with unusual properties, the correlation of Colburn [7, 1933], reproduced in another article [25], is recommended For the ordinary range of tube sizes, and for the usual hydrocarbon oils, the curves of Sieder and Tate [21, 1936] are convenient (Fig 3)

To use this chart it is necessary to calculate first the Reynolds number based on the viscosity of the fluid at the average of the inlet and outlet temperatures, μ_a If the Reynolds number is greater than 2,100, the flow is turbulent, and the heat-transfer coefficient for use with the logarithmic mean temperature difference can be calculated from the value of the ordinate by the substitution of the factors called for in the dimensionless groups To obtain μ_w it is necessary to estimate the pipe-wall temperature, for the case of heating oils with steam, this may be taken as equal to the steam temperature, as a first approximation, for other conditions, the temperature must be based on the relative thermal resistances in series, in accordance with equation (2) The line representing the data in the turbulent region may be extrapolated to higher Reynolds numbers by means of the following equation

$$\left(\frac{hD}{k}\right)\left(\frac{C\mu_a}{k}\right)^{-\frac{1}{3}}\left(\frac{\mu_a}{\mu_w}\right)^{-0.14} = 0.0262\left(\frac{DG}{\mu_a}\right)^{0.8} \tag{4}$$

If the Reynolds number is just above 2,100, it will be necessary to make an approximation for the length of the tubes (or the length of a single pass), and to chose the appropriate curve

If the Reynolds number is below 2,100, viscous flow prevails, and the heat-transfer coefficient depends on other factors than the Reynolds number, principally on the length/diameter ratio Moreover, the coefficient obtained from the chart is to be used with the *arithmetic* mean temperature difference from tube wall to fluid, not the logarithmic mean When a value of h has been obtained by means of a first approximation, and a value of the overall coefficient calculated, the resulting tube-length is used in a second approximation to obtain more nearly the exact value For extrapolation or interpolation in the viscous region the following equation may be used

$$\left(\frac{hD}{k}\right)\left(\frac{C\mu_a}{k}\right)^{-\frac{1}{3}}\left(\frac{L}{D}\right)^{\frac{1}{3}}\left(\frac{\mu_a}{\mu_w}\right)^{-0.14} = 1.86\left(\frac{DG}{\mu_a}\right)^{\frac{1}{3}}. \tag{5}$$

For the usual case where the oil-film resistance is the controlling factor and the surface temperature can be taken as equal to the steam temperature, the length of a (single) tube to give the required temperature rise can be estimated directly by a rearranged form of the above equation

$$\left(\frac{kL}{WC}\right) = 0.0625\left(\frac{t_2-t_1}{\Delta t_{a\,m}}\right)^{\frac{3}{2}}\left(\frac{\mu_a}{\mu_w}\right)^{-0.21} \tag{6}$$

where WC is the water equivalent of the oil flowing per tube It is obvious that the temperature rise cannot be more than twice the arithmetic mean temperature difference, where the surface temperature is constant The limiting value for a countercurrent exchanger depends on the relative heat capacities of the fluids The same equation may be used in approximating the length of tubes for a heat exchanger, provided an allocation of resistances is first made so that the terminal wall temperatures can be estimated.

If sufficient allowance has been made for dirt accumulations in calculating the overall coefficient, no additional factor of safety need be added in estimating the heat-transfer surface If one is added, the addition should be made to the length of the tubes and not to the number, since the reduced velocity in a greater number of tubes will give a lower (film) coefficient and so offset the greater surface area Additional tubes will, of course, provide for handling larger flows without excessive pressure drop Safety or 'ignorance' factors should be based on the degree of certainty which can be attached to the design data furnished

Pressure drop when heating or cooling liquids will not be the same as for isothermal flow Sieder and Tate recommend [21, 1936] that for turbulent flow the isothermal friction be multiplied by $1\ 02(\mu_a/\mu_w)^{0\cdot14}$, and for viscous flow by $1\ 1(\mu_a/\mu_w)^{0\ 25}$

B. Heat Exchangers

Heat exchangers differ from heaters only in that there are fluids (usually liquids, in petroleum technology) changing in temperature on both sides of the heat-transfer surface The design of exchangers differs from that of heaters only by the factors influencing heat transfer from the fluid outside the tubes

All the considerations set forth above with regard to length and diameter of tubes and calculation of inside film heat-transfer coefficients apply here and need not be repeated. It will only be necessary to discuss those factors having to do with conditions on the shell side

The heat-transfer coefficient on the outside of the tubes, as well as the pressure drop, is influenced by the velocity (and direction) with which the fluid flows through the passage between the tubes (hereafter referred to as the 'maximum velocity', i e at the closest approach of the tubes in a representative row) This velocity is controlled, in turn, by the number of tubes, their spacing, and the spacing of the baffles

Shell and tube exchangers can be built, of course, without baffles, in which case the flow can be considered as parallel to the heat-transfer surface, and calculations can be based on the formulae for flow inside tubes, using the 'equivalent diameter' concept (4 times the cross-section divided by the 'wetted' perimeter) The velocities so obtainable, however, are lower than desirable to make most effective use of the film heat-transfer coefficients possible inside the tubes for most ratios of fluid quantities, and so baffles are generally resorted to

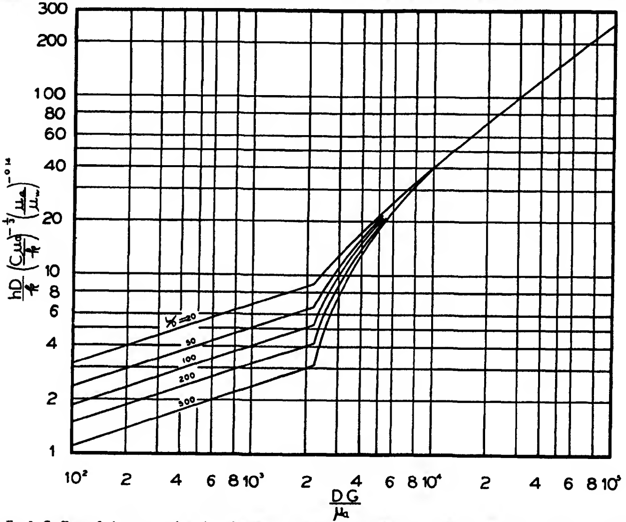


FIG 3 Coefficients for heating or cooling oils inside tubes (self-consistent units) L = length of tube, ft, D = diam of tube, ft, G = mass velocity, lb /(hr) (sq ft), h — tube wall-to-oil coefficient, B Th U /(hr) (sq ft) (° F), C = specific heat of oil, B Th U /(lb) (° F), μ_a = viscosity at mean oil temp, lb /(ft) (hr) = 2 42 × centipoises, μ_w = viscosity at wall temp, lb /(ft) (hr), k = thermal conductivity of oil, B Th U /(hr) (sq ft) (° F /ft)

Baffle arrangements are offered commercially in bewildering variety, but, so far as the authors of this article are aware, no data are available to show the superiority of one type over another Segmental baffles, arranged to give as nearly as possible an approach to true cross-flow conditions, permit the closest comparison with data obtained for such conditions, and only this type will be considered here.

Since the tube spacing influences the heat transfer, this dimension must be chosen with this in mind, as well as the minimum clearance allowable for secure fastening of the tubes (¼ in. was suggested above) or for ease of cleaning between the tubes. If cleaning must be provided for, a square arrangement of the tube bank is to be preferred to a staggered, and the clearance may be limited to ⅜ in. or even ¼ in. A square arrangement can be disposed so as to give the effect of a staggered bank if the flow is made to follow the diagonals instead of the sides of the squares on which the tubes are laid out. If fouling is not considered serious, and a staggered arrangement can be used, an equilateral triangular arrangement is as good as any. It is suggested that the minimum allowable clearance be chosen as a first approximation, and with the number of tubes chosen on the basis of an economic velocity inside the tubes, that an estimate then be made of the baffle spacing necessary to give a (maximum) velocity of a few feet per second outside the tubes. If this spacing is too wide to allow an approach to true cross-flow conditions, or if the pressure drop is too great for a reasonable baffle spacing, the tube spacing can be increased. It is not desirable to use a baffle spacing less than 1–2 in. Incidentally, the baffles may well be of the same metal as the tubes and of the same thickness as the tube wall. Chamfering edges of tube holes helps to prevent cutting of the tubes in service.

Data on heat transfer to or from fluids flowing directly across banks of staggered tubes have been correlated by Colburn [7, 1933], and the resulting curve is presented in another article [25]. It can be represented by the equation

$$\left(\frac{h}{CG_m}\right)\left(\frac{C\mu_f}{k}\right)^{\frac{2}{3}} = 0.33\left(\frac{DG_m}{\mu_f}\right)^{-0.4} \checkmark \qquad (7)$$

for values of (DG_m/μ_f) between 2,000 and 50,000. The viscosity called for in this equation is at the film temperature, i.e. at a temperature half-way between the mean fluid temperature and the wall temperature. For flow across tubes in square arrangement, the coefficient in the above equation is about 0.25. Here G_m is the maximum velocity (through the area at the closest approach of the tubes).

Results reported by Bowman [3, 1936] on a line of baffled exchangers are brought into agreement with the above equation when the velocity is corrected for leakage around the baffles.

$$G_m = \frac{W}{L_b[D_s - D_p(1.27N_t)^{0.5}] + 1.25KD_p N_t} \qquad (8)$$

When the other dimensions are measured in feet, K was found to have a value of 0.01.

More simply, but not so accurately, Bowman's results can be represented without this clearance factor by making the coefficient in equation (7) equal to 0.20. On the same basis, a baffled exchanger with tubes on square arrangement might be calculated by equation (7), using the nominal maximum velocity, with a coefficient equal to 0.15.

When film coefficient of heat transfer for the shell-side fluid has thus been estimated, it can be combined with that for the fluid inside the tubes, and with appropriate dirt-film conductances on *both* sides of the wall, to give an overall coefficient.

In the case of single-pass shell-and-tube heat exchangers the heating surface is determined, as for heaters, by the use of an estimated overall coefficient, U, and the logarithmic mean temperature difference, or, when U varies linearly with the temperature difference, by the use of equation (3). At first thought such procedure may seem unwarranted because the customary baffles make the shell-side fluid flow across rather than along the tubes as was assumed in the derivation of the rules. In practice, however, the baffles are commonly so numerous that a negligible change in temperature is incurred by a single transverse passage of the shell-side fluid between adjacent baffles. Hence for practical purposes the temperature of the fluid in the shell varies only in the direction along the tubes. In the unusual case of an exchanger with only one or two baffles, recourse may be had to the charts of D. M. Smith [22, 1934] for an estimate of the mean temperature difference by which the logarithmic mean should be replaced.

Multipass construction introduces a complication which cannot be neglected without serious error; indeed, such neglect often leads to specifications which are thermodynamically impossible. The origin of the trouble may be seen by considering a U-tube placed axially, the closed end extending upstream, within a jacketing pipe. If the fluid inside the U-tube is being heated, such an exchanger can actually operate with the exit temperature of that fluid above the exit temperature on the shell side; thus the direction of heat flow in one arm of the U may differ from that in the other. For exchangers of this type, i.e. single-pass shell with two passes through tubes (when overall coefficient is uniform, and the fluids do not vaporize or condense), Nagle [18, 1933] and Underwood [23, 1934] have shown that the correct mean temperature difference is found if the logarithmic mean calculated on the assumption of counterflow is multiplied by the function F of the temperatures and temperature differences which is given by Fig. 4 (*a*). The direction of flow in the shell does not influence the result, and the number of passes on the tube side, at least if an even number, has so slight an effect that it is negligible in practice.

When multipass construction is used on the shell side as well as on the tube side, or—what is the same thing—if several exchangers with one shell-pass and multiple tube-passes are connected in series, the correction factor F is the same for each shell-pass if each contains the same heating surface. This fact was utilized by Bowman [4, 1936] in constructing, from Fig. 4 (*a*), the analogous charts Fig. 4 (*b*, *c*, *d*, *e*) for exchangers with multipass shells. In the derivation it was supposed that the fluids flow from one shell-pass to the next in a countercurrent sense, as is usual within a single shell; the charts are therefore applicable to exchangers in series only if they are connected in a countercurrent sense. If there is only one tube-pass per shell-pass, the logarithmic mean obviously applies, provided all passes have the same number of tubes, &c., regardless of the number of passes (or shells) in series.

When, in a multipass exchanger, U cannot safely be supposed uniform, but can be approximated by a linear function of the temperature, it is easily possible to find an effective value of the coefficient which gives the correct heating surface if used with the temperature differences derived on the assumption of uniform U. The procedure was developed by Colburn [9, 1933] for use with single-pass counterflow exchangers and, according to Sieder and Tate [21, 1936], is substantially correct for multipass equipment. In following this procedure it is necessary to determine $U_2, \Delta t_2$ and $U_1, \Delta t_1$, the overall coefficients and temperature differences at the hot and cold ends respectively of the exchanger. The rate of change of U with the temperature of the fluid being heated is then estimated according to the equation

$$U = a(1+bt) \qquad (9)$$

A value is found for the function, C,

$$C = \frac{t_2 - t_1}{(1/b)+t_1}, \qquad (10)$$

and by means of Fig. 5 a value of F is estimated. This value multiplied by $(t_2 - t_1)$ and added to t_1 gives the temperature of the fluid being heated which may be used to calculate

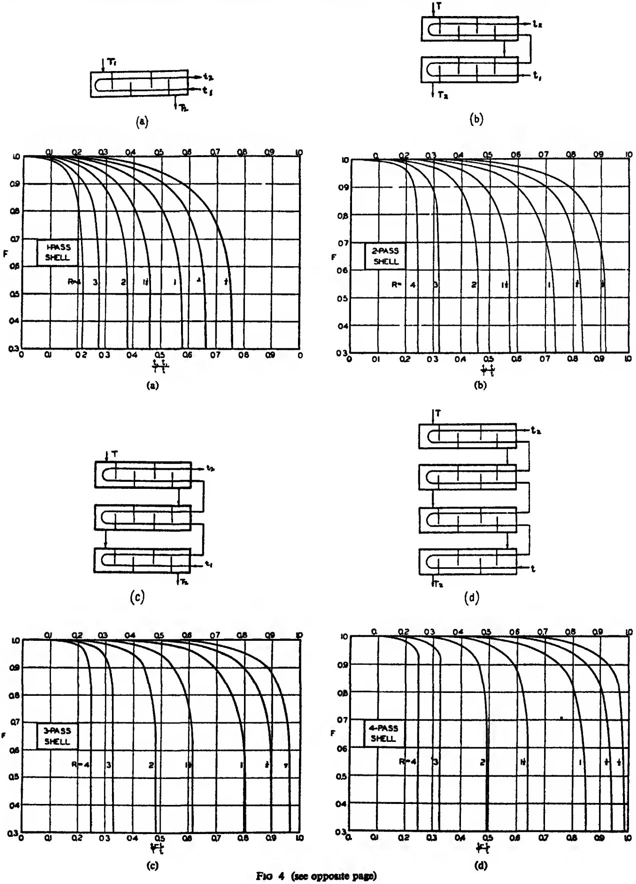


Fig 4 (see opposite page)

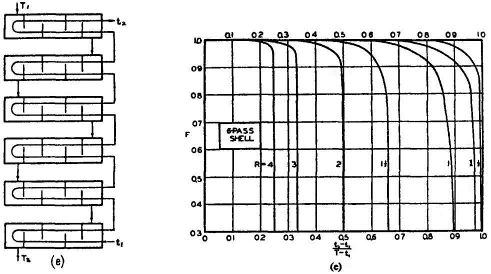


FIG 4 Correction factors, *F*, for use with logarithmic-mean temperature difference in countercurrent multipass heat exchangers having from 1 to 6 passes of the shell-side fluid and any even number of tube passes per shell pass, as shown in sketches below

T_2 - outlet temperature of shell-side fluid
T_1 - inlet temperature of shell-side fluid
t_1 — inlet temperature of tube-side fluid
t_2 = outlet temperature of tube-side fluid

$R = (T_1-T_2)/(t_2-t_1)$

True mean temperature difference

$$= F\left[\frac{(T_1-t_2)-(T_2-t_1)}{2\ 3\log_{10}\dfrac{T_1-t_2}{T_2-t_1}}\right]$$

a value of *U* which can be used with the logarithmic temperature difference, or one corrected as above for deviation from the countercurrent flow conditions

C. Condensers

The principles to be followed in the design of surface condensers are not different from those employed above Certain simplified methods can be employed, however, if, as is usually the case, water is employed as the cooling medium (If other materials, see above) Since condensing vapours are relatively clean, while water available for cooling may deposit solids, water is generally sent through the tubes of shell and tube condensers, or allowed to flow over the outside of S-bend coils—in either case to facilitate cleaning the water side

Coefficients of heat transfer for heating of water flowing through tubes can be conveniently obtained from Fig 6, which is based upon equations of the type proposed by Hinton [15, 1928] and on the data of Eagle and Ferguson [12, 1930] Table I will be of assistance in determining the actual water velocity from the weight of water required to effect the cooling, a velocity of between 3 and 5 ft per sec is desirable If the water trickles over banks of pipes, an approximation for the water-film coefficient may be obtained from the data of Adams, Broughton, and Conn [1, 1936], which may be represented by the equation

$$h_{a\ m} = a\Gamma^{0\ 39} \tag{11}$$

For the pipe sizes used the values of *a* were as follows

D = 1 in	2 in	4 in
a = 88 7	72 7	47 7

The equation may be used for values of Γ from about 250 to 1,000 lb /(hr.) (ft length of uppermost pipe) If, as was the practice in the early days of the petroleum industry, the cooling pipes are submerged in boxes containing more or less quiescent water, the coefficient can be estimated from the equation [24, 1927]

$$h = 67\ 5 = \left(\frac{\Delta t}{\mu}\right)^{\frac{1}{4}}. \tag{12}$$

In any event, a dirt-film coefficient of not more than about 500 should be included, and perhaps much less, depending upon the character of the water used and upon materials of construction

In contrast with steam condensers, where the water side presents the controlling resistance to heat flow, in condensers for organic substances the controlling resistance may be that of the condensing vapour film, or more precisely of the film of condensed vapour Coefficients for single pure vapours can be estimated from Nusselt's theoretical equations, as represented by the alinement chart [6, 1933], Fig 7, or for vertical surfaces, with allowance for turbulence in the condensate film, by Fig 8 [8, 1934]

Single pure vapours, however, are seldom encountered in the petroleum industry Kirkbride [16, 1933] recommends for petroleum fractions the use of the same equations, employing the boiling-point of the condensate under the prevailing pressure as the condensing temperature Condensing film coefficients observed by Kirkbride, reported in this manner, varied from about 175 to 360, with a maximum deviation from the theoretical values of 35% This procedure is doubtless satisfactory in arriving at an overall coefficient (in the absence of substantial amounts of non-condensing gases), though it should be recognized that the composition of the condensate is not necessarily that in equilibrium with the liquid vapour (except at infinitesimal rates of condensation), also that the composition of the vapour, in practical cases, varies as it travels through the condenser

If the mixed vapours separate into two layers on condensing, as in the very common case of condensing steam plus oil vapours, the resulting coefficient is still more difficult to predict. Kirkbride [16, 1933] proposes to compute a weighted mean coefficient from the separate theoretical coefficients for the two components, weighted according to the amount of heat received per unit time from each It has been pointed out, however, that there is here a possibility of dropwise condensation, dependent on surface conditions, which may invalidate this procedure [2, 1937]

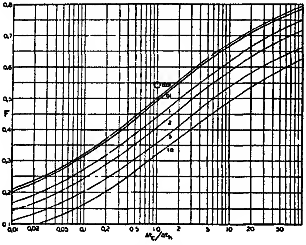


FIG 5 Plot of F vs Δt_c Δt_h

F = factor which multiplied by temperature rise, $t_2 - t_1$, and added to t_1 gives temperature associated with heat transfer coefficient, U, based on logarithmic mean Δt

Δt_c = temperature difference at cold end
Δt_h — temperature difference at hot end

$$C - \frac{t_2 - t_1}{1/b + t_1}, \text{ where } U = a(1 + bt)$$

In the presence of non-condensing gas, very much lower effective coefficients are obtained, due to the resistance of the gas film to diffusion of the vapour to the surface The design of a condenser on the basis of the theory and data for diffusional processes is straightforward, even if somewhat tedious It is necessary to equate, by trial and error, the equivalent heat transmitted to the condensate surface by sensible heat transfer and by the diffusing vapour to that transmitted thence to the cooling water, in order to arrive at the temperature of the condensate surface, for a number of points along the condenser When a number of such local values of heat transfer rate, $U\Delta t$, for several values of the cumulative heat transferred, q, have been obtained, the necessary surface area is found by graphical integration of the equation

$$dA = dq/U\Delta t \tag{13}$$

An example has been worked out by Colburn and Hougen [10, 1934], in which diffusion rates are estimated from the curves given by Chilton and Colburn [5, 1934] Values of vapour diffusivities may be estimated by the method proposed by Gilliland [13, 1934] Some suggestions for working out such cases may also be found in the paper by Kirkbride [16, 1933]

This method, while the only one recommended as reliable, is undoubtedly tedious Some figures may be secured as a guide to possible performance in petroleum condensers from Table II, taken from Higgins [14, 1936]

While overall coefficients in condensing pure vapours are not much affected by vapour velocity, effective coefficients for mixtures with non-condensing gases may be affected quite largely For this reason, if the mixture flows across the tubes, baffles should be used If the original mixture is mostly vapour, it may be desirable to use two units in series, the second of which is designed for high velocities with the much smaller throughput

D. Reboilers

Where vapours for distillation are supplied by means of indirect steam, a further class of heat-transfer equipment is needed, often called reboilers, or sometimes calandrias Data are not so well established for calculating this class of equipment as for those previously considered Overall coefficients, however, are relatively high They may range from 100 to 500 B Th U /(hr) (sq ft) (° F), the low values being associated with boiling liquids of higher viscosity, and with lower temperature differences, than the high values

It may be noted that liquids boiling under reduced pressure have high viscosities compared to the viscosity at the atmospheric pressure boiling-point, so that heat transfer coefficients for operation under vacuum will be low in comparison with those obtained at higher pressures, for the same temperature difference

While higher temperature differences, up to, say, 50° F overall, rapidly increase the heat transfer rate, it should be pointed out that too high a temperature difference, above, say, 100° F , will cause a decrease in the rate of heat transfer, on account of the formation of an insulating layer of vapour next to the hot surface [11, 1937]

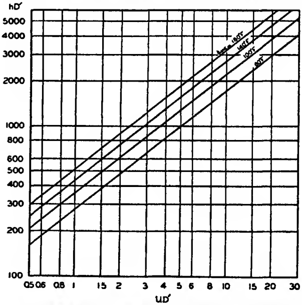
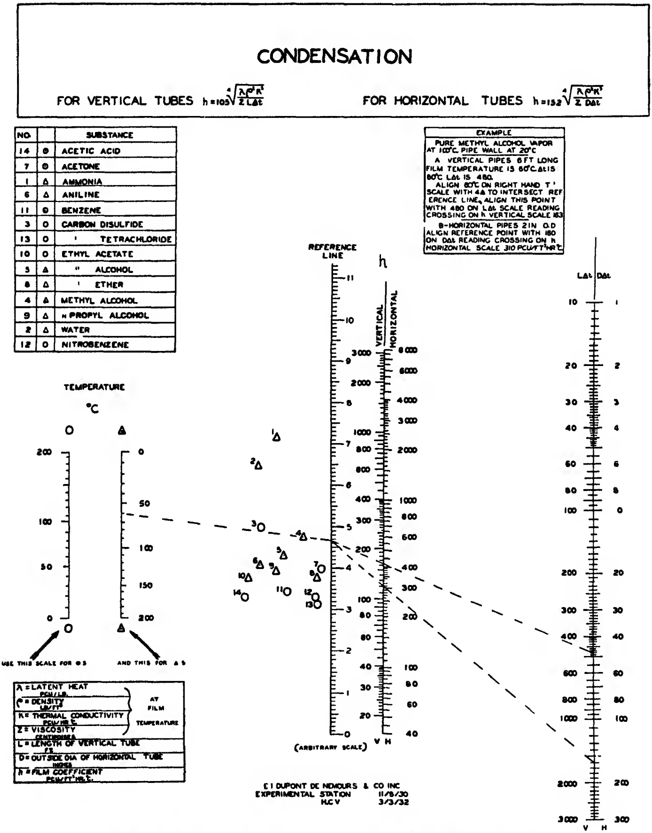


FIG 6 Coefficients for heating water inside tubes, the following units must be used

h = wall-to-water coeff , B Th U /(sq ft) (hr) (° F) D' = inside diam. of tube, inches u = linear velocity, ft /sec t_{av} = mean temp of water

If arranged for natural circulation, a reboiler may take the form of a shell containing a number of vertical tubes, of not too great length, perhaps not over 6 ft , and not too small a diameter, say not less than 1 in O D., with either an external return line of large cross-section or an ample internal downpipe A vapour disengaging volume designed to give 1 sec detention of the vapours evolved may be found adequate. The coefficients mentioned above will cover the practical range of values



CONDENSATION

FOR VERTICAL TUBES $h = 105\sqrt[4]{\frac{\lambda \rho^2 K^3}{Z L \Delta t}}$ FOR HORIZONTAL TUBES $h = 152\sqrt[4]{\frac{\lambda \rho^2 K^3}{Z D \Delta t}}$

NO.		SUBSTANCE
14	O	ACETIC ACID
7	O	ACETONE
1	Δ	AMMONIA
6	Δ	ANILINE
11	O	BENZENE
3	O	CARBON DISULFIDE
13	O	" TETRACHLORIDE
10	O	ETHYL ACETATE
5	Δ	" ALCOHOL
8	Δ	" ETHER
4	Δ	METHYL ALCOHOL
9	Δ	n PROPYL ALCOHOL
2	Δ	WATER
12	O	NITROBENZENE

EXAMPLE

PURE METHYL ALCOHOL VAPOR AT 100°C. PIPE WALL AT 20°C

A VERTICAL PIPES 6 FT LONG FILM TEMPERATURE IS 60°C. Δt IS 80°C LΔt IS 480.

ALIGN 60°C ON RIGHT HAND T' SCALE WITH 4Δ TO INTERSECT REFERENCE LINE, ALIGN THIS POINT WITH 480 ON LΔt SCALE READING CROSSING ON h VERTICAL SCALE 163

B-HORIZONTAL PIPES 2 IN O.D ALIGN REFERENCE POINT WITH 160 ON DΔt READING CROSSING ON h HORIZONTAL SCALE 310 PCU/FT²HR°C.

λ = LATENT HEAT PCU/LB.
ρ = DENSITY LB/FT³
K = THERMAL CONDUCTIVITY PCU/HR °C
Z = VISCOSITY CENTIPOISES
} AT FILM TEMPERATURE
L = LENGTH OF VERTICAL TUBE FT
D = OUTSIDE DIA OF HORIZONTAL TUBE INCHES
h = FILM COEFFICIENT PCU/FT² HR °C.

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EXPERIMENTAL STATION 11/8/30
H.C.V 3/3/32

FIG 7 Alinement chart for heat transfer coefficients for condensation of single pure vapours.

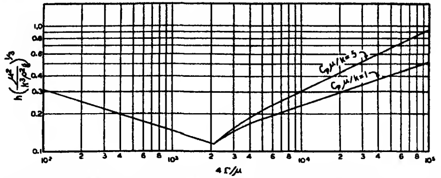

FIG 8 Theoretical vapour-to-wall coefficients for condensation of vapours on vertical walls (self-consistent units) Do not use for mixed vapours unless condensate is a single phase

h = vapour-to-wall coefficient, B Th U /(hr) (sq ft) (° F)
Γ = maximum weight flow of condensate per unit periphery, lb /(hr) (ft)
μ = viscosity of condensate at film temp , lb /(hr) (ft)
ρ = density of condensate, lb /cu ft
k = thermal conductivity of condensate, B Th U /(sq ft) (hr) (° F/ft)
g = $4\ 18\times10^8$ ft /(hr) (hr)
C_p = specific heat of condensate, B Th U /(lb) (° F)

If arranged for forced circulation, the reboiler may be designed by the formulae given above under Heaters, since under these conditions most of the heat is transferred as sensible heat, superheating the liquid, later to be removed by flashing in a separator

E. Performance Data

Table II, below, is taken from tests reported by Higgins [14, 1936] and may be used to furnish a rough guide for checking design figures, where conditions are given which are similar to the problem under consideration It must be recognized that conditions are seldom found to be identical, and that variations in viscosity of the oil, in cleanliness of the surfaces, in the character of cooling water, or in the proportion of non-condensable gas, may have such a preponderating influence that the figures given may be from two- to fivefold at variance or more

TABLE II

Tabulation of Shell and Tube Heat-Exchanger Tests Data of Higgins [14, 1936]

Test no	*1*	*2*	*3*	*4*	*5*	*6*	*7*
Service	*Stabilizer reflux condenser*	*Stabilizer reflux condenser*	*Stabilizer reflux condenser*	*Stabilizer reflux condenser*	*Absorption gasoline condenser*	*Naphtha condenser and cooler*	*Gasoline cooler*
Number of shells	2	1	1	2	2	2	2
Arrangement	parallel			series	series	series	series
Total surface, sq ft	3 880*	1 110	1,110	2,060	2 210	1,372	2,000
No of tubes per shell	1 880	566	566	640–414	478	291	426
Tubes, size	¾ in 14 B W G	¾ in 14 B W G	¾ in 14 B W G	¾ in 18 B W G	¾ in 16 B W G	1 in 14 B W G	⅝ in 16 B W G
Length of tubes, in	54½	120	120	120	144	144	144
Tubes, passes	6	4	4		6	1	1
Shell, O D , in	54	28	28		27 I D	20⅝	24 I.D
Shell, baffles, type	cross	¾ circle	¾ circle			cross	¾ circle
Shell, baffles, spacing, in		30 baffles	30 baffles				14 baffles
Shell, passes	6	2	2		2	1	1
Tubes							
Fluid	water	water	water	water	water	water	water
Amount, lb per hr	99 000	175,500	294,350	218,200	220,000		
Velocity, ft per sec at 60° F	0 7	2 97	4 99		5 32		
Operating pressure, lb per sq in	3	16	17	32			30
Temperature in, ° F	78 4	86	84 8	80	73	89	89
Temperature out, ° F	88 7	93 8	96 7	87	99	130	105
Heat load, B Th U per hr	1,020,000	1,404,000	3,532,000	1,525,000	5,730,000		
Pressure drop, lb per sq in	3 8	5 0	10·7	2			
Shell							
Fluid Amount, lb per hr	reflux 7,760 res gas 1,515	reflux 15,500 res gas 2,422	reflux 31,100 res gas 4,610	reflux 11,420 res gas 2,590	abs gaso 13,290 NC vapours 6,020 steam 2,360	nap 23,653 steam 2,530	62·9 API gaso 31,415
Velocity, ft per sec at 60° F							
Operating pressure lb per sq in	170	217	243	189	12	4	8
Temperature in, ° F	113	117	128	110	207	250	298
Temperature out, ° F	82 7	93 4	100	91	76	115	110
Heat load, B Th U per hr	1,148,300	2,175,000	4,502,000	1,504,000	5,735,000	7,421,000	7,250,000
Pressure drop, lb per sq in	4·0	4 5	6 2				
General							
Δt_m, ° F	11 55	13 5	22	16·25	29·4	61·4	77 5
U, B Th.U /(hr) (sq ft)	45 5†	93 7	144·6	45 6	88 2	87 5	46 8

* Data based on one exchanger,

† Tube sheets matted with hair and other debris.

TABLE II (*cont*)

Test no	*8*	*9*	*10*	*11*	*12*	*13*
Service	*Partial condenser*	*Partial condenser*	*Partial condenser*	*Partial condenser*	*Partial condenser*	*Stabilizer reboiler*
Number of shells	2	1	1	1	1	1
Arrangement	series					
Total surface, sq ft	2,238	1,256	1,256	1,256	1,216	1 798
No of tubes per shell	514–436	598	598	598	332	936
Tubes, size	1 in 14 B W G	⅝ in 16 B W G	⅝ in 16 B W G	⅝ in 16 B W G	1 in 16 B W G	¾ in 14 B W G
Length of tubes, in	144	144	144	144	168	120
Tubes, passes	4	6	6	6	4	2
Shell O D, in	28	28¼ I D	28¼ I D	28¼	33¾	60 I D
Shell, baffles, type	cross	cross	cross	cross	circular	none
Shell, baffles, spacing, in	9	16	16	16	4	
Shell, passes	2	1	1	1	2	1
Tubes						
Fluid	39 API crude	54 6 API nap	54 6 API nap	54 6 API nap	54 7 API nap	steam
Amount, lb per hr	124,400	100 500	154,000	129 700	69,500	3,260
Velocity ft per sec at 60° F	2 42	4 43	6 80	5 67	1 19	
Operating pressure lb per sq in	250				50	138 5
Temperature in, ° F	88	77	77	86	64	360
Temperature out ° F	213	151	147	172	121	360
Heat load, B Th U per hr	7 780 000	3,750,000	5,430,000	5 930,000	3,440 000	2 810,000
Pressure drop lb per sq in						
Shell						
Fluid	57 7 API gaso	62 3 API nap	62 3 API nap	62 3 API gaso	61 8 API gaso	58 2 API nap
Amount lb per hr	73 415				vap 33,700	53,300
Velocity, ft per sec at 60° F						
Operating pressure, lb per sq in	10	6	6	6	3	170 5
Temperature in ° F	311	204	212	210	280	300
Temperature out, ° F	298	193	198	204	204	340
Heat load, B Th U per hr						
Pressure drop lb per sq in						
General						
Δt_m ° F	147	80 5	90 2	70 6	129	33 5
U B Th U /(hr) (sq ft)	21 7	37 2	48 0	66 8	22	42 1

Test no	*14*	*15*	*16*	*17*	*18*	*19*
Service	*Stabilizer reboiler*	*Stripper reboiler*	*Rich oil preheater*	*Naphtha to naphtha exchanger*	*Naphtha to naphtha exchanger*	*Stabilized naphtha cooler*
Number of shells	1	1	1	1	2	1
Arrangement					series	
Total surface, sq ft	1 560	603	422	925	650	450
No of tubes per shell	795	314	220	1,670	168	680
Tubes, size	¾ in 14 B W G	¾ in 14 B W G	¾ in 14 B W G	¾ in 14 B W G	¾ in 14 B W G	¾ in 14 B W G
Length of tubes, in	120	120	120	36	120	42
Tubes, passes	2	2	4	18	4	10
Shell, O D in	50	32	23	54	18 I D	36
Shell, baffles, type	none	¼ circle	¼ circle	cross		cross
Shell, baffles, spacing, in.			4 baffles			
Shell, passes	1	1	1	14	2	10
Tubes						
Fluid	steam	steam	42 API abs oil	60 2 API nap	63 API nap	water
Amount lb per hr	4,875	1,300	26,100	45,100	58,500	76,000
Velocity, ft per sec at 60° F			1 40	1 39	4 61	2 68
Operating pressure, lb per sq in	168	146	72	176	214	12 9
Temperature in, ° F	374	364	247	91	91	78 2
Temperature out, ° F	374	364	339	264	284	86·3
Heat load B Th U per hr	4,150,000	1,120,000	1,443,000	4,446 000	6 270,000	1,092,500
Pressure drop, lb per sq in			13	5 0	24	11 6
Shell						
Fluid	57 API nap	37 4 API abs oil	steam	58 2 API nap	57 API nap	58 2 API nap
Amount, lb per hr		30,200	1,870	40,100	55,750	40,100
Velocity, ft per sec at 60° F				1 23		1 41
Operating pressure lb per sq in	190	54	110	165	190	168 5
Temperature in, ° F	308	294	346	344	350	143
Temperature out, ° F	350	343	346	143	164	86 3
Heat load, B Th U per hr			1,635,000	4,680,000	6 030,000	1,150,000
Pressure drop, lb per sq in				2 2	7	5 7
General						
Δt_m, ° F	41 4	40 8	31 8	64 6	69 3	23 1
U, B.Th U /(hr) (sq ft)	64 2	45 4	108	74 3	139	105*
F, by Fig. 4					0 91	

* Tube sheets matted with hair and other debris.

TABLE II (*cont*)

Test no	*20*	*21*	*22*	*23*	*24*	*25*
Service	*Stabilized naphtha cooler*	*Rich, lean oil exchanger*	*Absorption oil intercooler*	*Gas oil cooler*	*Kerosine cooler*	*Residuum crude exchanger*
Number of shells	1	3	1	1		1
Arrangement	series	series				
Total surface, sq ft	900	1,740	376	415	415	385
No of tubes per shell	450	302	196	176	350	164
Tubes, size		¾ in 14 B W G	¾ in 14 B W G	¾ in 16 B W G	¾ in 16 B W G	¾ in 16 B W G
Length of tubes, in	120	120	120	144	144	141½
Tubes, passes	2	4	2	1	1	2
Shell, O D, in		23	19	15¼ I D	32	15¼ I D
Shell, baffles, type		½ circle	¾ circle	¾ circle	¾ circle	½ circle
Shell baffles, spacing, in		4	4	3	1½	2
Shell passes		2	2	1	1	1
Tubes						
Fluid	water	42 7 API abs oil	water	water	water	39 API crude
Amount, lb per hr	117,500	41,200	33,400			124,400
Velocity ft per sec at 60° F		1 56	0 818			3 86
Operating pressure lb per sq in	38	72	26 3	30	30 max	250
Temperature in, ° F	80	103	79·0	89	89	192
Temperature out ° F	96	242	88 7	137	107	222
Heat load, B Th U per hr	1,880,000	3,423,000	324,000			1 940 000
Pressure drop, lb per sq in	11	8 0	3 9			
Shell						
Fluid	57 API nap	37 2 API abs oil	41 1 API abs oil	gas oil	43 8 API kero	13 API resid
Amount, lb per hr	55 790	38 400	30,800	18 860	14 353	14 700
Velocity, ft per sec at 60° F						
Operating pressure lb per sq in	183	50·3	97	5	2	2
Temperature in, ° F	164	325	114 6	395	338	598
Temperature out, ° F	101	143	90 5	152	118	370
Heat load B Th U per hr	1,810 000	3,730,000	367,000	2 680 000	1 722 000	2 010 000
Pressure drop, lb per sq in		2 5	4 4			
General						
Δt_m, ° F	40	58 8	17 7	109 5	97 5	262
U, B Th U /(hr) (sq ft)	52 3	33 5	48 8*	59	40 3	19 2
F, by Fig 4	0 96	0 95				

* Tube sheets matted with hair and other debris

Nomenclature

A — heat-transfer surface, sq ft
C — specific heat, B Th U /(lb) (° F)
D — diameter, ft
D_o — outside tube diameter, ft
D_s — inside diameter of shell
F — correction factor
G — mass (weight) velocity, lb /(hr) (sq ft)
K — leakage factor, equation (8) (ft)
L — length, ft
L_b — baffle spacing, ft
N_t — number of tubes
U — overall heat-transfer coefficient, B Th U /(hr) (sq ft) (° F)
W — flow rate, lb per hr
g — acceleration due to gravity, 4 18 × 10^8 ft /(hr) (hr)
h — individual film heat-transfer coefficient, B Th U /(hr) (sq ft) (° F)
k — thermal conductivity, B Th U /(hr) (sq ft) (° F /ft)
q — heat load, B Th U per hr
t — temperature, ° F
u velocity, ft per sec
Γ — flow per unit width, lb /(hr) (ft)
Δt — temperature difference, ° F
λ latent heat, B Th U per lb
μ — viscosity lb /(hr) (ft), = 2 42 × centipoises
ρ — density, lb per cu ft

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HEATERS

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THE earliest heaters for petroleum refining consisted of cylindrical shells set over a firebox, with the lower portion of the cylinder absorbing heat from the flame, the refractories, and the products of combustion that swept the lower rear portion of the shell on their way to the stack Because of a large volume of oil per unit of heat-absorbing surface and low velocities with which the surface was washed by the oil being heated, shell heaters were limited to low rates of heat input The permissible maximum was determined by the rate of free convection or convection induced by steam jets within the body of the oil, which even with boiling fluids was too low to permit rates much in excess of 3,000 B Th U per sq ft per hr without overheating the oil in contact with the heated portion of the shell Coke deposition and burning out of still bottoms almost invariably followed attempts to force shell heaters much above these rates The addition of internal flues to shell heaters to simulate a fire-tube boiler materially improved their operation and increased their capacity However, shell heaters were primarily batch heaters, and continuous operation, which gradually displaced batch operation in the larger refineries, could be accomplished with them only by operating a battery of shell heaters in series, each shell operating at a slightly higher temperature than its predecessor in the series With large-scale operation in some fields, such as California, batteries of shell heaters became too cumbersome

Comparatively successful application of tubular heaters on a small scale for dehydration and refining of emulsified oils led to the gradual adoption of tubular heaters for general refining purposes and eventual substitution for shell heaters for large-scale refining operations

The introduction of cracking, which called for heaters that could withstand higher pressures and higher metal temperatures than an externally heated shell, contributed greatly to the development of tubular heaters and definitely demonstrated their superiority over the shell type

The earlier tubular heaters varied little in their setting from shell heaters, the main difference being that the shell was displaced by a bank of tubes placed over the firebox However, since a definite velocity was imparted to the oil by pumping it continuously through the tube bank and the ratio of heating surface to volume was greatly increased, average rates of 5,000–6,000 B Th U per sq ft per hr were obtained without particular difficulties in the early tubular heaters in spite of the normally present zones of local overheating or 'hot spots' in some sections of the tubes directly over the fires with actual rates of 15,000–20,000 B Th U per sq ft per hr As the average rates of heat input and the oil temperatures were increased, the hot spots became more pronounced and troubles were encountered with failure of tubes in these hot spots, particularly in heaters where countercurrent flow of oil and gases was intended

The troubles were first attributed to radiation from the flames in the firebox, and a number of tubular heaters were built with the tube bank separated from the firebox by solid or perforated walls to protect the tubes from this radiation Because of more uniform heat distribution, greater average rates of heat input were obtained in these heaters than in heaters where the tube bank was directly over the fires in the combustion chamber, but it was soon found that even with the bank shielded from the visible flames, the tubes first coming in contact with the invisible products of combustion became easily over-heated unless the gas temperature was reduced below a certain minimum for the operation carried out

The next step in the development of tubular heaters was the reduction of the temperature of the gases entering the tube bank This was done in two different ways In the so-called 'convection' heaters where the heat was supplied by gases flowing over the tubes, the products of combustion were diluted first with excess air and later with returned or recirculated flue gases, to obtain the desired temperature of the gases entering the tube bank or the 'heating chamber' In other heaters 'radiant' tubes were installed in the combustion chamber to cool the products of combustion by absorbing radiant heat from the flame, the gases, and the refractories of the combustion chamber before the gases entered the 'main' or 'convection' bank of the heater, which was intended to supply the major portion of the total heat, and which was usually separated by a bridge wall from the combustion chamber Particular care was taken in these heaters to place the 'radiant' tubes out of the path of the products of combustion To reduce the rates of heat input which could be absorbed by the relatively small number of tubes used when subjected to the full radiation of the combustion chamber, the tubes were shielded from this radiation by surrounding either the tubes or the flames with refractory enclosures, which cut these rates approximately in two

High maintenance and operating costs of flue-gas recirculating equipment and frequent failures of the enclosures around the tubes, together with the comparatively satisfactory operation of some open-flame 'radiant' heaters without flue-gas recirculation and without shielding either the tubes or the flame, led to the gradual abandonment of the flue-gas recirculating and the shielded 'radiant tube' heaters and their replacement by the open-flame type Improvement in heat generation and distribution and better understanding of the laws of radiant and convection heat transfer greatly contributed to the success of the open-flame heaters, and at the present time such heaters are built almost exclusively The proportion of radiant heat input has gradually increased from 25% of the total in the early heaters to as high as 80% of the total Consistently long runs with heat transfer rates of 20,000 B Th U per sq ft per hr of internal surface for the radiant banks and 15,000 B Th U per sq ft per hr for the total internal surface of the heater are not uncommon, even with oil temperatures over 950° F Since modern heaters supply from 60 to 80% of the total absorbed heat by radiation, their operation is determined primarily by the rates of radiant heat transfer that can be obtained and safely applied to the oil

The rate of heat transfer by radiation is determined by the Stefan-Boltzmann law and can be expressed by the equation

$$q = 0.172A\left[\left(\frac{T_F}{100}\right)^4-\left(\frac{T_W}{100}\right)^4\right]F_e F_a,$$

where q is the heat absorbed by radiation, B Th U per hr ,

F_e = coefficient depending on the relative emissivity of the radiating and heat-absorbing surfaces,

F_s = coefficient depending on the geometrical arrangement of the surfaces,

A = equivalent effective heating surface, sq ft ,

T_F = effective furnace temperature, ° Rankine,

T_s = temperature of the heat-absorbing surface, ° Rankine

The laws of radiation and the evaluation of the various factors in this equation are dealt with in the article in this section, Principles of Heat Transfer, by Weir

In this equation the heat-absorbing surface is theoretically plane surface In practice, radiant heat-absorbing surface is ordinarily formed of banks of metal tubes spaced at intervals with sometimes as many as four rows of tubes per bank, with the banks often at different angles to the radiating plane Such heat-absorbing surface can be expressed in terms of equivalent effective heat-absorbing surface A by the use of coefficients which express the actual service conditions of the surface in terms of the theoretical

Fig 1 shows Hottel's curves [8, 1930] of relative effectiveness of tube banks with single and double rows of tubes placed on different centre-to-centre distances along a radiating non-conductive wall and irradiated from one side from a plane parallel with the wall If the area of the plane which might be considered to replace the tube bank is substituted for A in this equation, then the factor F_s is the ordinate of Fig 1 The effectiveness of a bank with a single row of tubes placed on a centre-to-centre distance of two diameters (the most common spacing) is 0 87 of a plane surface and each square foot of the circumferential area of the tube bank has an average effectiveness of $\frac{0\ 87 \times 2}{\pi}$, or approximately 0 55 With two parallel rows of tubes spaced on the same centres, and arranged as shown in the diagram, the effectiveness of the bank is 0 98, but since the amount of circumferential area is double that of a single row, the average effectiveness of each square foot of circumferential area is only 0 98 — π or 0 31 It will be noticed that little is to be gained by using more than two rows of roof tubes unless the spacing is very much greater than the usual 2 to 3 diameters

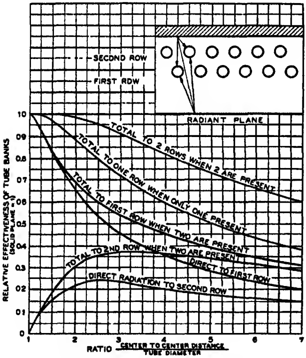

Fig 1 Relative effectiveness of tube banks compared to plane surface (Hottel)

Fig 2 shows Wohlenberg's curve [18, 1926, 19, 1935] of relative radiant heat-absorbing capacity of heaters as affected by the ratio of the effective heat-absorbing ('cold') surface to the projected area of the furnace envelope (cold surface plus refractory walls) This ratio is denoted by ψ and is called the 'cold fraction' of the furnace envelope as illustrated for a cube on Fig 3 With a given total liberation, a heater with the furnace envelope completely covered with cold surface (ψ - 1 0) will absorb by radiation the greatest proportion of the available radiant heat energy, which is unity on Fig 2 When ψ is less than 1 0 the total absorption of radiation is less but relative absorption per unit area is greater For instance, when ψ = 1 0 the absorption per cold face of a cube is 1 0—6 = 0 166, and when $\psi = \frac{1}{6}$ the absorption for this one face is 0 67

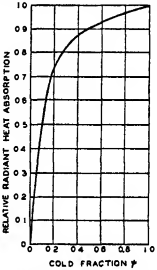

Fig 2 Relative effectiveness of heat-absorbing surface as function of 'cold fraction' (Wohlenberg)

Fig 4 shows the relative effectiveness of circumferential surface of tube banks with single and double rows of tubes spaced on two diameters and placed in a cubical combustion chamber when the cold fraction is varied from 0 166 to 1 0 The curves on this figure are derived from Figs. 1 and 2 according to the equation

$$E_{RS} = \frac{f_1 \times f_2}{n},$$

where E_{RS} = the relative effectiveness of circumferential surface,

f_1 = the relative effectiveness factor of circumferential area of tube banks, as derived from Fig 1 (0 55 for a single-row tube bank and 0 31 for double-row tube banks),

f_2 = the relative heat-absorbing capacity of heaters for the cold fraction involved as shown on Fig 2,

n = number of cold faces of the cube making up the cold fraction.

The values of relative effectiveness of tube banks and their circumferential area shown on Figs 1, 2, and 4 apply to banks irradiated from one side only and placed against a non-conductive wall which re-radiates to the bank all of the heat that passes between the tubes to this wall Under these conditions the effectiveness of the half of the circumferential area of the tubes facing the radiating plane (the exposed face) is many times that of the half receiving heat by re-radiation from the wall (the shielded face) For example, with a single row of tubes placed on a centre to centre distance of two diameters, the exposed face of the tubes has a relative effectiveness of 0 66, which is over 75% of the effectiveness of the total surface and three times the effectiveness of the shielded face With a bank having two rows of tubes on the same spacing, the exposed face of the first row has three times the effectiveness of the exposed face of the second row and sixteen times the effectiveness of the shielded face of the first row The average effectiveness of the total circumferential area of the first row is almost twice the average effectiveness of that of the second row

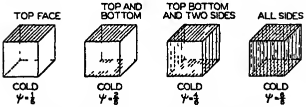

FIG 3 Diagrammatic illustration of 'cold fraction

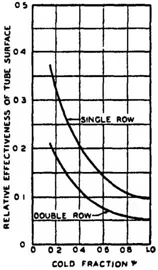

FIG 4 Relative effectiveness of circumferential surface as derived from Figs 1 and 2

With tubes irradiated from both sides, that is with the bank placed between two radiating planes, both halves of the circumferential area of the tubes become 'exposed' faces. With a single row of tubes irradiated on both sides and spaced on two diameters, the effectiveness of the bank is double that of the exposed face of a bank irradiated on one side, or 1 32 of the plane surface, which is approximately 52% greater than the effectiveness of a similar bank irradiated from one side only With two rows of tubes irradiated from both sides, each row has the same average effectiveness and the two rows have an effectiveness approximately 40% greater than two similar rows irradiated from one side only

In actual furnaces banks irradiated from both sides form, as a general rule, a smaller cold fraction of the total furnace envelope, the relative effectiveness of a bank irradiated from both sides is therefore further increased because of the greater effectiveness of a bank with a lower cold fraction Fig 5 shows the relative effectiveness of circumferential tube surface of single- and double-row tube banks as normally placed in the heaters using irradiation from one and two sides, the latter being marked 'Equiflux' in the figure The effectiveness of the circumferential area of tubes spaced on two diameters and placed in single rows along all six sides of a cube (cold fraction 1 0) is taken as unity in this comparison The effectiveness of banks irradiated from one side is derived on the basis of banks placed in a combustion chamber 18 ft wide, 16 ft high, and 40 ft long (cold fraction approximately 0 5), while the effectiveness of tubes irradiated from both sides is derived on a basis of the banks placed in the middle of a combustion chamber 8 ft wide, 12 ft high, and 40 ft long (cold fraction approximately 0 35)

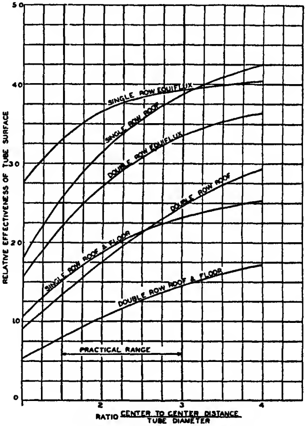

FIG 5 Relative effectiveness of circumferential surface with irradiation from one and two sides (equiflux)

Irradiation from both sides not only increases the effectiveness of single- and double-row banks, or makes both rows of a double-row bank of equal effectiveness, but tends to distribute the heat intensity around the circumference of the tube more uniformly, so that for a given maximum rate of heat transfer to any portion of the circumference higher average rates can be used, or with the same average rates, the maximum rate will be considerably lower as shown qualitatively on Fig 6

The effective furnace temperature T_F is theoretically the logarithmic mean temperature of the furnace as it changes from the flame-burst temperature to the temperature of exit gases from the radiant heat-absorbing chamber It is often referred to as the equilibrium temperature of the furnace Since the mean temperature is difficult to determine experimentally and rather cumbersome to calculate accurately it is substituted in the Stefan-Boltzmann equation by either the theoretical flame temperature or by the exit gas temperature, and the coefficient F_e is changed to accommodate the temperature chosen

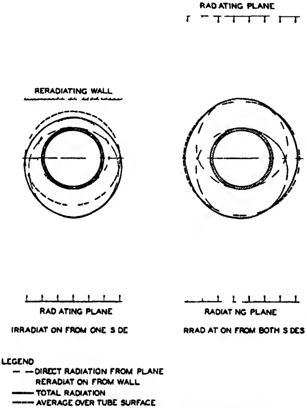

Fig 6 Flux distribution around tubes in a single row bank irradiated from one and two sides

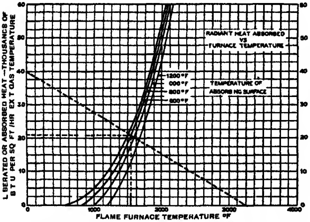

Fig 7 Radiant heat absorption relationships

Example

Flame burst temperature 3 200° F

Liberated heat per sq ft of equivalent effective surface, 40,000 B Th U

Temp of heat absorbing surface 800° F

Absorbed radiant heat per sq ft. of equivalent effective surface, 21 000 B Th U

Residual temp of gases, 1,550° F

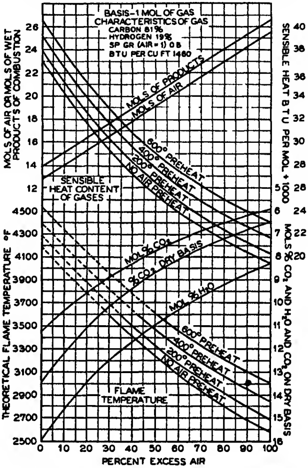

Fig 8 Combustion characteristics of cracking still gas

Fig 7 is an alinement chart showing the relationship between the theoretical flame temperature, the temperature of the heat absorbing surface, the quantity of generated heat per square foot of effective surface per hour (diagonal dashed line) the quantity of heat absorbed by radiation for a given liberation and theoretical flame temperature (horizontal dashed line), and the theoretical temperature of the gases leaving the radiant heat absorbing chamber, if no convection heat is applied to the surface in the chamber (vertical dashed line) The curves are derived from the Stefan-Boltzmann equation and the following simple approximate relationship between the total available heat, the heat absorbed by radiation, the theoretical flame temperature, and the exit gas temperatures—

$$\frac{Q_R}{Q_G}=\frac{T_G-T_F}{T_G-520},$$

where Q_G = the liberated heat above 60° F per sq ft of effective surface,

Q_R = the heat absorbed by radiation per sq ft. of effective surface,

T_G = the theoretical flame-temperature, ° Rankine,

T_F = the effective furnace temperature, ° Rankine.

Figs. 8 and 9 show the theoretical flame temperature obtained with different amounts of excess air and different air preheats when burning a representative cracking-still gas and cracked residue, and may be used with sufficient accuracy in conjunction with Fig 7 for any cracked gas or cracked residue normally burned in refineries

The residual heat in the products of combustion leaving the radiant heat-absorbing chamber is recovered either in supplementary tube banks, commonly called convection sections, or in air preheaters With high inlet oil temperatures both convection sections and air preheaters are often used, particularly at plants where fuel is sufficiently valuable to justify the installation of air preheaters

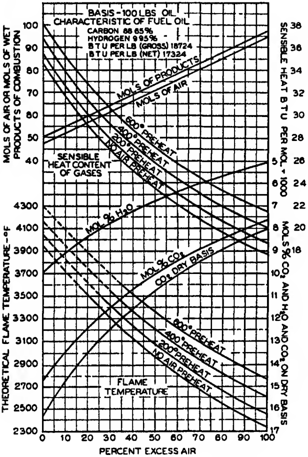

Fig 9 Combustion characteristics of cracked residuum

The mechanism of heat transfer in the convection sections is somewhat complex, in that with the average gas temperatures prevailing in convection sections of modern oil heaters (1,300–1,800° F inlet and 800–1,100° F outlet) a portion of the total heat supplied to the convection bank is by radiation from the gases, the amount depending on the gas temperature, the CO_2 and H_2O content of the gases, and the clearance between the tubes which determines the shape factor of the radiating gas layer. (See article on Principles of Heat Transfer, Weir, Table III) Figs 10 and 11 show the radiant heat absorption from products of combustion when burning gas and oil fuel, as in Figs 8 and 9, with 50% excess air and clearances of 2 in between the tubes (shape factor approximately 2.8)

The purely convection heat transfer can be expressed by the formula

$$q = T_M h_c,$$

where q = heat transfer, B Th U per sq ft per hr,
T_M = the mean log temperature difference of the gases and the outside metal temperature, ° F,
h_c = the coefficient of heat transfer, B Th U per sq ft per hr per ° F

The determination of the value of h is also discussed in the article referred to above, but a simple formula

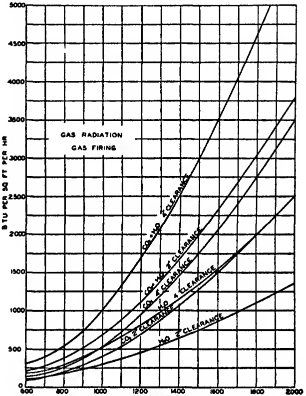

Fig 10 Radiant heat absorption from products of combustion of cracking-still gas

Example
Gas Temperature, 1,600° F
Surface temperature, 800° F
Clearance between tubes, 4 in
Total radiation from CO_2 and H_2O, 3,550 (at 1,600° F), 550 (at 800° F) – 3,000 B Th U per sq ft

proposed by Monrad [11, 1932] may be used to cover the present case, namely

$$h_c = \frac{1.6 G^{2/3} T^{0.3}}{D^{1/3}},$$

where G = mass velocity of the gases, in min cross-section, lb per sq ft per sec,
T = temperature of the gases, ° Rankine,
D = diameter of tubes, in

Depending on the above factors, h_c varies in practice between 2 and 4 B Th U per sq ft per hr per degree Fahr, and usually represents 30–60% of the overall heat transfer in the convection section

Modern petroleum heaters are, as a general rule, designed to meet definite service requirements covering not only total heat load, thermal efficiency, and performance of the heat-absorbing surface, but heat distribution and the time-temperature effect in the heater most suitable for the operation and the charging stock involved The time-temperature effect, which determines the degree of decomposition of the material heated, is often the most important service requirement and operating factor Petroleum heaters can be divided into three main groups, according to the amount of decomposition obtained

1 Heaters used for heating only with little or no decomposition
2 Heaters where in addition to the heating, substantially all of the decomposition desired for the refining process is obtained in the heater
3 Heaters where only partial decomposition is obtained in the heater, the remainder of the reaction being carried out in reaction chambers or soaking drums, usually not heated externally

Heaters of the first group are designed to obtain minimum time-temperature effect with the maximum temperature employed, and are used for non-destructive distillation where no chemical change of the overhead and residual products is desired, such as topping, atmospheric or vacuum distillation, re-running, &c

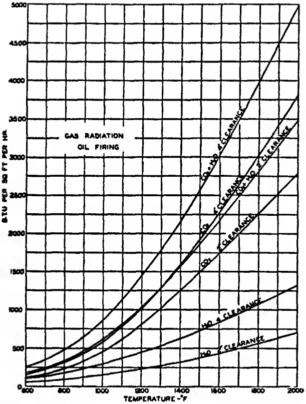

Fig 11 Radiant heat absorption from products of combustion of cracked residuum

Heaters of the second group are designed to give maximum time-temperature effect at the highest operating temperature employed, and are used with cracking units for the lighter overhead stocks where no reaction chamber is employed These heaters are usually so designed that the heating surface nearest the outlet from the heater is subjected to lower rates of heat input than the rest of the tube bank so as to provide an externally heated reaction or 'soaking' section in the heater, where very little or no increase in temperature is obtained

Heaters of the third group are the most difficult to design, particularly for residual cracking stocks which are highly sensitive to thermal treatment These heaters must be designed for a time-temperature effect that will permit the highest outlet temperatures, and consequently highest reaction chamber temperatures, to assure effective operation of the chamber, without excessive decomposition and the resultant coke deposition in the heating coil itself

With given cracking stocks, definite inlet and outlet pressures and temperatures, and definite quantities of material going through the heater, the time-temperature effect of a heater is closely related to its temperature curve or 'heating curve', which is obtained by plotting the temperature of oil against either the length, the amount of heating surface, or the volume of the coil Since the heating curve of a heater is determined by the relationship between the heat requirements of the oil and the rates of heat transfer at any point of the coil, the type of heating curve obtained in a heater is one of its main characteristics

As a general rule, the specific heat of hydrocarbons increases with temperature so that the sensible heat requirements per degree temperature rise are increased as the oil travels through the coil When change of phase occurs during heating, the increasing sensible heat requirements are augmented by increasing amounts of latent heat of evaporation If decomposition occurs during heating, resulting in conversion predominantly into lighter fractions, as is the case with cracking, the heat requirements are further increased by the heat of reaction and the higher specific heat and latent heat of evaporation of the lighter constituents formed In some instances, the heat requirements per degree temperature rise at the end of the coil are many times the requirements at the beginning of the coil, in which case, to obtain a uniform temperature rise throughout, it is necessary to apply at the end of the coil heat input rates many times the rates at the beginning of the coil

Fig 12 shows the most common types of heating curves obtained with different heat requirements and rates of heat input through the coil While smooth heating curves are actually obtained in most heaters, the change of heat transfer rates may be quite abrupt from zone to zone, so that the actual heat input rate curves of a heater may consist of a series of steps rather than the smooth curves or straight lines on Fig 12 Heating curve 12 *A* is obtained when the heat input into the oil increases at a greater rate than the heat requirements of the oil as it passes through the coil Heating curve 12 *B* is obtained when the heat input increases at the same rate as the heat requirement of the oil as it passes through the coil Heating curve 12 *C* is obtained with increasing heat requirements and uniform rates of heat transfer sufficiently high to maintain some temperature rise of the oil through the coil Heating curve 12 *D* is obtained with increasing heat requirements and decreasing rates of heat input The same type of heating curve may be obtained with uniform heat input rates and increasing heat requirements if these rates are sufficient to maintain a temperature rise of the oil only through the lower temperature range where the heat requirements are comparatively low

The coils of most commercial heaters can be represented as a series of sections with one of the above heating curves A bare tube convection section with countercurrent flow of comparatively high-temperature gases and comparatively low-temperature oil normally has a heating curve as shown on 12 *A*, with higher oil temperatures, the heating curve may be as 12 *A* in the bottom section and as 12 *B* in the top section, with concurrent flow of comparatively high temperature gases and high temperature oil, a heating curve as shown on 12 *D* may be obtained. Radiant sections with substantially uniform rates of heat transfer normally have a heating curve as shown on 12 *C*

In a heater where the oil passes first countercurrently through a convection section and then through a radiant section with substantially uniform and comparatively high rates of heat input, a heating curve as shown on 12 *E* is normally obtained This curve is a composite of curve 12 *A* for the convection section and curve 12 *C* for the radiant bank In many group 2 heaters where the temperature through the soaking section is maintained substantially constant and where the heat of reaction is the determining factor of the heat requirements a relationship of heat transfer rates, heat requirements and heating curve as shown on 12 *F* may be obtained particularly if the soaking section is located in a convection section with concurrent flow of oil and gases, or in a separately fired combustion chamber with lower average rates of heat input toward the end of the soaking section

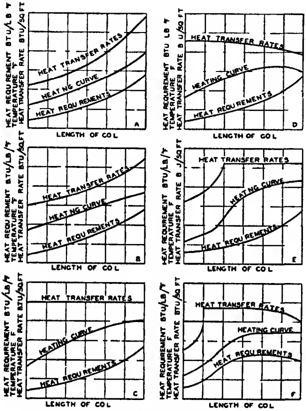

FIG 12 Relationships between heat requirements heat transfer rates and heating curve

A properly designed heater particularly a heater intended for group 2 or group 3 service is a heater where the relationship of heat transfer rates and heat requirements is such as to produce a heating curve that will give the time temperature effect most suitable for the service intended Failure to design a heater with this requirement in view may result in the heater being the limiting factor of the whole unit, which may have to be operated in a certain way to keep to a minimum troubles with the heater, such as local overheating, coke deposition in certain sections of the coil because of poor time-temperature relationship in the coil, low conversion per pass &c The design of heaters to meet a specific time-temperature relationship is a comparatively recent development and the data for such design are as yet jealously guarded secrets of the organizations engaged in this specialized work The discussion of the types of heaters commonly used in the petroleum industry has therefore to be limited to general principles

A number of typical furnace arrangements are shown below to illustrate the trend of development outlined above

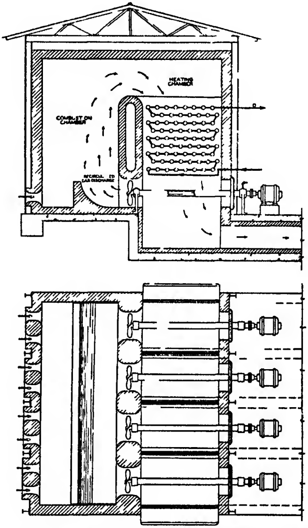

FIG 13 Flue gas recirculating furnace *I* oil inlet *O* oil outlet

Fig 13 shows a type of flue gas recirculating heater where the recirculated gases are introduced through the bridge wall directly from the tube chamber to the combustion chamber without auxiliary flues A number of small fans as shown, or steam injector jets, are used for flue gas recirculation As a general rule, this type of heater was used for group 3 service, and with countercurrent flow of gases and the oil with recirculating ratios below 2, gave a heating curve as shown on 12 *A* By increasing the recirculating ratio this heater can be operated to give heating curves as shown on 12 *B* and 12 *C*, the latter only with high oil outlet and comparatively low gas inlet temperature and gas-recirculating ratios of the order of 4 1

Fig 14 shows an early shielded radiant heat oil heater in which a roof bank was installed to absorb sufficient heat from the gases to permit their use without recirculation for heating the 'main' or the convection bank of the heater To

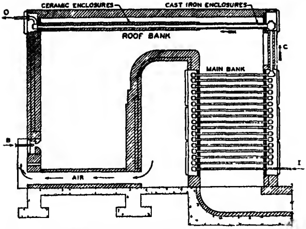

Fig 14 Early shielded tube radiant heat oil-heater *I*, oil inlet *O*, oil outlet. *C*, outside cross-over *B*, burners

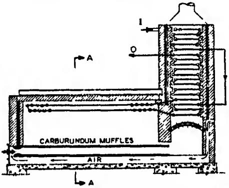

Fig 15 Early shielded flame radiant heat oil-heater *I*, oil inlet *O*, oil outlet *C*, outside cross-over

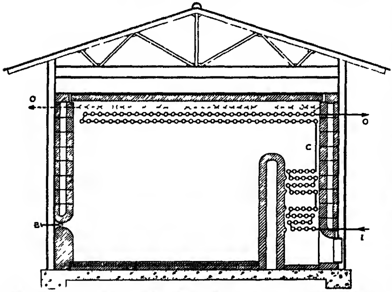

Fig 16 Early open-flame heater with roof tubes only Fraction cold, 0 26 Effectiveness of circumferential surface from Fig 4, 0 16 *I*, oil inlet. *O*, oil outlet *B*, burners

protect the roof bank from the full radiation in the combustion chamber, the roof tubes were covered with ceramic enclosures over the combustion chamber, where radiation was the most intense, and with cast-iron enclosures over the main bank. The heater was normally operated with comparatively high amounts of excess air (100%) to reduce the temperature of the gases entering the main bank This heater was used for group 1 service and had a heating curve similar to that shown on Fig 12 *C*

Fig 15 shows another type of an early shielded radiant heat oil-heater where carborundum muffles were placed around the flames to protect the comparatively small amount of radiant heat-absorbing surface from direct radiation The heater was intended for operation with low excess air to obtain high flame temperatures and the highest possible radiation through the carborundum With the flow as shown, the heater was primarily used for group 2 service to give a heating curve substantially as shown on Fig 12 *F*

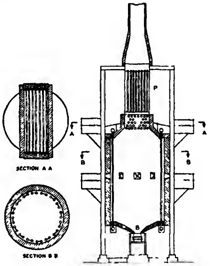

Fig 17 Updraught cylindrical heater Fraction cold, 0 85 Effectiveness of circumferential surface from Fig 4, 0 06 *I*, oil inlet *O*, oil outlet *B*, burner, *P*, air preheater

Fig 16 shows an early open-flame radiant heat oil-heater with a much larger combustion chamber than that of the heater shown on Fig 14, and with approximately one-half of the total tube bank located along the roof of the combustion chamber to permit the use of bare radiant heating tubes and open flames With two rows of tubes and the flow as shown, this heater is used for group 1 and group 3 service A heating curve intermediate between that shown on 13 *E* and 13 *F* is normally obtained With the reversed flow through the two-row roof bank, that is, with the oil entering the second row and leaving through the first, a heating curve intermediate between 12 *B* and 12 *C* is normally obtained. With three or more rows of tubes in the roof bank and with the oil entering the lowest row and leaving from the highest row, this heater is used for group 2 service and gives a heating curve approaching that shown on Fig. 12 *F*

Fig 17 shows an updraught heater consisting of a vertical cylindrical section with the tubes placed round the whole circumference of this section. The convection section when used is very small, and an alloy air preheater is usually employed to reduce the temperature of the gases going to the stack. This heater is used primarily for group 3 service and gives a heating curve of the type shown on Fig 12 *C*

The heaters shown on Figs 14 and 17 represent the complete range of proportions of radiant heat-absorbing surface to total surface used varying from a cold fraction of less than one-sixth to five-sixths, with the relative effectiveness of the radiant heat-absorbing surface varying from 0 35 to 0 06 The heater shown on Fig 14 had too little radiant heat-absorbing surface, so that shielding of the surface was required to protect these tubes from overheating The heater shown on Fig 17 has too much radiant heat-absorbing surface in proportion to the furnace envelope, with the result that the effectiveness of the surface is comparatively low

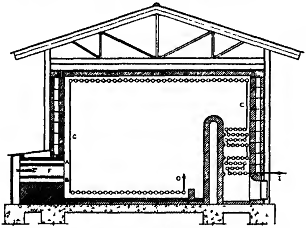

FIG 18 Single end-fired roof and floor tube heater Cold fraction, 0 41 Effectiveness of circumferential surface from Fig 4, 0 20 *I*, oil inlet *O*, oil outlet *C*, outside cross-over

Fig 18 shows a heater with approximately 50% of the total heat-absorbing surface located along the roof and the floor of the combustion chamber The tube banks in the combustion chamber form approximately two-fifths of the area of the furnace envelope With single rows of tubes used in the combustion chamber, the optimum effectiveness of the circumferential area is obtained As a general rule, the floor tubes of the heater are the tubes of the highest rates of heat input, and with the flow as shown a heating curve intermediate between 12 *B* and 12 *C* is normally obtained This type of heater is used on cracking units for group 3 service, particularly when processing heavy residual oils

This heater can be operated to obtain a limited control of the heating curve by changing the character of the flame and therefore their relative rates of heat input into the convection section, the roof tubes, and the floor tubes of the heater. The burners fire through three-compartment firing tunnels, of which the centre tunnel *F* is the firing tunnel proper and the upper and lower tunnels *A* and *B* are for admission of secondary air to the fuel after its ignition in tunnel *F* With all the air passing through compartment *F* as primary air, and short non-luminous flames, the rates of heat input into the floor tubes and the roof tubes near the firing wall are proportionally lower, and the rates of heat input into the convection section and the roof tubes over the bridge wall and near the back wall of the heater are proportionally higher than if only a portion of the air is sent through compartment *F* and the rest of the air used as secondary air through compartments *A* and *B* to produce luminous flames By restricting the flow of air through compartment *F* and admitting a large portion of the air through compartment *A*, semi-luminous flames with a hotter face toward the floor tubes is obtained This increases the rates of heat input into these floor tubes By restricting the primary air in compartment *F* and admitting all of the secondary air through compartment *B*, semi-luminous or luminous flames with a hotter face toward the roof tubes are obtained, which increases the rates of heat input into these tubes In this manner the heating curve for the complete coil can be varied from that as shown on 12 *E* to a composite of heating curve 12 *A* for the convection section and heating curves 12 *B* or 12 *C* for either the floor or the roof tubes

Fig 19 shows schematically one type of a multi-cell 'Equiflux' heater, in which each radiant heat-absorbing tube bank is heated from both sides, and a common convection section is used to cool the gases from the cells and preheat the oil entering the cells As many cells as the process requires may be used in the same manner or with separate convection sections for each cell As the heat-absorbing surface in the cells is irradiated from both sides it has a much greater average effectiveness for a given maximum intensity on any portion of the tube circumference than can be obtained in any of the heaters previously described (see Fig 6) As a general rule, the cold fraction of the tube bank in this type of heater varies from 0 24 to 0 35, which further increases the effectiveness of the surface used

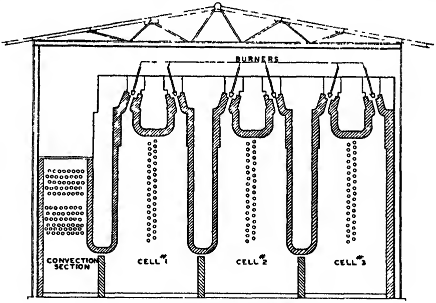

FIG 19 Multi-cell equiflux heater

The multi-cell arrangement permits a wide variation in the heating curves by altering the connexions between tubes in each tube-bank and between the different cells, by regulating the firing on each side of each tube-bank, and of course adjusting the relative heat input to the different cells

For instance, instead of connecting the tubes in a tube-bank all in series, criss-cross fashion, the oil may be arranged to pass first through one-half of the vertical bank and then in series through the other half, the heating curve can then be changed from 12 *B* to 12 *D* by regulating the heating on each side For large throughputs the oil can be made to pass through the two halves of each tube-bank unparallel and any desired heating curve obtained by suitably firing the different cells connected in series

The general design of petroleum refining equipment is toward larger, more efficient units that are responsive to accurate control of operating conditions, and that are sufficiently flexible to meet a comparatively wide range of these conditions to take care of the possible changes in stocks processed and final products desired With the constantly increasing demand for petroleum products that have to meet rigid specifications, and with these specifications changing rapidly, inflexible petroleum refining equipment may become obsolete and may require rebuilding or replacement long before it shows appreciable signs of wear and tear

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INSULATION

HEAT TRANSFER THROUGH INSULATION

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THE fundamental laws of heat transfer by conduction, convection, and radiation are discussed in the article 'Principles of Heat Transfer', the flow of heat through insulation is therefore treated as a specialized application of these principles to the particular conditions in this field Furthermore, since nearly all operations in the petroleum industry are now carried out by continuous processes, only steady state conditions will be considered in which the temperatures are steady throughout the system

One important feature in nearly all cases of heat transfer through insulation is that the whole of the temperature drop between the lagged surface and the outside air does not occur in the body of the lagging itself as there are other thermal resistances in the path of the flow of heat The most obvious of these is the thermal resistance at the external surface of the insulation There may also be a corresponding resistance caused by the poor mechanical contact between the inner surface of the insulation and the surface of the lagged body

Problems of this type are therefore clearly best treated as heat flow through thermal resistances in *series* according to the equation (equation (6) in the article referred to above)

$$q = \frac{(\theta - \theta')}{R_1+R_2+R_3+\quad+R_n}, \tag{1}$$

where q = rate of heat flow, B Th U per hr

$(\theta-\theta')$ = overall temperature difference, ° F ,

$R_1, R_2, R_3, \quad , R_n$ = thermal resistances (in series)

It may be of assistance to mention that there is an exact analogy to this equation to be found in Ohm's law which states that the current in a circuit consisting of a number of resistances connected in series is equal to the total potential difference divided by the sum of all the resistances in series

These thermal resistances may be regarded either as the resistance to heat flow of a given thickness X (ft) of material of thermal conductivity k (B Th U /sq ft hr °F for 1 ft thickness) having an area at right angles to the direction of heat flow A (sq ft), that is,

$$R = \frac{X}{Ak}, \tag{2}$$

or as the resistance to heat flow at a surface of separation of two media having a known coefficient of heat transfer h (B Th U / sq ft hr °F), in which case

$$R = \frac{1}{Ah} \tag{3}$$

The most general case normally met with in insulation problems is that represented by two surface resistances, one at each face of the insulation, and the insulation itself being made up of a number of layers of different conductivity In this case equation (1) may be written

$$q = \frac{(\theta-\theta')}{\frac{1}{Ah}+\frac{X_1}{A_1k_1}+\frac{X_2}{A_2k_2}+\quad+\frac{X_n}{A_nk_n}+\frac{1}{A'h'}}, \tag{4}$$

where θ and θ' are the temperatures of the media on each side of a composite wall of insulation of total thickness $(X_1+X_2+\quad+X_n)$

Linear Flow between Parallel Planes

The application of this equation to the case of a large plane surface covered with insulation of uniform thickness presents no difficulties because here the area through which the heat flows is constant, i e

$$A = A_1 = A_2 = \quad = A_n = A'$$

We can therefore divide both sides of equation (4) by A to obtain a new equation in terms of q/A, the rate of heat flow per unit area which we will denote by Q (B Th U /sq ft hr)

$$Q = \frac{(\theta-\theta')}{\frac{1}{h}+\frac{X_1}{k_1}+\frac{X_2}{k_2}+\quad+\frac{X_n}{k_n}+\frac{1}{h'}} \tag{5}$$

The terms in the denominator are now thermal resistances *for unit area* of path In this case $X_1, X_2, \quad , X_n$, the thicknesses of the various layers of insulating material, and $k_1, k_2, \quad , k_n$, their thermal conductivities, must be known The heat transfer coefficient at inner and outer surfaces, h and h', must also be evaluated as explained later The heat loss per unit area can then be calculated from the known overall temperature difference or vice versa

If there are other surface resistances such as might occur due to an air space between two layers of insulation, these can be allowed for by adding another term $1/h''$ to the denominator

Radial Flow between Concentric Cylinders

The other case of great practical importance is the radial flow of heat from a cylindrical surface such as a steam pipe through a layer of insulation of uniform thickness In this case the application of equation (4) is not quite so simple because the area through which the heat actually flows is no longer constant It is, however, convenient in practice to calculate the heat flow through all the various layers in terms of heat loss per unit area of *one* particular surface, and the *outer* surface of the pipe insulation is chosen for this purpose because this is the surface at which there is a surface resistance which should always be taken into account

The rate of heat transfer through a single layer of cylindrical insulation per unit area of *outer* surface may be written in the form (see equation (11) in 'Principles of Heat Transfer')

$$\frac{q}{2\pi r_2 l} = Q_2 = \frac{(\theta_1-\theta_2)}{\frac{r_2\log_e(r_2/r_1)}{k}}, \tag{6}$$

where

θ_1 and θ_2 = temperature of inner and outer surfaces respectively,

r_1 and r_2 = inner and outer radii respectively

If this layer is regarded as one of the intermediate layers of a composite pipe covering which has an outer radius r_n, the heat flow must then be expressed in terms of a rate of heat flow per unit area of this outer surface as follows

$$\frac{q}{2\pi r' l} = Q' = \frac{(\theta_1-\theta_2)}{\dfrac{r_n \log_e(r_2/r_1)}{k}}. \qquad (7)$$

It will be noted that the expression $r_n \log_e(r_2/r_1)$ occupies the same position in equation (7) as the thickness terms X_1, X_2, &c , occupy in equation (5) It has the dimensions of a length, and, in fact, this logarithmic term is frequently referred to for convenience as the 'equivalent thickness' It is numerically equal to the thickness of material on a flat surface which would be required to give the same rate of heat transfer per square foot as that passing through the outer surface of the cylindrical surface of the insulation on the pipe

The resistance of the cylindrical layer of insulation between r_1 and r_2 per unit area of *outer* surface will therefore be seen to be equal to $r_n \log_e(r_2/r_1)/k$

The coefficient of heat transfer h' at the outer surface can clearly be used without modification as a surface resistance $1/h'$

The surface resistance at the *inner* surface may also be quite simply expressed in terms of the rate of heat flow per unit area of *outer* surface It is easy to see that the effective value of this resistance is increased in the ratio of the outer to the inner radii We must therefore write $(r_n/r)\times(1/h)$ in place of $1/h$

The equation for a composite pipe covering consisting of a series of cylindrical layers of insulation of uniform thickness, with a surface resistance at the inner and outer surfaces, can now be written down in terms of the rate of heat flow per unit area of *outer* surface as follows

$$Q' = (\theta-\theta')\Big/\left\{\left(\frac{r_n}{r}\times\frac{1}{h}\right)+\left(\frac{r_n \log_e(r_1/r)}{k_1}\right)+\right.$$
$$\left.+\left(\frac{r_n \log_e(r_2/r_1)}{k_2}\right)+ \quad +\left(\frac{r_n \log_e(r_n/r_{n-1})}{k_n}\right)+\frac{1}{h'}\right\}, \qquad (8)$$

where Q' = rate of heat flow per unit area of *outer* surface,
θ and θ' = temperatures of inner and outer media respectively,
h and h' = heat transfer coefficients at inner and outer surfaces respectively,
r and r_n = inner and outer radii respectively,
$r_1, r_2, \quad , r_n$ = outer radii of successive layers of insulation,
$k_1, k_2, \quad , k_n$ = conductivities of successive layers corresponding to above,
i e k_1 = conductivity of layer r to r_1,

k_n = conductivity of layer r_{n-1} to r_n

The similarity between equations (8) and (5) is apparent when it is remembered that the expressions $r_n \log_e(r_1/r)$, &c , take the place of the thicknesses X_1, &c , in equation (5) Thus writing

$X_1 = r_n \log_e(r_1/r)$,
$X_2 = r_n \log_e(r_2/r_1)$,

$X_n = r_n \log_e(r_n/r_{n-1})$,

equation (8) becomes

$$Q' = \frac{\theta-\theta'}{\dfrac{r_n}{r}\times\dfrac{1}{h}+\dfrac{X_1}{k_1}+\dfrac{X_2}{k_2} \quad +\dfrac{X_n}{k_n}+\dfrac{1}{h'}}. \qquad (8a)$$

The rate of heat flow per unit area of the inner surface (the pipe surface) can be simply calculated, if required, by multiplying Q' by the ratio of the outer to the inner radius thus

$$Q = \frac{r_n}{r}\times Q' \qquad (9)$$

The logarithmic terms in equation (8) are evaluated in the usual way from ordinary log tables using the identity

$$\log_e(r_1/r) = 2\ 301 \log_{10}(r_1/r)$$

The application of equation (5) may be illustrated by means of a composite wall consisting of two layers with two surface resistances, as shown in Fig 1, and may be expressed as follows

$$Q = \frac{(\theta-\theta_0)}{\dfrac{1}{h}} = \frac{(\theta_0-\theta_1)}{\dfrac{X_1}{k_1}} = \frac{(\theta_1-\theta_2)}{\dfrac{X_2}{k_2}} = \frac{\theta_2-\theta'}{\dfrac{1}{h'}} \qquad (10)$$

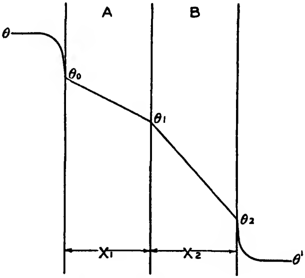

FIG. 1

If θ, θ', X_1, X_2 are known and h, h', k_1, k_2 can be estimated, it is possible to calculate the intermediate temperatures θ_0, θ_1, θ_2 by simple proportion Thus, working from the outside inwards, we have

$$\theta_2-\theta' = Q\times\frac{1}{h'} = (\theta-\theta')\times\frac{\dfrac{1}{h'}}{\left(\dfrac{1}{h}+\dfrac{X_1}{k_1}+\dfrac{X_2}{k_2}+\dfrac{1}{h'}\right)}, \qquad (11a)$$

and $\theta_1-\theta_2 = Q\times\dfrac{X_2}{k_2}$,

or

$$\theta_1-\theta' = Q\times\left(\frac{1}{h'}+\frac{X_2}{k_2}\right) = (\theta-\theta')\times\frac{\left(\dfrac{1}{h'}+\dfrac{X_2}{k_2}\right)}{\left(\dfrac{1}{h}+\dfrac{X_1}{k_1}+\dfrac{X_2}{k_2}+\dfrac{1}{h'}\right)}, \qquad (11b)$$

and similarly for θ_0 which is, however, more simply calculated from the inside temperature θ thus.

$$\theta-\theta_0 = Q\times\frac{1}{h} = \frac{\dfrac{1}{h}}{\left(\dfrac{1}{h}+\dfrac{X_1}{k_1}+\dfrac{X_2}{k_2}+\dfrac{1}{h'}\right)} \qquad (11c)$$

Alternatively, it may be simpler to calculate Q from equation (5) and then substitute successively in equation (10).

Calculation of Intermediate Temperatures

It is necessary to know the temperatures at intermediate points in a composite layer of insulation for two reasons Firstly, because the thermal conductivity of all insulating materials varies with the temperature and the mean conductivity of the material must therefore be known in order to calculate the heat loss Secondly, there is usually a fairly definite limit to the temperature at which any particular insulating material can be used, and as the high-temperature materials are the most expensive they are limited in practice to that fraction of the total thickness of insulation in which the temperature exceeds the safe temperature of the cheaper low-temperature material

In the cases under consideration there is the same rate of heat flow through each of the elements of construction of the composite insulation including the surface resistance The temperature drop across any individual element is therefore obviously proportional to its resistance

This simple method of calculating the intermediate temperatures assumes that the appropriate values for h, h', k_1, and k_2 are known beforehand As, unfortunately, these coefficients themselves depend to a considerable extent on the temperature they cannot be evaluated until the temperatures are known However, it is found in practice that if tables or curves are available giving the values of these coefficients over the range of temperature required, it is a simple matter to arrive at the correct solution to any problem by successive approximations

It must always be remembered in this connexion that in all practical calculations of thermal insulation there are usually several factors which cannot be evaluated exactly, so that, even if the thermal conductivity for the materials were accurately known, the calculation cannot be expected to be very exact For instance, it is impossible in practice to obtain perfect contact between surfaces, and therefore a slight difference in temperature between surfaces nominally in contact will always occur Unless a definite air space is formed between the layers of insulation, the contact resistance cannot be properly allowed for and has to be neglected The surface resistance at the external face of the insulation depends on various factors, as will be seen later, such as wind or draughts, surface emissivity, &c , and the effective temperature of the external medium θ' may be difficult to estimate, due, for instance, to the presence of hot radiating surfaces, sunshine, &c

Mean Conductivity

As already mentioned, the thermal conductivity of insulating materials varies with the temperature As a first step in any calculation the approximate temperatures of the materials are first guessed at and the corresponding thermal conductivities read from the tables or curves for the material. These conductivities are then used to calculate the temperatures in the lagging in order to choose the correct value for the conductivities

At this point we must decide what the correct conductivity is for use in the equations given above when there is a substantial difference in temperature between the two sides of any particular layer It is shown in the article on 'Principles of Heat Transfer' that the correct value in all such cases is the true mean value obtained by integrating the conductivity over the range of temperature However, in nearly all practical cases the conductivity can be taken to be a linear function of the temperature, at least over the range of temperature under discussion, in which case the true mean conductivity is equal to the conductivity at the arithmetic mean of the upper and lower limits of temperature.

Surface Resistance

Thermal insulation is applied in a great variety of circumstances in the petroleum industry, but there is nearly always one surface resistance to be taken into account, namely, at the outside surface of the insulation in contact with the air, as. for instance, with lagged steam pipes or fractionating towers In such cases, with the insulation fitting closely to the metal wall, this is the only surface resistance which need be considered because the temperatures of the metal walls are known

In other cases, such as the insulating walls of a cold-room or a duct carrying preheated air to a furnace, there is a similar surface resistance on the inside to be allowed for in calculating the transfer of heat from the air on one side of the insulation to the air on the other side

It will, of course, be realized that with properly designed lagging the surface resistance is only a minor factor in determining the heat flow, and in such cases only an approximate calculation is necessary On the other hand, the surface resistance is obviously the most important factor in controlling the temperature of the surface of the lagging, and this is of importance in the lagging of pipes carrying cold brine when condensation of dew from the atmosphere is to be avoided [5, 1936]

In this article only the usual case of heat transfer from a surface in contact with air will be considered Reference must be made to the article on the 'Principles of Heat Transfer' for methods of calculating the heat transfer coefficient in other circumstances and also for the principles underlying the radiation and convection of heat from solid surfaces which together determine the surface resistance

The heat transfer coefficient due to radiation h_r must be determined independently of that due to convection h_c as shown below The surface resistance for unit area is then given by $1/(h_r+h_c)$

Radiation Effect

Heat transfer by radiation is defined by the Stefan-Bolzman law, but for the present purpose it is required in terms of a heat transfer coefficient h as follows for British units

$$h_r = \frac{0\ 174\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]F_e F_s}{(T_1 - T_2)}, \qquad (12)$$

where h_r = heat transfer coefficient (B Th U /sq ft hr °F.),
T_1 = temperature of radiating surface (° Rankine),
T_2 = temperature of surroundings (° Rankine),
F_e = emissivity factor,
F_s = factor of geometrical arrangement

The factor F_s depends on the emissivities of the surfaces and the geometrical arrangement and varies between e_1, when the radiating body is small compared with the distance to the surroundings, and

$$\frac{1}{\frac{1}{e_1}+\frac{1}{e_2}-1},$$

when the distance is small compared with the radiating surfaces e_1 and e_2, being the emissivities of the radiating surface and the surroundings respectively

The factor F_s is equal to 1·0 when, as in the present instance, a complete body as distinct from elements of two radiating surfaces is considered

The emissivity of particular surfaces can be obtained from tables of this property, but it will be found that, apart from polished metallic surfaces, ordinary materials such as brick, wood, concrete, plaster, as well as all non-metallic paints irrespective of colour, have emissivities differing little from 0·90 to 0·95 The factor F_e will then vary between 0·95 and 0·81, and the value 0·90 may be used with sufficient accuracy in most cases

The value of h_r calculated by equation (12), using a value of $F_e \times F_s = 1{\cdot}0$, is shown as a family of curves in Fig 2 to save calculation, in which θ_1 and θ_2 indicate the temperatures in ° F corresponding to the absolute temperatures T_1 and T_2 in ° Rankine

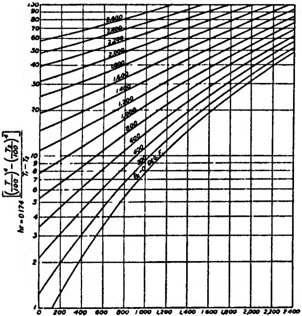

FIG 2

Convection Effect

The heat loss by natural convection from large surfaces is proportional to the five-fourths power of the temperature difference, and therefore the heat transfer coefficient is proportional to the one-fourth power For large vertical surfaces it is given with reasonable accuracy in British units by the equation

$$h_c = 0{\cdot}28(\theta_s - \theta_a)^{\frac{1}{4}}, \qquad (13)$$

where h_c = heat transfer coefficient (B Th U / sq ft hr °F),
θ_s = temperature of surface (° F),
θ_a = temperature of air (° F)

For horizontal surfaces facing upwards and hotter than the air or facing downwards and colder than the air the values given by equation (13) should be increased by 30%, and for horizontal surfaces facing upwards and colder than the air or facing downwards and hotter than the air the values should be decreased by about 30% [11, 1935]

For a hot ceiling or a cold floor the convection should theoretically be zero, but owing to convection currents from the walls and other sources of disturbance a good value to use appears to be about 35% of that given by equation (13)

For horizontal and vertical cylindrical surfaces the coefficient increases considerably as the diameter is decreased below about 2 ft , and the factor for use in equation (13) in place of 0·28 is shown in Fig 3

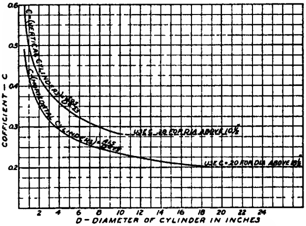

FIG 3

For short vertical surfaces the coefficient is also greater than for tall The percentage increase in the coefficient for vertical cylinders shorter than 2 ft is shown in Fig 4

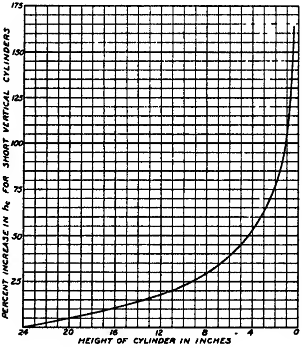

FIG 4

The effect of comparatively small air velocities past a surface is to increase the heat transfer coefficient at the surface very greatly

For the purpose of calculating the heat transfer coefficient for air velocities up to 1,000 ft per minute the following equation is recommended

$$h_{cv} = (1{\cdot}09 + 0{\cdot}0038V)h_c, \qquad (14a)$$

and above 2,000 ft per minute,

$$h_{cv} = (0\,022V^{0.78})h_c, \tag{14b}$$

where

h_{cv} = heat transfer coefficient for velocity V (B Th U / sq ft hr °F),
h_c = heat transfer coefficient by equation (13) (B Th U / sq ft hr °F),
V = air velocity in ft per minute

The curves in Fig 5 show the combined heat transfer coefficient due to radiation and convection for flat vertical surfaces by means of the above equations for a range of surface temperatures and air velocities, assuming an emissivity factor of 0 90 and a temperature of 80° F for the air and surroundings

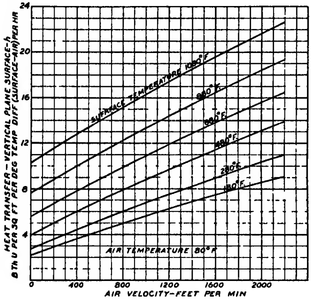

Fig 5

The above discussion as to effect of adjacent air movement on losses through insulation is based on flow of air over the surface of the insulation, and only applies to cases where the insulation is tightly sealed If the condition of the insulation is such that the air may circulate through cracks and crevices in the insulation, the increases may be far greater than those given above Therefore, it is essential that all insulation be sealed as tightly as possible this is particularly true of insulation located out of doors

Economical Thickness of Insulation

The engineer is frequently called upon to determine what thickness of insulation will give the most economical results under specified conditions of service It is apparent that beyond the limits of a certain thickness, the saving which will result for added increments of insulation will be insufficient to justify the additional cost The following rational method for arriving at the optimum thickness of material for use has been discussed in detail by McMillan [8, 1926]

The solution of a problem in the economics of insulation thickness involves the following controlling factors, each of which must be first definitely determined

1. **Hours of Operation per Year (Y)** When the equipment will not be in operation for the entire year, the actual number of hours per year that heat energy is supplied should be used

2. **Temperature Difference ($\theta_1-\theta_a$)** θ_1 is the temperature of the warmer surface to which the insulation will be applied and θ_a the temperature of the air surrounding the equipment The solution is not dependent upon the heat loss from the uninsulated equipment, but it does assume that θ_1 remains constant with varying amounts of insulation in place This condition is met exactly in some cases, such as for saturated vapour lines. For some other conditions, as in temperature-controlled furnaces, constancy of θ_1 is closely obtained

3 **Cost of Heat (M)** This factor will necessarily vary with the type of fuel burned, location of plant or equipment, &c The actual value of heat at the point where insulation is to be applied should be used, expressed in dollars per million available B Th U

4. **Conductivity of Insulation (k)** The actual value of this factor is necessarily dependent upon the mean temperature of a material of unknown thickness The inner surface temperature θ_1 will be known, and it is, therefore, necessary to assume a value for the mean temperature from which a determination of k is made by reference to curves or tables This assumed value can be readily checked after solution of the problem However, it is seldom found necessary to make a second determination, unless the conductivity of the material increases very rapidly with temperature

5. **Cost of Insulation (c)** This factor is the cost of the material plus its application costs, expressed in dollars per square foot per inch of thickness It should be remembered that the total applied cost for a greater thickness is less than would be expected from the list prices of the thicker insulation However, if it is assumed that the applied cost is directly proportional to thickness, this assumption should not affect the precision of the final result to such an extent as to require a second determination The thickness chosen for use will naturally be the commercially available thickness nearest that determined

6 **Per cent Annual Fixed Charges (d)** This factor includes the return desired on the investment, depreciation, insurance, &c Hence it is the total annual fixed charges as applied against the total applied cost of the insulation expressed as a percentage

7 **Thermal Resistance of Uninsulated Structure (R)** This factor is the sum of the resistances of all other elements in the construction, including any surface resistances

As the thickness of insulation applied to a piece of equipment or to a construction is increased, the cost of the heat lost per year is decreased, but the annual cost of insulation (first cost multiplied by per cent fixed charges) is increased Therefore, the thickness at which the sum of these two costs is a minimum is obviously the most economical or the optimum thickness Where only one material is desired for application to a flat surface, this thickness may be determined from the equation

$$L = \sqrt{\left(\frac{ak}{b}\right)} - Rk, \tag{15}$$

in which L is the optimum thickness, k is the conductivity, b is the annual cost of insulation per inch of thickness ($b = cd$), R is the combined thermal resistance of all other elements in the construction, and the factor

$$a = 10^{-6}Y(\theta_1-\theta_a)M, \tag{16}$$

in which the terms have been defined above Table I gives values of a for various temperature differences and various values of heat The value of Y is taken as 8,760, i e one full working year

TABLE I

Values of a

Temp diff, °F	Value of heat in dollars per million available B Th U									
	0 10	0 20	0 30	0·40	0 50	0 60	0·70	0 80	0·90	1 00
100	0·088	0 175	0 263	0 350	0·438	0 526	0 613	0·701	0 788	0 876
200	0 175	0 350	0 526	0 701	0·876	1 051	1 226	1 402	1 577	1 752
300	0 263	0 526	0 788	1 051	1 314	1 577	1 840	2 102	2 365	2 628
400	0 350	0 701	1 051	1 402	1 752	2 102	2 453	2 803	3 154	3 504
500	0 438	0 876	1 314	1 752	2 190	2 628	3 066	3 504	3 942	4 380
600	0·526	1 051	1 577	2 102	2 628	3 154	3 679	4 205	4 730	5 256
700	0 613	1 226	1 840	2 453	3 066	3 679	4 292	4 906	5 519	6 132
800	0 701	1 402	2 102	2 803	3 504	4 205	4 906	5 606	6 307	7 008
900	0 788	1 577	2 365	3 154	3 942	4 730	5 519	6 307	7 096	7 884
1,000	0 876	1 752	2 628	3 504	4 380	5 256	6 132	7 008	7 884	8 760

Composite Insulation

It is frequently necessary to apply more than one type of material to the hot surface of equipment In such cases the outer layer of material has high insulation efficiency, but its use is limited by the temperature at which physical or chemical alterations may occur Hence an inner layer of a more refractory material is first applied, which can withstand the higher temperatures, but which may have lower insulation efficiency This case has been analysed by Patton [9, 1932], who gives the following rational method of solution

The problem consists in first applying an inner layer of material of such thickness that its outside surface will be at a temperature sufficiently low for safe application of the outer layer of material, and second in making the selection of the optimum thickness of each material commensurate with the first condition It is obvious that the outer layer of the more efficient material should be applied as soon as the outer surface temperature of the inner layer will permit The solution of this problem then requires the following data additional to those outlined above

1. **Temperature between Layers (θ_2)** θ_2 is the temperature at which it will be safe to apply the outer layer of material This temperature will not be more than the temperature at which physical or chemical alteration of the outer layer will occur The temperature drop through the inner layer of material will then be $(\theta_1-\theta_2)$, while $(\theta_2-\theta_a)$ will represent the difference in temperature between that of the inner surface of the outer material and that of the surrounding air

2. **Conductivities of Materials (k_1 and k_2)** The conductivity of the inner and outer layers of material at their mean temperatures under the conditions of operation are k_1 and k_2 respectively

3. **Costs of Materials (c_1 and c_2)** The total applied costs, as above, per inch of thickness for the inner and outer layers of material are represented by c_1 and c_2 respectively

The optimum thickness of the outer layer of material applied to a flat surface can be expressed as

$$L_2 = \frac{1}{10^3}k_2(\theta_2-\theta_a)\sqrt{\left(\frac{YM}{dc_1k_1(\theta_1-\theta_2)+dc_2k_2(\theta_2-\theta_a)}\right)}-Rk_2 \tag{17}$$

The optimum thickness of the inner layer of the more highly refractory material may then be determined by the equation

$$L_1 = \frac{k_1(\theta_1-\theta_2)}{k_2(\theta_2-\theta_a)}(L_2+Rk_2). \tag{18}$$

In the case of pipe surfaces McMillan [8, 1926] states that the equation for economical thickness is not quite so simple, yet that it is by no means as formidable as it appears at first sight For one material, the cost of which may be expressed by the equation

$$\text{Cost per linear foot} = \frac{2\pi r_2 b}{12}(r_2-r_1)+(\text{a constant}), \tag{19}$$

$$\left(r_2\log_e\frac{r_2}{r_1}+R_sk\right)\sqrt{\left(\frac{2r_2-r_1}{r_2-R_sk}\right)} = \sqrt{\left(\frac{ak}{b}\right)} \tag{20}$$

All terms in these equations have previously been defined except R_s which is surface resistance $= 1/h$

The so-called 'Standard List Prices' of sectional pipe insulation are in reasonably close agreement with equation (19) for thicknesses greater than 1 in Prices of natural cork, rock cork, hair felt, mineral and rock-wool pipe coverings do not agree with 'Standard List', and therefore these equations, (19), (20), and (21), do not apply to these materials

Recognizing that the first term within the parentheses is equivalent thickness, the close similarity to equation (15) is at once apparent, since equation (15) may be written for one material

$$L+R_sk = \sqrt{\left(\frac{ak}{b}\right)}$$

Before proceeding with the solution of equation (20), the equation for economical thickness of the outer layer of insulation over one or more layers of materials having different conductivities will be written, since the same charts may be used for the solution of equations involving all such combinations This equation, given below, is written for a combination of two materials, but for more than two the equation is of exactly the same form The only difference will be the addition of other terms like the second term inside the brackets and the substitution of appropriate values of r where r_s appears in the equation

$$\left[r_s\log_e\frac{r_s}{r_2}+\frac{r_s}{r_1}\left(\frac{r_1\log_e\frac{r_2}{r_1}}{k_1}\right)k+R_sk\right]\sqrt{\left(\frac{2r_s-r_2}{r_s-R_sk}\right)} = \sqrt{\left(\frac{ak}{b}\right)} \tag{21}$$

In this equation all terms have been previously defined

The solution of equation (21) for 16-in pipe is illustrated in Fig 6, a, k, and b are established by the conditions of

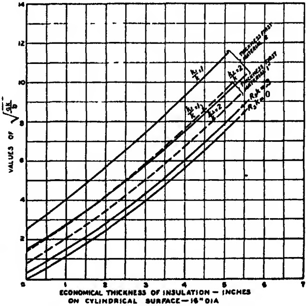

Fig 6

the problem. Knowing the value of $\sqrt{(ak/b)}$ the economical thickness may be read directly from the chart. For example, if $\sqrt{(ak/b)} = 4{\cdot}0$, and if no surface resistance is to be considered, the economical thickness is 3 03 in If $R_s k = 0\ 3$ in, the economical thickness is 2 80 in If there is a first layer of material 1 in thick, and if the conductivity of that layer is 2 0 times that of the second layer (and $R_s k = 0\ 3$), the economical thickness of the second layer is 2 38 in For intermediate values interpolations may be made Naturally the thickness chosen would be the commercially available thickness nearest the thickness found on the chart

The solution is graphical, it is true, and it may be asked why not, then, make a graphical solution in the first place by plotting the sum of the losses per year and costs per year for a number of thicknesses and taking the low point as the economical thickness? The answer is, that each solution by that or other equivalent methods requires a number of calculations, the plotting of a curve, and the location of the minimum point or the point where tangents are parallel, all of which is tedious, and the last step of which is likely to be highly inaccurate, while the solution described above requires but a few moments once the charts have been prepared

The chart illustrated in Fig 7 is applicable to the instant solution of most problems where a single material is involved It is based on $R_s k = 0\ 3$ in, which is fairly representative of good insulating materials under average still-air conditions Even if $R_s k$ for the given case differs considerably from the value of 0 3 in, the change in economical thickness will usually be so small as to be practically negligible However, if somewhat greater accuracy is required, correction may be made by adding to the thickness given by the chart the amount in inches by which $R_s k$ is less than 0 3 in or subtracting from the thickness the amount by which $R_s k$ exceeds 0 3 in Where absolute accuracy is required, and where combinations of materials are involved, it is necessary to use a chart such as Fig 6 for each pipe size

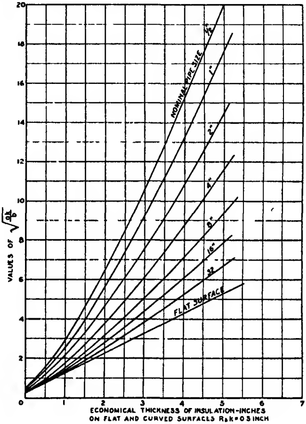

Fig 7

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INSULATION OF OIL INDUSTRY EQUIPMENT

By EVAN RINEHART

Johns-Manville Sales Corporation

OIL industry equipment may be insulated for one or more of several purposes, including fuel conservation, control of operating temperatures, reduction of thermal stresses, fireproofing of structural members and equipment, reduction of evaporation losses, maintaining low viscosity for pumping

The insulation of refinery equipment introduces the special problem of providing for the considerable expansion and contraction of the high-temperature pieces as well as securing a finish that is thoroughly waterproof and fireproof Many conditions also demand protection of the insulation against severe mechanical abuse

The economics of insulation brings in the relatively high equipment obsolescense in oil refining, which, however, is offset by the hard, driving service and the market value of refinery products per unit of equipment, meriting the best insulation procurable for the operating life of the apparatus

Since the objective with any insulation is generally to secure sustained efficiency, the material used should not be susceptible to either physical disintegration or increase in conductivity, under the conditions of service This implies stability in thermal characteristics and a resistance to cracking, shrinking, or settling which involves both the method of application and the type of insulating material used

With temperatures in the various classes of equipment from −60° F to 1,000° F, and with much higher furnace temperatures, several types of insulation are required Any one type is efficient only for a fairly definite range of temperature General practice is represented by the following table

Temp range, ° F	*Material*
—400–125	Cork
	Rock cork*
	Hair felt
125–600	85% Magnesia
	Asbestos-sponge felted
	Rock wool (up to 1,000° F)
600–1,600	Diatomaceous earth blocks
	Diatomaceous earth brick
	Insulating cements
1,600–1,900	Diatomaceous earth blocks
	Calcined diatomaceous earth brick
1,900–2,500	Calcined diatomaceous earth brick

* Rock cork is a material manufactured from a loose rock wool bonded with an asphaltic waterproofing compound

With greater ability of an insulating material to resist higher temperatures comes a decrease in its insulating property at lower temperatures Also, materials sufficiently refractory to remain stable at the higher temperatures are generally more costly than those suitable for lower temperatures Therefore, it is sound practice in the insulation of high-temperature equipment, such as the soaking drums of cracking plants, to use only enough thickness of the high-temperature insulator to reduce the temperature sufficiently on a supplemental layer of the more efficient (lower limit) material A standard combination of this type is diatomaceous earth blocks against the equipment followed by magnesia, the respective thicknesses of which can be varied to meet any temperature condition up to 1,900° F.

Insulation of Towers, Soaking Drums, Exchangers, &c.

Equipment insulation is used in the following forms

Blocks or sheets—(usually 24 in × 36 in, or fractions thereof), flat or curved to conform to equipment radius

Blankets—(usually 24 in × 96 in or fractions thereof) If made of rock wool it is enclosed in mesh wire or expanded metal

Cements—(in bags) of either asbestos, rock wool, diatomaceous earth or expanded mica base, combined with adhesive cements or clays and watered to trowelling consistency at the site of the work

Fillers—of asbestos or rock wool fibres (may be enclosed in metal containers)

Blocks and blankets are given a cement finish to afford a base for the final waterproofing agent For equipment such as vertical towers, soaking drums, or horizontal heat exchangers, the block type of insulation, laid up in broken joint construction, with each layer secured with wires, and finished off with cement and plastic waterproofing, is generally preferred Not only can the combination of high and moderate temperature blocks be varied in thickness to give the highest efficiency, but their application lends itself to standardized results However, the outstanding advantage of block or pre-moulded insulation is the uniformity of the product as it is manufactured under controllable conditions

Blankets are, by their nature, subject to non-uniformity of density as made, and to greater deformation as applied The lacing for securing their imposition is apt to produce bulges and flats, with eventual cracking of the cement coating and ingress of moisture A greater thickness of blanket insulation than is specified for pre-moulded block insulation is advisable

Cement insulation, termed 'monolithic', has had some degree of acceptance, due to its somewhat lower first cost and its workability around irregular surfaces The cement is applied in a series of ½-in to 1-in coats, each wire mesh reinforced, with a finish ¼-in coat and a final waterproofing

From an insulating standpoint, one objection is the considerable difference in density and conductivity which the various pressures in the trowelling exert on the cement Moreover, dehydration produces inevitable shrinkage cracks

From the standpoint of application, each cement coat must be separately dried before application of the succeeding coat, necessitating considerable steam on the interior of the vessel and prolonging the construction period far beyond that necessary for block application. Also, the cement insulation requires a greater attention to expansion joints

Insulating cements are readily available in such a form as to need only the addition of water for application. As such they are generally superior to cements composed of various ingredients that are ordered separately and mixed on the job, where the personal equation of the job labourer enters into the accuracy of measuring and the thoroughness of mixing, apart from the addition time and expense involved.

The cement form of insulation is particularly adaptable to treatment of tube plates and headers, the lining of tube doors, and the insulation of very irregular surfaces

Fillers in metal containers have not met with any degree of acceptance for the insulation of refinery equipment

The following table gives combinations and thicknesses of block type insulation representative of standard practice for the insulation of flat or slightly curved surfaces The diatomaceous earth type of block insulation is in itself satisfactory for temperatures up to 1,900° F, but for economy and efficiency it is combined with another lower limit material, as shown The thickness of the first layer should not be reduced below that shown in the table, to avoid excessive temperatures on the second layer The thickness of the second layer is an economic balance between normal costs of the complete insulation in place, and average values of heat saved, but can be increased or decreased for special conditions.

Typical Block or Sheet Type Insulation

Maximum temp of insulated surface, ° F	*Thickness of diatomaceous earth blocks in*	*Thickness of 85% magnesia or of asbestos-sponge felted, in*	*Total thickness including ½-in cement and 3/16-in W P in*
300		2	2 11/16
400		2½	3 3/16
500		3	3 11/16
600		3½	4 3/16
750	1½	2½	4 11/16
900	2	2	4 11/16
1,000	2½	2	5 3/16
1,200	3½	1½	5 11/16

For extreme conditions, such as those involving processing by electric heat, where much heavier insulation is desired, both inner and outer layer would be increased in thickness, since increasing only the outer layer raises the temperature of its inner face This is illustrated by Fig 1 in which 'Superex' is a typical diatomaceous earth-asbestos block made by Johns-Manville

The table below gives typical thicknesses for cement type insulation of the diatomaceous earth-rock wool or expanded mica types of cement, mixed with hydrated lime, Bentonite clay, or other binders

Temp range, ° F	*No layers of cement*	*Approx thickness per layer, in*	*Total thickness, in*
Below 150	2	¾	1¾
150–200	3	11/16	2¼
200–300	3	⅞	2¾
300–400	3	1	3¼
400–550	4	⅞	3¾
550–700	4	1	4¼
700–850	5	⅞	4⅝
850–1,000	5	1	5¼

Where used for fireproofing, the cement insulation is usually specified at 1¾-in minimum thickness including the weatherproof coat, which is to be about 3/16 in thick when dry

Application.

A 40-ft soaking drum at 900° F has lengthened about 4 in from the atmosphere temperature at which the insulation was applied Since no insulation material approaches the expansion coefficient of steel, this condition must be met by introducing workable expansion joints in the insulation. A typical joint is shown in Fig. 2.

Thorough waterproofing of exposed insulation is probably the most neglected of any of the essentials Not only does moisture markedly reduce the effectiveness of any insulating material, but it also imposes an additional heating load on the equipment

In order to secure a base for the actual waterproofing agent, it is necessary to apply several thin, wire-reinforced coats of cement to the insulation The first coat is customarily a long-fibre asbestos cement, for resistance to cracking The second coat is a mixture of asbestos cement and portland cement, trowelled to a hard finish To this, when the cement has set, is applied the actual waterproofing, which deserves consideration in its selection

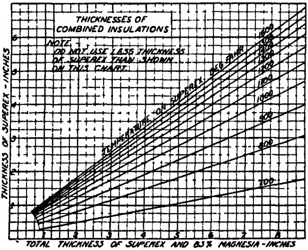


Fig 1 Thicknesses of combination insulation for high temperatures

Asphaltic paints will sag or run, or if of high melting-point, will check and crack Coal-tar pitches, with even lower temperature ranges, will oxidize under weather exposure Apparently the most satisfactory material is the manufactured mixture of properly processed emulsified asphalt and asbestos fibre This is trowelled on about ¼ in thick, usually with a reinforcing mesh wire incorporated The normal dehydration shrinkage leaves a tough, rubbery ⅛-in coating that is not only waterproof but also is fireproof

Fireproofness is another requisite of any refinery insulation particularly around a battery of stills This includes the piping insulation An ordinary roofing felt as weather protection on a pipe leading to overhead equipment offers a communicating link to any fire hazard at ground-level Such lines should be waterproofed as above described or wrapped with a fire-retardant (non-asphaltic) type of roofing jacket, or encased in metal

Some parts of heated equipment require removable and replaceable insulation, whether to admit of periodic inspection or for such operations as removal of manhole covers Since the heat loss at 800° F for only 3·0 sq ft approaches 15,000 B Th U per hour, the economy of providing covers for such locations is apparent Either quilted asbestos blankets or pre-cast block insulation is adaptable to removability and replacement.

Insulation of Towers and Drums

The general method of applying insulation to towers involves spot-welding angle clips circumferentially around the bottom head and boltıng thereto a curved ıron band This band iron serves as an anchor for the lacing wires supporting the insulating blocks on the head and as a support for the insulation on the shell above it

Similar circumferential band iron supports are located at intervals of not more than 15 ft on the height of the tower A band iron anchor for lacing wires is also located circumferentially around the top head Bent angle iron rings welded directly to the shell may be used instead of clips and band iron These arrangements are illustrated in Fig 3

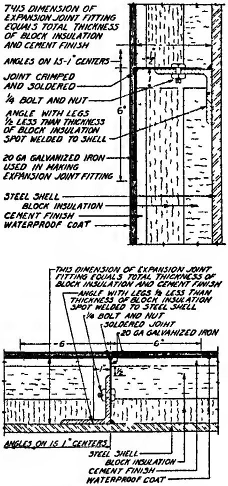


FIG 2 Insulation expansion joint for use on horizontal drums

Insulation on such heads is secured by means of lacing wires running diagonally between the band iron anchors and ⅜-in pencil rod iron around the manheads

Insulation on the shell is secured by circumferential lacing wires on 12-in centres. Flat metal straps approximately ¾ in × 0 020 in find excellent application in some of this work, and stranded wire cable is also frequently used

Where removable insulation over longitudinal or circumferential riveted seams is required, to permit caulking of rivets and joints, extra clip and band iron work is necessary

Fig. 3 shows block insulation method for manhole covers An asbestos blanket insulation cover, for use where manheads are frequently removed, secured with a spring inside the flange, is frequently used.

Insulation of Horizontal Vessels (Exchangers, Drums, Partial Condensers, &c.)

Horizontal vessels are insulated with the same type and thickness of insulation as indicated for towers Provision should be made for supporting the upper and lower halves of the main body insulation of large diameter drums by erecting angle iron channels, or band iron on angle clips along the centre line The insulation of the lower half is preferably supported by iron bands Where removability of the heads is a feature, angle iron or band iron is provided inside the bolt circle, punched for lacing wires Separate removable and replaceable flange covers are made of the insulating blocks and cement on wire mesh covered with ‘hardware cloth’

For vessels with permanent heads, angle iron clips are welded at intervals around the circumference, the clips being punched for lacing wires, at times being supplemented by ⅜-in pencil rod wire passed through holes in the clips

For resistance to mechanical abuse, steel jackets can be fitted over the main body, or over the removable heads or over both In such cases it is customary to omit the plastic waterproofing, but not the cement coats over the insulation

Because of the considerable movement and distortion of cylindrical shell stills, the insulating shells or blocks must be well secured and the furnace setting sealed at junction with the shell

In a continuous battery of these stills, each operating at a different temperature, it is customary to strike an average and insulate the entire battery with the same thickness of material This is of advantage since the operation of a battery is occasionally reversed

Interior Lining of Refinery Equipment

Pressure drums and reaction chambers are sometimes fitted with an interior lining as a protection against corrosion and as a means of securing a reduction in temperature on the inner steel face

Ceramic materials, either concrete or various mixtures of ganister or other refractories with cement and brick, are widely used The customary thickness is 2 in reinforced for a plastic application However, the high conductivity of such materials precludes any substantial temperature drop through them and the adhesion of the coke, with subsequent spalling of the lining, involves continual repairs

Asbestos cement blocks have been used with success, the surface offering less adhesion to the coke The blocks about 9 in × 18 in and 2 in thick are made with the proper curvature to fit the shell The blocks are supported vertically at approximately 6 ft intervals by circumferential bar iron or angle, welded to the shell

A ⅛ in thick layer of asbestos millboard is first cemented to the shell, and followed by a second layer, not bonded to the first, but with a plastic refractory cement coat on its inner face. The asbestos cement blocks are then placed, and pressed firmly into the plastic The blocks are laid up with a 1/16-in refractory cement joint The object of the two asbestos millboard layers, one bonded to the shell and the other to the blocks, is to provide for the relative movement of the blocks and the steel shell when heated to operating temperature Similar strips of the asbestos millboard at the angle supports allow for the difference in the expansions.

Blocks for the dome are made to conform to the double curvature, and are supported by a bar or an angle welded to the inside at the junction of cylindrical section and dome

Where a predetermined temperature drop of substantial amount through the lining is essential, a considerable thickness of insulating concrete is demanded In one instance where the shell was 40 ft high and 10 ft in diameter, the insulation consisted of 24 in of Sil-O-Cel C-3 Insulating Concrete on the sides and 36 in on the bottom.

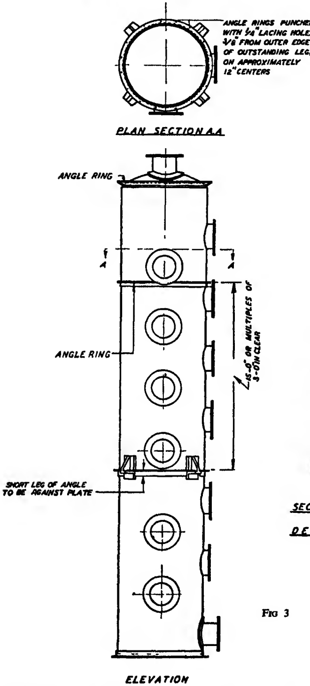


FIG 3

Insulation of Furnaces

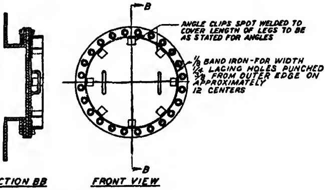
The main object of the walls of a furnace is to form a container or setting that is as free as possible from external heat losses. Owing to the fact that the conductivity of firebrick is over ten times that of a suitable insulating material, furnace construction should embody only the brickwork that is required for refractory purposes and of sufficient thickness to give this refractory structural stability For the great majority of designs, 13½ in of firebrick more than meets these requirements

With a 13½-in firebrick wall, at a furnace temperature of 1,600° F, the radiation loss to the exterior is about 750 B Th U per sq ft hr and at 2,400° F furnace temperature the radiation loss is approximately 1,300 B Th U per sq ft hr If exposed to an average ten-mile wind, these losses would be considerably raised

This means a clear loss of approximately 700 and 1,400 B Th U per sq ft per hour for the 1,600° and 2,400° furnace temperature, respectively However, by applying the conventional 3 in of diatomaceous insulating blocks and a suitable casing, the losses are reduced to 200 and 400 B Th U per sq ft per hour, respectively The insulation expense is saved in 12 to 18 months, aside from the other advantages mentioned later

Apart from the actual fuel conservation is the fact that the insulated wall maintains a higher inner face temperature, which by radiation maintains a more uniform temperature in the furnace

The objection is sometimes made to this that the temperatures of refractories are raised by the insulation For years boiler and industrial furnace manufacturers were of the same opinion, and yet to-day we find insulation applied to the exterior of steel-treating furnaces, to open-hearth regenerators, and to glass-tank regenerators, all with eminently satisfactorily results, and at much higher furnace temperatures From the standpoint of structural integrity, the application of insulation to a firebrick lining means the lessening of internal strains and reduction in spalling because of the smaller temperature difference between the inside and outside of the refractory Wall cracks, caused by uneven expansion and contraction, are fewer and smaller since sharp temperature changes are obviated and adjacent brickwork is protected against widely varying rates of expansion. Properly applied, the insulation tends to seal cracks in furnace walls and prevents infiltration of air or the extrusion of furnace gases



DETAIL OF MANHEAD COVER

The thickness of the insulation is governed structurally by its hot surface temperature limit or refractory value which, in turn, depends on (*a*) the thickness of the firebrick and/or insulating-refractory interposed between the furnace gases and the insulation, and (*b*) on the thickness of the block insulation proper

For instance, assuming a furnace temperature of 2,200° F diatomaceous earth-asbestos insulating blocks with a temperature limit of 1,900° F could be used 4½ in thick on a 13½-in firebrick wall, but only 2 in thick for a 4½-in firebrick wall, without endangering a break-down of the blocks

The thickness of the firebrick and/or insulating refractory brick also depends on a method of construction, height of the wall, and whether or not it has any load-bearing function Generally speaking, the calcined diatomaceous type of brick may be used with temperatures up to 2,000° F on it, erected either in place of firebrick, except for erosive fuel, or as insulation on the outside of firebrick

Diatomaceous bricks of higher calcination (such as Sil-O-Cel Super Brick) may be used for temperatures up to 2,500° F, with a firebrick lining, but not for direct exposure in place of firebrick

Uncalcined natural diatomaceous bricks such as Sil-O-Cel have a temperature limit of 1,600° F, as used with a firebrick lining for furnace work Diatomaceous earth-asbestos blocks are efficient for a maximum temperature of 1,900° F, with an interposed brick lining for furnace work

Combinations of diatomaceous earth-asbestos blocks and magnesia are often used outside the brick furnace lining, the various thicknesses being proportioned to give a maximum of 600° F on the magnesia

The use of insulating refractory brick, without any interior lining, in place of firebrick, is now well established for furnace temperatures up to the limit set by the brick manufacturer

Such construction makes possible thinner surface walls, improved efficiency, and lower operating costs It combines all of the characteristics essential to a highly efficient insulating refractory, including heat resistance, exceptional insulating qualities, low heat absorption, unusually high compressive and tensile strength, and ample load-bearing capacity under high temperatures

It must be borne in mind that, generally speaking, the higher the temperature limit of the insulating refractory, the lower its efficiency as an insulator, when such limit approaches that of a good grade firebrick, it is generally necessary to apply supplemental insulating in order to secure a low overall heat transmission

There are several methods of applying insulation over brick settings which are equally efficacious but applicable to different constructions All of these methods involve the use of insulating blocks or bricks, and care is taken in each case that the main supporting steel be left sufficiently exposed to the air so that its strength will not be affected by the heat

It has been found entirely satisfactory to apply suitable insulation between the brickwork and buckstays except at points of unusual thrust, such as opposite the arches, or where castings and steelwork are to be hung into the brickwork In such locations the firebrick is carried through the insulation to the outside of the furnace

When it is expedient to erect the furnace brickwork before the casing is applied, a space equivalent to the thickness of the insulation is left between the outside face of the brick and the inside face of the buckstays Then insulating blocks or bricks are erected to fill this space, and the transite or steel casing secured in place flush with the back of the buckstays by steel battens and toggle bolts, or by other suitable means

When the furnace brickwork is erected flush with the back of the buckstays, light angles may be clipped or spot-welded to the buckstays to allow the application of insulation between vertical steel members These angles serve to support the casing, which may be ⅜-in asbestos-cement sheets of ⅛-in steel A typical arrangement is shown in Fig 4

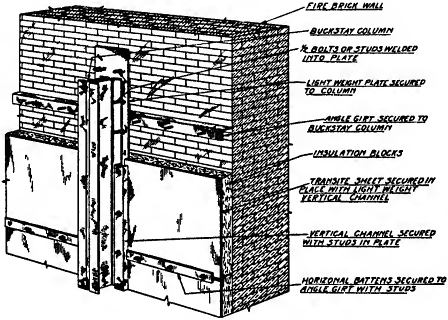


Fig 4

In oil-refinery practice it is customary to erect casings before brickwork The insulation is applied next to the casing and the firebrick laid snugly against the insulation

The designers of several of the well-known processes have found that ordinary brick settings may sometimes economically be replaced by air-cooled walls and suspended arches over the hotter portions of the furnaces In all these designs air is drawn over the exterior brick surface (suspended or otherwise) either by fans, by natural draft, or by burner induction The circulation varies with the different designs, but it is always necessary to make use of some sort of casing over the air-passages, whose function is to retain heat recovered by the air, furnish a suitable clearance for air travel so that adequate scrubbing action is obtained without undue friction loss, and to prevent the infiltration of air. Furthermore, the construction should be fireproof and able successfully to withstand abrasion, ordinary mechanical impact, and high temperature

A favourite casing specification is made up of outside panels of ⅜-in. asbestos-cement sheets, 1-in. high temperature insulating blocks, and inside panels of $\frac{3}{16}$-in asbestos-cement sheets Steel is sometimes used for the outside panelling This form of construction offers superior insulating qualities with a minimum of thickness

Development of oil-heating apparatus embodying radiant tubes along the furnace walls admitted of lighter wall construction, with the reduction in wall temperatures resulting from the heat absorption by the tubes At the same time, since the wall radiates heat directly to the closely adjacent tubes, and this radiation depends directly on the wall temperature, the wall should be thoroughly insulated to maintain it at as high a temperature as possible

The usual construction embodies an insulating refractory brick wall, veneered with diatomaceous earth block or a sectionally supported refractory tile wall, backed up with thicker insulation of diatomaceous block Either construction includes a final casing of steel or asbestos-cement sheets The low heat capacity of such walls is reflected in the economy and safety of operation

Unless well insulated, the furnace floor can materially contribute to the heat loss

A concrete foundation proper should be topped with at least 4 in of diatomaceous earth—Portland cement insulating concrete covered with firebrick or insulating refractory brick Alternatively a hydraulic setting refractory with half the thermal conductivity of firebrick can be used laid in monolithic construction 6 in thick for direct exposure to flame temperature up to 2,400° F

Tube plates and supporting members are usually insulated by high temperature insulating concrete, as a means of protection against the furnace temperature and gases The space between the header and tube plate is filled with diatomaceous earth blocks and cement

The tube doors are insulated with 2-in asbestos sheets, covered with $\frac{1}{4}$-in high temperature asbestos millboard, secured with bolts or studs and plate washers and with all edges sealed with a semi-refractory cement

Tank Insulation

While standard practice presumes insulation of the higher temperature asphalt tanks, the value of insulating tanks heated to only 150° F is not so generally recognized Although the cost of heating steam and the hours per year are determining factors, in general it is economy to insulate any equipment artificially heated to 125° F or over

For example, consider the desirability of insulating a 40-ft diameter by 30-ft high tank whose contents are maintained at 150° F, the tank being out of doors Assuming an average atmospheric temperature of 50° F, an average wind of 10 miles per hour, and a service heating season of about two-thirds of a year—6,000 hours With fuel oil at $1 00 per barrel of 5 5 million B Th U and 80% boiler efficiency and 5 0% transmission losses, the heating steam costs approximately $0 22 per million B Th U at the tank, exclusive of fixed charges, which would bring the cost of delivered heating steam to about $0 25 per million B Th U

The roof and sides, approximately 1,250 and 3,770 sq ft in area respectively, would lose about 9,650 million B Th U per year if left bare, but only about 800 million B Th U per year when insulated with 2 in thickness of magnesia blocks on the sides and 1½ in thickness on the roof

∵ Reduction of Heat Loss = 9,650 − 800 = 8,850 B Th U per year.

Value of heat saved = 8,842 × $0 25 = $2,212 50

Approx. cost of insulation—(in place) = $2,500 00

And therefore the time in which the insulation pays for itself is 13 6 months

For temperatures not exceeding 125°, cork, rock cork, or hair felt are commonly used (the latter for temperatures up to 150° F), as well as insulating lumber Higher temperatures are apt to affect such materials adversely and bring in the use of magnesia blocks, rock wool blankets, or plastic cements The latter are not particularly efficient, as their conductivity is relatively high and the large exposed area offers trouble from cracking Hollow tile is widely used because of cheapness and availability, as well as simplicity of erection However, tile or brick have comparatively poor insulating properties

Because of the exposure to wind and rain, the waterproofing of outdoor tank insulation should be most thorough To avoid eventual disintegration of the insulation around the bottom of a vertical tank, a 'boot' or seal of waterproofing felt is hot-mopped with asphalt to the tank sheets at the bottom before the insulation is applied, and later turned up and over the insulation The construction at this point is further heavily hot-mopped with asphalt. All tank openings such as manholes and vents should be sealed off from the insulation and the insulation carefully flashed

Insulated yard tanks exposed to mechanical abuse from trucks, &c, should be encased in a protective covering Hollow tile, brick, and asbestos-cement sheets are commonly used for this purpose

Insulation of Vertical Steel Tanks. Hot Tanks, 125 to 600° F

Eighty-five per cent magnesia blocks are recommended for roof insulation, and magnesia blocks or rock wool blankets for insulation of the side walls While the bare tank-roof temperature is lower than that of the sides, it should be insulated—usually to less thickness Though some prefer to leave the eaves bare on riveted tanks, eave insulation forms a tight connexion between roof and shell insulation, in addition to reducing heat loss With roof or eaves bare, special flashing is needed to weatherproof the shell insulation

The proper thickness of insulation to use on tank sides varies according to the maximum temperature Recommended thicknesses are as follows

Tank temperature, ° F	*Shell insulation thickness, in*
125–300	2
300–400	2½
400–500	3
500–600	3½

Roof insulation thickness is ordinarily ½ in less than that on the shell

For a finish, cement, waterproofed, is frequently used A $\frac{3}{4}$-in coat of cement composed of $\frac{7}{8}$ insulating cement and $\frac{1}{8}$ Portland cement by weight is applied on 1½-in hexagonal mesh galvanized wire netting, securely laced over the insulation Over the cement, when dry, is trowelled a smooth coat of plastic waterproofing, and applied $\frac{1}{4}$ in thick, painted with aluminium paint if desired On indoor tanks, the finish as described above may be omitted and insulating cement applied over the blocks in two coats with wire netting reinforcement, to a total thickness of $\frac{3}{4}$ in, the final coat being mixed with $\frac{1}{8}$ Portland cement by weight and trowelled to a smooth surface An asbestos-cement sheet-casing furnishes not only protection against fire, but against mechanical injury and severe weather conditions, and presents a neat appearance without painting or other maintenance

When insulating a tank roof the blocks are applied with fibrous adhesive and extend to the eave to lap over the side wall insulation If the side insulation is also 85% magnesia blocks, the roof insulation blocks are secured to them with wood skewers

Over the roof insulation, two coats of a cement composed of ⅞ insulating cement and ⅛ Portland cement by weight are applied to a total thickness of ½ in , the cement being carried down over the eave and the side-wall insulation for at least 9 in When the cement is dry it is coated with one coat of concrete primer Over the primed cement is thoroughly hot-mopped 15 lb asbestos waterproofing felt, lapped to form a two-ply protection, extending over the eaves to lap the side-wall insulation Around the rim of the eaves and around projections, plastic waterproofing is trowelled to a smooth finish

White top roofing is then solidly hot-mopped over the entire roof, with all joints closely butted Over the joints a coat of concrete primer is applied, followed by plastic waterproofing If a black finish is desired, the white top roofing is omitted, and asbestos waterproofing felt is used instead The top surface is finally given a mopping of hot asphalt

The following insulation specification is designed for tanks containing heavy oil, heated by steam coils, to a temperature not in excess of 125° F , and for tanks containing light distillates, gasoline, &c , at atmospheric temperature Usually such tanks rest on concrete base, and tank-roof decks are flat with no projecting curb or eave angle The recommended form of insulation for such tanks consists of cork, or rock-cork insulation, 1½ in thick applied with hot asphalt and (for vertical tanks) encased in flexible asbestos board on the sides The roof insulation should be protected by flashing plastic

Horizontal tanks should have the same insulation, but, in lieu of the foregoing finish, should be encased with Portland cement plaster, followed by a waterproof coat of suitable plastic waterproofing, trowelled on

In the case of vertical tanks, before application of the bottom courses, a waterproof 'boot' should be installed, consisting of two plies of 15-lb asbestos felt, hot-mopped solid to the tank side for a distance of 36 in After the bottom course has been applied to the face of the boot, the felts are turned up and over the cork bottom course and hot-mopped in place

As an alternative form of insulation for tanks containing casinghead or highly volatile gasoline, two ¾-in thick layers of hair felt stitched between layers of building paper has been used successfully

Insulation for Controlling Evaporation

The two main causes for evaporation of oil in storage are, first, 'wind-drift', or vapour circulation, through openings in roof and eave, and second, expansion and contraction due to temperature change in the vapour space above the oil and of the surface of the oil itself, called 'breathing'

Wind-drift losses are those caused by air currents entering through small openings at the eave or between the laps of metal deck plates, passing through the vapour space above the oil level, and escaping through openings in the opposite side of the tank These currents carry with them the lighter portions of the oil and not only appreciably reduce the volume of liquid in storage, but lower its gravity and consequently its market value

These losses from air circulation through the tank vapour space are greatest in wood deck tanks, where the roof openings are largest, but are almost as great in old style steel roofs with wide rivet spacing, and are appreciable even in caulked steel tanks

It is evident that expansion or contraction of either a steel or galvanized iron roof, due to change of outside temperature, will be greater in the surface of the roof directly exposed to the sun than in the circumference of the shell at the eave The filling and emptying of a tank also causes changes in the shape of the top ring with an attendant movement of the eave Both of these movements result in strains on all caulked joints, making it practically impossible to maintain them tight enough to hold gasoline vapour even though the best of workmanship was used in the original construction

'Breathing losses constitute the more important factor in the total evaporation loss as the tanks approach gas-tightness The mixture of air and oil vapour in the vapour space of the tank expands and contracts with daily changes in temperature

With an average variation of 30° F between the highest temperature during the day and the lowest temperature during the night, and a depth of oil of 28 5 ft in a 30-ft 55,000-bbl tank, the breathing from thermal expansion of the air and vapour mixture will be about 2,160 cu ft per day

The fresh air drawn in will become saturated with vapour and during the next 24 hours a corresponding amount of vapour-saturated air will be forced out A further loss due to small breathes is caused by intermittent sun and shade or showers

The breathing due to change in vapour pressure is greater than, and may even be more than double, that due to thermal expansion of the air and vapour mixture alone, and must be added to the breathing due to thermal expansion The effect of vapour pressure change is even greater on the evaporation loss than is made apparent by the increased volume of the breathing, because the result is to increase the proportion of gasoline vapour in the mixture breathed out of the tank

The chart in Fig 5 shows a typical reduction in variation of the temperature in the vapour space effected by insulating the tank top These temperatures were taken for one week in September and were registered by self-recording thermometers installed in the vapour space of each tank

Tests by a refinery near the Gulf Coast comparing evaporation losses from three steel-roofed tanks 90 ft diameter by 30 ft high, storing motor gasoline, showed the following losses over a period of nine months

	Average bbl lost per month
Tank with uncaulked bare steel roof	170
Tank with caulked bare steel roof	118
Tank with vapour tight insulated tank top •	79

All tanks were filled with 63 1° Be-gasoline at start of test The tanks were equipped with one screened breather vent and vapour tight hatches The uninsulated roofs were painted light grey

Because of the high A P I gravity of the gasoline in this test, the losses from all test tanks were rather higher than for ordinary motor gasoline, but the saving made by insulating the tank top over the uncaulked steel roof amounts to 91 bbl per month, and figuring the gasoline loss at $4.20 per bbl , the saving per tank over the 9-month period amounted to $3,439

Another method of reducing evaporation losses in crude and gasoline storage makes use of a 'sunshade' or housing around the shell only, with insulation of water on the roof.

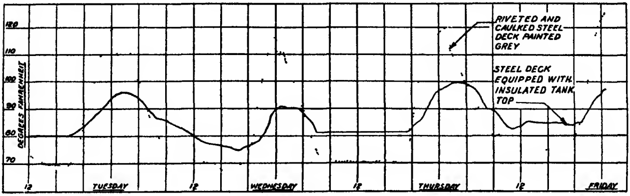
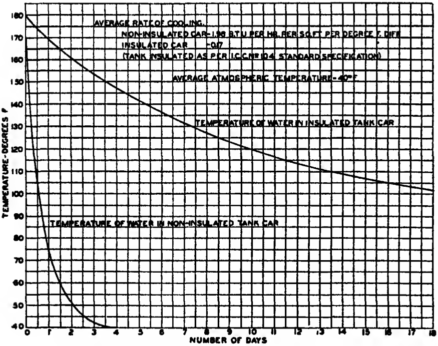


FIG 5

Corrugated asbestos sheeting has proved very satisfactory for such sunshades because of its light-coloured surface, durability without maintenance, and ease of application. In erecting the sheeting no welding is required, so that the tank contents need not be disturbed during the progress of the work.

Tank-car Insulation

Tank-car insulation is designed to keep the volatile contents of the car from heating up beyond a certain temperature or to keep the contents from cooling down below the temperature at which it can be unloaded. Statistics show that the average evaporation loss from an uninsulated tank car carrying casing-head gasoline amounts to 250 gal per shipment.



—CURVE SHOWING RELATIVE RATES OF COOLING IN INSULATED AND UNINSULATED TANK CARS

FIG 6

A suitable insulation for such work consists of two 1-in. layers of standard hair felt between three layers of 15 lb asbestos waterproofing felt, securely fastened to the tank and covered by a ⅛-in riveted steel jacket. Another similar material is loosely felted hair enclosed between two layers of waterproof paper which eliminates the operation of applying the waterproof felt.

Cars built for higher pressures are required to be insulated with a thermal efficiency equal to 4 in of compressed cork-board, made weathertight. Heater pipes attached to the tank should be insulated to half this thickness.

Cars carrying hot asphalt or petroleum products that are not explosive are insulated in accordance with the individual requirements of the particular case, the maximum thickness being the space allowed for insulation on the type of car. Standard hair felt is the most efficient heat insulation that can be used on these tank cars, but a 1-in layer of corrugated asbestos is often used as a first layer under the hair. At high temperatures asbesto-sponge felted must be used next to the tank to protect the hair felt. Between 250 and 300° F, 1 in of asbesto-sponge felted is normally used, between 300 and 400° F, 1½ in of asbesto-sponge felted, and over 400° F, 2 in of asbesto-sponge felted. In each case standard hair felt is applied over the asbesto-sponge felted if required to complete the thickness, and the entire insulation is properly waterproofed. Large sheets of moulded asbestos curved to the tank radius offer a substitute of light weight and low conductivity.

Rock wool blankets furnish the most widely used type of tank-car insulation, because of relative cheapness and ease of application. However, rock wool is open to the objection of settling and possible eventual disintegration from the continual vibration and exposure to moisture filtering through cracks in the overlaying metal casing.

Typical cooling curves are shown on Fig 6 for an insulated and bare tank car.

Fire Protection for Structural Steel

Structural steel becomes materially weakened between 800 and 1,000° F, which temperatures are far below those frequently encountered in plant fires In many industrial processes, and particularly in the oil industry, it has proved highly advisable to protect the supporting steel work where failure of any member might cause disastrous results

For this class of work certain insulation materials are fitted to meet fire conditions and give superior protection to the steel One such material is diatomaceous earth concrete which is made on the job and applied either by placing in wood forms, or by the cement gun method It has the following characteristics

(1) Applied to a thickness of 2 in it gives 6-hour protection for the steel members enclosed A 3-in thickness gives 10-hour protection

(2) It is a monolithic, strong, and self-supporting material

(3) It weighs only about 60 lb per cu ft Because of its relatively light weight it is easier to place than heavier materials, and lightens the load on supporting steel

(4) It withstands the action of water from a fire hose

The diatomaceous earth concrete fireproofing is usually applied in the following manner

The steel members are enclosed in 2 in × 2 in mesh 12-gauge electric weld wire, space ½ in from the steel surface The concrete is then applied over the entire surface of the steel members in monolithic construction allowing a minimum of 2 in (or 3 in) of protection at the extreme points and with no re-entrant angles After the concrete has set it is waterproofed

An alternative is high temperature block insulation and is recommended for protection up to six hours The blocks and cement are applied to the steel members as outlined below The hours of protection stated for these specifications are the time required for the steel to reach a temperature of 900° F, with the insulated member exposed to 2,000° F, on all sides, as determined from furnace tests A typical temperature chart is shown in Fig 7

For 4- to 6-hour protection, next to the steel are applied 1½-in thick 85% magnesia blocks wired in place, with all joints laid up in asbestos cement Over the magnesia a second layer of 1½-in thick diatomaceous earth blocks, secured by nichrome wire, are laid with asbestos cement, with all joints broken All voids between the steel and the insulation are filled with scrap insulation, poured in as the work proceeds It is important that all blocks be laid up with cement, actually buttering the joints, and not simply pointing them up after the blocks are in place Around the corners of the second layer of insulating blocks, asbestos sheet millboard is bent and stapled in place

Over the second layer of blocks is stretched 1-in hexagonal galvanized wire netting, followed by a ½-in thick coat of cement trowelled to a hard finish When the cement has set and is well dried out, it is waterproofed with a plastic applied ½ in thick and trowelled to a smooth finish A typical arrangement is shown on Fig 8

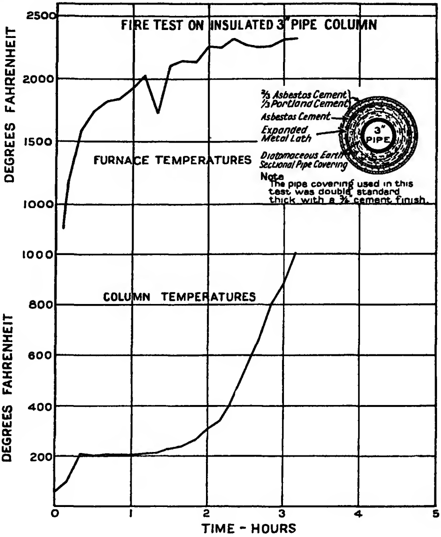


Fig 7

For protection up to 2½ hours, next to the steel are applied 1½ in thick diatomaceous earth blocks, secured in place with nichrome wire and laid up in asbestos cement Asbestos sheet millboard is bent around the corners of the insulating blocks and stapled in place, and a cement finish is applied over wire reinforcing and waterproofed as in the previous recommendation All voids between steel and insulation should be filled with scrap insulation, poured in as the work proceeds Typical arrangements are shown in Fig. 9

Rods for working valves are frequently carried some distance to give remote control in case of fire However, unless these rods are protected the possibility exists of their becoming useless through exposure to flame Control rods can be fireproofed as follows

Two layers of 1½-in thick diatomaceous earth pipe insulation (of the nominal pipe size equivalent to the diameter of the rod) are secured in place by nichrome wire All joints are sealed with asbestos cement Over the pipe insulation is stretched ½-in mesh galvanized wire netting, followed by a ¼-in thick coat of asbestos cement and trowelled to a smooth finish The cement is waterproofed with a plastic, applied ⅛ in thick and trowelled to a smooth finish

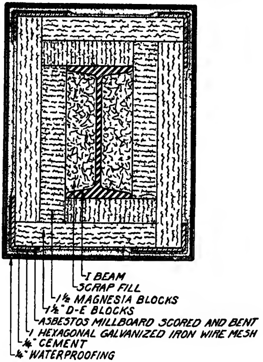


FIG 8 Protection of steel members for 4 to 6 hours

Valves, knuckles &c, are housed with ¼-in thick flat asbestos cement sheets and the space filled with scrap insulation

Stack Lining

During recent years many steel stacks have been lined with diatomaceous earth brick with very satisfactory results In industrial plants stacks are lined to prevent corrosion of the steel, increase the draft, and improve the operation of the equipment Corrosion protection is particularly important where flue gases have a highly acid condensate, such as those from oil sludge or high sulphur residues

Stacks are most usually lined with 2½ in of diatomaceous earth natural brick, but vitrified asbestos sheets curved to fit the radius of the stack are also used Prior to application of the brick insulation, circumferential angles, 2 in × 2 in × ¼ in, are placed in the stack on 37-in vertical centres, the outstanding leg punched with ½-in holes on 12-in centres After the inside surface of the stack is cleaned of all paint or other foreign material, the bricks are cemented to the stack with fibrous adhesive and further held in place by vertical wires, laced through the ½-in holes in circumferential angles

Over the surface of the brick is stretched 1-in hexagonal mesh galvanized wire netting, securely fastened to the lacing wires Two coats of asbestos cement are then applied to a total thickness of ½ in, the first ¼-in coat being left to dry with a rough surface before the application of the smooth finishing coat

Pipe Insulation

To be adaptable, pipe insulation must be of such form as to be easily applied It must have heat-resisting qualities sufficient to withstand successfully the highest temperatures to which it will be subjected It must be sufficiently strong and durable to assure long life Adaptability also depends upon many other conditions incidental to the particular application

Refinery pipe insulation must meet conditions of considerable mechanical abuse in ordinary service Also, certain lines around high-pressure cracking coil equipment, for instance, must be periodically inspected, necessitating the use of removable and replaceable type of insulation for these pipes and flanges

From the four basic mineral products—asbestos, magnesium carbonate, diatomaceous silica, and rock wool made from argillaceous limestone—insulation is manufactured in the forms of sectional pipe covering, insulating sheets, blocks, bricks, and blankets, as well as light-weight aggregate used with Portland cement for making insulating concrete Cork, rock cork, and hair felt products are used in the low temperature fields The insulation of cold piping, however, will be dealt with separately as an item in low temperature equipment

Eighty-five per cent magnesia is extensively used for

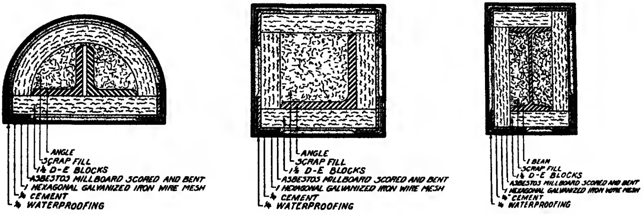


FIG 9.

steam-line insulation requirements in the oil industry where the insulation is not subject to mechanical injury, and where the temperatures do not exceed 600° F It is light, efficient, and low in price The asbesto-sponge felted insulation is an alternative type which can be used up to 700° F Its laminated construction gives sufficient mechanical strength to withstand severe usage and vibration, which makes it particularly desirable around stills and cracking plants where pipe insulation is often subjected to rough treatment Another advantage of asbesto-sponge felted is the fact that it can be taken off and placed on other pipe of the same size without deterioration from the consequent handling and transportation

In the range of temperatures so high that neither 85% magnesia or asbesto-sponge felted should not be used, diatomaceous earth-pipe insulation is the proper material Sometimes asbesto-sponge felted is used outside for mechanical protection of the diatomaceous earth insulation and to increase insulating efficiency Magnesia is used as an outside layer where the insulation is not subjected to abrasion, because it is lower in first cost

Rock wool pipe covering has had some acceptance, particularly when fitted in a metal casing or jacket to facilitate frequent removal However, on horizontal lines any fibrous form of insulation is very likely to sag, creating a tunnel along the bottom of the pipe, and thinning the insulation along the crown

The table of thicknesses which follows represents general practice in use generally on heated lines Exceptional conditions may make necessary thicker insulation Where piping is located outdoors it is customary to use insulation ½ in thicker than shown

		Thickness of 85% magnesia insulation (in)		
Steam pressure or condition	Temperature, ° F	Pipes larger than 4 in	Pipes 2–4 in	Pipes smaller than 2 in
Hot water		Std	Std	Std
0–25 lb	212–266	Std	Std	Std
25–100 lb	267–337	1½	Std	Std
100–200 lb	338–387	2	1½	Std
Low superheat	388–499	Dbl Std	2	1½
Superheat	500–600	3	Dbl Std	2

For temperatures above 600° F all pipes 1½ in and smaller are best insulated with a single layer of diatomaceous earth sectional pipe insulation 2 in thick Small fittings are insulated with asbestos cement For pipe sizes larger than 1½ in, at temperatures above 600° F, a combination insulation is best This consists of one layer of diatomaceous earth sections next the pipe, over which is applied a second layer of either 85% Magnesia or asbesto-sponge felted as conditions require Suitable thicknesses of each layer for the various pipe sizes are given in the table in the next column

Sectional insulation is applied to a pipe with joints, tightly butted and pointed up with asbestos cement Insulation is wired to the pipe with not less than three loops of 16-gauge annealed iron wire on pipe up to and including 6 in, and with not less than four loops for larger pipe sizes

When the insulation is applied in two layers both circumferential and longitudinal joints are staggered, with each layer wired in place as previously described

The insulation on bends should be given a thin finishing coat of asbestos cement to present a smooth, even surface. Insulation of flanges and fittings on lines over 4 in in diameter should be the same as the insulation on the line, surfaced with ½ in asbestos cement applied in two layers Canvas is stretched tightly over the cement and pasted On lines under 4 in the fittings and flanges are insulated entirely with asbestos cement to the same thickness as the adjacent insulation Flanges and fittings out of doors are waterproofed with a plastic applied in place of the second coat of cement, the canvas being omitted

Temperatures	600–699° F		700–799° F		800–1,000° F	
	Thickness of insulation (in)					
Pipe size, in	Diatomaceous earth	85% magnesia	Diatomaceous earth	85% magnesia	Diatomaceous earth	85% magnesia
1½ and smaller	2		2		2	
2	1¼	1½	1¼	2	1 9/16	1½
2½	1 5/16	1½	1 5/16	2	1 13/16	1½
3	1 9/16	1½	1 9/16	2	2 1/16	1½
3½	1 5/16	1½	1 5/16	2	1 13/16	1½
4	1 9/16	1½	1 9/16	2	2 1/16	1½
4½	1 5/16	2	1 5/16	2½	1 13/16	2
5 and larger	1½	2	1½	2½	2	2

Insulation on piping located outdoors or exposed to the weather is best finished with a heavy double-coated asbestos waterproof roofing jacket Joints in the jacket are lapped at least 3 in and sealed with lap cement and the jacket is securely wired in place On horizontal pipes the seams of the weatherproof jacket is placed at the side of the pipe with the lap turned down in order to shed the water Piping located close to the ground is best protected by a metal jacket

Where fire hazard must be considered and the application of ordinary roofing jackets is prohibited, due to the fact that flame may be carried along exposed piping when a fire occurs adjacent to lines so protected, an asbestos jacket or a steel jacket must be used

One form of asbestos jacket consists of one sheet of asphalt-saturated asbestos felt, over which has been cemented an unsaturated felt for an outer surface This material will not drip asphalt, carry flame, or support combustion

Flanges, fittings, and valves are generally insulated with the same materials as the adjacent piping

On piping 4 in and larger the bodies of flanged fittings and valves are insulated with block insulation to a thickness ½ in thinner than the insulation on the adjacent piping Hard finish asbestos cement is then applied to make the total thickness of insulation on the valve or fitting equal to that on the adjacent piping Pipe insulation should be stopped short of all flanges, and bevelled off to permit removal of flange bolts when necessary

In the case of flanges the insulation of which is to be of the removable and replaceable type, all flanges are insulated with sectional pipe insulation to a thickness equal to that of the insulation on the adjacent piping or with block insulation to a thickness ½ in thinner than the insulation on the adjacent piping, covered with ½ in hard-finish asbestos cement

On piping 3½ in and smaller, in place of blocks and cement as mentioned above, the entire insulation of flanged and screwed fittings and valves is best carried out with hard finish asbestos cement to a total thickness equal to that of the adjacent pipe insulation

Where it is necessary to make frequent inspection of hot oil-vapour lines, particularly those which connect the cracking oil with reaction chambers in the various cracking processes, asbestos pipe blanket insulation for temperatures up to 800° F is economical, due to ease of application and elimination of breakage The usual pipe blankets are made up of 2½ lb asbestos cloth on both sides, filled with brown asbestos fibre and quilted on approximate 9-in centres, with wire-inserted asbestos cord Monel metal hooks for lacing are secured to all longitudinal edges, on approximately 5-in centres with monel metal wire and copper disks The blankets are laced on the pipe or fitting with monel metal wire

Freezing of Water Pipes.

Built-up hair-felt insulation is used to protect water-pipes from freezing where the pipes are subjected to severe conditions This insulation consists of a suitable number of layers of 1-in standard hair felt securely bound in place on the pipe by means of heavy jute twine and finished on the outside with a waterproof jacket The following table gives some data on the protection afforded by insulation

Data on Freezing of Water in Pipes

Pipe size, in	*Insulation No of layers each 1 in thick*	*B Th U per deg temp diff, per hour per linear ft*	*Hours to cool to freezing-point from 60° F*	*Lb water flow per hour per linear ft to prevent freezing*
½	2	0 0895	0 417	0 537
	3	0 0747	0 500	0 448
	4	0 0660	0 565	0 396
1	2	0 1125	0 825	0 675
	3	0 0911	1 02	0 548
	4	0 0798	1 16	0 480
2	2	0 1586	1 94	0 952
	3	0 1244	2 48	0 747
	4	0 1063	2 90	0 638
4	2	0 2450	4 55	1 470
	3	0 1850	6 02	1 110
	4	0 1548	7 20	0 929
6	2	0 3302	7 35	1 981
	3	0 2434	9 88	1 460
	4	0 1984	12 20	1 191
8	2	0 4100	10 05	2 460
	3	0 2960	13 90	1 776
	4	0 2390	17 25	1 434
10	2	0 4930	13 00	2 960
	3	0 3536	18 10	2 122
	4	0 2830	22 70	1 698
12	2	0 5720	15 80	3 432
	3	0 4090	22 20	2 454
	4	0 3222	28 10	1 933

Where water must remain stationary longer than the safe length of time indicated, the only sure way of protecting the line is to provide a small steam or hot water line alongside the water line and then place insulation entirely round both lines In this case two-layer insulation is satisfactory and sufficient, as the heating line is the protection against freezing and the purpose of the insulation is to prevent excessive loss, and to keep the heat where it is wanted

Steam-heated Oil and Tar Lines

Oil, asphalt, tar lines, &c, in which it is necessary to maintain temperatures above outside temperature to ensure flow are protected from cooling by means of a small steam pipe running adjacent to the main pipe The two pipes are insulated together by applying sectional insulation of such diameter as just to fit around the pipes when bent to conform The insulation is held in place by 16-gauge iron wire loops All space between the joints is filled with asbestos cement

On inside piping, the insulation may be finished with rosin-sized paper over which is sewed an 8-oz canvas cover The canvas may be sized and painted if desired On outside piping, the insulation is covered with a weather-proof jacket

Insulation of Low-temperature Equipment.

A ton of refrigeration, the equivalent of 288,000 B Th U per 24 hours, often costs 10 times as much as the same number of B Th U produced for heating purposes The necessity for much heavier insulation on low temperature work than is customary for high temperatures is thus immediately apparent Furthermore, the cold processing of oils demands that temperatures be maintained within a narrow range, which control cannot be attained without the use of adequate insulation

Briefly, the requirements of a low temperature insulation are

1 The insulation must possess low conductivity at low temperatures and must have the ability to retain this low conductivity in service
2 It must not readily absorb moisture, as low temperatures involve condensation
3 It must permit thorough sealing against infiltration of air, for condensation within the material reduces its efficiency
4 It must have sufficient strength to be handled and applied without breakage, and it must be easily sawed and worked on the job
5 It must be vermin-proof and not susceptible to bacterial growth

Cork, with a long history of satisfactory performance, is the most widely used low temperature insulation It is manufactured in the form of sheets or lags mitred to the required curvature It should be thoroughly waterproofed, not only for maintenance of efficiency but also to prevent possible disintegration Granulated cork may be used as a filling material where conditions preclude the use of sheet or block insulation

Rock cork is of more recent development, having been introduced some 30 years ago It has since been used with entire success for all classes of low temperature insulation It consists of rock wool bonded with a waterproofing bitumen and is made in sheets or lags Possessing a considerable degree of waterproofness in itself, it is not so dependent upon the integrity of the final waterproofing surface

Hair felt, with an older history even than cork, offers portability, low weight, and relative ease of application due to the large units of area in which it is available In late years its use has been rather confined to equipment at atmospheric, or somewhat lower temperatures, although it has been satisfactorily applied to helium plant equipment operating at extremely low temperatures Hair felt is either manufactured as standard hair felt in rolls or with roofing paper stitched to both sides This insulation demands a better type of workmanship in its application than does either cork or rock cork At low temperatures its effectiveness is entirely dependent upon the completeness and integrity of the exterior waterproof envelope The efficiency is a function of the uniformity in thickness of such an easily compressible material

In a low temperature insulation the presence of moisture not only hazards eventual disintegration of organic material but also markedly impairs its insulating property Very low temperatures demand virtually an air-seal type of waterproofing to avoid moisture resulting from warm air filtering in through the outer surface and condensing in the insulation Once started, such action is always progressive, with a resultant frosting of the insulation throughout its depth

The conductivities of the three types of low temperature insulation are within fairly close agreement, varying somewhat with density and compression and, to some extent, with age when exposed to 'drying out'

For calculating the required thickness of insulation, the conductivity is usually taken to be 0 30 to 0 33 B Th U per hr sq ft °F for 1 in thickness

Where frosting of the exterior surface is a factor, the temperature of the surrounding atmosphere and its relative humidity at that temperature should be considered At times this would call for a greater thickness, but for general use, industrial practice has fairly well standardized the following thicknesses for tanks, brine coolers, chillers, refrigerated rooms, &c Cold piping is dealt with separately

Equipment temperature, ° F	**Thickness of cork or rock cork sheets or lags*
−60 to −50	12 in —three layers
50 to −30	10 in —three
− 30 to −15	8 in —two
−15 to 0	7 in —two
0 to 15	6 in —two
15 to 25	5 in – two
25 to 35	4 in —one
35 to 45	3 in —one
Above 45	2 in —one

* Add 1 in to above for corresponding thickness of hair felt to allow for compression

For vertical tanks 'Foundation cork is applied on a waterproofed concrete, normally about 25% thicker than standard to allow for its greater density and higher conductivity

For the walls of tanks 20 ft or greater in diameter cork or rock cork sheets are used, for tanks of smaller diameter, lags, formed of sheets of the same materials, mitred for the curvature, are preferable in order to secure close-fitting joints

The final exterior surface may consist of a suitable emulsified asphalt-asbestos cement waterproofing plastic, or roofing felts hot-mopped with asphalt For tanks over 20 ft in diameter, an asbestos-cement sheathing is usually added for mechanical protection, or hollow tile erected around the tank

Rock cork or cork sheets are applied horizontally to the side walls of the tank after dipping one face of the sheets in hot asphalt, and are further secured by metal straps If more than one layer of sheets is required, the second, and each subsequent layer, is secured to the previous layer by wood skewers, four to a sheet, driven at an angle, in addition to cementing with hot asphalt

The roof of tanks at low temperatures are usually insulated to the same thickness as the side walls The sheets are dipped on one face in hot asphalt in the same manner as on the side walls, and the second, and each succeeding layer, additionally secured to the preceding layer with wood skewers Over the finished insulation, waterproofing felt is applied in a manner generally similar to that for hot tanks

On horizontal tanks cork or rock cork lags, of the proper thickness and number of layers for the operating temperature, are securely attached to the shell of the cooler with hot asphalt, with each course further secured by circumferential metal straps Where two layers are necessary the attachment of the second layer to the first with hot asphalt is further reinforced by wood skewers driven in at an angle

When using hair felt insulation, after all leaks are made tight and all scale, grease, or other foreign matter removed with brushes and scrapers, the entire tank is first coated with concrete primer A first layer of felt is then hot-mopped to the ends of the tank A second layer is then hot-mopped to the first layer, each layer being cross-laced with wires on about 18-in centres, secured to ⅜-in twisted steel cables stretched circumferentially around the tank about 6 in from the ends The felt is applied to the body of the tank in a similar way, each layer being tightly laced with wire wound circumferentially around the tank on 18-in centres

Over the body and ends of the tank, 1½-in hexagonal wire mesh is stretched fastened to the lacing wires A ¾-in cement coat, consisting of two parts insulating cement and one part Portland cement by weight, is thoroughly worked into the wire mesh, and over the cement, ¼ in of plastic waterproofing is finally applied, trowelled to a smooth finish

Insulation of Refrigerated Rooms

Cork or rock cork sheets are usually used to insulate the floor, walls, and ceiling of refrigerated rooms

For floor insulation the sheets are applied over wood or concrete sub-floors, using the same method of application in either case The sub-floor is thoroughly cleaned and dried before applying the insulation Wood floors are first covered with two layers of heavy building paper Next, the sub-floor is flooded with asphalt, and the first layer of insulation applied while the asphalt is still hot It is then flooded with hot asphalt and the second layer applied, all joints being staggered and closely butted Further layers are applied in the same manner The top surface is flooded with a heavy coat of hot asphalt The floor insulation must always be covered with some type of wearing surface

Walls are usually prepared to receive the insulation in the following way Uneven stone or brick walls are trued up with a coat of Portland cement mortar brought to a float finish Frame walls are covered with two layers of waterproof building paper The cleaned, dry surface of masonry walls is coated with concrete primer

The insulation is then applied with hot asphalt All sheets are closely butted and pressed firmly into place to provide uniform adhesion, and outer layers are additionally secured to the preceding layer with wood skewers The interior finish for both walls and ceiling usually consists of ¼ in of asphalt-asbestos cement, evenly applied and trowelled smooth

Whenever several floors are being refrigerated, the floors should be supported separately from the walls, when possible, with space provided between the wall and floor slab to permit the continuance of insulation without a break at the floor-line. This makes it unnecessary to insulate floors and ceilings except at the bottom and top of the entire space being insulated Where the floor beams of intermediate floors must be supported in masonry walls, the insulation should be carried out on the beams from 3 to 6 ft, depending upon the temperatures to be held

Ceiling insulation should be applied on the top where this is possible When applied on the underside, advantage should be taken of all means of reinforcement, especially on the first layer, to ensure permanent construction Under wood-frame ceilings, two layers of waterproof building paper should be first nailed to the sheathing The initial layer of insulation is then applied with hot asphalt, and secured with galvanized nails and metal caps The following layers are applied with hot asphalt and secured to the preceding layer with wood skewers driven in at an angle

One method of insulating the under-side of concrete ceilings on new construction is to lay the first layer of insulation in the concrete forms before the slabs are poured Heavy galvanized wires with one end bent to form a cap are inserted in each sheet in such a manner as to form a key when the concrete is poured The top surface is given a coat of emulsified asphalt, after which the concrete is poured When the concrete has set and the forms have been removed the additional layers of insulation are applied underneath with hot asphalt and secured with wood skewers driven in at an angle

If concrete floor slabs have been poured without provision for supporting insulation, and it is necessary that the insulation be applied to the under-side, the most satisfactory method is to drill holes in the concrete and secure 2 in × 3 in nailing strips to the slab with expansion bolts The entire surface is then given a coat of concrete primer, and the first layer of insulation erected in asphalt between the nailers, and toe-nailed to them at each edge The second layer is applied in asphalt, nailed to the strips, and in addition secured to the first layer with wood skewers, driven in at an angle Any further layers are applied with asphalt and wood skewers

Around doorways and along passages, particularly where trucks are wheeled, it is advisable to provide protection for the insulation For places where the blows are not severe, a reinforced cement wainscot, ¾ in to 1 in in thickness will suffice Where the abuse is continuous and extreme, wood studs, to which parallel wood battens of sufficient strength are nailed, will serve Generally this protection need extend up the wall only about 4 ft

Insulation of Cold Piping

While pipe insulation for low temperatures embraces the same types of insulation as used for low temperature equipment, the thickness and methods of application differ considerably

Cork pipe insulation is most generally used on piping conveying cold fluids The thickness depends on the temperature involved and on other considerations, but the usual thicknesses are given in the following table, which may be taken to apply also to other forms of insulation for cold piping

Temperature °F	*Thickness designation*	*Approximate thickness, in*
Above 25	Ice water	½–2
25 to 0	Brine	2–3
0 to 20	Heavy brine	3–4
−20 to −40		5
−40 to −60		6

Cork pipe insulation is furnished in single layer, semi-cylindrical or segmental sections, to fit standard pipe sizes Cork jackets are furnished to fit screwed and flanged fittings. They are usually made in two half-sections for small sizes, and in segments for large sizes

An alternative type of insulation to cork for low temperatures is known as rock cork, a material manufactured from a loose rock wool, bonded with a waterproof asphaltic compound It is usually furnished with a factory applied waterproof jacket and in this form it has a high resistance to moisture infiltration The same raw material is also made into a soft felt about 1 in thick consisting of loosely felted rock wool also impregnated with asphalt

This rock wool felt is particularly useful for the insulation of flanges and pipe fittings as it can be packed round irregular-shaped surfaces It is often used in this way in conjunction with sectional pipe covering for the straight lengths of pipe It is applied in several layers to build the insulation up to the required thickness, each layer being covered with waterproof tape before the next layer is applied so as to form a very thorough protection against moisture

The sectional pipe covering is first applied and the ends of the last sections thoroughly coated with waterproofing compound before covering the pipe fitting The insulation over the fitting is finally bound with a layer of waterproof tape covered with a trowelled coat of plastic waterproof compound This is illustrated in Fig 10

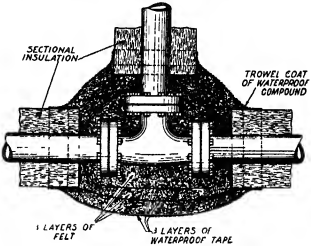


Fig 10

A built-up form of insulation is also sometimes used consisting of several layers of insulating hair felts carefully applied and sealed by interposing layers of a specially impregnated waterproof tape The finishing layer of tape is additionally waterproofed

All pipe hangers should be erected on the outside of the cork, which should be protected from each hanger by a sheet iron shield, approximately 6 in wide, shaped to fit the curvature of the insulation and extending half-way up the sides of the pipe Lines may be supported on wood blocks set in the hangers until the insulation is applied

Unused, or infrequently used, branch or by-pass lines, leading off from lines being insulated, should be insulated to a distance not less than 3 ft from the main pipe-line

Longitudinal joints in the pipe insulation are made at the top and bottom of the pipe All insulation is securely wired in place with copper-covered annealed iron wire and joints and seams cemented and spaces filled with bitumen or paraffin-cork mastic The completed insulation is then finished as desired, usually with asphaltic paint

After application the insulation should be inspected, preferably twice a year, and loose wires tightened, any places where seams are not tight puttied up with seam-filler, and the covering given a coat of asphaltic paint

SECTION 34

METALS AND ALLOYS IN REFINERY EQUIPMENT

FACTORS TO BE CONSIDERED IN SPECIFYING STEEL FOR REFINERY SERVICE

By T McLEAN JASPER, and CHARLES W WHEATLEY, *A O Smith Corporation*

THE use of steel for refinery service covers a wide variety of equipment To help the refinery engineer to select the most suitable material requires an appropriate knowledge of the problems associated with steel production as well as those associated with the fabrication and service of equipment

Steel of various kinds have peculiar limitations Certain steels are more sensitive than others to temperature variations, and cannot be so easily cast into large ingots without surface cracking or the occurrence of other defects Such steels are almost invariably difficult to roll into plates Other steels, which will cast satisfactorily into ingots, may still present a serious rolling problem Metallurgists who are working with small crucible or electric heats will not become aware of such limitations in the experimental stages of investigating steels, and for this reason considerable disappointment may be associated with an endeavour to bring such experimental steels into service, especially where heavy plates for large vessels are considered

In the selection of steel, it might be said, in general, that the refiner can very satisfactorily confine himself, for his load-carrying work, to carbon, and low alloy steels Where corrosion is of major importance, special steels of high alloy content are available which cannot, at present, be produced from large ingots, nor can they be used in any but thin sections without excessive fabrication costs Means, however, have been devised to attach such thin plates to ordinary commercial steel by rolling, spot welding, or other means

The designing engineer, who writes the steel specifications for his equipment, should be acquainted with the above facts in order not to specify uneconomical materials It should be understood that unnecessary restrictions which call for closer specified limits than necessary should be avoided since they increase the price of steel without obtaining sufficient economical returns This principle is very often disregarded and the writing of specifications is cumbered with expensive restrictions which sometimes have little or no real practical service value The American Society for Testing Materials has taken it upon itself to produce steel specifications for service These specifications are the result of a joint committee of members comprising steel producers, equipment manufacturers, and equipment users Such specifications, when they become standards, have at the back of them a record of having been proposed, investigated by a committee of men vitally interested in expanding the use of steel, and advanced through a period of trial as Tentative Standards

Until recent years specifications for quality thick plates were not available When this type of material was needed, steel fabricators of thick-wall vessels had to resort to considerable experimentation in co-operation with the steel mills before a satisfactory material specification was developed In the early stage of this development excessive mandatory precautions were taken to safeguard the steel, with the result that the price was high Later the quality factor was established on the basis of chemical and physical tests which had been established by experience as properly safeguarding the material, with the result that greater latitude was available to the steel producer so that his ingenuity in the production of steel could play a more important part The result was an improved steel mill practice and a reduction in the cost of production and price This could only be brought about by a close co-operation between the user and the producer of steel

Common load-carrying steels made in heats of fifty tons or more cannot be commercially produced with such small chemical and physical specification ranges as can special steels Therefore, the question of allowable impurities in the two cases is of an entirely different order of magnitude Special steels may vary in price from 20 cents to $1 25 per lb , and therefore the point of view of the metallurgist habitually servicing such steel production and use must be greatly modified if he is to service the commercial production and use of tonnage steels which carry a price in the neighbourhood of from 2 to 4 cents per lb

In dealing with the details of specification writing, the chemical tolerances which have been accepted as satisfactory for the economic production and use of tonnage steels will be considered Such tolerances can undoubtedly be reduced if so desired The advantages gained by such a reduction, however, must be eventually balanced against the increased cost of steel production In general, it is more economically appropriate to shift the commercial range of tolerances up or down the scale of these requirements rather than to narrow this range

The following table gives the typical commercial tolerances which are used on general steels for the petroleum service and cover chemical composition exclusive of high alloy steels

Chemical Tolerance Range

Carbon	0 10% for low carbon requirements
	0 15% for high carbon requirements
Manganese	0 30% for manganese requirements
Sulphur	0 05% maximum for all plate steel
Phosphorus	0 04% maximum for all plate steel
Nickel	0 20% for low nickel content,
	0 50% for medium nickel content
Chromium	0 30% for low chromium content,
	0 50% for medium chromium content
Molybdenum	0 10% for general plate steel
Vanadium	0 15% minimum
Silicon*	0 40% for Silico Manganese Steels,
	0 15% minimum for general plate steel when required,
	0 30% maximum for general plate steel when required

* Not specified in most plate steels

When the above tolerances are adhered to, it has been found that the physical properties can be expected to be within satisfactorily close limits so that the engineer can design his equipment from the standpoint of safety with considerable definiteness as to strength It is generally known that the physical strength will vary, with the same chemical composition, depending on the gauge of the finished plate The following table illustrates this point, and is based on a considerable number of test results on 0 20 to 0 30% Carbon Steel, in which case all of the chemical elements were restricted by standard tolerances

It is seen by the table that, as the thickness of the plate is reduced to ½ in and under, a higher minimum strength can be specified

Relation between Strength of Plates as received and Thickness of Plates for 0 20 to 0 30% Carbon Steel

Thickness	*Ultimate strength lb per sq in*	*Yield-point lb per sq in*
¼ in	68,000	47 000
½ in	65,500	42,500
1 in	62 000	39,500
1⅛ in	60,000	38,500
2 in	59,000	38 000
3 in to 6 in	57,000	37 500

ALLOYED CAST IRONS IN PETROLEUM REFINING EQUIPMENT

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A GREAT deal of progress has been made in the last 10 years in the quality and properties of cast iron, and the petroleum refining industry has been quick to use or seek to employ these improvements to the fullest extent in step with the progress in its own field and the demands upon its production departments for economy and efficiency This does not mean that the output of the grey iron shops has suddenly swung completely to a product of a high order of excellence any more than that the output of the oil refinery has swung completely to premium gasolines A great deal of plain cast iron is still produced and the modest 20,000 lb per sq in strength, requiring no appreciable degree of pressure tightness, can be secured without much concern on the part of either producer or consumer The broad range of properties available in modern cast iron—such as a strength of 20,000 to 60,000 lb per sq in , or up to 80,000–100,000 lb per sq in when heat-treated, and a range of hardness from 100 to 500 Brinell, with other physical properties improving correspondingly, gives the equipment manufacturer or refinery constructor an opportunity to build up to the new properties now being obtained.

In addition these properties are available in high-grade cast iron at a moderate or no increase in cost, for the reason that raw materials needed do not vary appreciably in cost, and alloys deliver more value per dollar when employed in castings than when used in wrought shapes Sometimes it is possible to improve a poor or average grade of iron by alloying it directly and depending upon the alloys to correct inequalities in the base composition Nickel, chromium, and molybdenum, singly or grouped, can be applied in unbalanced proportions to bring an unbalanced cast iron into a compositional equilibrium and at the same time impose some of their influence upon the resulting product A better and more economical procedure, one which is customarily followed in steel making, consists of first producing the best possible base composition, then adding the alloys—properly balanced—to do their bit. Unfortunately, cast iron and steel cannot be treated in the same way, and the same proportions of alloys used for one as for the other One exception, if there may be one, is in the nickel alloyed irons, simply for the reason that nickel acts largely upon the iron component instead of the carbon of the complex iron-carbon-silicon combination that constitutes cast iron

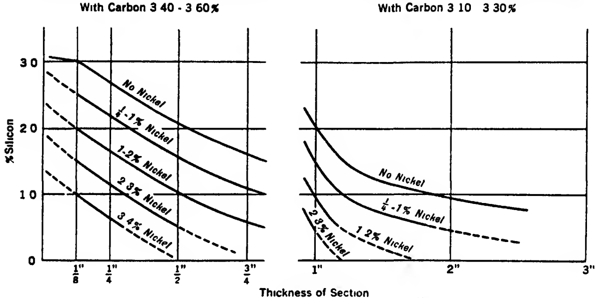

FIG 1 FIG 2

Percentages of silicon and nickel required to render castings of different section completely grey and machinable

An effort to outline the action of important chemical elements composing cast iron is made as follows Most important is carbon, which is present in commercial cast iron from 2 5 to 3 5% In a grey cast iron of the usual type, at least two-thirds of its carbon is desired in the form of graphite This graphite content would not be present if it were not for the action of the element silicon Cast irons contain 0 5 to 3% of silicon, which reduces the solubility of carbon in iron Since thin castings cool rapidly, they require a higher silicon content to achieve adequate graphitization An excessive silicon content causes a corresponding excessive graphitization, coarsening of the precipitated graphite, and an accompanying 'openness' of grain leading to porosity, leakage, and poor physical properties

The carbon content is important in controlling the strength of the cast iron Low-carbon irons contain less graphite and are consequently stronger Foundrymen can vary both the silicon and carbon contents of their irons within commercial limits of ±5% by suitable adjustments of the mixtures they are melting Figs 1 and 2 illustrate in a general way the influences of silicon and carbon on machinability and strength

Nickel additions to properly balanced cast irons range from 0 25 to 5%, sometimes accompanied by one-third as much chromium, i e from 0 1 to 1 5%, or molybdenum replacing chromium when desirable to avoid embrittlement or to reduce machining troubles In special cases, as in the corrosion resisting cast irons, nickel additions up to 20% may be employed, and where low or high expansivity is needed, up to 40% may be employed It is worth mentioning at this point that foundrymen have mastered the production of these highly alloyed irons without recourse to the use of special melting equipment

Alloying elements are classified as graphitizing types or carbide-forming types, depending upon whether they promote the action of silicon in precipitating graphite from the iron-carbon solution or oppose this effect and form carbides There seems to be no neutral position, and any element inactive in this iron-carbon system is likely to be considered inert and of little significance in affecting the important physical properties of cast iron Of the three most important alloying elements—nickel, chromium, and molybdenum—nickel is a graphitizer, chromium and molybdenum carbide formers The intensity of their respective effects may vary within the carbon-silicon ranges outlined above Thus, one part of nickel possesses approximately the force of $\frac{2}{3}$ to $\frac{1}{3}$ part of silicon as a carbide destroyer Chromium resists silicon upon a point-to-point basis Molybdenum is somewhat less powerful than chromium as a carbide former These alloys after being balanced to maintain equilibrium as regards graphitizing power, begin to exert their important secondary effects upon the iron-carbon-silicon solution by strengthening, hardening, toughening, &c

A perfectly balanced plain cast iron makes an excellent base to build from If nickel alone is to be added, it would be desirable to reduce silicon or carbon to maintain a proper balance In some cases foundrymen are compelled to run their soft irons, and then nickel with chromium and/or molybdenum additions are necessary, one element being the complement of the other as regards balance, while the effect of the alloys is cumulative Collateral properties of cast irons such as machinability, density, corrosion resistance, &c, require separate consideration and treatment and will be discussed first

Machinability

Machinability, grain refinement, density, uniformity, are undefinable, yet important properties of castings All these are interrelated Usually 0 5 to 2% of nickel is used to develop them As mentioned above, nickel exerts a graphitizing effect similar to silicon, but, unlike silicon which may completely free an iron of combined carbon, it exerts a greater solvent power for carbon Dissolved carbon must be diffused and not allowed to concentrate into lumps or colonies of carbides Pure nickel will dissolve carbon while silicon will not, and the presence of as little as 3% silicon in iron almost completely destroys the solid solubility of carbon in iron Since much of the body and strength of an iron and the effect of alloys upon it depend upon the presence of dissolved carbon in it, nickel exerts a positive but restrained influence in compelling complete graphitization of carbide residues, yet relinquishing its graphitizing power as soon as this lumped carbon is diffused and in solution

The step-bar casting, Fig. 3, offers a practical means of illustrating these principles An iron correctly balanced for the $\frac{1}{2}$-in section will be coarser grained than desirable in the 1-in section and ungraphitized and unmachinable in the $\frac{1}{4}$-in section, as well as unmachinable along the edges of the $\frac{1}{2}$-in sections, because the effective section through the corner is approximately equal to half the flat section Thus the radius through the corner of the $\frac{1}{4}$-in section is approximately equivalent to a round bar $\frac{1}{8}$ in in diameter

Strength and Combined Carbon in Castings of Varying Section

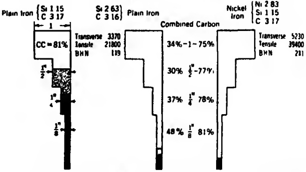

FIG 3 Plain iron and alloy iron of equal chilling tendency and of approximately equal machinability in castings of varying thickness (Black area is 'white unmachinable iron Spotted area is 'mottled' and unmachinable)

If the dominating section of the casting is $\frac{1}{2}$ in thick and requires 2% silicon with 3 3 total carbon, then the $\frac{1}{8}$-in section should contain at least 2 75 silicon Since this silicon would promote a coarse grain and openness, possibly leakage in the $\frac{1}{2}$-in and larger sections, the corrective of applying 1 5% nickel to the 2% silicon iron maintains the close grain of this composition for the $\frac{1}{2}$-in or larger sections and produces the necessary graphitization in the $\frac{1}{4}$-in and $\frac{1}{8}$-in sections to permit rapid machining For example, piston rings, individually cast, are frequently made $\frac{3}{16}$ in to 1 in thick with a 2% silicon iron and 2 to 0 75% nickel, viz

TABLE I

Example of Improving Density, Machinability, and Wear Resistance

			Section					
			Alloyed to improve density and machine well			*Alloy hardened to resist wear*		
	Plain iron, well balanced	*Plain iron, poorly balanced*	*$\frac{3}{16}$ in*	*$\frac{1}{2}$ in*	*1 in*	*$\frac{3}{16}$ in*	*$\frac{1}{2}$ in*	*1 in*
T C	3 20–3 50	3 30–3 50						
Si	1 80–2 20	2 40–2 70						
Ni			1 50	1 0	0 60	2 0	1 50	1 0
Cr						0 30	0 30	0 30

In another case, grease-gun cylinders—expected to be machined at high speeds, ends threaded, finished smooth, with sections $\frac{1}{4}$ in to 1 in in the casting—were made of a well-balanced base mix similar to the above with 1 to 1 5% nickel to maintain the close grain, pressure tightness, and machinability required of this exacting production job

Density—Pressure Tightness

Pistons for reciprocating pumps, engines, and compressors represent another common problem in obtaining dense, pressure-tight castings The following description and outline illustrate the case Automotive pistons (Fig 4) always light in section along the skirt and heavy sectioned in the piston-pin boss, have a characteristic habit of revealing porosity in the neighbourhood of the bosses, or between the head and boss The condition is not discovered until considerable machining is done and the casting skin removed or the shrink spots reached when the ring grooves are cut The soft iron needed to keep the skirt machinable opens the grain and encourages shrinkage in the heavy sections A reduction in silicon content of 0 1 to 0 3%, readily achieved by using a sufficient quantity of steel scrap in the charge, promotes a closing of the grain, while a nickel addition equal to double the amount of the silicon removed restores the necessary structure and machinability Where foundry mixtures cannot be changed, nickel-chromium additions, slightly out of balance but certain to maintain machinability at a somewhat reduced rate due to the accompanying hardening effect, can be applied as shown in Table II

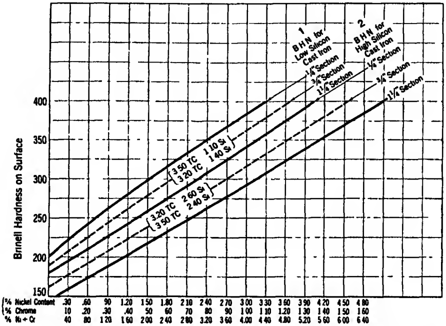

FIG 5 Hardening thin sections by direct alloying Thin sections ¼ in to 1¼ in (1) Low silicon cast iron, (2) high silicon cast iron (Diagram shows quantity of Ni Cr to be added)

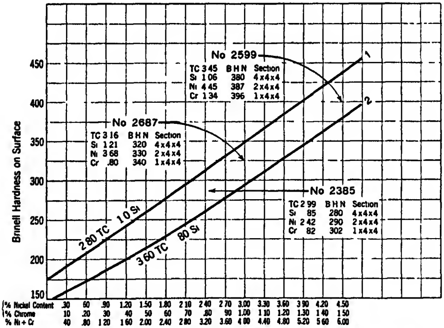

FIG 6 Hardening thick sections by direct alloying Heavy sections up to 4 in (1) Low-carbon cast iron, (2) high-carbon cast iron (Diagram shows quantity of Ni + Cr to be added)

Wear Resistance

Table I illustrates in general the manner in which hardening is accomplished Hardness may not be synonymous

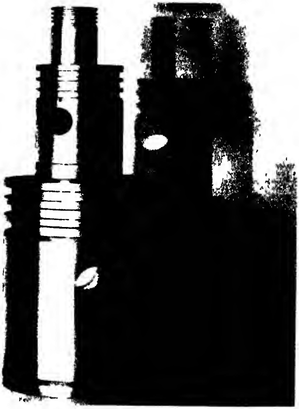

Fig 4 Nickel cast iron pistons

Fig 8 Centrifugal alloy iron liners

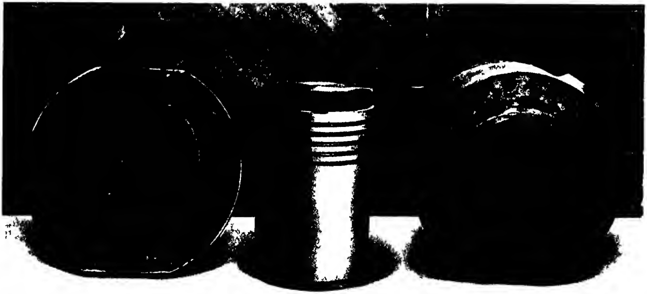

Fig 7 Nickel-chrome cast-iron cylinder heads and piston used in gas engine

TABLE II

Improving Density with Ni *or* Ni-Cr *Additions*

Plain iron	*Skirt section with nickel* *Light ½ in*	 *Medium 1 in*	 *Heavy 1½ in*	*Skirt section with Ni–Cr* *Light ½ in*	 *Medium 1 in*	 *Heavy 1½ in*
T C 3 10–3 40						
Si 2 20–2 40	2 20	1 90	1 40	2 40	2 40	2 40
Ni	0 75	1 25	2 0	0 75	1 25	1 50
Cr				0 30	0 50	0 60
Approximate strength lb /in ² Number	30,000	35,000	38,000	30,000	35,000	40,000
Brinell hardness number	160	175	190	175	190	210

with wear-resistance if microstructure is ignored, but hardening an iron by preserving its basically good structural qualities and building up hardness by means of balanced additions of alloys as illustrated above (Table II) has repeatedly demonstrated an ability to resist wear It might be interesting to add that these correctly balanced alloyed cast irons are not only hardened but strengthened and toughened as well A good wearing machinable hardness of 200 to 280 Brinell in the 'as cast' condition can be selected from an inspection of Figs 5 and 6 Pump liners, valve parts, engine and compressor castings (Fig 7), are typical refinery castings treated in this way

Results of wear tests [4, 1932] made in the working parts of pumps illustrate in the following data the practical application of the principles described

TABLE III

Wear of Plain or Alloy Iron

		T C	Si	Ni	Cr	*Brinell*	*Wear–weight loss, mg per sq in , after 20 hr*
Plain iron	cast	3 40	2 20			170	75
Alloy iron	cast	3 42	2 28	1 23	0 21	200	35

Similar evidence has been presented by Bornstein [2, 1929] from operating tests on tractor-engine cylinders Nickel-chromium alloy iron cylinders containing 0 68% of nickel and 0 22% of chromium were 26 points higher in Brinell hardness and showed only 68% of the wear of plain cast-iron cylinders

Heat Treatment

Some castings, such as pump and engine liners, camshafts, &c , are heat-treated either to develop strength or hardness for resistance to wear (Fig 8) Castings may be softened by an annealing at 1,100–1,300° F , after which they are rough machined at a hardness of 170 to 220 Brinell They are then gradually heated to 1,450–1,550° F, oil quenched to a maximum hardness, after which they are tempered and toughened by heating to some temperature between 400 and 1,000° F The procedure is limited to simple and symmetrical shapes Cored-out castings of complicated shapes are too susceptible to warping and cracking to be heat-treated They are best strengthened or hardened by the direct alloying procedure described in Figs 5 and 6 and Table II.

Tensile Strength

The strength commercially obtainable in grey iron has gradually and consistently been moved up from a 20,000 to 30,000 lb per sq in level to as high as 50,000 to 60,000 lb per sq in Most of the common cast irons to-day are produced in the 25,000 to 35,000 lb per sq in tensile range, but where strengths are important the upper levels have been developed without much difficulty In special cases cast irons possessing strength exceeding 65,000 lb per sq in and heat-treated grades up to 100,000 lb per sq in are being made (Table IV)

TABLE IV

Effect of Quench and Drawback upon the Tensile Strength of High Strength Nickel Cast Iron

Specimen	*Total carbon, %*	*Composition* *Silicon, %*	 *Nickel, %*	*Tensile strength in lb per sq in* *Original as cast*	*Quenched oil 1,500° F drawn at* *600° F*	 *800° F*
No 1	2 46	1 98	2 44	59,300	84,700	88,320
No 2	2 84	1 98	1 44	55,600	75,560	78,840
No 3	2 78	1 79	2 28	68,000	84,600	84,240
No 4	2 89	2 02	2 44	66,200	75,560	78,840
No 5	2 68	2 26	2 69	64,200	72,000	73,400
No 6	2 81	2 02	3 08	69,606	63,200	82,100
No 7	2 56	3 06	3 14	60,100	69,200	75,960

Alloys are almost indispensable to the everyday production of high-strength irons One of the outstanding characteristics of nickel-alloyed irons is their ability to level off irregularities in production conditions such as occur due to minor shifts in composition, pouring temperatures, shake-out, and cooling conditions, &c , which may adversely affect the strength of ordinary cast irons

Piwowarski [7, 1934] describes these effects thoroughly, and emphasizes the effectiveness of nickel with chromium or molybdenum in obtaining uniformity and reproducibility in high-grade cast irons

The American Society for Testing Materials in 1932 issued A S T M Tentative Specifications for Gray Iron Castings (A 48–32 T) [8, 1932] including castings for high-strength applications The data of Table V are abstracted therefrom

TABLE V

*Classifications of Cast Iron, from A S T M Tentative Specifications A 48–36**

Class	*Minimum tensile strength, lb per sq in*	*Transverse strength, lb load for 1 2 in diam bar × 18-in span*
20	20,000	1,800
25	25,000	2,000
30	30,000	2,200
35	35,000	2,400
40	40,000	2,600
50	50,000	3,000
60	60,000	3,400

* Am Soc Testing Mats Stds , 1936, p 757

The class 40 and 50 range of properties is met easily by nickel-chromium cast irons as is evidenced by the data of Table VI taken from a technical bulletin of the International Nickel Company

TABLE VI

High-test Alloy Cast Iron

Tensile Strength 40,000 per sq in to 48,000 per sq in

Section	¼ to ½ in	¼ to ½ in	¼ to ½ in	½ to 1 in	½ to 1 in	½ to 1 in	1 to 2 in	1 to 2 in	1 to 2 in	2 to 4 in	2 to 4 in	2 to 4 in.
Brinell hardness	180	220	260	180	220	260	180	220	260	180	220	260
Machinability	readily	good	economically	readily	good	economically	readily	good	economically	readily	good	economically
Wear resistance	good	very good	excellent	good	very good	excellent	good	very good	excellent	good	very good	excellent
Total carbon	3 20–3 40	3 10–3 30	3 00–3 20	3 10–3 30	2 90–3 10	2 80–3·00	3 00–3 20	2·90–3 10	2 80–3·00	2 90–3 10	2 80–3 00	2 70–2 90
Manganese	0·55–0 75	0 55–0 75	0 55–0 75	0 75–0·95	0 75–0 95	0·75–0 95	0·75–0 95	0·75–0·95	0 75–0 95	0 75–0 95	0 75–0·95	0 75–0·95
Silicon	1 60–1 80	1 40–1 60	1 20–1 40	1 20–1·40	1 10–1 30	1 00–1 20	1 00–1 20	1 00–1 20	0 90–1 10	0·90–1 10	0 80–1 00	0 70–0 90
Nickel	1 25	1 25	2 00	1 25	1 75	1 75	1 25	1 75	1 75	1 25	2·00	2·00
Chromium	none	none	none	none	none	0 26–0 35	none	none	0·25–0 35	0 25–0 35	0 35–0 45	0·50–0 60

Note The harder compositions attain top strength easily, but machine less freely

Class 60 specification or better is met readily in nickel alloyed grey cast irons through the agency of special melting involving the use of over 60% of steel in the cupola This type of iron has been trade named 'Ni-Tensyliron' A great many foundries are producing it to meet the 50,000 lb per sq in specification, and several are bettering the 60,000 lb per sq in specification regularly By special heat treatment 15,000 to 25,000 lb per sq in additional tensile strength is obtainable as shown in Table IV

The composition of Ni-Tensyliron may be varied over a fairly wide range to accommodate varying sizes and thicknesses of castings The general range is given in Table VII

TABLE VII

Composition of Ni-Tensyliron

Total carbon	2 50–3 15%
Manganese	0 50–0 90%
Phosphorus	0 15% max
Sulphur	0 12% „
Silicon	1 20–2 75%
Nickel	1 00–4 00%
Chromium or molybdenum	0 0–0 50%

In some cases slightly higher strengths are obtained, particularly in heavy sections, with additions of 0 35 to 0 5% of either chromium or molybdenum

The full ranges of properties obtainable in irons of this class are given in Table VIII The relation between composition and strength ranges is outlined in Fig 9

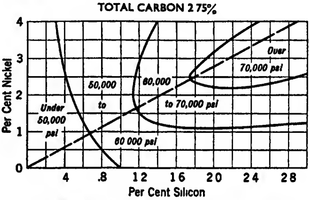

FIG 9 Ranges of silicon and nickel in which high-strength iron is obtained

TABLE VIII

Physical Properties of Ni-Tensyliron

Transverse breaking load*	4,500 to 8,000 lb
Deflection	0 11 to 0 25 in
Tensile strength (arbitration bars*)	50,000 to 75,000 lb per sq in
Compressive strength	165,000 to 190,000 lb per sq in
Elastic modulus (tension and compression†)	20,000,000 to 23,000,000 lb per sq in
Brinell hardness‡	220 to 320
Fatigue limit	50% to 57% of tensile strength

* 1¼ in round—12 in centres

† Up to proportional limit or up to 25% U T S

‡ Particular value obtainable depends upon silicon and nickel content

U T S = Ultimate Tensile Strength

The uniformity of Ni-Tensyliron in heavy sections is shown by the data of Table IX which is due to MacPherran [5, 1929], who has shown that the Brinell hardness of plain grey iron varies from 22 to 30 points from the outside to the centre of 4-in rounds, whereas high-strength nickel cast iron is uniformly hard throughout similar sections The strength throughout the heavy section is well maintained while the strength of ordinary cast iron may decrease 50% or more in the core of heavy sections

TABLE IX

Properties of Cast Irons in Heavy Sections

Property	Plain iron	High test iron	Ni-Tensyliron A	Ni-Tensyliron B	Ni-Tensyliron C
Total carbon	3 25	2 95	2 60	2 70	2 92
Silicon	1 40	1 00	1 57	1 71	1 45
Nickel	none	1 10	1 34	2 42	4 01
Tensile strength 4 in round per sq in					
Outside	29,000	41,800	59,000	68,600	55,000
Centre	16,150	31,400	45,600	48,200	42,200

The Ni-Tensyl type of cast iron finds application for pumps, compressors, engines, valves, and other pressure castings subject to considerable load.

Impact Resistance

Some cast-iron applications such as valve, pump, plug-cock, and compressor parts, require more than an ordinary degree of toughness Curiously enough, the high-strength alloy irons of the Ni-Tensyliron type generally possess a high deflection and resist impact well. Frequently the impact strength of the Ni-Tensyliron types will be two or three times better than that of the plain irons The impact test committee of the A S T M [9, 1929], reporting upon some 30 tests in which a plain and nickel-alloyed cast iron were included, compared various cast irons by dropping a 100-lb weight from successively higher levels on a 4-in span of a 1 2 in diameter bar A comparison of Ni-Tensyliron and plain iron follows

	Tensile strength	*Drop—in*	*Average*
Plain cast iron	33,500	6 to 10	7 2
Ni-Tensyliron	61,600	11 to 20	16 2

Additional data appear in Table X

Low-temperature Impact

Some operations have been conducted at temperatures reaching −50° F Many materials become brittle at these temperatures, and while cast iron is not affected to the same degree as steel, it loses some toughness The nickel-alloyed high test and Ni-Tensyliron types not only possess better impact resistance at normal temperatures but retain more of their toughness at low temperatures, as shown in Table X

TABLE X

Low-temperature Impact Properties of Alloyed and Plain Cast Iron

	T C	Si	Ni	Cr	Cu	*Foot-pounds** *Room temp*	*Foot-pounds** *−45° F*
Plain C I	3 44	1 96				39	29
Nickel C I †	2 76	2 02	1 75			44	38
Ni-Resist C I	2 73	1 59	13 76	1 95	6 0	55‡	50
Invar C I	2 50	1 40	30 00	4 00		81	70

* Bar 1 20 in dia × 6 in —broken 'as cast'

† High test type (develops up to 60 ft lb)

‡ Values as high as 70 ft -lb have been developed in softer grades

For service at freezing temperatures, therefore, cast-iron equipment which operates successfully at normal temperatures should be constructed of alloyed, high-test nickel cast iron, or Ni-Tensyliron Compressors, pumps, filters, and other parts of the refrigeration and circulation systems have been built of these tougher alloy-irons

High Temperature

Cast iron operates in many of the hot, unfired, low-pressure applications under the traditional limit of 450° F set by several engineering committees If specifications limiting the degree of growth and including an outline of an acceptable composition range are not set, the 450° F temperature limit would better be retained However, cast irons are available which can be employed for unfired pressure vessels at temperatures up to 700° F and with special care for temperatures up to 900° F The low-carbon, low-silicon types described as pearlitic irons make the best base compositions, to which suitable additions of heat and deterioration resisting alloys, such as nickel and chromium in proper balance, are added Tables XI, XII, XIII, XIV and Figs 10, 11, and 12 illustrate the difference in deterioration rate

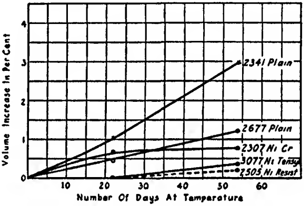

FIG 10 Plain cast iron of 2% silicon showed greatest growth subjected to steam at 900° F A nickel-copper-chromium cast iron showed the least See Table XII

Cylinder heads, compressor parts, valves, regulators, low-pressure return bends, exchanger and condenser castings, pumps, &c , subjected to long periods of heating may not require irons of unusual strength, but do require that their original physical properties do not deteriorate appreciably

Fig 13 summarizes results of quick, elevated temperature tests upon a number of cast irons No 6 is a malleable iron base specially processed, while nos 7 and 8 would

TABLE XI

Stability of Cast Iron at 1,000° F

Material	*Composition, %* *Total carbon*	*Silicon*	*Nickel*	*Chromium*	*Volume increase % after indicated time* *72 hr*	*185 hr*	*303 hr*	*422 hr*	*542 hr*	*662 hr*	*Brinell Hardness after indicated time* *Start*	*113 hr*	*231 hr*	*350 hr*	*422 hr*	*542 hr*	*662 hr*
Plain iron	3 44	1 96			2 16	2 97	3 74	3 86	4 12	4 17	179	103	95	102	105	89	101
Nickel-Chromium iron	3·41	1 97	1 73	0·60	0 68	1·06	1 57	1 57	1 78	1 82	217	179	163	168	165	156	156

TABLE XII

Heat no	*Type*	*Analysis* T C	Si	Ni	Cr	Cu	*Volume increase %* *After 22 days*	*After 54 days*	*Tensile strength lb per sq in* *Original*	*After 22 days*	*After 54 days*
2,341	Plain	3 48	2 02				1 01	2 99	18,400	13,840	10,600
2,677	Plain	3 36	0 82				0 45	1 22	32,900	32,840	27,200
2,307	Nickel-Chromium	3 04	1 39	0 96	0 33		0 68	0 78	43,000	39,720	41,300
3,077	'Ni-Tensyliron'	2 89	2 45	1 45			0 00	0 36	47,000	54,760	55,200
2,505	'Ni-Resist'	3 04	1 64	13 63	3 23	6 48	0 00	0 23	24,050	27,720	28,400

TABLE XIII

Growth of Cast Iron in an Oxidizing (CO_2) *Atmosphere at 1,500° F (815° C)*

Heat no	Type	Analysis					Volume increase % after indicated number of cycles (below)			
		T C	Si	Ni	Cr	Cu	7	16	27	39
2,361	Plain cast iron	3.26	2.02				7.87	15.62	22.08	24.39
2,349	Nickel-Chromium cast iron	3.43	1.08	2.33	0.49		1.36	3.96	12.59	17.10
2,335	Nickel cast iron	3.82	0.45	3.97			6.54	5.99	7.62	9.76
2,317	'Ni-Resist'	2.88	1.72	14.31	3.92	5.37	2.17	0.59	1.30	1.99

TABLE XIV

Scaling of Cast Iron in an Oxidizing Atmosphere at 1,500° F (815° C)

Heat no	Type	Analysis					Original weight of specimen in g	g of scale formed after indicated no of cycles			Cumulative scale formed % of orig wt of specimen after indicated no of cycles		
		T C	Si	Ni	Cr	Cu		12	28	44	12	28	44
2,361	Plain cast iron	3.26	2.02				115.49	9.81	29.36	41.24	8.50	25.40	36·60
2,343	Ni-Cr cast iron	3.53	1·97	1.52	0.40		114.13	5·98	18.45	33.61	5.25	16·15	29.50
2,327*	'Ni-Resist'	2.60	0.48	13.17	1.48	6.50	122.49	1.83	9.22	9.73	1.50	7.56	7.95

* While this particular test sample was low in silicon it may be stated that the standard 1 to 2% Silicon Ni-Resist composition is more satisfactory in that it requires no special foundry mixtures and produces equivalent results

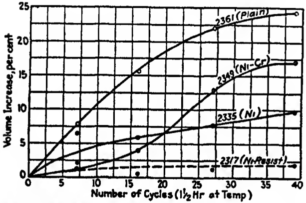

FIG 11 Resistance to growth in an oxidizing atmosphere of carbon dioxide at 1,500° F See Table XIII

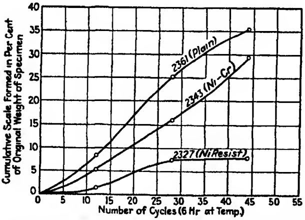

FIG 12 Inhibition of scale formation in cast iron (oxidizing atmospheres at 1,500° F) is important in applications requiring transfer of heat. See Table XIV

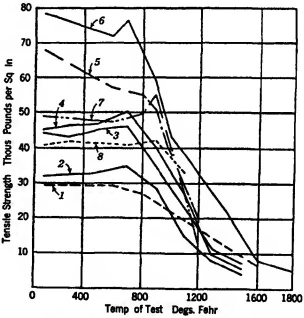

FIG 13 Short-time tensile strength tests at elevated temperatures of irons of the following compositions

Number	1	2	3	4	5	6	7	8
Total carbon	2.95	3.40	3.20	2.95	2.78	2.60	2.40	2.61
Manganese	0.85	0.75	0.85	0.75	0.80	0.25	0.70	0.82
Silicon	1.64	1.50	1.15	2.45	1.79	0.90	1.57	1.20
Nickel	13.02		1.50		1.59	1.25	1.34	2.39
Copper	6.29							
Chromium	3.55					0·40		
Temp of falling off in strength, °F	600	700	700	700	800	800	900	900

require special melting methods other than the cupola It is evident from a comparison of cupola irons 2 and 3 and also from a comparison of high-test types nos 4 and 5 that low-silicon, low-carbon alloyed cast irons are best fitted for high-temperature loading

Creep tests were made by Allen [1, 1931] on three of the irons described above It is interesting to compare the low-silicon, nickel alloyed, moderate strength grey iron with its unalloyed companion as shown in Fig 14 and Table XV It is apparent that a high-test iron, sufficiently low in silicon, and fortified with alloys in the manner illustrated in Iron no 5, above, would excel the unalloyed high-test iron both in initial strength, creep strength, and resistance to deterioration An outline of suitable compositions is suggested in Table XVI below

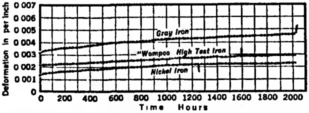

FIG 14 Time-deformation curves for three irons carrying 10,500 lb per sq in Load at 700° F 'Grey Iron corresponds to no 2 of Fig 13 'Nickel iron' corresponds to no 3 'Wompco' corresponds to no 4

TABLE XV

After 2,015 hr under Load at 700° F the Test Bars were removed from the Creep-test Apparatus and subjected to the Tension Test at Room Temperature

	Tensile strength at room temperature, lb per sq in			*Brinell hardness*	
	Before creep testing		*After creep testing*	*Original*	*Measured at room temperature after 2,015 hr at 700° F*
	Maximum	*Minimum*			
Grey iron	33,900	31,500	29,750	197	156
'Wompco' high-test iron	48,300	45,000	48,250	237	217
Nickel iron	48,100	47,400	47,400	230	216

TABLE XVI

Limiting Temperature 450° F A S T M Class 30 or less, i e under 30,000 lb per sq in

	T C	Si	Ni	Cr *and/ or* Mo
Light sections down to ½ in	3 40 max	2 50 max	1 50*	0 15* to 0 30*
Heavy sections up to 2 in	3 40 max	1 50 max	1 50*	0 40* to 0 70*

* Optional for lower strength range Necessary for stability at upper strength range

Limiting Temperature 600° F A S T M Class 30 to 60, i e 30,000 to 60,000 lb per sq in.

	T C	Si	Ni	Cr *and/ or* Mo
Light sections down to ½ in	3 20 max	2 10	1 25–2 0	0 15–0 35
Heavy sections up to 2½ in	3 20 max	1 60	1 25–2 0	0 30–0 60

Limiting Temperature 750° F A S T M Classes 40 to 60, i e 40,000 to 60,000 lb per sq in

	T C	Si	Ni	Cr *and/ or* Mo
Light sections down to ½ in	3 00 max	2 00 max	1 50–2 50	0 15–0 35
Heavy sections up to 2½ in	3 00 max	1 20	1 50–2 50	0 30–0 60

Where creep may proceed to the extent of several per cent , as in some unfired pressure vessels such as heat exchangers, valves, pumps, return bends, fittings, &c , close specifications upon composition, strength, and growth are obviously necessary, or irons which possess one of these qualifications, such as strength, might readily fail in resistance to creep or growth Good practice suggests further that castings for elevated temperatures be subjected to a stress-relief anneal, consisting of heating slowly to some temperature up to 1,000° F max , but above the highest casting operating temperature, to eliminate stresses introduced during casting

Where machinability is unimportant as for firebox and still tube supports, which are not excessively heated or loaded, alloy additions to low-silicon (under 1 5%) irons containing from 1 25 to 2 5% nickel and 0 6–1 % chromium give good results (Table XVII)

The upper alloy ranges shown in Table XVII produce a hardening of the cast iron which limits the degree of heat resistance obtainable, particularly where machinability is important, and the improvement illustrated by Tables XI, XIII, and XIV can then be excelled only by employing one of the high-alloy types of cast iron such as Ni-Resist, which is described more fully later

TABLE XVII

Composition Range for Castings requiring Moderate Heat Resistance not subject to Internal Pressure and Non-machinable

	%
Total carbon	3 10–3 25
Silicon	0 75–1 50
Manganese	0 60–0 80
Nickel	1 00–2 50
Chromium	0 50–1 25

The nickel-chromium cast irons illustrated in Table XVII, in the relatively simple composition shown and in about a 1 to 1½-in section, would be completely destroyed in about 12 to 15 months at 1,100° F , while the plain cast iron would fail in about 6 months Several courses remain open to deal with this problem

First, limit the working temperature to a maximum of 900–1,000° F

Second, employ about twice the alloy content, i e 3 to 4% nickel with 1 to 1 25% chromium to obtain a corresponding improvement

Third, use Ni-Resist which, as described later, possesses 8 to 12 times the resistance to deterioration shown for plain cast iron and may be employed for somewhat higher temperatures than 1,100° F

Fourth, equip entirely with heat-resisting alloys of the steel type, such as shown in Table XVIII

These separate suggestions require a little amplification The second one, recommending a 4% Ni, 1 25% Cr, type of cast iron is being employed as kiln liner in the cement industry where its hardness helps to resist abrasion as well as heat It should not be employed if extensive machining is necessary because its hardness may exceed 350 Brinell, although it is grey and possesses the toughness of grey cast iron in comparison to the brittleness of white non-graphite irons

If high degree of permanence is necessary the Ni-Resist composition, austenitic, non-magnetic, and corrosion resistant as well as machinable, can be applied for temperatures above 600° F and under 1,300° F as shown in Tables XI, XIII, and XIV, Figs 10 and 11 taken from Wood's [11, 1933] work After making a growth test on a series of commercial materials, Wadman [10, 1930] selected Ni-Resist for furnace parts heated at 900–1,300° F, and heat-resisting alloys for higher temperatures Results of his tests appear in Fig 15

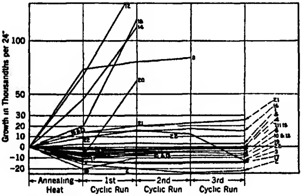

FIG 15 Growth after 30 days' heating Annealing heat = 1,400° F for 96 hr 1st cyclic run = raise temperature in 8 hr from 900 to 1,400° F Hold 8 hr at 1,400° F Cool 8 hr to 900° F Repeat daily for 10 days, 2nd and 3rd cyclic run = same as first

Compositions in Fig 15

No	Fe	Cr	Ni	Si	C	Mn	Cu
1	72–70	28–30					
2	62	25	10	3			
3	52	23	23	0·5	0 8	0 5	
4	67	21	12		0 25		
5	50–41	18–22	30–34		0 4	2–3	
6	16–14	18–20	65	0 6		1	
7	41	18	38	1 25–1 5	0·4–0 5	0 75–1 0	
8	44–39	17–19	37–39	1		1	
9	48	15	35	1–1·4	0 45–0 65	0 5–0 7	
10	55	14 6	30		0 26		
Ni-Resist		4·07	14 26	2 05	3 16		6 34
12		0 5	0 3	2·0	3 3	0 65	

13, 14, 15, 16—Heat-resisting castings
17, 18, 19—Stainless steels
20 21—Cast irons
22—Structural steel welded

The toughness of Ni-Resist is considerably greater than that of ordinary cast iron, as indicated in the impact data of Table X as well as in deflection tests Its strength is about the same as that of plain cast iron, and at best reaches a 30,000 to 40,000 per sq in tensile level At elevated temperatures, quick or short-time tests (Fig 13) show that its strength falls rapidly in the range of 800–1,400° F as is true of all cast-iron base materials Most important in connexion with its use at elevated temperatures is the fact that its strength remains unchanged over a long period of time, while the low-alloyed irons and plain irons deteriorate rapidly so that after a few months' service at high temperatures their strength and body are completely destroyed, as shown in Tables XII and XIII In order to summarize these facts and outline suitable compositions, Table XVIII is offered, based upon castings of 1-in sections

TABLE XVIII

*Firebox and Still Castings**

Temp ° F	T C	Si	Ni	Cr	*Type*
A—up to 600	3 10–3 40	1 20–1 75			plain
B—600–900	3 10–3 40	1 20–1 75	2 0	0 75	Ni-Cr
C—900–1,300	2 60–3 10	1 50	14 5	3 50	†Ni-Resist
D—1,300–1,800	under 0 35		10–12	24–28	heat resisting
E—1,800–2,000	under 0 35		35	15	,, ,,

* Tube supports, firebox castings, dampers, stack rings, &c Heat resisting alloys D and E are used interchangeably depending upon condition of atmosphere, particularly of sulphur, in furnace

† Contains 6% copper or 20% nickel

Corrosion Resistance

Almost every conceivable form of corrosion is encountered in refinery operation Acids, caustics, saline solutions, liquids, tars, hot, cold, aerated, agitated, turbulent, stagnant, erosive, wet, dry, vapours, represent some of the conditions encountered Fortunately, nearly all of the mildly alloyed nickel or nickel-chromium cast irons possess a moderately good resistance to most corrosives Some of the improvement is due to the inherent resistance conferred by the alloys, the remaining improvement comes from an attendant refinement in the structure and texture Many castings, such as condenser pipe sections, fittings, manifolds, traps, regulator valves, pumps, bubble caps, and trays, &c, are moderately alloyed to obtain a mild increase in corrosion resistance ranging from 20 to 200% In most cases light castings such as thin-walled pipe or condenser castings, &c, will contain

Thickness	T C	Si	Ni	Cr
⅛–½ in	3 10–3 40	1 80–2 20	0 50	0 20

Heavier castings such as pumps, bubble caps, valves, and control devices will contain three times as much alloy to compensate for their thicker section, viz

Thickness	T C	Si	Ni	Cr
½–2 in	3 00–3 40	1 20–2 00	1 50–2 50	0 50–0 75

When chromium or silicon are not particularly useful, as in caustic, hydrochloric, or similar corrosives, chromium free, low-silicon compositions may be most useful, viz

Thickness	T C	Si	Ni
½–1 in	3 10–3 50	1 40–1 80	1 0–2 50
1–3 in	2 80–3 40	0 60–1 40	2–4 50

Where conditions are especially severe the Ni-Resist composition of the nickel-copper-chromium or copper-free type are employed, viz

Section	T C	Si	Ni	Cu	Cr
½–1 in	2 60–3 10	1 40–1 80	13–15	5–6	1 50–2 50
Copper free	2 60–3 10	1 40–1 80	18–22	under 0 30	2 00–3 00
1–2½ in	2 60–3 10	0 60–1 40	13–15	5–6	2 00–3 50
Copper free	2 60–3 10	0 60–1·40	18–22	under 0 30	2 00–3 50

In many instances the characters of the corrosives encountered defy definition. They may be mildly acid one day and caustic or brackish the next. In such cases a great

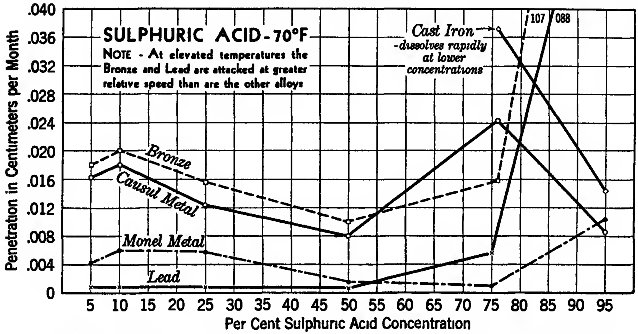

FIG 17 Corrosion rates of valve construction materials in sulphuric acid solutions at 70° F 'Causul metal' is a special grade of alloy of the Ni-Resist type

deal of useful data has been obtained by means of the corrosion spool test In this test a series of cast-iron specimens are prepared, weighed, and mounted on an insulator with insulating spacers between them to eliminate electrolytic or galvanic corrosion After a long enough period of exposure to eliminate the effects of day-to-day variations, the spool is removed and the specimens cleaned, weighed, and critically examined In some cases the advantage of one composition over another is so distinct upon visual inspection that further work is hardly necessary Fig 16 illustrates this The superior performance of Ni-Resist in these pilot tests leads to its gradual introduction and finally widespread adoption for many refinery applications Its greater resistance to wear, Table XIX, over the ordinary cast irons or the soft brasses and bronzes, and its ability to ensure hotter temperatures rapidly increased its commercial usefulness Ni-Resist worked well against most corrosives whether acid base or salt, and the ever-shifting character of some refinery solutions made it more or less an all-purpose, low-cost construction material Figs 17, 18, and 19 indicate its acid, caustic, and salt-water performance A summary of tests upon typical refinery corrosives has been separately prepared [6] Cooper-Bessemer Corporation prior to its application of Ni-Resist for compressor heads, cylinders, and pistons made the test summarized in Table XX

TABLE XIX

Weight Loss in grams of Austenitic and Ordinary Cast Irons under Erosive Conditions (Mather and Platt, Ltd)

Mixture	*'Ni-Resist' type alloy*	*Cast iron*
Sand and water 50–50	145	320
Coal dust and water 50–50	18	84
Clinker and water 50–50	144	320

TABLE XX

Exposure to Saturated Hydrogen Sulphide in Water at 180° F [10]

Weight Loss, grams per square metre

Material	*100 hr*	*200 hr*	*300 hr*	*400 hr*
'Ni-Resist'	59 68	83 45	83 45	83 45
Semi-steel (12½% steel)	79 05	189 10	221 65	248 00
Piston-ring cast iron	156 55	215 00	252 65	294 50
Machine steel (0 35 to 0 45% carbon)	85 25	217 90	310 00	362 70

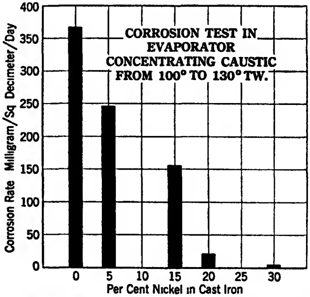

FIG 18 Effect of nickel additions to cast iron 'Ni-Resist' of 20% nickel–2% chromium resists boiling caustic corrosion

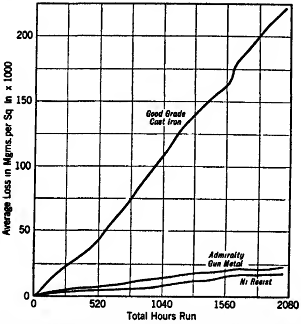

FIG 19 Diagram showing corrosion rate of Ni-Resist compared with cast iron and gun metal in aerated sea water (*Metallurgia*, 8, 45 (1933))

Shaffer and Pollock, reporting upon extensive tests of condenser materials, wrote

'A few ferrous alloys tested in the stream from distillation of acid-treated naphtha showed that metals of the 18–8 (chromium-nickel) type show good resistance and that cast iron is more resistant than steel, while small additions of copper to cast iron appear to lessen its resistance, low-chrome steel shows only low resistance to this type of corrosion. An alloy cast iron of the following composition, nickel 12–15%, chromium 2·4%, copper 5–7%, silicon 1·5%, total carbon 3% and the remainder iron, has proved very resistant in such a service. Cast iron, on account of its low cost and moderately long service, is reasonably economical, but a trial of the above alloy may justify the higher capital expenditure.'

More recent work by Pollock, Camp, and Hicks was reported in the February 1935 A.I.M. and M.E. Symposium on 'Metals in Oil Refining Equipment'. An attempt to abstract some of the data on cast iron is made in Table XXI, but for complete information the reader is referred to the 200 or more samples and approximately 35 test conditions compiled by the staff of Humble Oil & Refining Company as a contribution to progress in the oil industry.

Harnsberger [3, 1935], 'Materials Used in Refinery Pumps', in a report surveying pump materials refers to the successful application of Ni-Resist among other materials

TABLE XXI

Results of Refinery Corrosion Tests

No	Type	*Penetration in inches per year*										
		Fresh water	*Salt water condenser box*	*Salt water condenser box*	*Steam*	*Crude oil vapour*	*Naphtha (liquid)*	*Cracking coil bubble tower*	*Debutanizer Vapour*	*Debutanizer Liquid*	*5% HCl*	*5% HCl plus acid sludge*
70	Plain	0·0005	N D	0·0044	0·0089	0·0136	0·0111	0·0054	N D	N D	3·6813	0·0975
139	Low silicon	0·0029	0·0154	0·0046	0·0090	0·0066	0·0057	N D				
116	C N I	0·0019	0·0074	0·0047	0·0061	0·0144	0·0060	0·0051				
179	Ni 4%			0·0037		0·0037	0·0120	0·0078				
173	Pipe			0·0046		0·0090	0·0084	0·0051				
71	12½% Ni special		0·0078	N D	0·0024	0·0046	0·0053	0·0001	N D	N D	0·3297	0·1563
117	Ni resist	0·0001	0·0030	0·0036	0·0001	0·0145	0·0022	0·0030	0·0001	0·0003	0·0456	0·0312

N D = not determined

No	Type	*Plant caustic 15° Bé*	*Wash water from treaters*	*Wash water from treaters*	*Wash water from treaters*	*Rerun naphtha acid treated still (vapours)*	*Rerun naphtha acid treated still (liquid)*	*Plant caustic 10° Bé*
117	Ni resist	0·0002	0·1330	0·0172	0·0285	0·0003	0·0004	0·0002
158	88–10–2 bronze	0·0006	0·0155		0·0135			0·0027
A–3	77–8–15 „	0·0013	0·0246	0·0087	0·0157			0·0007
70	Plain					0·0018	0·0057	

Analyses

No	Type	T C	Si	Mn	Ni	Cr	Cu	Sn	Pb
70	Plain	2·61	1·75	0·95					
139	„	3·00	2·00	0·60					
116	C N I	3·30	2·40	0·65	0·40	0·25			
179	1 to 4% Ni				1–4				
173	Pipe	3·40	1·80						
71	12½% Ni special	2·78	2·17	0·47	12·41				
117	Ni resist	2·80	2·00	1·00	13 to 15	2 to 3	5 to 6		
178	„	2·80	2·00	1·00	13 to 15	2 to 3	5 to 6		
A–3	Bronze						77	15	8
158	„						88	10	2

No 71 under-alloyed Ni-Resist type

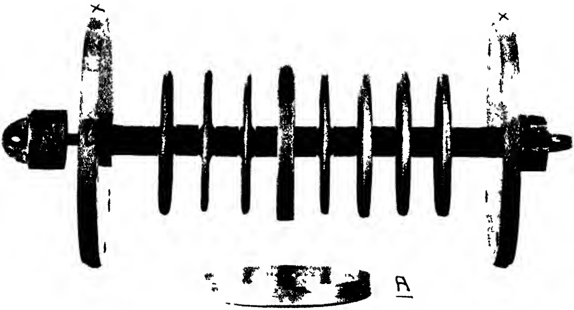

FIG 16 Results of 78 days test of cast iron in acid treated naphtha stream Disks X X are Bakelite end rings All specimens originally same size as specimen A Thick specimen in centre of spool is Ni Resist

FIG 20 Condition of 8 in pipe after several months handling hot hydrogen sulphide contaminated brackish water

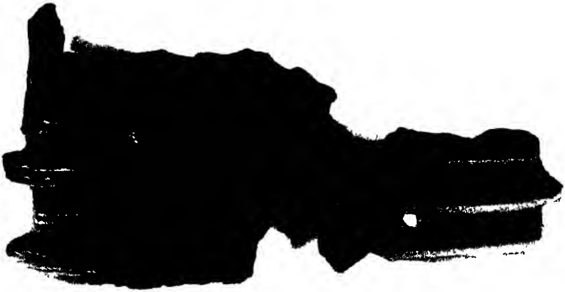

FIG 21 Corroded condenser section after 1½–2 years in condenser box handling gasoline vapours at 600–700° F Exterior cooled by brackish well-water

for liners, fluid ends, valves, wearing rings, shaft sleeves, &c, in cold service, reflux, hot-oil pump liners, and gas-absorption plants Bubble caps of Ni-Resist are being tested in a number of refineries

Exposure tests of 6 months' duration of Ni-Resist at 300 lb per sq in pressure and 700° F, in a tower taking gas oil charging stock from mid-Continent crude, gave the following results

TABLE XXII

Bubble Cap Corrosion

Cap	*Weight in ounces* *Original*	*Final*	*Loss*
Top	180	179	1
2	180	178	2
3	180	174*	6*
4	176	176	0
5	175	173	2
6	182	178	4

* Weight loss includes broken tooth

The trays of cast iron in the lower end of this tower were badly attacked

The tests are being repeated with Ni-Resist in the bottom trays

In another large mid-western refinery a tower operating on all kinds of stock at a pressure of 300–50 per sq in and a top temperature of 650–750° F and a bottom temperature of about 750° F showed the following results after cleaning (by sand blasting) and weighing caps that had been in service for 3,135 hr

TABLE XXIII

Bubble Cap Corrosion

Tray no	*Average weight loss oz per cap* *Cast iron*	*Ni-Resist*	*Ratio of corr* *C I v Ni-R*
Top	12	4	3 0
2	14	6	2 4
3	17	8	2 2
4	broken	12	
5	22	11	2 0
6	24	7	3 4
7	21	7	3 0
8	20	8	2 5
9	23	6	3 9
10	22	11	2 0
11	23	10	2 3
Bottom	19	9	2 2
Avg (excluding no 4)	19 7	7 9	2 5

Caps had been grouped in accordance to their positions on each tray and average weight losses measured In addition, observations were recorded to the effect that nearly 25% of the plain cast iron caps were cracked or broken and that all caps were badly pitted, indicating localized corrosion of greater severity than registered by the average weight loss The caps have been replaced and will be corroded to destruction The tests thus far indicate that a further advantage over the two to fourfold improvement will accrue to the Ni-Resist caps, as their better surface condition resists the reception and retention of corrosive vapours

Condenser corrosion is a troublesome matter in many refineries, especially in the top sections where temperatures are high and the vapours begin to be converted into liquid Figs 20 and 21 show some of the conditions of corroded pipe and condenser sections after a short time in service Condenser sections, pipe, pumps, valves, meters, traps, filters, bubble caps, &c, are typical castings regularly being produced of Ni-Resist

Abrasion Resistance

An extremely hard, white cast iron, unmachinable and possessing, when sand cast, a hardness in excess of 600 Brinell, has been developed and trade named 'Ni-Hard' It contains approximately 4 to 5% of nickel and 1 5 to 2% of chromium and is achieving increasing importance in castings subject to abrasive conditions

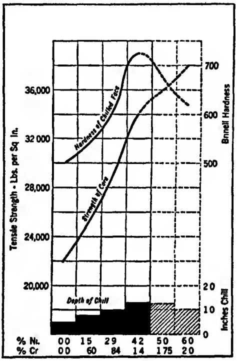

FIG 22 Properties of 'Ni-Hard' and plain cast iron Total carbon approximately 3 5%, silicon, 0 95 to 1 0%

A comparison of its strength and hardness with plain cast iron is shown in Fig 22 Its properties are summarized in Table XXIV

TABLE XXIV

Properties of Alloyed Chilled Iron

	High carbon	*Low carbon*
Brinell on chilled surface	650–700	575–650
Tensile strength of grey core	30,000 lb /in^2	40,000 lb /in^2
Total carbon	3 00–3 50	2 50–3 00
Silicon	0 50–1 0	0 50–1 0
Nickel	4 25–4 75	4 25–4 75
Chromium	1 40–1 80	1 40–1 80

The Ni-Hard type of alloy cast iron attains Brinell hardness values on the chilled face of from 500 to more than 750 At the same time strength and toughness are increased greatly, so that it is a very useful material for resistance to wear and abrasion Up to a hardness of about 500 Brinell the alloy can be machined with carboloy tools There are certain places in refinery operation where this material could be useful, for example in pumps handling clay, Fuller's earth suspensions, gritty oil, such as sludge-coke mixtures or gritty water and in tube cleaners

Appendix

Typical Applications of Ni and Cr in Cast Iron

	T C	Mn	Si	Ni	Cr	TS* *1,000 Lb*	BHN	% *steel in charge*†
Grate bars, stoker parts	3 30	0·60	1 50	1 50	0·60	36	210	15–30
Light cams	3 10	0·55	1 50	1 25	0 30	35	200	20–30
Heavy cams	3 10	0 60	1 50	2 00	0 60	42	200	50–80
Air-cooled cylinders	3 30	0·60	2 35	2·00	2 20	28	200	0–15
Automotive light cylinders	3 30	0 55	2 10	0 75	0 30	36	200	15–25
Heavy automatic cylinders	3 30	0 65	1 85	1 75	0 50	36	220	20–35
Light compressor cylinders	3 30	0 55	2 10	1 25	0 45	36	210	15–20
Light Diesel cylinders	3 30	0 65	1 85	1 75	0 50	36	220	20–35
Light brake drums	3 30	0 65	2 10	1 50	0 40	35	220	15–25
Heavy brake drums	3 10	0 80	1 80	2 25	0 50	38	220	15–25
Clutch and hoist drums	3 00	0 85	1 10	1 25	0 30	40	220	30–70
Cylinder heads	3 30	0 55	2 10	1 25	0·45	38	220	15–20
Light cylinder liners	3 25	0 55	2 00	1 75	0 50	36	220	20–40
Exhaust manifolds	3 50	0 65	1 80	2 00	0 75	36	200	0–20(C)
Clutch plates	3 30	0 65	2 10	1 50	0 40	35	220	15–25
Caustic pots	3 30	0 50	0·70	1 50	0 60	38	230	30–50
Lead, zinc aluminium pots	3 30	0 65	1 00	2 00	0 75	40	230	250–0

* In arbitration bar section

(C) Anneal at 1,400° F

† A wide range in steel content has been given since the exact amount required to obtain the recommended T C content will depend on the characteristics of the individual furnace in which the material is produced The extremes given have, however, been successfully used, and the foundryman can determine the exact amount with a knowledge of melting conditions in his own unit

*Application of High-test Alloy Cast Iron**

Casting	% *steel in charge*	*Total carbon*	*Silicon*	*Nickel*	*Chromium*
Brake drums	60	2 90–3 10	1 40	2·00	0–0 30
Cams	60	3 10	1 10	0·90	0–0·30
Cylinders					
Air ammonia and CO_2	60–70	2 80–3 00	1 10	1 00–1 50	0–0 30
Hydraulic compressor	50–60		1 00	1 00	None
Printing press	50–60		1 00	1·00	„
Steam	60	2 75–3 15	0 90–1 10	1·00–1 25	0–0 30
Diesel engine					
Liners and heads					
Medium	60	2 90–3 10	1 00–1 20	1 50	0–0·30
Heavy	60	3 00	0 90–1 00	2·00	0·50
Gears					
Medium and heavy	50		0 80–1·00	2 00	0·60
, ,	75		1 00–1 20	1 25	None
Plungers—hydraulic press	50–60		1·00	1 00	„
Pumps					
Medium and heavy	50	3 00–3 15	1 20	0 75–1 00	„
Medium and light	80	2 75–3 00	2 00–2 25	1 50–2 00	„
Valve bodies	50	3 05–3 15	0 90–1 00	1 50	,
Valve bodies	60	3 00–3 15	1 25–1 50	0 75–2 50	„
Valve bodies, extra strong	70–80	2 75–3 00	1 25–2 25	1 50–2 00	„

* See Table VI

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FERROUS METAL TUBES FOR REFINERY SERVICE

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(*a*) Introductory Remarks

THE technology of petroleum refining has advanced tremendously within the last 10-year period Demands for quality lubricants, for high anti-knock, gum-free gasoline, and for other more specialized petroleum products have led to many changes in refinery apparatus Units for topping, cracking, re-forming, and stabilizing have been continuously changed and improved so as to obtain quality products and high yields The dewaxing of lubricating oil, solvent-refining processes, hydrogenation, and, more recently, polymerization of refinery and natural gases to produce polymer gasoline have added to the complex problems involved in securing adequate materials of construction The search for suitable materials has been governed by the service requirements of the particular part and by the ever-present need for safety and economy

Oil refining is mainly a series of thermal processes, combined, in some cases, with chemical processes The severe nature of the service requirements and the rapid changes occurring in crude-oil supplies and in refinery processes themselves have made it essential that engineers, research workers, and refinery technologists keep abreast of requirements

Tubes and pipe for topping stills and cracking furnaces, vapour lines, refinery piping, and heat exchangers and condensers form important items of the equipment used This article concerns itself with a critical review of the properties of alloy steels in present use in these forms and considers only 'seamless' tubing, which is almost exclusively used because of its well-known features of safety and reliability

(*b*) Historical Sequence of Development

Until 1928, plain low-carbon steel was the only ferrous tubular material in common use Even to-day it may be considered the basic material for service where the corrosive conditions are mild and where temperatures and pressures are not excessive The demands for higher temperature operating conditions and the excessive corrosion of carbon steel, encountered when processing sour crudes, led to a trial, during 1927, of 16 5–18% chromium-iron alloy tubes A few months' service indicated that such an alloy had exceptional corrosion resistance, but developed brittleness which led to several failures during cleaning operations Because of this disadvantage the alloy was found unsuitable for general application Alloys of 20–30% chromium with iron exhibit the same tendencies towards brittleness and have not found extended use except for certain vapour-phase gas-cracking operations In this service the tubes are carefully guarded from shock when cold. According to Curme [13, 1927], their high chromium content inhibits undesired catalytic effects at operating temperature, and thus retards deposition of carbon within the tubes

In spite of considerable investigation, the tendency towards brittleness of plain chromium-iron alloys containing over about 16% chromium has remained characteristic of these alloys. Consequently, they have been used to a limited extent only, and, when used, this tendency towards embrittlement is taken into account

The 18% chromium–8% nickel alloy, generally referred to as 18–8, was introduced to the refining industry in 1928 Since then it has made an enviable record under severe operating conditions because of its excellent resistance to oxidation and corrosion, and its high creep strength Abuse and lack of knowledge of the alloy's characteristics caused early failures but, when certain changes in operating practices and furnace construction were made, the alloy became much more reliable Many of the original tubes suffered little or no corrosion in 6 to 7 years' operation The results of these and other installations indicate that length of life under proper conditions of operation is indefinitely long A brief summary of characteristics of the 18–8 alloy is given in a later section of this article

During the period between 1928 and 1930 experiments were carried on, notably by Dixon [16, 1934], who investigated the possibilities of alloys of lower chromium content Tubes of 4–6% chromium type alloy came into commercial use during 1930, and modifications containing tungsten, developed by Malcolm [24, 1933], and molybdenum, as proposed by the writer [30, 1933, 32, 1935], made their appearance shortly thereafter. A steel containing a higher chromium content—with a tungsten addition, nominal composition 12% chromium–3% tungsten—has been advocated by Browne [8, 1933] Tubing of such material is claimed to bulge prior to bursting when overheated, and in this respect is similar to tubing of plain carbon steel Intended as a substitute for the 18–8 alloy, it has not found extended application, for the reason that it is practically as expensive as 18–8, but has lower strength and somewhat inferior resistance to corrosion and oxidation

In the past 3 years lower alloy steels for oil cracking have been developed These steels contain smaller percentages of chromium than those mentioned above In addition to chromium they contain molybdenum, generally 0 5% or more, to improve strength and to eliminate any tendency towards cold embrittlement In some cases silicon is substituted in part for chromium to increase resistance to scaling Carbon steel has also been improved in high-temperature strength by the addition of molybdenum, but this element does not enhance resistance to corrosion or scaling

In short, a wide variety of steels having special properties have become available for refinery work within the past 7 years These range from plain steel to a highly alloyed steel containing 25% chromium and 20% nickel, which alloy has only recently become available in tubing made by the seamless piercing process

(*c*) Influence of Alloying Elements

Davenport [14, 1935] described the characteristics of alloy steels before the Sixteenth Annual Meeting of the A P I , 1935 A somewhat more concise description of the influence of the principal alloying elements with relation to their effects in tubing material for high-temperature service is given herein. Alloy steels are practically indispensable to safe and economical refining operations, and the trend is towards their increasing use as operating conditions become more severe. The increase in operating temperatures and pressures in various cracking processes, the handling of sour crudes and corrosive products, with the consequent necessity of improved strength and resistance to corrosion and oxidation, are factors tending to increase the use of suitable alloys. In short, modern operating practice demands alloy steels for safety and economy.

While there are numerous elements which affect hardenability, mechanical properties, corrosion and scale resistance, and other properties of iron-carbon alloys, the most important elements, in so far as they refer to refinery tubing, are chromium, nickel, molybdenum, silicon, and, to a lesser extent, tungsten, vanadium, manganese, copper, aluminium, titanium, and columbium.

The effects of these individual elements when added to low-carbon steel are given briefly in the following statements.

Chromium.

Chromium is perhaps the most important element that is added to refinery steels. Its effect, with or without the addition of nickel, in increasing the resistance of iron alloys to corrosion in various media is well known and is exemplified in the wide variety of stainless steels now available—steels containing about 12 to 30% chromium. Chromium is particularly effective in increasing resistance to hydrogen sulphide, elementary sulphur, and organic sulphur compounds at elevated temperatures. Dixon [17, 1935] has published a curve, reproduced in Fig. 1, showing that even small amounts of chromium are of value in increasing resistance to corrosion by corrosive crudes at high temperature and pressure. When the chromium is increased to 18%, as in the 18–8 alloy, the metal becomes practically non-corrodible by the most corrosive oils. Mead, Shaffer, and Camp [26, 1930] have contrasted the corrosion of 18–8 tubes with carbon-steel tubes when operating on West Texas gas oil, stating that 18–8 tubes under the most severe conditions show but slight increase in inside diameter, whereas carbon-steel tubes had to be frequently replaced because of internal corrosion.

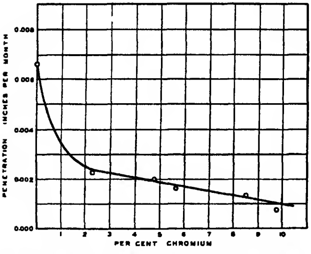


FIG. 1. Relation of corrosion rate to chromium content of steels when handling certain corrosive crudes at high temperature and pressure. (*After E. S. Dixon.*)

The enhancement in corrosion resistance conferred by chromium is accompanied by greater resistance to oxidation at high temperatures. The mechanism by which chromium creates resistance to oxidation is similar to its action in conferring corrosion resistance through formation of a passive surface film. This undoubtedly involves formation of a tight surface layer of oxide which protects the underlying metal from attack. With extremely high chromium contents, i.e. 20% or more, this protection extends to temperatures of 2,000° F or higher. A correspondingly lower degree of protection obtains as the chromium content decreases. At intermediate temperatures about 1,600° F a chromium content of 16 to 18% is sufficient for practically complete protection. Laboratory tests recently performed by the writer [1, 1935] show that improvement in resistance to oxidation may be gained with substantially lower amounts of chromium, as shown by tests on certain chromium steels at 1,200° F. The comparative results are shown by Fig. 2.

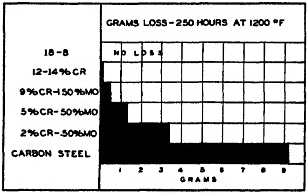


FIG. 2. Relative oxidation resistance of various steels containing chromium at 1,200° F., as determined by scale loss on heating 250 hours.

Chromium confers certain changes in the physical properties of steel at ordinary temperatures and also at elevated temperatures, not, however, in proportion to the amount added. For example, the addition of 1% or more may cause appreciable air-hardening, which may make welding problems more difficult. The air-hardening is proportional to the chromium and carbon up to about 14% chromium content, above which the low-carbon alloys become non-hardening, but are subject to reduced impact value and poor ductility on heating to temperatures in the vicinity of 900° F. In consequence it becomes particularly important to take these peculiarities into consideration before applying such material.

Nickel.

Nickel, in small amounts, does not add to the high-temperature strength of alloy steels, nor does it contribute appreciably to resistance to corrosion or oxidation. Furthermore, nickel itself is not particularly resistant to attack by sulphur, the principal corrosive agent in refinery service, and pure nickel rapidly becomes embrittled through intercrystalline attack when in contact with sulphur compounds at elevated temperatures. Nickel is therefore omitted entirely from the lower chromium-steel alloys for refinery service or is added in relatively large amounts for the specific purpose of rendering them austenitic in structure, i e so that they become non-magnetic, non-hardenable steel alloys possessing great strength at high temperatures, great toughness, and excellent corrosion- and oxidation-resistant qualities Alloys of this type are 18–8 and the 25% chromium–20% nickel alloy Nickel thus becomes a toughening agent and strengthener for the 16% chromium or higher chromium content alloys, which are more or less brittle in the absence of nickel Nickel, in low-alloy steels, detracts rather than adds to high-temperature strength properties.

Molybdenum, Tungsten, and Vanadium.

These elements are carbide formers (also ferrite formers), and their chief action in refinery steels is to make such steels more resistant to 'creep' or flow at elevated temperatures They tend to provide resistance to softening on tempering and act as restrainers of grain growth Molybdenum is perhaps the most effective element of the group in increasing strength for a given cost and is unique in its ability to render chromium steels less susceptible to temper embrittlement (cold brittleness) For these reasons the molybdenum steels are finding distinct favour for high-temperature use, although certain steels containing tungsten and vanadium have been used successfully in high-temperature applications Molybdenum improves both creep and short-time ultimate strength A specific example of this effect may be cited in a recent study made by the writer on steels containing 9% chromium [33, 1936] The effect of various quantities of molybdenum on the short-time strength of 9% chromium steel is shown by Fig 3

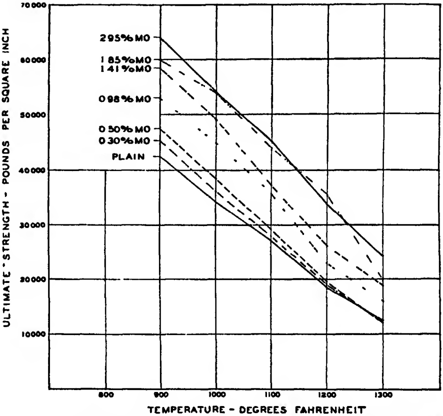


FIG 3 Graph showing the effect of molybdenum on the short time ultimate strength of steel containing 0 15% maximum carbon and 9% chromium (*After the author*)

Manganese and Copper.

Manganese tends to strengthen ferrite at ordinary temperatures and adds slightly to creep strength at slightly elevated temperatures It is not effective above about 950° F in raising creep strength, and it adds nothing towards corrosion resistance or oxidation resistance Increased manganese content, according to Greaves and Jones [19, 1925], is likely to increase susceptibility towards embrittlement, consequently, the amount of manganese in refinery steels is generally limited to the amount necessary for satisfactory deoxidation Manganese has been suggested by Becket [5, 1934] as a substitute for nickel for stabilizing austenite to produce chromium alloys similar in characteristics to 18–8 Such alloys are stated to be more resistant to gases containing sulphur at elevated temperatures due to the absence of nickel With equivalent chromium content, these manganese alloys are somewhat less resistant to corrosion and scale than similar alloys containing nickel and are less resistant to creep. They have not as yet found application in oil-cracking service

Copper in small amounts improves the resistance of steel to dilute acid solutions of a reducing character and also its resistance to atmospheric corrosion It also is stated by certain investigators to improve resistance towards oxidation, the influence on oxidation resistance is slight however Copper is non-resistant to sulphur compounds at elevated temperatures, consequently it has not been used in steels for high-temperature service The lack of resistance of copper-bearing steel to corrosion is confirmed by Egloff and Morrell [18, 1927], who report results of a corrosion test covering a period of 20 days when cracking oil containing 1% sulphur at 460° C. (860° F) The samples tested were suspended in the vapour zone of the reaction chamber The copper-bearing steel lost more than plain steel, and hence did not show promise for this service

Silicon.

There are insufficient data to indicate the value of the addition of silicon to iron alloys for resistance to corrosion

This is especially true with reference to corrosion that occurs at high temperatures in oil refining Results secured in acid corrosion tests of iron-silicon alloys have been inconsistent [21, 1933] Generally speaking, corrosion resistance of such alloys is but little improved by the addition of ordinary amounts of silicon, i e up to 3% or more Silicon alloys containing 12% or more of silicon are, however, quite resistant to acid From the data available it can be inferred that silicon cannot entirely replace chromium in providing resistance to corrosion when used in ordinary amounts

That silicon appreciably improves scale resistance of iron alloys at elevated temperatures is exemplified by the well-known silicon-containing automotive valve steels It may be substituted in part for chromium in low-alloy steels used in refinery service to provide additional resistance to scaling Low-carbon steels containing over 2% silicon are more or less brittle, and, when silicon is used in conjunction with ferrite-forming elements, such as chromium and molybdenum, the amount should be restricted to somewhat under 2%, so as to ensure satisfactory ductile properties Silicon stiffens ferrite and provides resistance to tempering at temperatures up to 1,000° F At higher temperatures silicon causes softening and probably reduces creep strength, as indicated by the fact that high silicon-chromium valve steels have good scale resistance, but relatively poor high-temperature strength properties

Aluminium, Titanium, and Columbium.

Aluminium, like chromium, silicon, titanium, and columbium, has the power of forming tightly adhering refractory oxide scales when added to steel alloys It thus markedly improves resistance to scaling It is difficult to add appreciable quantities of aluminium to steel without producing certain undesirable effects, consequently, it is used mainly as a deoxidizing agent and for the purpose of controlling grain size rather than as an alloying agent Aluminium in ordinary amounts does not improve corrosion resistance, and it greatly detracts from creep strength at high temperature Aluminium is more beneficial when applied to tubing as a surface coating, as in the calorizing process [9, 1935]

Titanium and columbium are carbide-forming elements and also serve as ferrite formers They are used in plain chromium steels containing up to 14% chromium to reduce air-hardening tendencies and to assist oxidation resistance In chromium-nickel austenitic steels, such as 18–8, these elements act as stabilizers to fix carbides and thus retard or prevent intercrystalline corrosion Under ordinary conditions of cracking-still service, columbium and titanium are not necessary to successful operation of cracking-still tubes of 18–8, but these elements might improve the alloy under inordinately severe conditions For a more extended discussion of the effect of these elements the reader is referred to articles by Bain *et al* [4, 1933] and Becket and Franks [6, 1933, 7, 1934]

(*d*) Requirements of Tubing for High-temperature Service

The following outline indicates the general requirements of an alloy tubing material for service at elevated temperatures

1. (1) It shall be adequately resistant to corrosion, especially towards corrosion by the media encountered in oil refineries
2. (2) It shall be resistant to oxidation at temperatures up to the maximum for which it is designed
3. (3) It shall have adequate creep strength
4. (4) It shall be stable at operating temperature and free from cold embrittlement, i e it shall show no tendency for grain growth or structural changes which will appreciably affect its ductility and resistance to shock
5. (5) The alloy shall be ductile and of such nature that it can be fabricated into tubes of good workmanship and quality.

Fundamental characteristics, such as thermal expansion conductivity, and structural type (i e whether ferritic or austenitic), are dependent solely on composition and must be accepted with the other properties gained Weldability is important for vapour lines and refinery piping, and, although many of the chromium steels are air-hardening, suitable methods of welding and annealing in the field have been worked out Ability to be flanged, expanded, and bent is also important

It is obvious that all the characteristics enumerated cannot be achieved in any one alloy and, this being the case, it is necessary to sacrifice certain features to obtain other more desirable ones This, in reality, means that a number of alloys are necessary to cope economically with the variety of services existing in modern oil-refining operations Furnace tubes under heat input operate under more severe conditions than piping or heat-exchanger tubes, and, in consequence, strength may be diminished or oxidation resistance dispensed with in the latter in favour of such other attributes as corrosion resistance, ease of welding, &c The economical selection of a suitable alloy for a particular purpose requires the close co-operation of the metallurgist and the refinery engineer

(*e*) Characteristics of Carbon and Carbon-molybdenum Steels

The properties of carbon-steel tubing are known from long experience to be satisfactory as to workability (ductility), ease of welding, and resistance to impact after long heating Furthermore, carbon steel is inexpensive and, in many cases, entirely satisfactory where the service conditions are relatively mild For this reason a large percentage of the tubing used in refinery construction is of plain low-carbon steel (Analyses and properties of carbon and alloy steels referred to in this article are given in the section on Tables of Data)

The bulk of furnace tubes and pipe of carbon steel are manufactured by direct hot-rolling, although, in certain instances, 'cold-drawn' tubes are specified in order to obtain closer tolerances and smoother surface finish These cold-drawn tubes have given service life commensurate with their increased cost according to various reports on their operation It is the usual practice to employ cold-drawn tubes in the smaller sizes, for condensers and heat exchangers, although small-sized, hot-finished tubes have become available and certain economies may be gained by their use Furnace tubes are generally made to Manufacturers Specification no 100 (A S T M A 161–35 T) or equivalent, and cold-drawn condenser and heat-exchanger tubes are made to A S T M A 179–35 T.

Carbon steel has relatively poor resistance to corrosion and oxidation and has low strength at elevated temperature Tubes of this steel should be applied for the milder services, and, even then, careful operation is necessary to prevent tube losses Steel furnace tubes may fail because of internal corrosion, oxidation, or creep, or a combination of these effects Figs 4 and 5 show typical sections of carbon-steel still tubes that failed principally because of creep and oxidation Fig 6 shows a still tube that failed because of 'end-corrosion'

Carbon-steel tubing 'as rolled' has a lamellar, pearlitic structure, but when operating at temperatures approaching 1,000° F, or higher the pearlite tends to spheroidize, which results in a loss of creep strength. The representative structural appearance of steel tubes before and after service are shown in the micrographs in Fig 7 The effect of this

Fig. 4 Typical appearance of furnace tubes which failed because of oxidation and creep

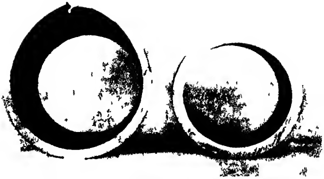
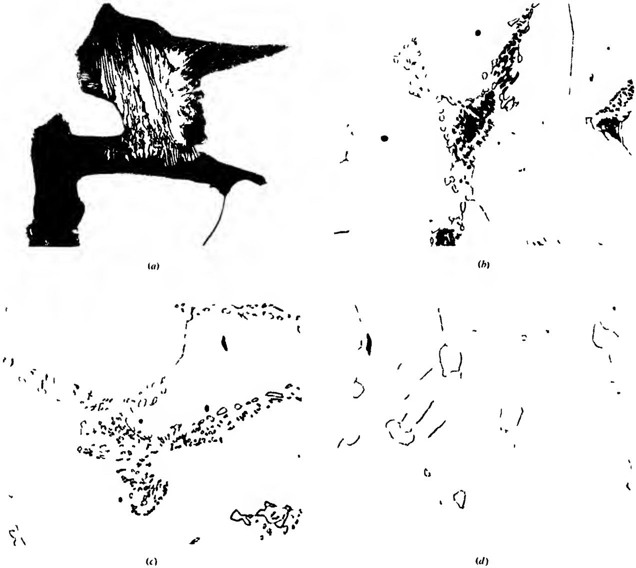


Fig. 5 Sections through a steel still tube which enlarged by creep. Photograph shows original and enlarged diameters

Fig. 6 Failure of a steel still-tube through excessive corrosion near the rolled end of the tube. This is a more or less common occurrence in units handling certain oils and is due to changes in velocity of the oil stream in the vicinity of the header connexions

Fig. 8 Typical brittle fractures in plain 5% chromium steel tubes. Failures occurred through cleaning operations when the tubes were cold



(a) (b) (c) (d)

Fig. 7 Representative changes in structure of the pearlite areas of carbon-steel tubes after long heating above 1,000° F All structures etched with nital 2 000

(a) Lamellar pearlite of hot rolled tube – before service (b) Incipient spheroidization of cementite (Fe_3C) – after service (c) Complete spheroidization of Fe_3C in still-tube (d) Complete spheroidization and coalescence of Fe_3C in tube which failed by creep change in structure on creep properties will be discussed in more detail under 'Creep'

Closest to plain steel from the standpoint of composition, properties, and cost is carbon-molybdenum steel, which has been used for furnace tubes and vapour lines for the past two or three years This steel first attracted attention for elevated temperature service in Europe, where it has been employed for superheater tubes in the Loeffler high-pressure boiler It has been recommended for this service by Vitkovice Mines, Steel and Iron Works Corporation, Czechoslovakia [20, 1932], and by Bailey and others [2, 1931]

The addition of molybdenum to steel in amounts up to 1 00% produces a definite advantage in elevated temperature strength over that of plain steel Corrosion or oxidation properties are little, if at all, improved thereby, so that such material should be used under mildly corrosive conditions and at moderate temperatures to avoid excessive scaling It offers higher creep strength than plain steel and is readily weldable, hence it provides additional safety in vapour lines and hot-oil piping At room temperature, low-carbon molybdenum steels are slightly stronger than carbon steel of equivalent carbon content (see Table II, section (1)), but for all practical purposes may be considered as having about the same physical characteristics

So far as is known, carbon-molybdenum steels are entirely free from cold embrittlement and do not suffer loss of ductility after long periods of operation at elevated temperature This might be expected from the known beneficial effect of molybdenum and from the structural similarity of molybdenum steels to carbon steel Carbon-molybdenum steel has frequently been used as a base material for calorizing, and this process of surface alloying with aluminium provides greatly increased resistance to scaling and corrosion [9, 1935] The higher creep strength of the carbon-molybdenum steel provides increased ability to meet the stresses at higher temperatures, which the calorizing process makes possible through its protection of the surface of the metal

The surface coating of iron-aluminium alloy formed on the tube, whether it be carbon or alloy steel, is more or less brittle, and care must be exercised to avoid cracking in expanding or otherwise deforming the tube A two-cycle calorizing treatment which involves diffusion of the aluminium is helpful (U S Pat 1,988,217), and annealing as a final operation is also helpful, especially in the case of alloy tubes, in restoring ductility to the base metal Special expanding tools may be provided for rolling which lessen the danger of cracking the coating In some cases the calorized layer is removed from the inside of the tube to permit ease in rolling into the header

(*f*) Five per cent. Chromium Steels

As previously related, steels of this type originated with Dixon [16, 1934] Such steels may be modified with tungsten or molybdenum Recently additions of titanium or columbium have been made, the latter elements being used to reduce air-hardenability The plain 4–6% chromium steel is subject to brittleness when cold, and this feature has been described by Wilten and Dixon [46, 1934]. More recently an extended study correlating the notch impact test with service failures has been made by Wilten [45, 1935], who shows that the plain 4–6% chromium alloy and the tungsten modification have a high susceptibility ratio which increases as the temperature is reduced below 200° F. Cleaning or knocking of tubes of these types while warm (above 200° F) is recommended to avoid breakage of tubes due to reduced toughness when cold The typical appearance of tubes cracked in cleaning is shown in Fig 8

The 4–6% chromium alloy containing tungsten has been successfully used for valves and valve parts The properties of this alloy have been described by Malcolm [23, 1931] A few installations of tubes of this alloy have been made, and these have operated successfully except for some breakage of tubes which were cleaned while cold The higher cost of this modification, however, and its tendency towards cold brittleness have made it less favoured for tubing than the molybdenum alloy

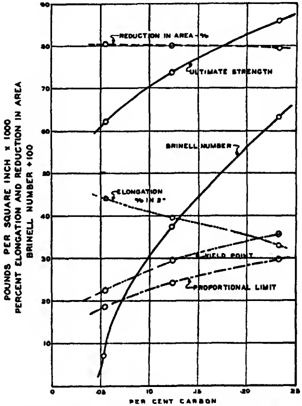


FIG 9 Curve showing the effect of carbon content on the room temperature physical properties of 5% chromium, 0 50% molybdenum steel, annealed Tests made on 1-in rd

The 4–6% chromium steel with 0 50% molybdenum has been used with decided success for furnace tubes, vapour lines, hot-oil piping, and heat-exchanger tubes This alloy contains sufficient chromium to be fairly resistant to moderately and even fairly corrosive oils Service reports show its corrosion resistance to be from 4 to 10 times that of carbon steel, depending on the nature of the oil handled, velocity of flow, temperature, and other factors The molybdenum addition provides increased strength and freedom from cold brittleness [30, 1933], making it the preferred type for tubing application The effect of carbon content on the physical properties of annealed 5% chromium–0 5% molybdenum steel is shown by Fig 9

Wright has shown that the air-hardening properties of 5% chromium steel are proportional to both chromium content and carbon content [47, 1932] In furnace tubing which is installed in the annealed condition this feature is not important, as a soft-annealed tube will not harden until the temperature exceeds 1,400° F. This is considerably above a safe operating temperature for alloys of this type.

Annealing of tubes of this alloy after hot working, forging, Van Stoning, and welding is required to restore ductility and toughness. In consequence, welding of vapour lines and the like requires careful handling to avoid difficulties. A brief description of procedures found to be satisfactory is as follows.

Welding Procedure. Welding shall be done by the electric-arc process, using properly covered electrodes of 4–6% chrome, ½% molybdenum. No bare-rod electric-arc welding is permissible. Direct-current-type welding equipment is preferable to the alternating-current type. While the electric-arc welding process is generally favoured, gas welding may also be used.

Welders shall be qualified in accordance with the requirements of paragraph 527 of the 1935 issue of the American Tentative Standard Code for Pressure Piping.

Alloys of the 4–6% chromium-molybdenum type are manufactured in several grades with respect to carbon content, the carbon ranges being 0.1% maximum to 0.25% maximum. This alloy is distinctly an air-hardening alloy, and, as carbon enhances its air-hardening properties, the lower carbon ranges of the alloy are generally chosen for parts that are to be welded. However, it should be stated that even the high-carbon material may be welded by the fusion-welding process, providing a high preheating temperature is employed and the weld is heat treated immediately after completion.

The main problem in welding, assuming the availability of satisfactory electrodes, is the prevention of cracking of the weld metal during welding, which may be accomplished by preheating the parts to be welded, either locally or uniformly, to a temperature of at least 300° F., the higher the temperature the better, and maintaining the temperature until the welding is completed and the part placed in the furnace for annealing. This should be done before the part cools, otherwise stress cracking may appear.

If possible, backing-up strips or rings should be used, and the walls of the joint kept apart to permit fusion to the backing-up strip.

When castings of this material are to be welded, they should be preheated to at least 500° F. before welding and maintained above this temperature during welding.

Heat-treating. Due to the extremely hard weld metal and affected zone of the parent metal in the as-welded condition, the Brinell hardness of which is of the order of 400 to 500, the welded part must be annealed. The physical properties of the weld metal will vary with the heat treatment, maximum softness being obtained by a full anneal from approximately 1,600° F. Slow cooling is essential if the material is heated to 1,600° F. for full annealing, as this temperature is above the critical, and hardening will be induced if the cooling is rapid.

The manner and rate of heating of this alloy steel is immaterial, except that uniform temperatures over the affected zone should be obtained. Rapid heating to the chosen annealing temperature is preferable, and scale may be reduced by using a slightly reducing atmosphere within the furnace.

Complete heat-treating following welding. The entire piece should be inserted in a suitable furnace immediately after welding and before allowing the piece to cool from the preheating, and the temperature should be properly controlled to close limits as follows:

> Heat the entire piece uniformly to a temperature between 1,550 and 1,650° F. (preferably to 1,600° F.) and hold the temperature for 1½ hours per inch of maximum metal thickness. Then cool in the furnace at a rate not in excess of 50° F. per hour to 1,300° F., and continue to cool in the furnace to 1,100° F. at a rate of cooling not in excess of 100° F. per hour. Remove from furnace and cool in still air.

Local heat-treating following welding. When temperatures below the critical point are employed for softening, the properties of the alloy will depend upon the time it is held at temperatures during the heat treatment.

Where it is impossible completely to heat-treat the entire piece and it is necessary to heat-treat the material locally, use the following heat treatment and control the furnace temperature closely:

> Heat uniformly to 1,325 to 1,400° F. (*Caution*.—Do not heat alloy over 1,450° F. or it will air-harden on cooling.) Hold temperature for 1 hour or more and then cool in still air.

It is, however, preferable completely to heat-treat the material after welding than to heat-treat it locally.

The reduction of carbon to 0.1% maximum and the incorporation of titanium in a ratio of 4 to 6 times the carbon content partially eliminates air-hardening in the 5% chromium steels. Alloys with this amount of titanium are sufficiently free from the structural transformations producing hardening for simple annealing treatments to suffice in restoring ductility after hot-working. The titanium addition also improves scale resistance. The difficulty of controlling the proper ratio of titanium to carbon in melting the alloy has hindered its adoption, and service tests have been too limited to indicate the value of this modification at this time. It may be stated that certain difficulties are encountered in welding the alloy in spite of its non-hardening features. Further, impact values are likely to be erratic if the prescribed ratio of titanium to carbon is not maintained. This has led to investigations on the use of columbium. A somewhat higher ratio of columbium to carbon (7 to 9 times carbon) than when titanium is used is required to produce the non-hardening features (see note at end), but control in melting is said to be better and welding characteristics are somewhat improved. The value of either of these modifications still remains to be determined in refinery applications.

(g) Eighteen per cent. Chromium—eight per cent. Nickel Tubes

Tubes of this highly alloyed steel have been used perhaps longer than tubes of any other alloy steel in refining operations. A complete description of this material, including a discussion of its advantages, limitations, and disadvantages, has been previously given by the author [28, 1931].

This alloy has exceptional properties of corrosion and oxidation resistance and has strength at elevated temperatures that far exceeds that of the lower alloy non-austenitic steels. Offsetting these desirable properties are the characteristics of a high thermal coefficient of expansion and low thermal conductivity, and these must be taken into account to avoid certain difficulties in operation. When 18–8 tubes are used in conjunction with plain steel headers or return bends, leakage is likely to result which requires constant attention Further, to avoid danger from overheating, with the possibility of tube ruptures, furnaces in which 18–8 tubes are used should be designed for uniform heating of the tubes, and relatively low rates of heat transfer should be employed

Dixon [15, 1931], by means of a questionnaire directed to refiners and others, concluded that the alloy has many desirable properties, but that exceptions to its use were taken because of its lack of ductility under tensional deformation when overheated and overstressed J L Marek [25, 1933], in his article 'Safety at Petroleum Cracking Plants', also pointed out this lack of ductility The writer has studied the high-temperature ductility of many austenitic alloy combinations [31, 1935] (variations of chromium and nickel content with and without addition elements), and concludes that the lack of ductility of 18–8 is not a special characteristic of the composition, but a fundamental property of all low-carbon alloys of austenitic type In fact, 4–6% chromium steels and even ingot iron exhibit the same tendencies at temperatures corresponding to their transformation to gamma-iron (austenite) Creep strength of the lower alloy-content non-austenitic steels is so low that failure generally occurs before the temperature can rise to a point where transformation to austenite occurs In other words, the ductile alloys fail in the range where their structure consists essentially of alpha-iron

Some improvement in the ductile characteristics of 18-8 may be gained by special methods of processing designed to produce a small grain size in the tube prior to use This has been shown by studies on the effect of grain size undertaken by the writer [29, 1931–2] As a consequence tubes manufactured in recent years are much more reliable than those made previously The low ductility of austenitic 18–8 tubes under stress at temperatures exceeding 1,300° F is a property now recognized as characteristic of the material, and tube failures through abuse and overheating rest entirely with refinery operators Such failures are entirely preventable with proper operating practice, which connotes frequent cleaning to remove coke films and proper firing and combustion conditions to avoid exceeding safe tube temperatures

Many tubes have operated on sour crudes or corrosive gas oils for over 40,000 steam hours with little or no loss due to corrosion If fuels are used containing appreciable sulphur, the external surfaces of tubes may show some incipient intercrystalline attack This attack is superficial except where acid sludge is burned, as ordinary gases of combustion containing lower amounts of oxidized sulphur compounds attack the metal very slowly

The alloy undergoes a slight structural change, and all furnace tubes gradually precipitate carbides and become slightly magnetic This does not detract from their utility, nor does it cause appreciable change in physical properties, unless the carbon content is high For several years all 18–8 tubes for high-temperature operation have been limited to a maximum carbon content of 0 07%

All 18–8 tubes operating in the range of temperatures at which carbide precipitation occurs become susceptible to intercrystalline corrosion and, if removed from service and placed in mild acid solutions or salt cooling water, they will quickly disintegrate This condition of structure can be corrected by heat-treating if further use at low temperature is contemplated Despite carbide precipitation, tubes will operate thousands of hours at high temperature without [illegible] n The corrosion encountered in oil streams or vapours at elevated temperatures is non-ionizing and non-conducting, consequently, intercrystalline corrosion of tubes in this service is but rarely encountered In fact, it has been entirely absent except in isolated cases confined to large-grained upset tube ends operated under unduly severe corrosive conditions This type of corrosion might be combated by the use of tubes of 18–8 stabilized with titanium or columbium, but its occurrence is such a rarity that plain 18–8 tubes have so far sufficed for all needs For a more extended discussion of the structural features of the alloy and the effect of carbide precipitation the reader is referred to B Strauss *et al* [37, 1930] and Bain and Aborn [3, 1930] The effect of titanium has been discussed by Bain *et al* [4, 1933], and the effect of columbium by Becket and Franks [7, 1934]

Tubes of the alloy are particularly useful where temperature and pressure conditions are high The high strength of the alloy eliminates the necessity of using excessively heavy walls to provide the desired safety This in turn permits greater quantities of charge to be handled The alloy may also be recommended for use where the stocks to be handled are excessively corrosive The alloy has also been used successively in the hydrogenation of petroleum products

(*h*) Intermediate or Low-alloy Steels

In this classification of steels are placed those containing varying amounts of chromium below the range of the 4–6% chromium steels Molybdenum is added to such steels in addition to chromium to improve strength properties and to obviate any tendency towards cold brittleness. In certain cases silicon is substituted for chromium as a means of improving scale resistance at nominal cost A steel containing 1 25% chromium, 0 5% molybdenum, and 0 75% silicon has been described in various articles by Clark, White, and Wilson [41, 1932, 42, 1934] Such material has good strength properties for a steel of the pearlitic class, and also has somewhat better corrosion and oxidation resistance than plain steel This material is calorized in many cases, because of its low chromium content, to provide it with a higher degree of resistance to scaling and corrosion A somewhat similar steel with a slightly higher molybdenum content has also been proposed for tubes for high-temperature service, mainly for boiler construction [10, 1934] By increasing the chromium content to about 2% [1, 1935], a considerable increase in corrosion resistance is achieved that obviates the necessity for calorizing, except where furnace conditions are such that excessive scaling is caused At present, considerable tubing of these intermediate grades is being used This tubing is available with chromium content varying by small increments up to 3%

Due to the large amount of sweet oil being processed, these intermediate alloy steels are finding distinct favour. Their strength properties at high temperatures are, in most cases, equal to or better than those of 5% chromium, 0 5% molybdenum steel, and they are sufficiently corrosion resistant to be economical under mildly corrosive conditions Wilson [44, 1935] has recently described a 2 5% chromium-molybdenum-silicon steel, and some production has been attained with a 3% chromium alloy containing 0 8–1% of molybdenum There are thus 5 alloys available between 1 25% chromium and 3% chromium This situation is somewhat confusing to the refinery engineer faced with the selection of a material in this range of composition The prices for these materials increase in proportion to this alloy content Perhaps, in time, the industry and producers will co-operate in standardizing on one or two steels in the range, which would result in benefit to both

The intermediate steels are free from cold brittleness and have adequate ductile properties for forming and rolling They are somewhat air-hardening, and good practice necessitates annealing after welding to restore ductility and impact properties Welding procedures suitable for the 5% chromium steels are recommended

The intermediate steels should be applied for mildly corrosive service where strength properties in excess of those of mild steel are required In this connexion the intermediate steels may be used economically in many places where 5% chromium materials have been found adequate, so that their use is likely to increase so long as sweet or mildly corrosive stocks are being charged

(*i*) Higher Alloys

In order to provide a higher degree of corrosion resistance than is provided by 4–6% chromium steels, with a corresponding increase in strength properties and oxidation resistance, the author has studied the properties of steels containing about 9% chromium, the strength properties of which have been improved by a relatively large addition of molybdenum [33, 1936] The normal analysis of this steel is 9 25% chromium, 1 5% molybdenum, and 0 12% carbon It is intended as an intermediate between the 4–6% chromium alloys and 18–8, both as to properties and cost It is recommended for use where the corrosion resistance of 4–6% chromium alloys is not sufficient or where scaling has been encountered in alloys of lower chromium content

This material is quite similar in physical properties and weldability to the 5% chromium-molybdenum alloy, but its higher chromium content places it more nearly in the stainless-steel class with respect to resistance to corrosion and oxidation Service tests are now being conducted in twelve different refineries to obtain data on the alloy At present the installations have not operated sufficiently long to classify the material accurately as to its utility and economy Indications are that it will find a field in the handling of sour crudes and corrosive gas oils where the high-creep strength of 18–8 is unnecessary

In the class of steels having extremely high-alloy content, an austenitic steel containing 25% chromium and 20% nickel has recently become available in seamless tubes in the usual range of sizes used for furnace tubes This material has been in use several years in the hydrogenation of petroleum products, but the tubes for these installations were manufactured by a forging and boring process

The 25–20 alloy is quite similar to 18–8 in many of its properties, but it has substantially better resistance to corrosion and oxidation Its creep strength is slightly better than that of 18–8, and it is more resistant to carbon absorption (carburization), which will permit it to extend the operating range above that for which 18–8 is suitable It is probable that the alloy will find a field of usefulness in dehydrogenation and polymerization processes where it is desired to operate at high gas temperatures and at high pressures

(*j*) Heat Exchangers and Condensers

The metallurgy of ferrous materials has not advanced an appreciable extent in supplying corrosion-resistant tubing materials for heat exchangers and condensers This is particularly true with regard to condenser equipment of the shell-and-tube type Powell [36, 1935] has recently given a résumé of the subject which indicates that this problem is a troublesome one Maintenance costs and tube replacements are generally high for condensers handling unneutralized fractions or when operating in Coastal refineries using brackish water for cooling purposes

The conditions tubular material must meet for this service may be enumerated as follows

1. (1) Sulphide corrosion from vapours, crude oils, and fractionated products
2. (2) Hydrochloric acid from the hydrolysis of magnesium chloride which is carried over to end products and condensed out This is particularly troublesome at condensation temperatures, but may be nullified by neutralization, generally with ammonia
3. (3) Corrosion from air-saturated cooling waters
4. (4) Corrosion from salt or brackish water which is also likely to be air saturated

These conditions do not take into consideration mechanical difficulties of various sorts—erosion, contact electrolysis, plugging of tubes from deposits in the water, or heavy sludge and tar from oil products—all of which affect tube life and increase the maintenance cost of equipment

Tubes of admiralty brass and plain steel have been largely used, the steel tubes being used mainly in heat exchangers handling sweet crudes and in condensers where the cooling waters are of a non-corrosive nature Admiralty tubes have been installed in exchangers where acid corrosion and sour products are encountered and mainly in condensers using saline waters as the cooling medium Brass tubes are not particularly resistant to sulphide corrosion, but are more resistant than steel in unneutralized fractions containing acids They are also more resistant to salty and other cooling waters than steel, which tends to corrode rapidly, with pitting, in waters containing oxygen Brass tubes are subject to dezincification, especially in salty cooling waters, and many tubes eventually fail from this cause Mechanical wear due to the cleaning of tubes plugged or fouled with deposits, erosion, and corrosion of the types previously enumerated all tend to shorten tube life Tubes of certain modified brasses and other non-ferrous alloys have been used, but it is beyond the scope of this article to discuss their merits

The use of tubes of plain 5% chromium or 5% chromium-molybdenum has extended life in exchangers handling oils or vapours where hydrogen sulphide is the active corroding agent In condensers the 5% chromium alloys are not generally economical, as their resistance to corrosion by cooling water or acid is not sufficiently better than that of plain steel to warrant their extra cost A test installation in a condenser cooled by sea-water gave relatively short life, indicating that this type of material should not be used in brackish or salt-water

Steel tubes and cast-iron pipe have been employed in submerged-type condensers, and although corrosion is rapid, especially in salt-water, their life is extended by using exceptionally heavy walled tubes. Use has been made of discarded 18–8 still tubes for submerged condensers, in which case the tubes are reheat treated prior to use to improve their corrosion resistance

Tubes of stainless materials, especially the 18–8 alloys, have given disappointing results in condensers and ex-

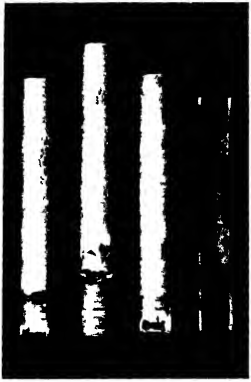


Fig. 10 Circumferential stress cracking in 18–8 tubes operating in a gas-oil to crude exchanger. Failure due to temperature stresses through lack of freedom for expansion of the tubes

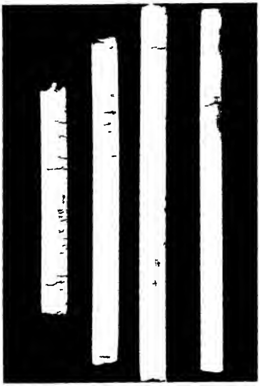


Fig. 11 Fatigue cracks in 18–8 tubes which operated in condenser or exchanger units without adequate freedom for expansion of the tubes. (Repickled to show cracks)

Fig. 12 Internal pitting with stress-cracking (corrosion-fatigue) of 18–8 condenser tube which operated in contact with brackish water

Fig. 13 Typical microstructure of cracked 18–8 condenser or exchanger tube, showing transcrystalline nature of cracks—etch—chrome-regia ×175

changers of the shell-and-tube type The difficulties which have arisen are largely mechanical, and are due to the alloy's characteristics of high thermal expansion and low conductivity These features introduce mechanical stresses that are not provided for in present designs of equipment, with the result that tubes are not free to expand This causes buckling of tubes and transverse fracture through fatigue

This difficulty has been especially noticeable in multi-pass units in which tubes are subjected to unequal temperatures across the tube bundle Temperature variations and pump pulsation produce alternating stresses which may lead to rapid failure Careful consideration of design from the standpoint of freedom for expansion and equality of temperature distribution should be given before application of these alloy tubes is contemplated

While remarkably resistant to sulphide corrosion, stainless steel alloys will not resist hydrochloric acid in unneutralized condensed fractions, and they are subject to localized attack (pitting) in salt-waters In the latter case deposits containing chlorides from the waters collect on the tube surfaces, and those points thereby deprived of oxygen become de-passified, i e the corrosion-resistant film to which chromium alloys owe their corrosion resistance breaks down and local corrosion in the form of pitting results This pitting, together with the mechanical stresses previously mentioned, causes failure through 'corrosion fatigue', the pits acting as stress-raisers Failures which have occurred from these causes are illustrated by Figs 10, 11, and 12 The structural condition of the metal has been satisfactory with proper heat treatment applied before installation, and all cracks have been transcrystalline, typical of fatigue, as shown by Fig 13

In natural cooling waters saturated with oxygen the stainless alloys are quite resistant, as oxygen, contrary to its pitting action on ordinary steel, tends to passivate the high-chromium alloys, and corrosion thus is retarded That the high expansion rate is the most important factor retarding the use of 18–8 tubes in heat exchangers in which corrosion due to sulphide occurs has been proved by substituting plain 18% chromium-iron tubes In certain exchangers of the multi-pass type, in which the heat transfer is from gas oil to crude, 18–8 tubes failed in as short a time as 10 days because of mechanical stresses When tubes of plain chromium alloy were substituted the service has extended to 5 years with no signs of failure from mechanical or other causes It should be borne in mind that 18% chromium-iron alloy becomes embrittled in the temperature range between about 650° F and 950° F, so that the contemplated use should exclude this range Tubes of 18–8, in larger diameters than those ordinarily used in shell-and-tube units, have been successfully employed in high-pressure, high-temperature exchangers of special design.

(*k*) Creep and Short-time Properties

Perhaps the most important property of material intended for elevated temperature service under pressure is its ability to resist deformation when stressed at elevated temperature over long periods of time Due to the influence of temperature, steel at sufficiently elevated temperature becomes a plastic or viscous material rather than an elastic material, and hence will continuously flow or stretch at any given elevated temperature at a rate which is dependent on the load applied This stretch or 'creep', as it is ordinarily known, has been defined by Tapsell [38, 1931] as deformation of a material occurring with time under and due to an externally applied stress Considerable investigation has been conducted on this phenomenon during the last 10 years, and it is by this property that materials are classified as to their ability to sustain loads at high temperature

Creep tests take ordinarily from 1,000 to 5,000 hours for completion, and certain tests are now being continued for 10,000 hours or more by the Joint Research Committee of the A S M E and A S T M to determine the effect of an inordinately long period of testing In certain cases preliminary properties are evaluated by short-time test methods This is essentially a quick physical test that takes approximately an hour and gives values which are comparative if the test procedure has been standardized Such tests give values which are far above the true breaking loads as determined by the long-time creep test Design of parts has been predicated on these short-time values, in some instances by making large allowances for safety factors, but generally the actual creep or flow rates are now being used for design purposes except where data are lacking

Some attempt has been made to shorten the time for evaluating creep rates by such means as Hatfield's time-yield, by determination of proportional limit, and by accelerated creep tests wherein the rate of flow is taken during some arbitrary time period, as, for instance, between the third to sixth hour or twenty-fifth to thirty-fifth hour These methods have not found favour with American investigators, who prefer measuring the rate of flow over much longer periods of time The Joint Research Committee of the A S M E and A S T M on Effect of Temperature on the Properties of Metals has formulated codes (A S T M E 21–34 and E 22–35 T) for both the short-time and creep tests, and this is enabling different investigators to arrive at values which more or less correspond for materials of similar composition and condition

Many factors influence creep properties of metals, among which may be mentioned

(1) Influence of method of manufacture
(2) Effect of composition
(3) Effect of heat treatment, grain size, &c
(4) Effect of segregation or banding or other non-homogeneity

Differences in creep values for any given material, as shown by various investigators, may be due to the above influences or to errors in the actual determination, due to lack of precision of equipment, temperature control, &c As previously mentioned, the testing codes recently adopted are tending to bring about better correlation of data and to make the values obtained more reliable

Molybdenum improves creep in pearlitic steels, and carbon seems to have a more minor influence Norton [34, 1929] has grouped the steels into austenitic high-creep-strength materials and medium-creep-strength materials, with a third group of plain or low-alloy steels having low resistance to creep The group into which the individual alloy falls depends on the elements making up its composition. The values for low carbon 18–8 shown by Norton have been closely checked by Cross [11, 1934]. Clark and White have studied the influence on creep of grain size, carbon content, method of loading, and other factors, including the effect of time on rate of creep [40, 1934, 43, 1935] In connexion with the last-mentioned factor it has been shown that the rate of creep of a chromium-silicon-molybdenum steel at 1,000° F may accelerate under high loadings when the tests are continued for long periods This change in rate is apparently due to loss of strain-hardening effect with spheroidization of the carbides under stress as the time of heating the specimen continues This results in a marked drop in creep resistance Clark, White, and Wilson have also studied the creep of carbon-molybdenum steels as used in refinery service [41, 1932, 42, 1934]

Cross and Johnson [12, 1934] have investigated the creep properties of 5% chromium-0 5% molybdenum steel, using specimens cut from cracking-still tubes These investigations have shown that increased carbon content improves creep strength in this alloy and that furnace-cooled (annealed) metal had properties superior to those of normalized and drawn metal They have also shown that longitudinal specimens had better creep resistance than transverse specimens from the same tubes, but that the differences were small, being less than 10% greater Norton [1, 1935] has determined creep properties of many of the refinery steels, using, in some cases, strip specimens cut from tubes which were in the annealed condition

In general, it may be stated that at temperatures of about 1,000° F, or above, annealed steels have the best creep properties, whereas below 1,000° F the reverse may be true, and heat-treated material may be superior Whether or not this is true is dependent on the composition of the particular alloy Fine-grained materials are less creep resistant than coarse-grained materials at the higher temperatures, but coarse-grain steels may show inferior ductility and impact properties Quality and uniformity of material, both as to structure and composition, are desirable for uniformity of strength properties Through the work being done on this subject, more reliable data and a better understanding of flow of metals at high temperatures may be expected in the future

The gradual change in microstructure under prolonged heating and stress leads to a reduction of creep strength According to Tapsell [38, 1931], Bailey has found a reduction of creep strength amounting to 25% when lamellar pearlite in carbon steel changed to spheroidized cementite More recently Jenkins and Mellor [22, 1935] studied the mechanism of flow of various low-carbon steels and irons under creep, and confirm the loss of creep strength due to spheroidization When the pearlite changes to rounded globules of iron-carbide, it has but little stiffening effect on the ferrite phase Norton has shown that long-time service does not alter the creep strength of the 18-8 alloy [35, 1934], but in certain unpublished work there has been noted a considerable reduction in creep strength of 5% chromium-molybdenum and carbon-molybdenum steels at 1,000° F due to prolonged exposure above that temperature This would indicate that the creep properties of pearlitic steels should be determined on completely spheroidized-stabilized material so that no further changes would occur in heating which would result in strength losses not anticipated when the material entered service This stabilizing prior to testing would apply to furnace-tube materials operated at 1,000° F, or above, as structural reactions below 1,000° F proceed at a much slower rate In many cases heat-treated alloys or parts may be used at the lower temperatures with no appreciable change in structure or loss in strength, providing the alloys are selected on the basis of reliable test data

The use of creep or short-time data in the design of tubing for high-temperature service is a highly controversial subject There are several schools of thought on the matter, and engineers may be at wide variance with each other as to the proper formula or constants to employ in developing wall thickness of tubing for any given set of operating conditions The formulas of Claverino, Barlow, the A S M E, Dahl, and others have been used In some cases temperature stresses are allowed for and extra thickness is generally added to compensate for corrosion and oxidation or for wear due to cleaning In all cases a great deal of practical experience is applied in the selection of size and thickness of tubes for high-temperature refining operations There is a distinct need for clarification and standardization on this important subject, which could be well undertaken by some engineering body It is beyond the scope of this article to discuss the subject at greater length, and for further details the reader should consult the references given in Section II of the bibliography

(*l*) Tables and Charts of Data, &c.

The following section includes tables and charts of data covering chemical composition, physical properties, short-time strength, creep strength, thermal expansion coefficients, and conductivity of certain of the alloys described The data are not complete in all cases, but should prove useful They have been collected from various sources which are acknowledged

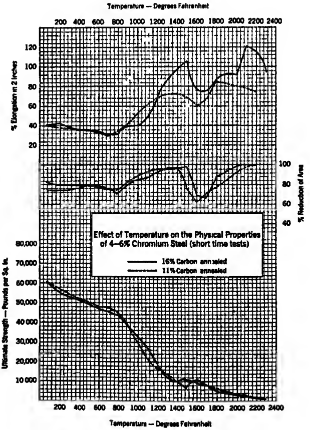


FIG 14 Physical properties of plain 4-6% chromium steel at various temperatures as determined by short-time tests (*After the author*)

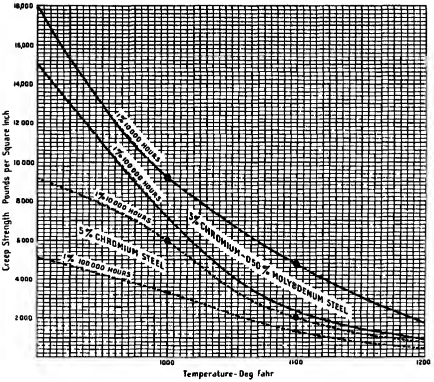


Fig 15 Curves showing comparative creep properties (1% in 10,000 and 100,000 hours) of plain 5% chromium steel and 5% chromium, 0.50% molybdenum steel (*After Norton*) Both materials soft annealed prior to testing

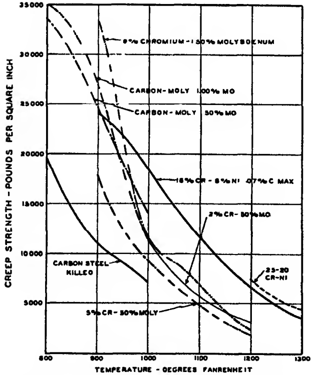


Fig 16 Creep strength of various steels for a rate of 1% in 10,000 hours (*After Norton*)

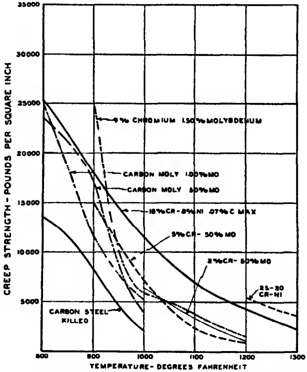


Fig 17 Creep strength of various steels for a rate of 1% in 100,000 hours (*After Norton*)

TABLE I

Chemical Composition of Alloys available for Oil Refining (Tubes)

Material	C	Mn	S	P	Si	Cr	Mo	Ni	W
(1) Carbon steel (killed)	0 10–0 20	0·30–0 60	0·045 max	0·040 max	0·25 max				
(2) Carbon-molybdenum (0 50% Mo)	0 10–0 20	0 30–0 60	0 045 „	0 040 „	0 25 „		0 45–0 65		
(3) Carbon-molybdenum (1·00% Mo)	0·10–0 20	0 30–0 60	0 045 ,	0·040 „	0·25 „		0 90–1 10		
(4) Chromium-silicon-molybdenum (1 25%Cr)	0 15 max	0 30–0 60	0·030 „	0·030 „	0 50–1 00	1 00–1 50	0 45–0 65		
(5) Chromium-molybdenum-silicon (1 75%Cr)	0 10–0 20	0 40–0 60	0·040 „	0 025 „	0 45–0 75	1 50–2 00	0 60–0 80		
(6) Chromium-molybdenum (2% Cr 0 50% Mo)	0 15 max	0 30–0 60	0 035 „	0 030 „	0 50 max	1 75–2 25	0·45–0 65		
(7) Chromium-silicon-molybdenum (2 5% Cr)	0·15 „	0 50 max	0 030 „	0 030 „	0 50–1 00	2 25–2 75	0 45–0 65		
(8) Chromium-molybdenum (3% Cr, 0·90% Mo)	0 15 „	0 30–0 60	0 030 ,	0 030 ,	0 50 max	2 75–3 25	0 80–1 00		
(9) 5% chromium (plain)	0·15 ,*	0 50 max	0 030 ,	0 030	0 50 „	4 00–6 00			
(10) 5% chromium-tungsten	0 15 ,*	0 50 „	0 030 „	0 030 ,	0 50 ,	4 00–6 00			0·75–1 25
(11) 5% chromium-molybdenum	0 15 „*	0 50 „	0 030 ,	0 030 „	0 50	4 00–6 00	0 45–0 65		
(12) 9% chromium, 1 50% molybdenum	0 15 „	0 50 ,	0 030 ,	0 030	0 50	8 00–10 00	1 25–1 75		
(13) 18% chromium, 8% nickel	0 07 „	0 60	0 030 „	0 030 ,	0·75 „	17 00–19 00		8 0–10 5	
(14) 25% chromium, 20% nickel	0 15 ,	1 00	0·030 ,	0 030	0 75	24 00–26 00		19·0–21·0	

* Also available in 0 10% max 0 20% max and 0 25% max carbon These alloys can also be obtained with titanium or columbium additions, as can 18–8

TABLE II

*Typical Physical Properties at Room Temperature, Annealed**

Material	*Ultimate strength, lb per sq in*	*Yield-point,† lb per sq in*	*Elongation, % in 2 in*	*Brinell hardness*	*Charpy impact ft -lb*
(1) Carbon steel (killed)	55,000	35,650	48 0	113	46 0
(2) C-Mo (0 50% Mo)	65,800	41,200	45 0	126	
(3) C-Mo (1 00% Mo)	67,000	42,500	44 0	128	
(4) Cr-Si-Mo (1 25% Cr (DM))	70,800	50,200	40 0	137	
(5) Cr-Mo-Si (1 75% Cr)	70,000	45 000	30 0 (min)	140–60	(normalized and drawn)
(6) Cr-Mo (2% Cr, 0 50% Mo)	68,500	42,000	40 0	137	52 0
(7) Cr-Si-Mo (2 5% Cr)	74,400	40 650	38 5		(1-in bar stock)
(9) 4–6% Cr (plain)	62,200	28,500	46 0	131	46 0
(10) 4–6% Cr, 1 00% W	75,500	39,100	43 0	156	50 0
(11) 4–6% Cr, 0 50% Mo	73,200	33,400	44 0	148	56 0
(12) 9% Cr, 1 50% Mo	78,500	43,400	38 0	169	38 0
(13) 18% Cr, 8% Ni	95,600	40,100	60 0	175	84 0
(14) 25% Cr, 20% Ni	98,500	48,000	55 0	160	

* Properties typical of values obtained on annealed heavy-wall tubes Values for materials 5 and 7 were obtained on 1-in rd

† Yield-points determined by 0 2% permanent set

TABLE III

Short-time High-temperature Tensile Properties

Description of material	*Temp ° F*	*Ultimate, lb per sq in*	*Yield, lb per sq in*	*Elongation, % 2 in*	*Red of area, %*	*Ref*
0 10–0 20% carbon steel (killed)	750	58,000	24,600	34 0	67 0	[39]
1-in rd , annealed 1,550° F	900	45,500	23,500	38 0	70 6	
	1,000	36,500	20,100	42 5	76 9	
	1,100	27,200	14,250	56 5	82 2	
	1,200	20,000	10,200	54 0	89 1	
	1,300	13,550	7,375	59 5	91 6	
	1,400	9,025	3,750	69 5	76 9	
O H carbon steel (killed)	900	30,150	13,850	54 5	84 4	[1]
Analysis	1,000	23,500	12,110	61 0	88 8	
C 0 10%	1,100	15,630	8,020	64 5	95 0	
Mn 0 40%	1,200	11,490	6,415	82 0	98 0	
Si 0 10%						
1-in rd , Brinell 95						
Carbon-molybdenum steel	750	68,100	23,500	28 5	61 7	[39]
Analysis	900	58,200	22,300	29 5	67 8	
C 0 10–0 20%	1,000	50,400	22,800	32 5	77 6	
Mo 0 45–0 65%	1,100	42,000	22,500	40 5	81 4	
Si 0 25% max	1,200	28,100	15,100	56 0	88 6	
1-in rd , annealed to 126 Brinell	1,300	19,000	10,400	68 0	92 6	
	1,400	11,700	5,900	82 5	89 0	
Carbon-molybdenum steel	800	70,500	14,140	27 5	71 5	[1]
Analysis	900	63,500	12,600	27 5	75 8	
C 0 17%	1,000	57,500	11,620	29 0	76 6	
Mn 0 59%	1,100	45,100	10,570	38 0	83 9	
Si 0 18%	1,200	27,000		60 0	88 3	
Mo 0 52%	1,300	16,180		82 5	93 9	
1-in rd forged	1,400	8,720		94 0	85 8	

Description of material	*Temp °F*	*Ultimate, lb per sq in*	*Yield, lb per sq in*	*Elongation, % 2 in*	*Red of area, %*	*Ref*
Carbon-molybdenum steel	800	66,900		28 5	66 2	[1]
Analysis	900	63,250		29 5	68 4	
C 0 10%	1,000	57,390		32 0	73 5	
Mn 0 42%	1,100	50,500		38 0	75 3	
Si 0 22%	1,200	38,000		46 5	71 9	
Mo 1 09%						
1-in rd , Brinell 129						
Chromium-silicon-molybdenum steel	750	71,650	26,400	27 0	67 8	[39]
Analysis	900	67,500	25,600	26 0	66 0	
C 0 15% max	1,000	57,750	24,900	25 5	73 3	
Cr 1 50% ,,	1,100	47,500	23,100	31 0	82 5	
Si 0 50–1 00%	1,200	33,300	16,000	36 5	88 2	
Mo 0 40–0 60%	1,300	22,800	11,100	61 8	94 5	
1-in rd , annealed at 1,550° F , Brinell 123	1,400	13,800	7,000	72 0	98 5	
Chromium-molybdenum-silicon steel	700	67,200	40,500	22 0		[10]
Analysis	800	65,500	39,200	22 0		
C 0 10–0 20%	900	62,000	38,000	29 0		
Cr 1 50–2 00%	1,000	52,500	33,500	38 0		
Mo 0 60–0 80%						
Si 0 45–0 75%						
Normalized at 1 600° F , reheated 3 hr at 1,350° F , Brinell 140–60						
Chromium-molybdenum steel	800	64,300	22,875	26 5	62 5	[1]
Analysis	900	61,600	22 250	30 5	71 7	
C 0 11%	1,000	55,300	21,000	35 0	76 9	
Mn 0 30%	1,100	44,250	20,650	40 0	72 0	
Si 0 20%	1,200	30,850	19,300	58 0	87 8	
Cr 1 79%	1,300	19,380	17 700	76 5	91 8	
Mo 0 60%	1,400	10,500	9,740	86 0	97 8	
1-in rd , annealed, Brinell 125						
Chromium-silicon-molybdenum steel	750	62,450	26,600	30 5	67 4	[39]
Analysis	900	53,000	24,300	38 3	75 2	
C 0 15% max	1,000	45,100	22,850	42 5	79 9	
Mn 0 50% ,	1,100	36,500	20 000	50 3	85 4	
Cr 2 25–2 75%	1,200	28,600	16 000	57 0	90 0	
Si 0 50–1 00%	1,300	19,600	11,500	69 0	93 6	
Mo 0 40–0 60%	1,400	12,900	7,500	75 0	96 0	
1-in rd , annealed, Brinell 143						
4–6% chromium–1% tungsten steel	800	46,350	20,650	32 5	71 2	(B & W Tube Co data)
Analysis	900	40,940	15 350	38 0	69 3	
C 0 12%	1,000	34,750	11,250	48 0	77 2	
W 0 92%	1,100	27,750	10,580	55 5	84 9	
Cr 5 00%	1,200	20,550	9,190	66 0	91 3	
1-in rd , annealed, Brinell 123	1,300	12,850	8,550	77 5	94 7	
4–6% chromium–tungsten steel	800	50,400		26 0	63 5	[39]
Analysis	900	46,950		26 0	73 5	
C 0 15% max	1,000	41 250		32 0	78 3	
Si 0 50% ,,	1,100	34,500		38 0	85 8	
Cr 4 00–6·00%	1,200	21,875		37 0	91 7	
W 0 75–1 25%						
1-in rd , annealed at 1,550° F , Brinell 131						
4–6% chromium–0 50% molybdenum steel	750	51,800	21,050	30 5	76 7	[39]
	900	48,400	19,600	28 5	76 9	
Analysis	1,000	44,400	17,300	28 5	73 5	
C 0 15% max	1,100	34,400	15,400	38 5	87 3	
Si 0 50% ,,	1,200	25,800	11,300	46 0	91 0	
Cr 4 00–6 00%	1,300	19,100	9,500	65 0	94 6	
Mo 0 45–0 65%	1,400	13,300	7,250	65 0	95 9	
1-in rd , annealed at 1,550° F , Brinell 128						
4–6% chromium–0 50% molybdenum steel	800	60,500	26,750	28 5	66 8	[1]
	900	53,350	23,500	36 5	73 6	
Analysis	1,000	45,350	20,600	46 0	83 2	
C 0 16%	1,100	31,700	15,800	60 0	90 2	
Mn 0 36%	1,200	24,450	11,350	69 5	93 7	
Si 0 37%	1,300	17,800	7,250	78 5	96 6	
Cr 5 13%	1,400	11,370	8,250	78 0	98 8	
Mo 0 58%	1,500	11,890	8,400	22 5	73 5	
Specimens from heavy wall tube Furnace annealed, Brinell 143						

TABLE III (*cont*)

Description of material	*Temp ° F*	*Ultimate, lb per sq in*	*Yield, lb per sq in*	*Elongation, % 2 in*	*Red of area, %*	*Ref*
4–6% chromium–molybdenum steel						
Analysis						
(1) C 0 14%	1,000	41,300	17,100	46 0	79 9	[11]
Si 0 35%	1,100	32,500	15,150	45 5	86 5	
Cr 4 63%	1,200	25,100	12,600	66 8	87 2	
Mo 0 54%						
Furnace cooled from 1,550° F , Brinell 130						
(2) C 0 18%	1,000	44,700	18,750	45 0	83 1	
Si 0 33%	1,100	36,300	16,900	42 3	87 3	
Cr 4 96%	1,200	26,600	13,100	55 8	87 9	
Mo 0 49%						
Furnace cooled from 1,550° F , Brinell 138						
9% chromium–1 50% molybdenum steel	900	58,500	24,190	35 0	74 6	[1]
Analysis	1,000	49,300	24,320	37 0	81 1	
C 0 12%	1,100	37,380	20 550	54 0	88 0	
Si 0 09%	1,200	26 200	17,300	71 0	95 0	
Cr 9 42%	1,300	18,800	13,030	81 0	97 1	
Mo 1 41%						
1-in rd , annealed, Brinell 143						
18% chromium–8% nickel	800	67 025		45 2	68 8	[1]
Analysis	900	64,480		40 2	69 1	
C 0 07% max	1,000	61 625		44 5	69 0	
1-in rd	1,100	53,730		40 7	64 8	
	1,200	44 375		46 7	64 1	
	1,300	35,610		50 7	58 2	
	1 400	23,640		53 2	47 2	
	1,500	17 210		54 5		
25% chromium–20% nickel	800	84 250		33 5	56 5	[1]
Analysis	900	84,700		32 0	54 8	
C 0 10%	1,000	80,450		32 5	51 4	
Mn 0 52%	1,100	73,200		36 0	50 8	
Si 0 97%	1 200	64,250		34 0	48 9	
Cr 24 96%	1,300	51,300		36 5	54 4	
Ni 21 45%	1 400	44,450		45 0	58 8	
⅞-in rd (hot rolled), Brinell 179	1,500	34 620		47 0	50 3	
	1,600	24,050		46 0	47 6	
	1,700	16 240		49 5	49 9	
	1,800	11,630		54 5	46 7	
	1 900	8,745		66 5	48 1	
	2,000	7,000		62 5	49 6	

TABLE IV

Creep Properties—Data from Various Sources

Material and condition	*Temp ° F*	*Creep stress,* lb per sq in*		*Ref*
		1% 10,000 hr	*1% 100 000 hr*	
Carbon steel (killed), 0 10–0 20% C	800	26,800	18,500	[39]
	900	16,900	12,800	
	1 000	5,750	2,700	
	1,100	1,800	840	
	1,200	920	290	
Carbon steel (killed), 0 18% C, 0 09% Si Brinell 103	800	19,500	13,500	[1]
	900	11,000	8,400	
	1,000	7,200	2,150	
Carbon steel (killed), 0 15% C (tube) Normalized and drawn 168 hr at 1,200° F	1,000	3,400	1,800	[40]
Carbon-molybdenum steel, 0 10–0 20% C, 0 45–0 65% Mo, 1-in rd , Brinell 126	800	26,000	15,500	[39]
	1,000	17,800	10,700	
	1,200	2,000	480	
Carbon-molybdenum steel, C 0 16, Mo 0 54% Brinell 131	800	33,500	23,500	[1]
	900	24,500	17,200	
	1 000	14,000	4,000	
Carbon-molybdenum steel, C 0 16, Si 0 23, Mo 0 42% Normalized and drawn	1,000	16,000	9,225	[40]
C 0 15, Mo 0 50% Normalized and drawn 168 hr at 1,200° F	1,000	8,800	4,750	

* Note Values shown in nearly all cases were extrapolated from rates of 0 01% and 0 10% elongation per 1,000 hours

Material and condition	*Temp °F*	*Creep stress,* lb. per sq in* 1% 10,000 hr	*Creep stress,* lb. per sq in* 1% 100,000 hr	*Ref*
0.50% molybdenum steel calorized	1,000	7,000	2,700	[9]
	1,200	1,650	470	
	1,300	840	210	
1.00% molybdenum steel calorized	1,200	2,600	1,100	
	1,300	2,000	840	
	1,400	750	380	
1.00% molybdenum steel	800	35,000	25,000	[1]
	900	27,000	11,500	
	1,000	11,500	5,200	
Chromium-silicon-molybdenum steel, C 0.07, Si 0.72, Cr 1.25, Mo 0.54% Annealed	800	29,500	20,000	[39]
	1,000	24,000	15,000	
	1,200	3,950	1,950	
Chromium-silicon-molybdenum steel, C 0.10–0.20, Si 0.45–0.75, Cr 1.5–2.0, Mo 0.60–0.80%	800		30,000	[10]
	900		15,400	
	1,000		9,400	
2% chromium–0.50% molybdenum steel annealed tubing Brinell 143	1,000	11,400	6,300	[1]
	1,100	5,650	3,320	
	1,200	3,150	1,100	
Chromium-silicon-molybdenum, C 0.15 max Si 0.50–1.00, Cr 2.25–2.75, Mo 0.40–0.60% Annealed Brinell 143	800	25,000	20,000	[39]
	1,000	8,600	5,400	
	1,200	2,325	1,000	
4–6% chromium steel (plain)	1,000		6,500	[39]
4–6% chromium steel C 0.15% tube Annealed at 1,600° F Drawn 168 hr at 1,200° F	1,000	6,600	3,750	[40]
4–6% chromium steel (plain), 0.20% C Annealed Brinell 126	800	22,000	10,200	[30]
	900	9,200	5,100	
	1,000	6,000	3,300	
	1,100	2,000	1,320	
	1,200	840	450	
4–6% chromium-tungsten steel	1,000		6,000	[39]
4–6% chromium-tungsten steel, C 0.08, Si 0.20, Cr 4.88, W 1.10% Annealed	1,000	8,400	5,650	[40]
4–6% chromium-tungsten steel, C 0.11, Cr 5.82, W 0.92% Brinell 121	900	9,800	6,800	(Norton)
	1,000	6,700	5,000	
	1,100	3,500	1,600	
	1,200	2,400	740	
4–6% chromium-molybdenum steel, C 0.15% max Annealed Brinell 128	800	22,000	14,250	[39]
	1,000	10,250	7,000	
	1,200	2,500	900	
4–6% chromium-molybdenum steel, C 0.15, Cr 4.0–6.0, Mo 0.50% Annealed tube at 1,600° F Drawn 168 hr at 1,200° F	1,000	9,500	4,200	[40]
4–6% chromium-molybdenum steel, C 0.14, Cr 4.63, Mo 0.54% Annealed	1,100	4,200		[11]
C 0.18, Cr 4.96, Mo 0.49% Annealed	1,100	5,170		
4–6% chromium-molybdenum steel, C 0.15, Cr 5.23, Mo .56% Tubing annealed Brinell 143	900	17,900	15,000	[1]
	1,000	9,200	7,200	
	1,100	4,800	2,400	
	1,200	1,800	900	
9% chromium–1.50% molybdenum steel, 0.15% C max Annealed Brinell 152	900	33,250	24,750	[1]
	1,000	11,650	5,800	
	1,100	6,950	3,775	
	1,200	2,300	1,600	
18% chromium–8% nickel steel, 0.07% max C 0.053, Cr 17.57, Ni 8.70% Hot rolled Brinell 187	800		25,300	[1]
	900	24,000	18,000	
	1,000	18,300	11,500	
	1,100	11,550	7,100	
	1,200	6,600	4,250	
	1,350	2,500	1,600	
18% chromium–8% nickel steel, C 0.067, Cr 18.21, Ni 9.56% Rolled and water cooled from 2,000° F	1,000	17,520		[11]
	1,100	13,600		
	1,200	7,100		
25% chromium–20% nickel steel (hot rolled)	1,200	7,400	5,400	[1]
	1,350	3,300	2,800	
	1,500	1,100	800	

* Note Values shown in nearly all cases were extrapolated from rates of 0.01% and 0.10% elongation per 1,000 hours

TABLE V

Coefficient of Thermal Expansion

Material	*Temperature range,° F*	*Average coefficient in per in per 1° F*
Carbon steel, 0·10–0·20% C	32–390	6·89 × 10^{-6} Ref 1
	32–570	7·22 × 10^{-6}
	32–750	7·55 × 10^{-6}
	32–932	7·89 × 10^{-6}
	32–1,112	8·13 × 10^{-6}
C-M, 0·50% Mo	70–450	7·92 × 10^{-6}
	70–750	8·18 × 10^{-6}
	70–1,050	8·86 × 10^{-6}
	70–1,150	8·95 × 10^{-6}
1·25% Cr, 0·75% Si, 0·50% Mo	at 900	9·34 × 10^{-6} Ref 2 True
	at 1,000	9·74 × 10^{-6} or inst co-
	at 1,110	10·14 × 10^{-6} efficients
2% Cr, 0·50% Mo	70–450	7·45 × 10^{-6}
	70–750	7·78 × 10^{-6}
	70–1,050	8·45 × 10^{-6}
	70–1,150	8·50 × 10^{-6}
4–6% Cr, 0·08% C, 0·16% C	100–1,000	6·80 × 10^{-6}
	70–1,310	7·10 × 10^{-6}
4–6% Cr, 0·50% Mo	100–1,000	7·00 × 10^{-6}
	70–1,112	7·16 × 10^{-6}
9% Cr, 1·50% Mo	70–300	6·29 × 10^{-6}
	70–600	6·67 × 10^{-6}
	70–900	7·00 × 10^{-6}
	70–1,200	7·30 × 10^{-6}
18% Cr, 8% Ni (0·07% C max)	68–500	9·73 × 10^{-6}
	68–700	10·00 × 10^{-6}
	68–900	10·15 × 10^{-6}
	68–1,000	10·20 × 10^{-6}
	68–1,100	10·30 × 10^{-6}
	68–1,200	10·41 × 10^{-6}
	68–1,300	10·55 × 10^{-6}
25% Cr, 20% Ni	105–1,320	9·20 × 10^{-6}
	70–1,832	10·60 × 10^{-6}

Ref 1—Joint Research Committee A S M E–A S T M (1931)
Ref 2—Timken Steel & Tube Co—Digest of Steels (1934)
Other data from Babcock & Wilcox Tube Co, Beaver Falls, Pa

TABLE VI

*Thermal Conductivity of Various Materials**

No	*Composition of material*	*Thermal conductivity in Watts cm $^{-1}$ deg $^{-1}$*				
		100° C	*200° C*	*300° C*	*400° C*	*500° C*
C_1	Basic O H iron C 0·02, Mn 0·03, S 0·005, P 0·042	0·665	0·607	0·549	0·491	0·435
S_1	H C steel C 0·83, Mn 0·27, S 0·015, P 0·017, Si 0·16	0·458	0·435	0·413	0·390	0·367
S_6	4–6% Cr steel C 0·10, Mn 0·45, S 0·017, P 0·013, Si 0·18, Cr 5·15	0·366	0·358	0·351	0·343	0·336
A_1	15% Cr steel C 0·08, Mn 0·35, S 0·017, P 0·020, Si 0·20, Cr 15·19	0·261	0·262	0·262	0·262	0·263
A_2	12% Cr steel C 0·07, Mn 0·09, S 0·010, P 0·015, Si 0·09, Cr 12·00	0·249	0·259	0·268	0·277	
A_4	26% Cr steel C 0·10, Mn 0·40, S 0·008, P 0·013, Si 0·45, Cr 26·00	0·209	0·219	0·229	0·238	0·243
A_7	18–8 low carbon C 0·07, Mn 0·27, Cr 18·16, Ni 9·10	0·164	0·177	0·190	0·203	0·216

1–1 Watt cm –1 deg –1 = 1 Watt/(sq cm) (deg C/cm) = 0·239 Cal/(sec) (sq cm) (deg C/cm) 1 Watt cm –1 deg –1 = 57·9 B Th U/(hr) (sq ft) (deg F/ft)

* Extracted from table by Shelton, S M, and Swanger, W H, *Trans A S S T* 21, 1066, 1067, 1070 (1933)

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NOTE

Since this article was written, experiments show that both the titanium and columbium containing alloys are hardenable if a sufficiently high temperature is reached They are, however, substantially non-hardenable from temperatures producing drastic hardening in the usual 5% chromium molybdenum steel

CHOICE AND DESIGN OF TUBING FOR FURNACES AND SHELL AND TUBE EXCHANGERS

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INTRODUCTION

SEAMLESS tubing is standard for use in oil furnaces and heat exchangers Refineries are large users of lap-welded pipe for tankage and miscellaneous lines, but this article is confined to heating tubes in furnaces, exchangers, and condensers

The fundamental soundness of a good piece of seamless tubing is everywhere appreciated, and it is the only tubing permissible for severe service

FURNACE TUBING

A. Refinery Requirements

In 1931 questionnaires were sent to some 250 refineries and 20 manufacturers of refining equipment in order to obtain their views on the needs of the industry [4, 1931] with reference to metal products in general use at high temperatures Necessarily, the replies dealt in large measure with heater tubing A general summary of views as to the important properties of tubing is given below

Corrosion Resistance. Metal should be resistant primarily to anhydrous hydrogen sulphide, which corrodes plain steel rapidly at elevated temperatures, particularly above 600° F

High-temperature Strength This is, of course, an essential attribute of a furnace tube

Stability of Properties. These requirements are that the metal does not become embrittled, or otherwise develop undesirable strength or ductility characteristics in pressure and temperature service For example, 18–8 % chromium-nickel alloy is usually limited to 1,200° F because of lack of stability at high temperatures The common 4–6% chrome alloy frequently develops a cold brittleness due to service, so that sometimes furnace tubes are found which were fractured on down periods by knocking tools used in cleaning out the coke deposits Some manufacturers add other alloys—tungsten, molybdenum, &c —for which various claims are made Laboratory tests show molybdenum is very effective in improving the toughness of 4–6% chrome steel

Indications of Impending Failure This refers to the fact that oil-furnace tubes occasionally are overheated, bulge, and split, it is very desirable that the tube give appreciable warning by gradual swelling so that the operators can be forewarned and shut down the unit prior to failure

Ease of Fabrication. Under this head are grouped desirable qualities such as weldability, cold and hot bending, flanging, and flaring properties Mild carbon steel, for example, is readily cold worked to a remarkable degree, and if worked hot or welded requires no annealing The 4–6% chrome alloy is air hardening if worked hot or welded, and is then dangerously brittle until annealed It may be cold worked without difficulty when in the annealed state Due to development in field annealing, it is now being welded and annealed in place on the job

The 18–8 % chrome-nickel alloy is ductile, but susceptible to hardening by cold working, and welding may impart undesirable properties difficult to remove by heat treatment

Thermal Expansion Due to the wide use of carbon steel, the coefficient of expansion of alloys should be near that of mild steel

Scaling Resistance. The metal should not oxidize or scale readily The resistance of carbon steel is not satisfactory above 1,150° F in the furnace Up to 1,300° F the 4–6% chrome alloy appears satisfactory, and higher chromium content is required for resistance at higher temperatures

Cost Since carbon-steel tubing costs about $0 05 per lb , any alloy to supplant it must be fairly reasonable in price

The above properties are not developed to the fullest degree in any one metal Carbon steel is deficient with respect to corrosion resistance and high-temperature properties, the familiar 18–8% chromium-nickel alloy is almost ideal with respect to corrosion resistance, scaling resistance, and strength, but has a bad record in respect to high-temperature stability and swelling prior to bursting Where corrosion as experienced in pressure distillation, i e from hydrogen sulphide in the absence of liquid water, becomes a factor, many refineries are using one of the 4–6% chromium-steel alloys, which in addition to corrosion resistance have higher strength at elevated temperatures than carbon steel, and are otherwise quite similar to mild steel Carbon steel and the 4–6% alloy at present constitute the great majority of tubes in actual service, and for this reason are treated herein at greater length than other materials

Where corrosion is not a factor and great strength at high temperatures is desired, special alloys are being offered by the tube mills It is thought that the use of extremely thick tubes at high temperatures can be avoided, with saving in weight, cost, &c

These alloys may be regarded as first-quality mild carbon steel to which are added small percentages of molybdenum, chromium, manganese, &c , to enhance the high-temperature strength

Interested parties should apply to the steel and tube mills for detailed information to solve their particular problems, because as yet the industry has little practical experience to report, on other than chrome alloys

Surface Coatings. Tubes surface coated inside and out with calorizing and chromium plating are available These must be regarded as in the experimental stage until a few years of successful service are reported.

B. Choice and Design of Tubing

Corrosion.

There is no corrosion problem, relatively speaking, when sweet oils are processed For oils having a low sulphur content, plain carbon-steel tubes are satisfactory in nearly all heaters But as the industry goes to sour and sulphur-bearing oils, especially at temperatures above 600° F , corrosion usually becomes appreciable Steel gives a life from 3 to 8 years in the former service, but in the latter it may last less than 1 month Most Mid-Continent crudes (especially those from the south and west) are corrosive at the high temperatures of cracking coils, but not particularly corrosive in pipe-still furnaces If the corrosion is of the usual type, due to sulphides, 4–6% chrome can be expected to give a life several times that of carbon steel In general, the greater the sulphide corrosion of mild steel, the greater the relative life of the 4–6% alloy Table I below illustrates this point

TABLE I

Approximate Life of Tubes subjected to High-temperature Sulphide Corrosion

Service	*Life carbon steel*	*Life 4–6% chrome*	*Ratio*
Mild	8 years	10 years	1 25 1
Moderate	2 ,,	8	4 1
Severe	½ year	3	6 1
Extra severe	⅕ ,,	2	10 1

The chrome-nickel (18–8) alloy is very definitely resistant to sulphide corrosion, in extra severe corrosion it would last, probably, upwards of 20 years On the other hand, the cost of this alloy is so high and the restrictions as to temperature of use so exacting that it is not being advocated as widely as formerly, except where extreme strength at temperatures below 1,200° F is essential

Corrosion agents other than anhydrous sulphides may be met occasionally

(1) Chlorides yielding hydrochloric acid, in the presence of water
(2) Sulphur dioxide in the presence of water
(3) Sulphides in the presence of water
(4) Miscellaneous acids

Chromium in the alloy is not likely to improve the steel in the face of these corrosives

The behaviour of metals in corrosive service frequently cannot be predicted from theoretical consideration, laboratory test of the stocks, &c It is far better to run a preliminary test in service, following the procedure developed by the General Committee on Corrosion of the American Petroleum Institute [6] The test specimens should include mild steel, 4–6% chrome alloy, 18–8, and others as desired So far as we know, alloys containing appreciable percentage of chromium are the only ones of value in resisting corrosive attack except in the cases listed above

The general demand for chrome steels has recently brought to the market 2 and 8% chromium alloys, whose properties and cost are believed to be roughly proportional to the percentage of chrome content

Allowing for the variation of corrosion with temperature of the oil, some heaters are built in part with chrome tubes, the remainder mild steel Where temperatures at the inlet are below 700° F , carbon-steel tubes might be used up to the point when 700° F is reached, then a chrome alloy Then later in the coil, where there is a decided coke film, it might pay to use carbon steel again because of the decrease in corrosion rate under a coke film.

When past experience is not available and tests cannot be run, modern practice is to build the heater of carbon steel in locations where corrosion is doubtful and retube with an alloy when necessary.

High-temperature Strength.

In recent times the trend has been towards progressively higher pressures and temperatures, in various heating processes, and to longer battery runs These are serious factors in tube failures, nevertheless, there probably are as yet few heaters operating in which carbon steel would not give a good account of itself in respect to strength.

Alloys, however, are being introduced for their value in resisting stress at high temperature as well as corrosion

High-temperature properties and design problems will be discussed with reference to several elements below

Design Formula. A variety of formulae are available, ranging from the simple Barlow formula

$$S = \frac{PD}{2t}$$

to extremely complicated expressions involving heat transfer, elastic moduli, conductivity, &c On the basis of both theoretical and practical considerations the Clavarino formula is recommended This is given below in a form which assumes Poisson's ratio to be 0 3 This formula is used satisfactorily for lines and heater tubes In the latter case the theoretical calculations of many authorities [8, 1931] show that a large and serious 'thermal stress' can exist, in fact, bulging of tubes is reported and attributed to thermal stressing in at least one case [5] in a boiler furnace On the other hand, other authorities [2, 1930, 3, 1932] discuss theoretically thermal stressing, and conclude that it is unimportant

Practical experience in cracking heaters confirms this conclusion, so that the Clavarino pressure-stress formula is found amply conservative

Allowable Stress Steel in temperature service in boilers was traditionally designed for a working stress determined by dividing the ultimate tensile strength at room temperature by a factor of safety ranging from 4 to 6 At the higher temperatures of oil heaters (and modern boiler practice, also) the concept of creep is considered very important

There is a wealth of literature describing the creep of metals, this being a very slow deformation or flow exhibited under stress at high temperatures [9, 1934] The essential and generally agreed on facts are outlined below

(1) Most authorities believe that all metals even at ordinary temperatures and ordinary design stresses (say, 16,000 lb per sq in in steel) undergo gradual deformation, but at an extraordinarily slow rate

(2) It is a provable fact that, at moderate temperatures, keeping the temperature constant and increasing the stress markedly increases the rate of deformation

(3) Keeping stress constant and raising the temperature will markedly increase the rate of deformation

(4) With the usual specimen of mild steel in a tensile test machine at a temperature of 1,000° F , exposed to a stress of about 6,000 lb per sq in , the creep or extension of the specimen in 1,000 hours is about 0 1%, or 1/1,000 in per in This would become about 1% in a year, at this rate, and such an amount of deformation may be serious

Although creep is recognized as of real importance, it is not at the present time herein recommended as the sole basis for allowable stress in tube design

This decision is a matter of several years' practical experience.

Several reasons are

(1) In the past, due to the lack of a standard test procedure, the different authorities and the different vendors of tubing were publishing quite different values for creep

properties of the same metals, values which differed from one another by several hundred per cent

(2) Many perplexities about creep still exist, referring in particular to the procedure for extrapolating a 1,000-hour test to 30,000 hours' service, the effect of cycles of temperature and stress, hysteresis, compound stress, &c A standard procedure is now available and the laboratories and vendors are publishing values which agree with one another, so that in time reliable creep design will be practical

(3) The allowable stress problem cannot be entirely dissociated from the tube-temperature problem, this point is discussed later, under Metal Temperature

(4) Finally, a practical analysis of the creep situation may be set up in two thoughts First, the tube is not to fail suddenly with an explosive burst as it operates under temperature This can be prevented by a working stress obtained by dividing the ultimate strength of the metal at the high temperature by a generous factor of safety Secondly, at a reduced stress so computed the tube at the worst will do no more than swell slowly during days and weeks of operation, and the operators and inspectors will detect the swelling and remove the tube

In practice bulging by *creep* is not found to be an expensive problem, failures and split tubes happen occasionally, and these are found to be due to extra thick coke inside the tube, or flame impingement, the local heavy scaling of the tube testifying to unusual and excessive metal temperatures, Fig 1 is a typical example

Objections can be raised against basing high-temperature design on the ultimate tensile strength determined in a short time-test, but, from a practical point of view, when the factor of safety is chosen properly to avoid excessive failures from bulged or split tubes, then creep and similar considerations give little or no trouble to the operators

The computation of numerical values of allowable stress is given on a later page

Metal Temperature.

The temperature of an insulated line containing hot oil or vapour is practically the same as that of the oil or vapour If the line is bare, or in a hot furnace, so that heat conduction is taking place, the temperature of the metal will be proportionately less or greater than the oil temperature In practice the actual oil temperature is used, except inside a furnace In the latter case the temperature had best be actually measured with appropriate thermo-couple equipment [5]

Some heaters are operated by tube metal temperature readings These are taken by alumel-chromel wires inserted in small drill-holes in the tubing, the tubing being peened with a centre punch around the drill-holes so as to contact and hold the wires securely The couple wires are insulated by porcelain and surrounded by a protector-tube, usually of 18–8 alloy This latter is securely welded to the heater tube to exclude furnace atmosphere An installation of this type requires calibration in actual service, which is carried out by installing three alumel-chromel couples as near as possible to each other, one each of 20-gauge, 12-gauge, and 8-gauge wire Simultaneous readings of the several couples taken under operation are plotted and then extrapolated to zero diameter wire This is considered the true temperature and compared with the tube-enclosed assembly to give a correction to be added or subtracted at any future time when true temperatures are desired

Many measurements of tube temperatures have been made, showing in exceptionally severe cases that the heater-tube metal temperature may run almost to the furnace temperature, 1,450° F, 500° above the oil temperature Measurements further show that the tube wall operates through a range of temperature, starting fairly close to the oil temperature and generally ranging upwards throughout the run, due to coke deposition Coke is the real 'bugaboo', the cause of excessive temperatures and split tubes

Coke deposition in the tubes affects the tube metal temperature so as to require process handling of various kinds, viz the charging to cracking units of stock specially selected for cleanliness as to coke, or 'clean circulation' type of units, in which the charge oil is cleaned up prior to passing through the furnace tubes, shielding of the coking zone, so that the group of tubes in which coke deposits is shielded from high furnace temperatures, finally, as a last resort, the use of excessively thick or strong tubing so as to withstand almost the full furnace temperature

Because of the many varied means of handling this situation simple rules of thumb or arbitrary determinations of the tube metal temperature cannot be laid down here In general, the effect of the coke must be determined by the refinery engineer for his each individual application, taking into account the type of cracking or distillation cycle, nature of the charge oil, location of tubes in which coke deposits, thickness and nature of the deposit, the rate of heat transfer in the furnace, and the likelihood of flame impingement On a later page is outlined a type of calculation which can be used when these factors can be reasonably evaluated

It is also this factor of uncertainty which makes it highly advisable to base allowable stress on ultimate tensile strength divided by a factor of safety A creep-strength figure appertains to some one particular temperature, but, as stated, a tube does not ordinarily operate at a definite temperature, rather it operates through a range of temperature

The designer of tubing predicts the metal temperature, and then uses a factor of safety to protect against uncertainties in allowable stress and adverse furnace conditions

Minimum Practical Thickness.

Even if a tube metal should be developed giving an extraordinarily high tensile strength, no one would consider operating tubing down to a razor-blade thickness Actual corrosion is characterized by a certain amount of pitting, and is nearly always decidedly uneven in one way or another It is rarely proper to assume that the inspectors will locate the thinnest point in a line, so that in practice lines are condemned at quite appreciable thickness Fig 2 illustrates an occasion when the inspector did locate the pit, obviously, one should not rely on always doing so

Other considerations enter, such as likelihood of the line or tube being torn loose by weight, by thermal expansion, or by pressure surges A rational scheme for lines in general is to classify the units into extra hazardous and ordinary types, for the former, the minimum practical thickness will be set at the thickness for operation at 700 lb per sq in at 950° F, for the latter, minimum thickness will be required for operation at 200 lb per sq in at 700° F. This system is detailed later

Money Value of High-temperature Strength.

The balance between the cost and the value of high-temperature strength cannot be struck with precision.

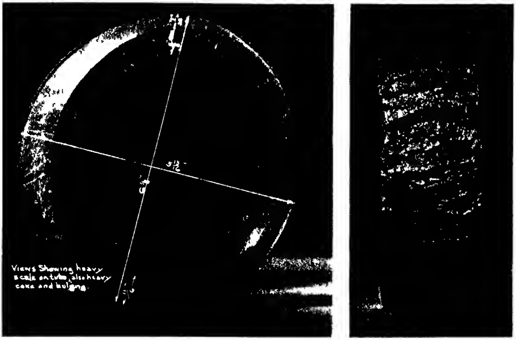
5 13/16"
Views Showing heavy scale on tube, also heavy coke and bulging.

FIG. 1


View Showing Pit Located By Inspector.

FIG 2

The published values of such strength are not yet reliable, the uncertain metal temperature is a factor, and, finally, the minimum practical thickness will usually condemn heater tubing before the theoretical design strength comes into play Added strength is certainly worth a premium, because it increases the factor of safety against adverse conditions, reduces fire, reduces tube renewals, and increases safety

Practical experience in specific locations is required to settle this point, and beyond a word of caution in pointing to minimum practical thickness in the above paragraph the matter is otherwise left to the individual designer

Outline of Tubing Design

The following outline should be modified freely to conform to local and individual applications

Calculate allowable internal pressure for the allowable maximum stress by Clavarino's formula

$$P = S\frac{10(D^2-d^2)}{13D^2+4d^2}$$

P = allowable pressure, lb per sq in ,
S = allowable working stress at the temperature of operation, lb per sq in ,
D = outside diameter of tubing, in ,
d = inside diameter of tubing, in

Allowable stress

$$S = \frac{TS}{FS}$$

TS = ultimate tensile strength, from short time-test at high temperature

Design values for 0 10–0 20% carbon steel and 4–6% chrome, and 18–8% chrome-nickel are tabulated below Values are for material in a soft, ductile condition suitable for tubing

Ultimate Tensile Strength

Tempera-ture	*Carbon steel*	*4–6 % Chrome**	*18–8 %* Cr-Ni
0–500°	Use 60 000 lb per sq in	Use 60 000 lb per	Use 90 000 lb per sq in
550°	„	59 520 sp in	
600°		58 500	
650°	„	56 760	
700°	57 990	54 300	72 000
750°	54 480	51 720	71 000
800°	49 980	48,420	68 000
850°	45 000	45 000	66 000
900°	40 020	41 700	63 000
950°	34 980	38,400	61 500
1,000°	30 000	35,040	60 000
1 050°	25 260	31 740	58 000
1 100°	21 240	28 320	56 000
1 150°	17 400	25 020	53 000
1 200°	14 220	21 720	49 000
1 250°	11 760	18 300	46 000
1 300°	10 020	15 000	41 000

* The tabulated values apply to plain 4–6% chrome The addition of molybdenum or tungsten strengthen the steel as regards creep resistance, but not materially as regards the strength necessary to resist the type of temporary overloading which actually causes the majority of tube failures

FS = the factor of safety. The value depends on the certitude with which safe operating stresses are derived by past experience, and with the reliance to be placed on the estimation of true metal temperatures, &c

A value of 6 is suggested for use in cracking process heaters

Some authorities recommend increasing the factor of safety at higher temperatures, and this step is recommended as in accordance with the trend developed by creep tests.

Metal Temperatures.

For tubing outside a furnace zone, use the temperature of the oil or vapour carried by the line

In a furnace the metal temperature is computed from the oil temperature, coke thickness, and the rate of heat transfer into the tube in question In the absence of better and more specific information about the job he is working on, the designer may use the following scheme

Temp of oil $T°$ F (1)

Temp drop through liquid film $\frac{Q}{150}$ (2)

" " coke $\frac{Q \times L}{20}$ (3)

Temp of metal—Sum of above terms

Q = maximum rate of heat transfer into oil, B Th U per sq ft per hr
L = coke thickness, in

Minimum Practical Thickness.

The establishment of this thickness depends somewhat on local conditions For example, in the presence of extremely uneven or spotty corrosion some companies have found it practical to renew tubes or lines on the basis of a definite number of hours of operation, rather than attempt tedious drilling and callipering

The system outlined below, however, is based on hammer testing and careful callipering by competent inspectors The minimum practical tube metal thickness for each tube or line is to be computed for the temperatures and pressures listed in the following outline, depending on the service of the unit on which the line is located

Classification of Refining Units.

A Pressure units (high temp , high press , or both).
  1 Heater tubes
    a In furnace—Radiant zone
      Convection zone
      Clean circulation—no coke
    b In junction box or header
  2 Units operating above 200 lb per sq in
    a Lines above 650° F —Use 700 lb per sq in. at 950° F
    b Lines below 650° F —Use 800 lb per sq in. at 650° F
  3 Units operating below 200 lb per sq in
    a Lines above 650° F —Use 500 lb per sq in. at 1,000° F
    b Lines below 650° F —Use 600 lb per sq in. at 650° F
B Non-pressure units (crude stills, pipe stills, &c)
  1 Heater tubes
    a In furnace
    b In junction box
  2 Lines (fractionating towers 25 lb per sq in or less)—Use 200 lb per sq. in at 700° F.

The above classification requires an arbitrary table for heater tubes, somewhat as follows

It is understood that each tube or line will stand on its own merits, that is, will be renewed on the basis of the actual temperature, pressure, and thickness before the minimum practical thickness is reached, if actual computations call for such a step

Heater Tubes

O D of tubing	*Pressure units (High press or high temp)*		*Crude topping pipe stills*	
	In furnace	*In box*	*In furnace*	*In box*
2½ in			0 12 in	0 10 in
2¾ ,,			0 12 ,,	0 10 ,,
3¼ ,,	0 16 in	0 12 in	0 12 ,,	0 10 ,,
3⅜ ,,			0 12 ,,	0 10 ,
3½ ,,	0 18 ,,	0 15 ,	0 12 ,,	0 10
4	0 20 ,	0 16 ,	0 12 ,,	0 10 ,,
4½ ,,	0 22 ,,	0 17 ,,	0 14 ,,	0 12 ,,
4¾ ,,			0 15 ,,	0 13 ,
5 ,,	0 27 ,,	0 21 ,	0 16 ,,	0 14 ,,

It is further the practice in preheater design to purchase new tubes always with a corrosion allowance, this being an added thickness of metal over what is theoretically demanded for strength, as the tubes thin due to corrosion, bulged and possibly split tubes will begin to show in a gradual manner and indicate the need for retubing irrespective of any theory

Practical considerations of this nature must be watched carefully, in view of the present-day imperfect development of high-temperature design

Cost of Tubing.

The cost and value of tubing are primarily to be correlated with corrosion resistance The following table [1, 1934] is a rough picture of the situation

Material	*Cost ratio**	*Corrosion-life ratio†*
Carbon steel	1	1
Carbon-molybdenum	1 5	1–1 25
2% chrome ,,	2 1	2–2 5
4–6% ,, ,	3 29	4 25–6 75+
8–10% ,, ,,	8 66	10–12 5
18–8	10 6	16–25+

* Approximate—based on car-load quantities

† From service records and estimates

C. Inspection Methods

The safe operation of tubing in corrosive service at high pressure and temperature demands a detailed inspection system This should involve a chief inspector and other men as necessary for actual inspection and keeping of records After every run of a unit certain lines and nipples are hammered to detect thin spots, and special care is taken in the inspection of all the furnace tubes which are heavily fired Badly scaled tubes are sometimes removed because of scaling alone, usually they also show a bulging and a sagging If the swelling is uniform, an increase in diameter up to about 5% is often permissible If the bulge is in any degree irregular, the tube is removed Crooked tubes are rarely removed because of sagging alone

The frequency and the rigour of inspection depend largely on the nature of the corrosion and the hazard to life and property A pressure battery in moderately corrosive service is completely overhauled every 6 months, in addition to the necessary attention after each run The thicknesses of all lines and tubes are checked by drilling or by callipering, at as many points as necessary Special care is given lines near welds, valves, bends, or other points of turbulence Furnace tubes have been found to undergo accelerated corrosion at the following points in or near the junction box, on the flame side, on the top of the tube, on the bottom of the tube, in other words, almost anywhere in the tube

After a field check of lines and the necessary renewals, the engineering office carefully computes the allowable temperatures and pressures of operation and notifies the operating department of their findings A diagrammatic sketch of the unit showing all lines and connexions is made New lines are coloured black, lines far above minimum thickness are coloured green, lines one stage thinner are coloured yellow, and tubing approaching minimum thickness is coloured red for warning The chart is posted in the control house for ready reference of the operators, inspectors, and craftsmen on the unit

Increasing use is being made of 'Sentry Drilling' of lines This is the drilling of numerous small holes, appropriately spaced, into the wall of severe-duty tubing, the holes are drilled almost through the minimum allowable thickness of the tube in question, so that when corrosion has thinned the line to where it becomes unsafe—rather, undesirable for safe operation—there is a small blow-out through the drill-hole These blow-outs are mild, perfectly safe to operating personnel, and a very effective warning of otherwise unsuspected corrosion

Sentry drilling is to be regarded only as adjunctive to regular inspection methods

D. Purchase

Seamless carbon-steel tubing is purchased under several specifications, the designations of these are listed below in the order of decreasing quality

1 Association of American Steel Manufacturers, MSS no 100 This is of the highest grade, suitable for heater tubing Actually, it is extensively used for all tubes and oil-lines on hazardous refining units, up to 1,200° F It will usually be satisfactory to order hot rolled, 'average wall' tubing

2 American Society of Testing Materials A 106, Specifications for Seamless Steel Pipe This material is furnished with less rigid grading, but is quite suitable up to 750° F

3 A S T M A 53 Specifications for Seamless Steel Pipe These apply to material for service where ordinary lap-welded pipe could be used, say, to 350° F, but the seamless line is preferred

Alloy tubes of 4–6% chrome are ordered by A A S M, Manufacturers Standard Specification no 200, for heater tubes and all lines Several points deserve mention

(*a*) This material is air hardening, and care must be taken to receive annealed tubing which can be cold rolled and flared into the header boxes successfully A Brinell Hardness no of 170 maximum will ensure ease of rolling

(*b*) No objections are found in service to the less expensive 0 20% maximum carbon variety for heater tubes, the 0 15% maximum carbon is preferred for welded lines

(*c*) The 4–6% chrome-molybdenum variety is to be preferred where freedom from brittleness in the cold is desirable Brittleness can be temporarily inhibited in all types of this alloy by heating to 300° F for decoking by knocking, but the possibility of cold splits [10, 1934] returns when the metal cools again

The corrosion allowance will depend theoretically on the corrosion rate for the type alloy, the life desired, and a host of unknown factors which may come into play in the future

We recommend, in the absence of better information, the purchase of tubing about ¼ in thicker than the minimum practical thickness for the size and intended service, this ⅛ in in general serves as the usual corrosion allowance In the case of outside lines in the larger sizes, particularly when costly fabricated pieces are involved, a more generous corrosion allowance than ⅛ in will be economical

Corrosion allowance should be ample, because

1 Recovered tubing is always of value
2 Added thickness is a factor of safety against bursting
3 If the allowance is on the light side and unexpectedly corrosive stock is encountered, the whole corrosion allowance might be used up in a single battery run, before the fact could be discovered

HEAT EXCHANGERS

In most refinery distillation equipment a large number of various makes of shell and tube exchangers and condensers are installed In view of certain limitations, particularly costly tube replacements, shell and tube exchangers in several recent large installations were confined to oil and vapour service, none being installed to use water for cooling In the latter case submerged coils of thick tubing were used But in many cases the efficiency of these exchangers and condensers is such as to warrant their use, although costly replacement of tubes is experienced In one refinery alone approximately 130,000 tubes are in use Popular sizes are ⅝ in × 18 gauge, ¾ in × 16 gauge, and 1 in × 14 gauge, and lengths vary from 5½ to 20 ft, with 12 ft being the usual length

Various kinds of metals have been tried, but for most purposes brass (Red Brass and Admiralty) and steel are standard, other alloys are expensive and their performance does not justify their use, except in the face of oil-to-oil corrosive service

An idea of the replacements may be estimated by considering the 130,000 tubes mentioned above These tubes have an average life of 3 years, which means that 45,000 tubes will be the yearly replacement requirement in the refinery mentioned Not only is the expense of purchasing new tubes and labour for replacement an important item, but operating time on valuable units is lost due to the failure of tubes This is particularly true on an oil-to-oil exchanger where the cooling medium may materially contaminate the distillate A unit charging 10,000 to 15,000 bbl per day may come down prematurely while exchangers or condensers are unheaded, and tubes plugged or replaced, also considerable engineering and mechanical work have to be performed to stop leaky bundles Even when repairs are accomplished there is no knowing just how long before the unit must again come down for some other tube failure in the same or a different bundle This process of shutting down a unit, repairing bundle, and going back on the line is soon repeated unless great care is used in the proper selection of tubes

Several reasons for tube trouble are listed as follows

(*a*) Corrosion within the tubes (water or oil)
(*b*) Corrosion outside the tubes (oil or vapour)
(*c*) Mechanical failures (erosion, cracking, buckling, and pulling from tube sheet)

Corrosion within the Tubes (Water or Oil).

Corrosion from the water is prevalent in the Gulf Coast region where brackish water for cooling prevails A particular type of corrosion on brass tubes using brackish water is that known as dezincification, whereby plugs of copper are formed in a brass tube either by substitution of copper for zinc or by dissolving of the whole brass and redepositing, in place, the copper in the form of a plug This type of failure is well known in services other than refinery service, such as marine service This is particularly severe in a refinery because it increases with the temperature. Practically 90% of the Admiralty failures in condensers in the Gulf Coast region, where brackish water is used, are due to dezincification

Another important feature with respect to failure of condenser tubes is the plugging of the inside of the tube with a scale formed from solids borne in solution by the cooling water This deposit must be removed periodically before it completely plugs the tube A preferred means of removal is pumping through weak, hot hydrochloric acid treated with inhibitor to prevent corrosion of the metal Also, sandblasting is used with a short, tapered nozzle sufficiently small to be driven into the end of the tube If cleaning should be delayed too long it becomes necessary to drill out deposits in the tube with an auger attached to a long rod Tubes in oil-to-oil exchangers frequently have the inside nearly plugged with tarry matter or coke This may be cleaned by steaming, benzol washing, or as indicated above

Corrosion on Outside of Tubes.

This consists of two kinds, acid and sulphide The acids are usually formed during processing of oil and are the results of hydrolysis of certain salts originally in the crude—magnesium chloride being the principal offender Acid corrosion must be combated by neutralizing by the injection of some alkali in the oil stream—ammonia being frequently used It is of interest to note that corrosion by acid is particularly severe at the temperature at which condensation of vapour to liquid takes place, above this temperature, or below it, tubes are much less attacked

Sulphide corrosion results from action of H_2S on the metal Hydrogen sulphide is either originally present in the crude, or it is formed from sulphur-bearing oils during the cracking or distilling process The temperature at which tubes operate has an influence on the rate of corrosion from sulphide

Mechanical Failures.

These consist of erosion, radial cracks, and buckling Erosion is prevalent in those tubes adjacent to the vapour inlet of the exchanger and is due to the rush of vapours exerting a cutting action on the tubes To reduce this erosion some method of protection must be resorted to, such as installing a baffle on the tubes to act as a target for the impingement of the vapours as they enter the exchanger Transverse cracks are common in only one type of tube, viz the 18–8 alloy, and are characteristic of this metal The susceptibility of this metal to such cracking is sufficient to forbid extensive use of the alloy, although generally its properties are otherwise excellent Transverse cracking in 18–8 alloy is apparently not affected by the kind of oil or cooling medium, but is usually the result of temperature change Buckling is due to frequent change of temperature and to uneven temperature distribution Individual tubes which have become overheated expand more than the adjacent tubes, and buckle, thereby obtaining a permanent bow When temperatures are reduced the contraction naturally pulls the distorted tube from the tube sheet The latter has occurred only in a very few instances

Choice of Tubing

In general the following requirements are necessary for satisfactory exchanger or condenser tubes

1 Easily obtainable
2 Reasonable price
3 Resistant to brackish water corrosion
4. Resistant to sulphide corrosion
5 Easily installed in bundle

A large number of tubes of various analyses have been tested experimentally, and for one reason or another they have failed to replace steel and brass Steel is used commonly in sweet crude for exchanger service in oil to oil Brass is commonly used among the more sour crudes, particularly where acid is experienced which may not be completely neutralized Brass is also used in water-to-oil coolers and condensers In spite of the large amount of experimentation with various alloys none has been found to replace brass or steel, although there is great need for a more satisfactory metal It is difficult to state the life of a brass tube In some classes of service tubes are replaced as early as 6 months, in other classes of service they last as long as 5 years, for the entire refinery, 3 years would be a rough estimate of the life of a brass tube in the Gulf Coast region where water is used as a cooling medium. Many key bundles, however, require replacement after 12 to 18 months' service

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PRESSURE VESSELS FOR THE PETROLEUM INDUSTRY

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THIS article will consider the history of development, codes of good practice, materials of construction, problems of design, fabrication methods for combating corrosion of pressure vessels, as well as factors which are associated with the economical use and safety of their operation

The petroleum industry is one involving severe service requirements because of its hazardous nature and because of the demands for economical production of gasoline and other petroleum products

General History of Petroleum Vessels

The development of modern processes of oil refining has been accompanied by, and to some extent has been dependent upon, improvements in materials and methods of construction of equipment As long as the refining process consisted of the distillation of the light fractions of oil at comparatively low pressures and temperatures, small vessels of relatively light construction were adequate To-day, refinery vessels of large size and complicated designs must withstand a large range of operating conditions Operating temperatures may range for certain processes from atmospheric to 1,000° F, and for other processes from atmospheric to −50° F These temperature variations may and usually do occur rapidly during the period when vessels are put into or taken out of operation Operating pressures of several hundred pounds per square inch are common, and they may be as high as several thousand pounds per square inch

The history of the petroleum industry shows the use of nearly every type of vessel construction in existence Vessels for this service have been fabricated by riveting, hammer or forge-welding, hollow forging a large ingot, and autogenous welding For the most severe service in the petroleum industry, riveted and hammer-welded vessels are giving place to the autogenous welded and forged vessels, due largely to the great improvements made during the past few years in construction methods of the latter types and to the safety assured by the specifications and codes which have been produced to cover these construction methods No less than four large groups of users have by relatively recent codes and specifications covered the latter types of vessels

The limitations of the forged vessels are associated with the size of steel ingots which can be cast and with the size and flexibility of the forging equipment available for fabrication. The size of the autogenous welded vessel is limited only by transportation and erection facilities By far the larger number of current vessel inquiries specify autogenous welding because this method of fabrication lends itself to considerable variation in designs, and to the use of materials which are peculiarly suitable to the great variety of refining processes in use in the petroleum industry. Other determining factors in the selection of methods of construction are service reliability and cost Although the metallic arc has been known and used for a considerable time, the modern type of arc-welding is comparatively new. The oil industry was the first to recognize arc welding on a large scale in spite of the fact that such equipment is subjected to perhaps the most severe service of any equipment

The arc-welded pressure vessel for high temperatures and high pressures, and having strong ductile welds was first built for the petroleum industry in 1925 Since that time several fabricators have become proficient in this type of construction The relatively recent standardization of codes and specifications has safeguarded the construction of such vessels, so that the question of reliability has been established on the basis of inspection by the use of radiographs, periodical tests on welded plates, and proof tests on the finished vessels

Codes of Good Practice

The most recent specification or code for the construction of pressure vessels has been established by the American Petroleum Institute jointly with the American Society of Mechanical Engineers This specification or code considers the question of materials, design, and construction factors as well as the inspection and maintenance of equipment in service It is intended to apply to vessels constructed for petroleum liquids and gases There are five major divisions, which pertain to the following items

W Design and construction of Fusion-welded Vessels
R Design and construction of Riveted Vessels
F Design and construction of Seamless-forged Vessels [1]
I Inspection, Repair, and Allowable Working Pressure of Vessels in Service
S Material and other Specifications [1]

It is intended that these specifications be kept up to date by a relatively small working group comprising an equal number of users and fabricators of pressure vessels and assisted by sub-groups who are particularly interested in certain phases of the industry pertaining to pressure vessels In this manner, the petroleum-pressure vessel will clothe itself with the maximum of safety consistent with sound economic requirements for the service of the industry and will also make use of improvements in design and methods of fabrication which may become available from time to time

There are a few points which pertain to the code referred to which can be appropriately emphasized and which give the fundamental basis for its utility. The code is the result of the work of experienced fabricators and users of pressure vessels who have pooled their experience, which comprises tests on materials and designs as well as knowledge in various methods of construction and the hazards associated with operation The aim of the code is to state the requirements of vessels and outline methods of testing and inspection which will ensure that the requirements are met without going into intimate constructional details Knowledge gained from the testing of large full-size vessels is incorporated in the requirements for designs Materials, depending on the precautions taken in their production, are given quality factors consistent with the quality of such materials as are discovered from service as well as from fabrication experience The joint efficiencies which are allowed are made consistent with the care exercised in their production, and in this manner the tendency is developed to encourage the use of the highest quality joint as being the most economical The safety factors are based on the failure strength of the vessel as a whole, and not on the calculated cylinder strength which formerly was considerably greater than the strength of the vessel at some other location Allowable working stresses at elevated temperatures are based on long-time strength-values for steels at such temperatures In the periodic inspection requirements, allowance is made for the effects of corrosion and deterioration of equipment so that vessels are automatically retired from a particular service when the allowable pressures are below the requirements of the process The requirement as to the frequency of inspection is made dependent on the hazards of the service and on the deterioration rate of various types of equipment

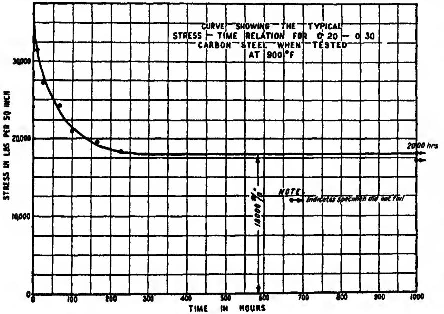

FIG 1

The following discussion will deal largely with the arc-welded pressure vessel because of the fact that the authors are particularly familiar with this phase of the subject, and because the older methods of fabrication have been described in engineering literature, and the fundamental qualities of these methods of construction have been understood, appreciated, and utilized over a great number of years

With particular reference to the codes on autogenous-welded vessels, the type of data which will explain the basis for specifications will be given in detail under the following headings

Materials of construction
Problems of design
Fabrication methods
Methods for combating corrosion

Materials of Construction

The load-carrying steels most appropriate for pressure vessel fabrication are those which can be satisfactorily rolled into large plates The manufacture of steel plates for pressure-vessel construction has been profoundly influenced by the adoption of electric arc-welding for fabrication This has involved mainly the production of larger ingots than had heretofore been produced in this quality, and it is now possible to secure plates up to 6 in in thickness of the correct analysis to give the physical properties required, with a satisfactory surface condition and good weldability So satisfactorily has this been accomplished that the vessel manufacturer is now assured of a reliable source of plate stock for all commercial requirements Much credit is due to the steel producers for the skill and enterprise they have put into this phase of vessel fabrication The load-carrying materials include carbon and minor alloy steels The carbon steels, are, in general, the least expensive Where light weight, relatively thin sections, or resistance to certain fluids or shock is required, the low alloy steels may be economically permissible because of their relatively improved physical properties or improved resistance to corrosion and deterioration The discussion of the production and specifications for suitable load-carrying steels is treated under a separate article

Highly corrosion-resistant steels are necessary under certain conditions because no suitable substitutes have been discovered These steels are expensive and are limited in economical application as load-carrying materials They need not be cast into large ingots because they are applied in relatively thin sections Where the operating conditions permit of a thin wall, the entire vessel may be made of these more costly materials The majority of petroleum vessels subjected to corrosion, however, require considerable thickness, and, therefore, make it more economical to use carbon or low-alloy steels for load-carrying purposes with the addition of a lining of some corrosion-resistant steel or other material which may be applied as a protection against corrosion.

To answer the question pertaining to the use of steel at various temperatures, a careful study of the test results available is required It is well known that at elevated temperatures, steel may have an ultimate strength considerably below its strength at ordinary temperatures, and that its long-time strength is considerably below its short-time strength This relation between long- and short-time strength is clearly illustrated by Fig 1, which shows test data for a 0 20–0·30% plain carbon steel at 900° F The method of testing to produce the above type of curve is to take several specimens of a particular steel and at a definite temperature to load each to a different stress until failure occurs The time for failure and the test stress for each specimen is then plotted and the resulting curve drawn The value of stress, obtained from that portion of the curve which is parallel to the time axis, represents the stress that the steel can carry for an indefinitely long period at the temperature of test This method of testing was first outlined by Mr H J. French [1, 1925], when on the Staff of the Bureau of Standards Fig 1 indicates that at 900° F. the short-time ultimate strength is about 35,000 lb per sq in , while the long-time ultimate strength is 18,000 lb per sq in

Fig 2 shows the test data which were obtained in a different manner and represents the long- and short-time limit of proportionality for this steel at 900° F This method of testing was first used by one of the authors in 1928 Each stress-strain curve represents a different rate of loading the test specimens The value of the limit of proportionality for each rate of loading is plotted along the stress axis, and the time during which each increment of load was allowed to exert itself is plotted along the time axis It will be noted that the proportional limit is higher for the more rapid rates of loading and approaches a constant value as the time interval between loadings increases The constant stress which the curve approaches has been called the long-time limit of proportionality By this means the long-time proportional limit at 900° F can be obtained on a single specimen if the interval between load-increment applications is greater than 9 hours From Fig 2 it may be seen that the long-time value is 11,700 lb per sq in , and the short-time value 18,000 lb per sq in

Another method of obtaining test results for elevated temperature operations is known as creep testing A great number of workers have used this method, and since it has been very ably and comprehensively covered in a book entitled *Creep of Metals* by Tapsell (Oxford University Press, London, 1931), a detailed description will not be attempted here The reliability of the results obtained by this method depends largely on the use of very sensitive and accurate measuring instruments and temperature-control devices, and on the elimination of oxidation of the test samples during the period of testing

A committee of the American Society for Testing Materials has been working on the testing of metals at elevated temperatures for a considerable period of time Other groups in Europe have also done much work along this line, so that a very large amount of test data is available to help the designing engineer in selecting appropriate working stresses for various steels at elevated temperatures

The curve shown in Fig 3 has been adopted by the joint API-ASME Code Committee as a practical and safe interpretation of the test data available It may be said in general that the values represented are based on a large experience with carbon steels and a lesser experience with normal load-carrying alloy steels Since it is a characteristic of most alloy steels to maintain higher relative strengths at elevated temperatures, the application of the curve in Fig. 3 to load-carrying alloy steels will compensate for this lesser experience until such time test data become available

The long-time ultimate strength and the long-time limit of proportionality would seem to be most useful criteria in selecting working values for elevated-temperature operations Such values are obtainable on equipment in which no extraordinary precautions are necessary, and the results are reproducible if reasonable laboratory precautions are used in the operation of equipment

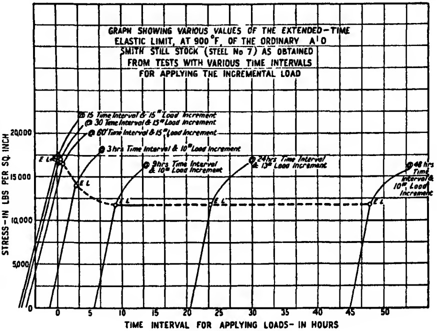

Fig 2

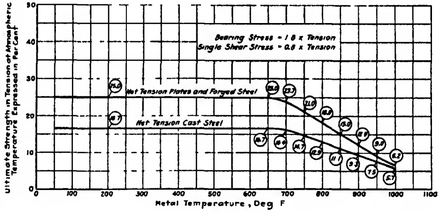

Fig 3

The use of steel for low-temperature refining processes has brought about the practice of low-temperature testing The question of strength at low temperature is not as crucial as it is at elevated temperatures because it is well known that this physical property is not impaired as the temperature is decreased to low values Shock resistance and ductility, however, may be greatly reduced in steels operating at very low temperatures In some steels the rate of decrease of these properties is much less than in others For this reason, testing methods have been devised and utilized to select appropriate steels for low-temperature operation when shock resistance and ductility are required The impact test has been used most particularly to eliminate undesirable steels from low-temperature service Fig 4 shows typical impact values for 2½% nickel-steel plates and 0 20–0 30% carbon-steel plates at various temperatures [3, 1934] The carbon steel shows a very much greater decrease in value at low temperatures than does the nickel steel While the notched-bar impact test may not represent service conditions, it is useful in selecting types of steel that have inherent superior shock-resisting qualities When once this information is secured the type of steel can then be specified largely on the basis of chemical composition and heat treatment Impact values have not been used in steel-mill specifications because the resultant cost would have been increased to a degree which is not warranted

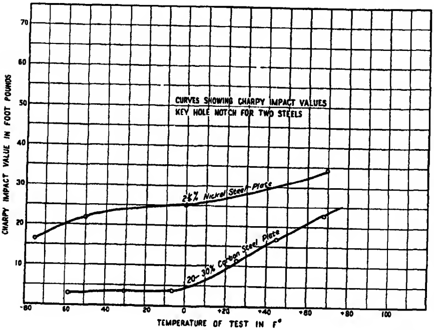

Fig 4

Problems of Design

Test results on full-size vessels have greatly helped the engineer on his design of pressure vessels Figs 5 and 6 are self-explanatory and bring out clearly the very considerable value of such tests Burst-test data on vessels, as published in the literature by a considerable number of engineers, have confirmed the advantages to be obtained by correctly shaping the vessels and adequately reinforcing the openings Fig 5 shows the relative strength of the cylinder wall, an unreinforced opening, and a dished head Fig 6 shows similar information taken when the opening was properly reinforced and when an elliptical head of proper proportions was used The safe operation of pressure vessels is more nearly assured if attention is paid to designs which bring all parts of the vessel to a balanced load-carrying value Adequate attention to such details may make vessels from 60 to 100% stronger with little or no additional expense The authors would like to cite one series of repeated pressure tests made by the Babcock & Wilcox Company under the supervision of Prof H F Moore [4, 1931], which confirms the importance of the adequate reinforcing of even small openings if full advantage is to be taken of available safety measures These tests show conclusively that lack of reinforcement may very materially reduce the strength of the unreinforced small opening This method of testing, as used by Prof Moore, affords a means for determining weaknesses in designs of pressure vessels It is not intended to convey by this reference that the petroleum vessel in general presents a problem in which repeated change of pressure enters as a major factor

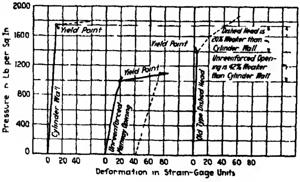

Fig 5

Vessels used at elevated temperatures, even though correctly designed, require care in operation to prevent too rapid temperature changes especially at openings This source of danger resulting from high differential stress is too little appreciated A number of fractures have occurred at points where pipes introduce cold or hot liquids into vessels at the start or finish of operations If a temperature differential of several hundred degrees occurs in the vicinity of an opening or other locations, a stress exceeding the strength of the steel can be set up

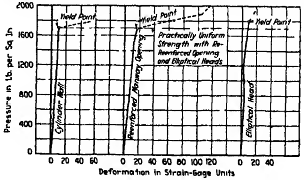

Fig 6

The oil-refining industry is confronted with occasional conditions during operation tending to cause high pressures which are, no doubt, well understood and guarded against by the careful operator For instance, if by mischance a slug of water should be introduced into an operating vessel, a very rapid increase of pressure may occur with which

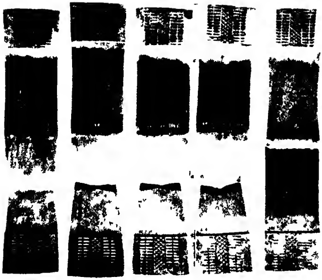

FIG. 7 Tensile test on specimen cut across a weld joining plates 6 in. thick. The area through the weld was reduced various amounts by drilling holes. Each hole is 0.2 in. in diameter.

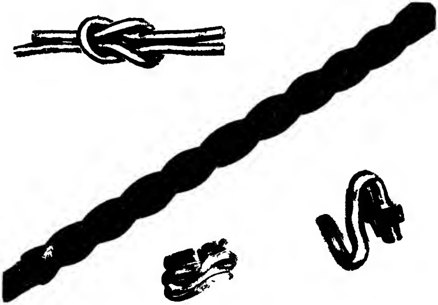

FIG. 9 Specimens cut entirely from deposited weld metal showing the typical ductility of the Smith weld

safety valves may be unable to cope, with the result that the vessel is very materially overstressed. Almost complete elimination of air is necessary when bringing cracking equipment into operation, otherwise as the temperature increases a condition may be reached which will result in an internal explosion It may seem unnecessary to draw attention to these conditions which are so generally known and so easily guarded against by the industry at large It is done simply to point out that correct design does not relieve the operator from maintaining a vigilant campaign for safety

Fabrication Methods

The typical refinery vessel consists essentially of a cylinder with heads It also has various openings ranging in size from small pipe-connexions to manholes 24 in or more in diameter

The cylindrical portion of the vessel may be an assembly of a number of shorter cylinders or it may be made up of longitudinal plates which are pressed to form parts of the cylinder Short cylinders or rings may be made by expanding a pierced ingot by forging or rolling, but the method most commonly used is that of rolling a plate into a cylinder and welding the longitudinal seam The heads are either spun or pressed from plates, and such parts as nozzles, manholes, &c , may be made of plates, forgings, or castings Before fabrication starts, the materials are given a thorough inspection to ensure that they meet the specifications, after which they are cut to size by torch or machine The plates, in so far as is practicable, are scarfed in the flat to produce the welding groove, and are then formed to shape Care is taken not to work the material too severely while it is cold, and therefore it is considered necessary to heat the heavier plates prior to forming

The equipment necessary for the building of thick-wall pressure vessels must be large and powerful in order to fabricate them in the most satisfactory manner Large furnaces equipped with accurate temperature control are necessary to heat the plates uniformly so that no damage occurs to the material and so that good commercial tolerances in fabrication may be maintained To form plates into cylinders or heads, the work should be done in as few operations as possible to avoid embrittling the plate surfaces Rolls or presses capable of forming plates up to and above 6 in in thickness are, therefore, necessarily massive and powerful

After the parts are prepared and formed, they are assembled and tack-welded to hold them in place for the welding operation The butt type of joint is used for the longitudinal and circular seams on the shell sections and also for the longitudinal seams on manhole and nozzle necks Fillet welds are used around reinforcing pads and to some extent in joining detail parts and fittings to the vessel proper For butt joints in heavy material the U-groove, so called because the cross-section of the groove is the shape of the letter U, is used, whereas a V-shaped groove is often used on thin sections The material may be scarfed or grooved from one side only or from both sides When the welding is to be done from one side only, a backing-up strip is used to permit full penetration When both sides of the seams are accessible some welding is generally done from the reverse side On Code vessels, the unfused lip at the bottom of the original groove is removed before any welding is done on the reverse side, thus assuring complete penetration and fusion at all points

Proper preparation facilitates the welding operation, but the mechanical properties of the weld metal and also of the joint produced depend upon the equipment used, upon the training and skill of the personnel, and, to the greatest degree, upon the type of electrode used

The equipment available for welding has been greatly improved during the last few years Welding machines for either alternating or direct current are available in any size required, and first class welding is being done with either A number of welding heads for feeding the electrode are on the market and the equipment required to move either the work or the arc is readily obtained or built

Some skilled operators and experienced supervisors may be available from time to time, but it is generally necessary for the individual manufacturer to train men in the use of his particular process

A large variety of electrodes ranging from plain bare wire to a number of types of heavily coated wire are on the market Where reliability and high mechanical properties are required of the weld metal, the heavily coated electrodes are necessary The increased use of welding during the last ten years is due primarily to the intensive development work on electrodes Even with modern equipment and the skill of the present day operator, it is not possible to produce commercially the quality of welds required for the construction of Code vessels with the types of electrodes in general use ten years ago

So far as serviceability is concerned, the quality of the weld is determined by its mechanical properties and its corrosion resistance In Code vessels the metal in the weld and at the junction of the weld and the plate have strength properties at least the equivalent of the plate material used This is of great importance because if either the weld metal or the junction were weaker than the plate, proper allowance would have to be made for this inferior strength and the full working strength of the plate would not be utilized In addition to the necessary strength, the weld metal has ductility approximately equal to that of the plate stock which insures against local failure if the structure is accidentally overstressed Ductile welds are not damaged by such occasional overstressing, since they are able to adjust themselves, but brittle welds such as may result from bare electrodes are susceptible to failure under such circumstances

For the purpose of comparison, average mechanical properties obtained on several specimens of bare wire-welds and of welds made with heavily coated electrodes are given in Table I These welds were made in 1-in. plates of 0 20 carbon steel by skilled operators using modern equipment

TABLE I

	Tensile test			Bend test % elong
	Y P	*Ult*	*% elong*	
Bare wire—all weld	42,200	43,300	2 5	*
Bare wire—across weld	25,900	29,500	1 5	5 2 failure
Covered electrode—all weld	47,100	56,900	34 0	*
Covered electrode—across weld	32,000	52,000	48 1	40 5 no failure

* Bend tests were not made

The tensile test specimens taken across the welds made with the covered electrodes failed in the plate material and the values given are, therefore, the properties of the plate, while for the bare-wire weld specimens the values give the properties of the weld It will be noted that the yield point and the ultimate strength of the welds made with the covered electrodes are substantially higher than those of the plate material The average elongation of the tensile specimens is in the range that may be expected of mild steel The bend tests were not carried to failure and the average value given does not represent the possible elongation Similar specimens have been bent flat on themselves without failure The mechanical properties of the bare-wire welds are all low compared to the corresponding properties of the plate material and the elongation values are particularly low The bend tests for these specimens were carried to failure Bare-wire welds in thin materials show relatively much higher physical properties than those given in Table I In such cases ultimate strengths of 50,000 to 60,000 lb per sq in and elongation from 6 to 12% in 2 in are obtainable under favourable conditions

With covered electrodes, it is possible to control the strength of weld produced, and this strength is independent of the thickness of the plate welded When strength is the primary requirement, the electrodes are generally designed to give an ultimate strength about 10% higher than the plate The results of the proper design of weld rods are illustrated in Figs 7 to 9 Fig 7 shows a series of five specimens taken across a weld in a plate 6 in thick The cross-section was reduced by drilling one, three, five, and seven holes, 0 2 in in diameter, through the weld Even with five holes, the specimen failed in the plate material Fig 8 shows the test results obtained in specimens of weld and of plate in which the specimens were taken parallel to the weld Fig 9 demonstrates the ductility of metal deposited by properly coated electrodes

Resistance to corrosion by the weld metal comparable to that of the steel is necessary if the welded equipment is subjected to corrosive conditions If the weld corrodes more rapidly than the plate material, its thickness and hence its strength may eventually become less than that of the stock even though the mechanical properties of the weld metal are equal to those of the plate Corrosion tests of specimens of 0 20–0 30 carbon steel welded with bare wire and with heavily covered electrodes have shown that the bare-wire weld corrodes very rapidly compared to the plate material, whereas the weld made with correctly covered wire corroded less rapidly than the plate material, and hence stands out in relief Fig 10 shows the typical appearance of some of these specimens after test Welds made with covered electrodes in vessels that have been in service for a number of years have consistently shown a corrosion resistance equal to or greater than that of the plate material Some such welds which were originally ground flush now stand out in relief

Some explanation of the difference in physical and chemical behaviour of weld metal deposited with bare wire and with properly covered electrodes is given by a metallurgical examination

Fig 11 is a photograph, natural size, of a cross-section of weld made with a covered electrode in 1-in plate. This section was etched lightly to bring out the layers of weld metal and the zone of refined plate stock adjacent to the weld A more intimate view of the weld metal is shown in Fig 12 The metal is seen to be clean and sound, and of a fine and uniform grain structure

A better conception of the structure of the weld metal is obtained from Figs 13 and 14, which show it at magnification of 100 × and 1,000 × respectively The former shows that the metal is exceptionally fine grained The small dark areas are typical of the low-carbon content of the metal. This structure is shown to better advantage in Fig 14, which brings out more clearly the individual grains and the carbide areas The small round dots in this picture are tiny inclusions of silica which act as a beneficial dispersion to keep the grain structure fine, even though portions of deposit are heated nearly to the fusion temperature by the welding operations

A point of great importance is the manner in which the weld deposit fuses to the plate stock An example of such a junction is shown in Fig 15 The transition from weld to plate stock is seen to be so gradual that the line of demarcation is scarcely perceptible at a magnification of 100 ×

Some photographs of the structure of bare-wire welds are also reproduced to bring out the more important weld metal defects which have been overcome by the modern methods of welding Fig 16 shows a typical section of a bare-wire weld in 1-in plate stock This section was polished and etched lightly to bring out the structure of weld metal as deposited by this rod To the naked eye (magnifications of 1 ×) this metal looks fairly sound, though the macrograph, Fig 17, at a magnification of 9 × shows it is porous It is seen that a major portion of the deposit is in a coarse condition, while it will be recalled that the weld made with the covered electrode shown in Fig 13 is fine grained Fig 18 shows that certain portions of this weld deposit are fine grained, however, a magnification of 1,000 × as shown in Fig 19 brings out two serious defects typical of bare-wire weld metal The small round grey inclusions have been identified as iron oxide, FeO This dispersion of iron oxide is similar in appearance to the dispersion of silica in the covered electrode weld metal, but the iron oxide is harmful instead of beneficial Weld metal which contains this iron oxide type of inclusion alone, is hot short and it is also brittle when cold if contaminated by such large amounts as are found in bare-wire welds The dark patches in Fig 19 have been identified as a nitride constituent, which occurs when large amounts of nitrogen are present in the metal It is well known that nitrogen lowers the ductility of steel, and the brittleness of bare-wire weld metal is undoubtedly due in part to the nitrogen it contains This nitrogen may also produce certain harmful ageing effects, but when the metal is initially as brittle as bare-wire weld metal, this ageing effect becomes of little significance in a practical way

The junction between weld metal and plate stock in the bare-wire weld is shown in Fig 20 The dark band is a carbide segregation The microscopic examination shows clearly that the bare-wire weld metal contains large amounts of the harmful constituents, oxygen and nitrogen This is readily accounted for by the lack of protection afforded the metal as it passes through the air from the electrode to the weld At the high temperature at which this transfer takes place, the iron readily dissolves both of these gases in large amounts Some gas is given off again during the solidification of the metal in the deposit, but sufficient remains behind to produce the structures noted above [2, 1935].

After the properties of weld metal deposited by a definite process have been established as being satisfactory, by a sufficient number of tests of welds made in materials similar in composition and thickness to that to be used in the vessel, it is only necessary to show by inspection methods that the welds in the vessel are sound. This is generally accomplished by the use of pressure tests, visual inspection, and radiographic examination. The amount of

FIG. 12 Same as Fig 11 at centre of the weld × 9

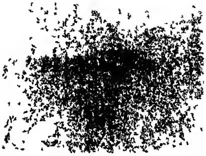

FIG. 13 Same as Fig. 11 showing refined weld metal × 100

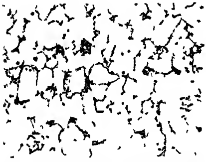

FIG. 14 Same as Fig. 11 showing details of the structure The small dark spots are the silica dispersion × 1,000

FIG. 15 Same as Fig 11 showing junction between weld and plate stock × 100

FIG. 17 Same as Fig 16 at centre of the weld × 9

FIG. 18 Same as Fig 16 showing refined weld metal × 100

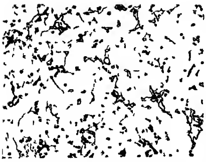

FIG. 19 Same as Fig 16 showing details of the structure The dark spots are iron oxide The dark patches are a nitride constituent × 1,000

FIG. 20 Same as Fig 16, showing junction between weld and plate stock × 100

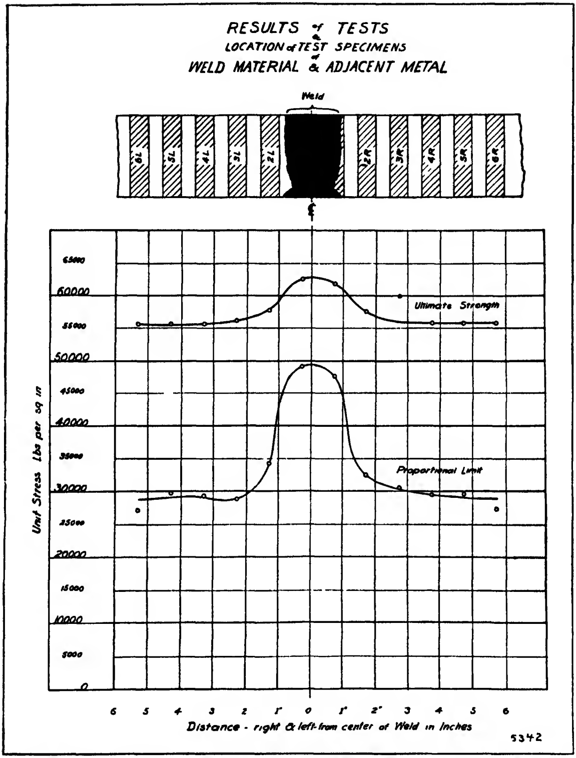

FIG 8 Test results on specimen from welded plates 2½ in thick Test specimens were cut at 1-in intervals parallel to the weld and pulled in the same direction

radiographing required and the standards of soundness for welds are fixed by codes such as the joint A P I -A S M E Code This Code also provides for test plates, to be welded at the time the vessel is fabricated, from which the mechanical properties of the weld can be determined For some types of service the Code does not require radiographing, but lower joint efficiencies are assumed for such vessels

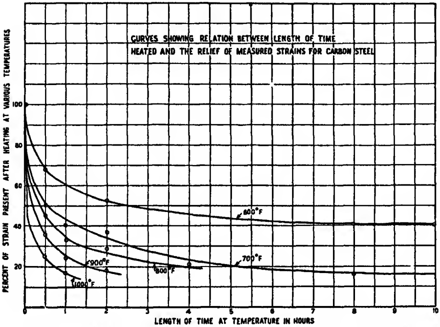

Fig 21 Curves showing relation between length of time heated and the relief of measured strains for carbon steel

After the vessel is fabricated, the next step is stress-relieving unless the vessel is made of thin material Vessels of certain types and wall thickness may be stress-relieved or not, but the A P I -A S M E Code puts a premium on stress-relieving by permitting higher joint efficiencies for the vessels that are stress-relieved

The need for stress relief and the basis for the procedure in use is shown by Fig 21 which reproduces unpublished data obtained in 1926 It shows the percentage of the initial stress remaining in the steel after heating to various temperatures for different periods of time The maximum initial stress could not have been above the yield point at room temperature because at such stresses relief would occur by yielding These tests have been taken to indicate that a temperature of between 1,100° F -1,200° F, is sufficient to reduce the stresses to a negligible amount if the vessel is held at this temperature 1 hr per in of main-wall thickness Other tests made to determine the ability of the vessels to maintain their shape have shown that only relatively thin or relatively long vessels are likely to distort at the stress-relieving temperatures There is no need of stress-relieving very thin vessels, but if stress-relief is desired, it should be performed at lower temperatures or special means of supporting the vessel should be used

In the inspection of the finished vessels, measurements of roundness and straightness are taken The Code has fixed reasonable commercial tolerances on the shape It is recognized that lack of straightness or roundness may introduce stresses during service of considerable magnitude especially in thick-walled vessels

The final step of the inspection is a proof test During this test, all welded seams are hammered while the vessel is under a pressure which may be two to three times its working pressure

The properties of weld metal previously discussed pertained to 0 20-0 30 carbon steel Equally satisfactory results are obtainable with many of the low-alloy steels, with various grades of stainless steel and with some other alloys especially suitable for corrosion resistance Mechanical properties characteristic of a number of these materials and suitable welds are given in Table II

Although the ductility of high strength welds is not as great as the ductility of welds in 0 20-0 30% carbon steel, this reduction of ductility usually accompanies an increase of strength A similar relationship is found for steels of various strengths The ductility of a properly made weld is of the same order as that of the corresponding plate material

Each of the alloy steels presents its own welding problem, but with proper care and technique all the steels commercially available and suitable for pressure-vessel service can be satisfactorily welded

Table II

Showing Typical Properties in Plate and Weld Metal for Various Tests

	Steel Properties			*Weld Properties*		
Kind of steel	*Yield-point lb per sq in*	*Ultimate strength lb per sq in*	*Elong % in 2 in*	*Yield-point lb per sq in*	*Ultimate strength lb per sq in*	*Elong % in 2 in*
Carbon steel C Max 0 20%	25,000-35,000	45,000-55,000	40-50	40,000-50,000	50,000-60,000	35-45
C 0 20-0 30%	30,000-40,000	55,000-65,000	30-40	45,000-55,000	60,000-70,000	25-35
C 0 35-0 45%	40,000-55,000	70,000-85,000	20-30	50,000-65,000	70,000-85,000	20-30
Manganese steel Mn 1 0-1 5%	40,000-60,000	60,000-90,000	25-35	50,000-75,000	65,000-95,000	15-30
Nickel steel Ni 1 0-2 0%	40,000-50,000	60,000-70,000	40-50	45,000-55,000	60,000-75,000	25-35
Ni 2 0-3 0%	45,000-60,000	70,000-80,000	30-40	50,000-65,000	70,000-85,000	20-30
Ni 3 0-3 8%	50,000-65,000	80,000-100,000	25-35	65,000-80,000	85,000-100,000	15-25
Chrome-vanadium steel Cr 0 80-1 10%	55,000-65,000	85,000-95,000	25-35	65,000-80,000	85,000-100,000	15-25
Chrome steel Cr 16-18%	40,000-55,000	85,000-95,000	20-40	55,000-65,000	75,000-90,000	15-25
Chrome nickel steel Cr 17-20% Ni 7 10%	30,000-45,000	80,000-95,000	45-65	35,000-50,000	70,000-90,000	20-45

Fig. 10 (*a*) Weld of heavily coated weld rod
Fig. 10 (*b*) Weld of bare wire weld rod

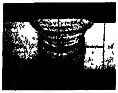

Fig. 11 Cross-section through weld made with covered electrode Lightly etched 1

Fig. 16 Cross section through weld made with bare wire electrode Lightly etched 1

Fig. 22 Alloy buttons before and after corrosion test

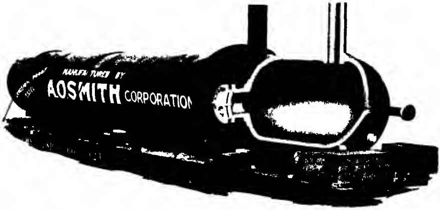

Fig. 23 Cut away view of Smithwelded-Smithlined still for Texas Co., Port Arthur, Texas Inside diam 5 ft wall thickness 3 in plus $\frac{7}{64}$ in alloy lining, overall length 41 ft, weight 96,300 lb

In the welding of corrosion-resistant alloy steels the resistance to corrosion is more important and often presents a more difficult problem than that of obtaining suitable mechanical properties However, with a controlled welding procedure and, in some cases, suitable heat treatment of the finished product, these difficulties have been overcome for the wrought alloys most suitable for refinery service

Methods of Combating Corrosion

Corrosion has been a source of great concern to the oil industry and particularly to refiners operating high-pressure equipment Experiences resulting in economic loss, personal injury, and loss of life have proved the seriousness of deterioration on such high-pressure equipment The consideration of ways for controlling this deterioration is the duty, not alone of the refiner, but also of the equipment manufacturer The effects of corrosion, various methods of controlling these effects, and means for eliminating corrosion will be discussed

Corrosion in equipment is the source of greatest hazard in that it reduces the wall-thickness of vessels and tubes, it attacks the surfaces unevenly, and, in general, it is the factor which is most active in rendering equipment unsafe for operation The danger to personnel through leaks, fires, and explosions would be greatly reduced if corrosion were absent

Costs of replacement and maintenance of equipment are appreciably decreased by a proper control of corrosion Property damage resulting from corrosion includes destruction of surrounding property by explosions and fires as well as the destruction of the defective equipment Expenditures for inspection are appreciably decreased if adequate corrosion protective measures are taken

The cost of refining is increased through the effects of corrosion Corrosion reduces the effective thickness of a vessel, and in consequence the operating pressure and/or temperature must be reduced in order to maintain adequate safety There is an optimum pressure and temperature for economical operation which is dependent on the charging stock and on the product desired A reduction from these optimum operating conditions decreases the throughput of oil Decreased conversion yield may also result from this lowering of the pressure or temperature Thus, the flexibility of the equipment for various operations (the adaptability of equipment for use with various types of charging stock and for the production of various products) may be greatly limited if the optimum operating conditions cannot be maintained The everchanging competitive market necessitates this flexibility of operation Shutdowns for inspection, repairs, or replacements during rush seasons are reflected in the burden costs and also entail loss of production A lowering of morale following leaks, fires, and explosions results in personnel inefficiency.

The method for compensating for corrosion is to reduce the allowable working pressure and/or temperature each time inspection shows it to be necessary Even though some means of protection against corrosion is used, periodic inspection is necessary to determine the effectiveness of this protection and to decide upon the safe operating conditions should any part of the equipment be reduced in thickness

A number of methods for combating corrosion have been used with varying degrees of success Among these are the removal or neutralization of the corrosive ingredients in the charging stock, the application of temporary protective coatings to the inner surfaces of vessels, and the use of permanent corrosion-resistant materials in the construction of vessels or liners.

The removal of corrosive ingredients by chemical reaction is very difficult to apply and prohibitive in cost Neutralizing agents applied directly to the charging stock have had a limited application because of economic and technical objections

The practice of installing vessels with excess initial wall thickness to compensate for corrosion is often used This compensation may be adequate when refining relatively non-corrosive oils or medium-corrosive oils in conjunction with temporary protection such as ganister linings This added wall-thickness is beneficial in conjunction with temporary linings since corrosion may occur at local areas due to failure of the temporary linings

Ganister liners have been extensively used in recent years Such liners are composed of a mixture of inert aggregates with a cement binder and are applied in thicknesses of 1 in or more to the inside of a vessel on a reinforcing grid They are installed at the refinery and can be renewed from time to time when necessary

Thin coatings of a few thousandths inches in thickness usually fail because of porosity and inability to resist mechanical abuse This accounts for the fact that paints and platings have given less satisfaction than have the thicker coatings Relatively thick deposits of sprayed aluminum have had a fair life where the surfaces were not subject to mechanical abuse Such metal-sprayed coatings can be applied in the refinery whenever replacement is necessary

An inspection facility for use in all vessels built without permanent liners consists of non-corrosive alloy buttons as shown in Fig 22, which are fastened to the inner surface of the vessel at convenient locations As corrosion progresses, the buttons stand out in relief, thus enabling the inspector, with the aid of templates, straightedge, and scale to determine cheaply and accurately the corrosion loss and any distortion of the vessel The drilling of holes to determine the extent of corrosion produces inspection scars which introduce weaknesses in the vessel The use of alloy buttons eliminates the necessity for drilling such holes in vessel walls to determine wall-thickness

Vessels fabricated entirely of corrosion-resistant alloys are generally too expensive for use with high temperatures and pressures because of the amount of costly material required Where light weight, or relatively thin sections are sufficient, the corrosion-resistant steels may be economically permissible

The majority of oil-cracking vessels require considerable thickness, and thus make it more economical to use carbon steel for load-carrying purposes and a permanent alloy stainless-steel liner of appreciable thickness as a protection against corrosion A construction which has been in satisfactory use for several years employs thin sheets of corrosion-resistant alloy electrically welded at frequent intervals to the interior of the carbon-steel vessel in such a manner as to make the lining an integral part of the vessel wall (Fig 23) Such a liner may be applied to any desired portion or to the entire inside surface of the vessel The high chromium and the high chromium-nickel steels which have been used remain, for all practical purposes, unattacked under service conditions It is preferable to use alloy steels that are not subject to inter-granular corrosion since this may in time limit the protection Alloy welds used in joining the liner sections are readily made equal in physical- and corrosion-resistant properties to the alloy sheet Liners that are welded at close intervals have demonstrated their permanency of attachment over a wide range of operating conditions

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NOTE

[1] These divisions are not as yet completed in the 1934 edition of the Code

SECTION 35

CORROSION

THE PRINCIPLES OF METALLIC CORROSION

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PRACTICAL cases of metallic corrosion are best studied in the light of the general principles involved, which have been considerably clarified within recent years. In discovering causes and attempting prevention of particular cases of corrosion, it is no longer necessary to proceed empirically, and much time and labour can often be saved by a preliminary survey of existing facts and theory. The purpose of this article is to present a critical summary of the present-day knowledge of the mechanism of corrosion and protection. For reasons of space, little work prior to 1920 is discussed, and much of the more recent work receives scanty treatment. Fuller information should be sought in the books by Evans [23, 1926, 24, 1937] and Speller [67, 1926] on general corrosion, Hedges [42, 1932] on protective films, Palmaer [56, 1929, 1931] on acid corrosion, and Glasstone [40, 1930] on electrochemistry, and in the bibliography compiled by Vernon [73, 1928], as well as in the many original papers cited.

Metallic corrosion may be comprehensively defined so as to include all processes by which metals pass from the elementary to the combined state. There are two main classes of such processes, viz. attack of metals by (1) gases, (2) aqueous media. It will be convenient to consider these separately, though it should be borne in mind that no hard-and-fast distinction can always be made, as for instance in the case of so-called atmospheric corrosion, which is treated in a separate section.

Attack of Metals by Gases

When a freshly prepared metallic surface is exposed to air or oxygen, a surface film of oxide at once commences to build up, at a speed determined partly by the actual rate of chemical reaction of oxygen with the metal and partly by the degree of porosity of the oxide-film to oxygen. Pilling and Bedworth [61, 1923], who studied high-temperature oxidation, pointed out that if the volume of a given amount of oxide is less than that of the metal from which it is formed, the film will be discontinuous and highly porous, and will scarcely hinder further attack, whereas if the volume of the oxide exceeds that of the metal from which it is formed a dense laterally *compressed* film will be produced which will greatly hinder access of oxygen to the metal, and become an important factor limiting the rate of attack. The ratios oxide volume/metal volume for a number of common metals are given in Table I.

TABLE I

Ratio Oxide Volume/Metal Volume

Na	Ca	Mg	Al	Pb	Sn	Cd	Zn	Ni	Cu	Fe	Mn	Co	Cr
0·32	0·78	0·84	1·28	1·31	1·33	1·32	1·59	1·68	1·70	2·06	2·07	2·10	3·92

In support of the theory, Pilling and Bedworth showed that the rates of attack of calcium and magnesium by oxygen are constant with time, indicating that the oxide-film is very porous and that the net rate of attack is determined solely by that of the chemical reaction, but that copper and nickel are attacked at a diminishing speed, the amount of attack being proportional to the *square* of the time, a fact simply explained by the ordinary laws of diffusion if it be assumed that the rate of diffusion of oxygen through the ever-thickening compact film is the limiting factor. The theory was further confirmed by Finch and Quarrell [34, 1934], who showed experimentally by electron diffraction methods that the oxide-film initially formed on zinc is actually in a state of lateral compression.

At the ordinary temperature, oxide-films whose volume exceeds the corresponding metal volume (e.g. those on Cu, Fe, Cr) build up rapidly for a few seconds or minutes, but soon become nearly impervious to oxygen and cease to thicken at sensible speed before the film has reached visible thickness. Nevertheless, such films can be detected by the gravimetric method of Vernon [75, 1926], and by the optical method due to Freundlich, Patscheke, and Zocher [37, 1927] and developed by Tronstad [71, 1929, 72, 1932], which is based on the principles of the reflection of polarized light worked out by Drude [18, 1890]. Furthermore, the films are rendered visible if removed from the brightly reflecting metallic basis; Evans [25, 1927] achieved this in the case of iron by dissolving away the underlying metal with iodine, while Evans and Stockdale [33, 1929] removed films from copper and nickel by anodic treatment.

At somewhat higher temperatures, studied by Evans [22, 1925], Dunn [19, 1926, 20, 1931], and Wilkins and Rideal [82, 1930] thicker films are formed. These give rise to interference tints whose colour depends on the thickness and refractive index of the film; the 'temper-colours' of iron and steel are a familiar example of such tints, which may also be readily obtained on copper and nickel. At still higher temperatures, serious cracking of the film often leads to the formation of comparatively thick oxide scale, and other factors besides pure oxygen diffusion may become important. Pfeil [58, 1929] showed that in the case of iron, diffusion of *metal* upwards through the scale is at least as important a factor as diffusion of oxygen down, in determining the progress of attack. Wagner [80, 1933] put forward evidence that such oxygen and metal movement is really *ionic migration* in a galvanic cell. The outside of the oxide-film is an inert basis for the cathodic ionization of oxygen, the metal surface is the anode, while the oxide-film, which conducts electricity both electronically and ionically, provides both 'metallic' connexion and electrolyte for the cell. This theory gives equations for the rate of film-growth of the same form as the Pilling and Bedworth equations, but the electrical specific resistance of the film appears as an important factor.

The attack of metals by halogens depends on similar considerations. The Pilling and Bedworth principle was extended to these cases by Fischbeck [35, 1933], who pointed out that sodium can be kept almost unchanged in bromine for a year, the ratio bromide volume/metal volume being 1·36. Again, tinplate scrap is detinned commercially by dry chlorine; at the temperature used, the liquid stannic chloride imposes no hindrance to the attack of the tin, but when this has been removed, a nearly non-porous solid film of ferric chloride forms on the iron and prevents more than superficial attack

Many kinds of attack are met with due to mixtures of gases, particularly when moist Discussion of some of the more important cases will be found under the heading 'Atmospheric Corrosion'

Attack of Metals by Aqueous Media

1. Breakdown of the Oxide-film.

Since a metal surface which has been exposed to air is covered with a thin film of oxide, the first effects of immersion of the metal in an aqueous solution concern the oxide-film This film is practically impermeable to oxygen molecules, and if a chance crack or hole appears in it and allows the passage of oxygen, the further oxide formed heals the pore and prevents further attack But the film is usually easily penetrated by ions, and if these can react with the metal below to produce a soluble salt, undermining of the film may occur and further metal be exposed to attack Such a condition occurs when, for example, iron is exposed to sodium chloride solution Wherever there is a pore in the film, a minute cell of the type

CATHODE		ANODE
Oxide-film	NaCl solution	Iron

is set up (Fig 1), the oxide-film is a moderately good conductor and acts as cathode to the metallic anode Iron therefore dissolves as ferrous chloride at the base of the pore, which results in undermining and further breakdown of the film The ferrous ions diffuse and migrate outwards and meet the hydroxyl ions which have been formed cathodically at the oxide-film surface, ferrous hydroxide is precipitated outside the pore, and is oxidized to rust by any dissolved oxygen which is present corrosion has commenced (Fig 2) But if sodium phosphate is the solution used, the initial anodic product is sparingly soluble ferrous phosphate, which being precipitated within the pore tends to repair the film and stifle further attack

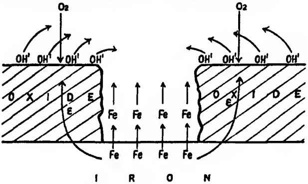


FIG 1

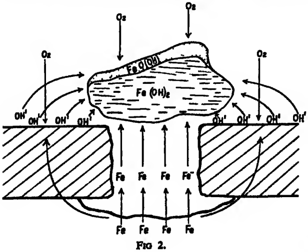


FIG 2.

The state of breakdown or repair of the oxide-film of a metal immersed in an aqueous medium can be determined very simply by the electrochemical method due to May [52, 1928] and extended by Evans [27, 1929], Bannister and Evans [3, 1930], and Hoar and Evans [46, 1932] Since the oxide-film is always more 'noble' than the basis metal in any solution, metal specimens covered with a nearly complete film show more noble electrode potentials than those where the film has broken down Thus, if the potential of a specimen against a standard half-cell be measured by means of a potentiometer or an electrometer over a period of time from the initial immersion in the medium, a falling potential indicates that the film is breaking down, while a rising potential shows that repair is occurring It is found that chloride and sulphate ions are particularly active in promoting the breakdown of most oxide-films, whereas phosphate, hydroxyl, and chromate ions, which usually form insoluble compounds with metals, normally give rise to film-repair by plugging the pores Naturally, however, sulphate ions tend to *repair* the film on lead owing to the insolubility of lead sulphate, while hydroxyl ions if present in quantity will completely *remove* the films on aluminium and zinc, with formation of soluble aluminate and zincate Solutions containing large amounts of hydrogen ions—i e acid solutions—very often dissolve the basic oxide-film directly, in some cases, e g the ferric-oxide film on iron, the film is probably first reduced by nascent hydrogen to a lower oxide that is more readily soluble in acids

Evidence for the mechanism of film-repair has been obtained by direct chemical methods Bannister [2, 1928] removed oxide-films from aluminium which had been treated with sodium phosphate, and found that they contained a small percentage of aluminium phosphate Similarly Hoar and Evans [45, 1932] found 0 1–1 0% tervalent chromium in films stripped from iron treated with potassium chromate The percentage of chromic oxide was greater in films from iron specimens which had had only a short exposure to air before immersion in chromate than in those from specimens pre-exposed to air for 24 hours, also, addition of chloride ions to the chromate solution produced films containing more chromic oxide In fact, the more repair needed by the film, the more chromic oxide was it found to contain, though the amount never exceeded 1 0% of the total weight of the film This indicates that the nearly continuous air-formed ferric-oxide film is repaired by plugs of chromic oxide in its pores

It is obvious that if a given set of conditions produce film-repair, no corrosion can take place the metal is said to be 'passive'. Nevertheless, it must be emphasized that film breakdown as deduced from potential measurements indicates only the *liability* of the metal to corrode, and gives little or no clue to the *distribution* or the *velocity* of corrosion Factors governing these will now be considered.

2. Distribution of Corrosion.

The initial distribution of corrosion on a metal surface will depend on to what extent the oxide-film breaks down.

Three fairly well-distinguished cases arise—(*a*) complete dissolution of film general attack, (*b*) partial removal of film attack on large, well-defined areas, (*c*) penetration of film attack at isolated points

(*a*) **Complete Dissolution of Film: General Attack.** Complete film dissolution usually occurs in strong non-oxidizing acids, and also in strong alkalis if the oxide is amphoteric, e g aluminium, zinc, and stannic oxides Attack proceeds more or less uniformly over the entire metal surface, although a certain amount of pitting is not infrequent, especially at a 'water-line' Hydrogen is usually evolved, and this kind of corrosion is known as the Hydrogen Evolution Type The hydrogen probably comes from special points sporadically distributed over the metal surface, as discussed later, but does not interfere to any extent with the general dissolution of the metal

(*b*) **Partial Removal of Film: Attack at Large Well-defined Areas.** When iron or zinc is immersed in an alkali-metal chloride or sulphate solution open to the air, corrosion is mainly of the Oxygen Absorption Type, little hydrogen being evolved Attack commences at the most porous parts, or 'susceptible points', of the oxide-film These are found at stressed or jagged parts of the metal, in the case of cut strips, the edges constitute especially susceptible points Even in carefully machined or polished specimens with no cut edges there will still be some pores in the film which are larger than others, and attack begins there Now although the oxygen dissolved in the salt solution will have some tendency to repair pores in the film, it is not alone a sufficient agent except in special cases But when the metal dissolves anodically at the base of an especially large pore, the equivalent of alkali is formed outside by the cathodic dissolution of oxygen at the oxide-film electrode, according to the *net* reaction (which doubtless takes place in several stages)

$$O_2+2H_2O+4\epsilon \rightarrow 4OH^-$$

This alkali, spreading over the neighbouring surface, tends to heal up any smaller pores by precipitating as hydrated oxide any metallic ions which have been produced there Thus, the largest pores alone suffer continued attack, for here the ferrous ions are produced too rapidly to allow their precipitation as an adherent, non-porous corrosion product in contact with the metal The film around them becomes undermined, and flakes off but the continued production of cathodic alkali protects a greater or smaller part of the film, sometimes indefinitely, and this part of the metal remains unattacked

Aston [1, 1916] pointed out that those parts of a metal corroding in an aerated salt solution which have become covered with loose corrosion products will be partially screened from access of dissolved oxygen, and will therefore tend to be less noble than the parts where oxygen has free access This effect, called by Evans [21, 1923] 'Differential Aeration', leads to the formation of a cell of the type

CATHODE		ANODE
Aerated metal	Salt solution	Non-aerated metal

Evans demonstrated the current flowing in such a cell by using *separate* pieces of metal, one aerated, the other not, electrically connected through a galvanometer, the current was quantitatively correlated with the amount of anodic dissolution of the non-aerated electrode by Evans, Bannister and Britton [28, 1931], and Evans and Hoar [30, 1932] On a single corroding specimen, anodic attack proceeds underneath the screening corrosion products, the reaction being in essence

$$Me \rightarrow Me^{+}+\epsilon,$$

while at the aerated cathodic parts the net reaction is

$$O_2+2H_2O+4\epsilon \rightarrow 4OH^-$$

The production of alkali at the cathodic parts maintains the oxide-film (which is the true 'inert' basis of the oxygen-electrode type cathode) in good repair, and the metal is unattacked Hydroxyl ions migrate towards the anode, and meeting metallic ions near there, precipitate them as hydroxide or hydrated oxide corrosion product (Fig 3) Thus the corrosion process itself produces alkali in the cathodic, unattacked zones, which maintains these parts unattacked, and it also produces corrosion products of a non-protective, but oxygen-screening, type upon the anodic zones, hence maintaining these anodic This explains why a distribution of corrosion once set up by considerations of the initial breakdown of the film tends to persist for a more or less indefinite time, unless in fact so much corrosion product accumulates that it begins to 'blanket' the entire metal At this stage the particular conditions as to the relative ease of supply of oxygen to the various parts of the metal surface must determine where the cathodic reaction takes place and where the anodic attack proceeds

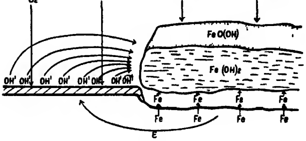


FIG 3

It should be noticed that the Differential Aeration principle explains why, in corrosion of the Oxygen Absorption Type, *those parts of the metal where oxygen has most access often suffer the least attack*, a phenomenon of frequent occurrence in practice

Bengough [4, 1933] criticized the Differential Aeration mechanism on several grounds He maintained that corrosion products, since they are penetrated by ions, must be penetrated as easily by oxygen this argument is not valid, for *charged* anions *migrate* through the thick solid-liquid suspension or 'mud' of corrosion products under a *potential* gradient, whereas *uncharged* oxygen molecules can only *diffuse* under a *concentration* gradient Furthermore, Evans and Mears [32, 1934] showed conclusively, by direct experiment, that the diffusion of oxygen through a stagnant salt solution is greatly hindered by the presence of a mud of a number of different metallic corrosion products

(*c*) **Penetration of Film: Attack at Isolated Points.** The attack at large areas which occurs on iron and zinc in aerated chloride and sulphate solutions does not occur with metals which have more robust air-formed oxide-films, such as nickel, tin, and aluminium. Although the oxide-film is penetrated by the anion, attack is so slow that little undermining occurs, and the attack is confined to comparatively few small points, usually localized at cut edges, &c., where the film is weakest Similar attack is found on iron and zinc when the chloride solution contains also a small amount of a film-repairing anion such as chromate, hydroxyl, phosphate or silicate, here the initial anodic product at the base of the pore may be a sparingly soluble body Evans and Hoar [31, 1934] discussed the question of whether hydroxyl or salt-forming ions take part in the anionic discharge from solutions containing both, they concluded that, as well as high pH, the tendency of the metal salt to hydrolyse is a factor favouring preferential hydroxyl ion discharge, which may of course lead to film-repair and localized attack Such metals as tin, antimony and bismuth give salts very prone to hydrolysis, and usually suffer highly localized attack

When conditions are favourable to localized attack, this is often particularly prevalent at a 'water-line' such as exists on metal partially immersed in a corroding medium According to Evans [23, 1926], there is here a tendency for precipitated corrosion product, which would elsewhere be formed so close to the metal as to repair the film, to cling instead to the liquid-air interface So far from being protective, this corrosion product may form a tiny canopy as shown in Fig 4, so setting up differential aeration attack by screening the point of initial break-down from air Of course, when conditions produce the faster, less localized attack dealt with in section (*b*), this inherent weakness of the water-line is more than compensated by the rapid production of cathodic alkali there, where oxygen is in greatest supply, the water-line then remains immune

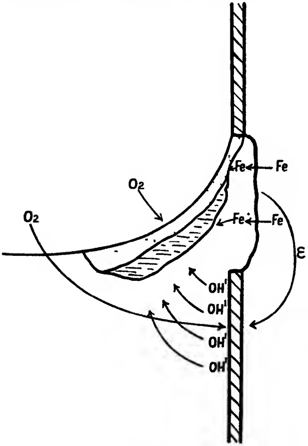


Fig 4

3. Velocity of Corrosion.

It will be convenient first to discuss the velocity of corrosion in relation to the three kinds of distribution just described

(*a*) **General Attack.** The most common case of general attack is the dissolution of electronegative metals in acids with the evolution of hydrogen Broadly speaking, the rate of dissolution is found to increase with increasingly electronegative properties in the metal, increasing hydrion concentration of the acid, rise of temperature, presence of impurities in the metal, and of oxygen or other oxidizing agent in the acid

It is generally considered that the hydrogen is evolved from specific points on the metal surface which act as cathodes towards the rest of the surface they may be heterogeneous impurities in the metal, a case studied in detail by Palmaer [56, 1929], or they may be merely special parts of the metal itself, such as grain-boundaries or corners, as suggested by Pietsch and Josephy [60, 1931] and Pietsch, Grosse-Eggebrecht, and Roman [59, 1931] Current flows between the cathodic points and the rest of the (anodic) metal, with evolution of hydrogen at the cathodes according to the reaction

$$2H^{+} + 2\epsilon \rightarrow H_2,$$

and with the equivalent dissolution of the metal where it is anodic,

$$Me \rightarrow Me^{+} + \epsilon$$

The corrosion velocity is equivalent to the current flowing, and is thus determined by the electrical characteristics of the numerous small local cells of the type

CATHODE		ANODE
H_2	H^+, Me^+	Metal

The unpolarized p d , *on open circuit*, of this cell, in a solution normal in both hydrion and the metallic ion, would theoretically be equal to the standard electrode potential of the metal on the normal hydrogen scale Table II shows some of the more common standard potentials, taken mainly from *International Critical Tables*, vol vi, pp 332, 333 But in the case of a corroding metal, the corrosion-current produces polarization of both electrodes, that of the cathode no doubt following the laws of hydrogen discharge worked out by Tafel [70, 1905], Bowden [13, 1930], and Gurney [41, 1931] Fig 5*a* shows schematic cathodic and anodic polarization curves, *C* and *A* The acting e m f, E_0, when the corrosion-current i_0 is flowing, is probably very small, because the internal resistance E_0/i_0 of the many local couples in parallel must be small The compromise potential of the corroding metal, as measured against an independent standard half-cell, will lie between the close limits E_c and E_a, and will

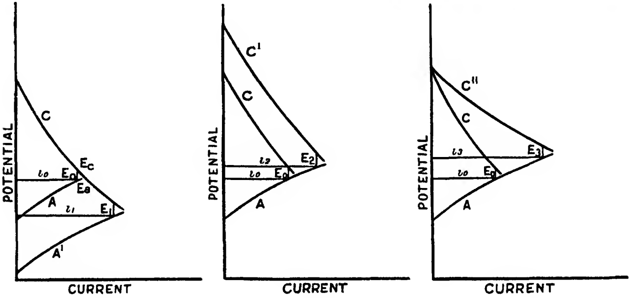
TABLE II

Standard Electrode Potentials

	Volts		*Volts*
Na, Na^+	−2 715	Ni, Ni^{++}	−0 231
Mg, Mg^{++}	−1 55	Sn, Sn^{++}	−0 136
Al, Al^{+++}	−1 33	Pb, Pb^{++}	−0 122
Mn, Mn^{++}	−1 1	H_2, H^+	±0
Zn, Zn^{++}	−0 762	Bi, Bi^{++}	+0 226
Cr, Cr^{++}	−0 557	Cu, Cu^{++}	+0 344
Fe, Fe^{++}	0 441	O_2, OH^-	+0 398
Cd, Cd^{++}	0 401	Ag, Ag^+	+0 798
Co, Co^{++}	−0 29	Au, Au^{+++}	+1 36

therefore be almost equal to the acting cathodic and anodic potentials.

Now consider a more electronegative metal. This will give rise to a lower anodic polarization curve *A′*, Fig. 5 *a*. If all other things are equal, the corroding potential will be more negative, and the e.m.f. and current will have larger values E_1 and i_1. The increase in corrosion velocity with increase in the electronegative properties of the metal is thus readily explained. It may be noted that presence of ions which remove the metal ions as stable complexes renders the metal effectively more electronegative, and thus increases its corrosion rate, as discussed by Riley [63, 1934] for copper and by Hoar [44, 1934] for tin.



(*a*) (*b*) (*c*)

FIG. 5

It will also be clear that any factor which raises the cathodic polarization curve will also increase the corrosion current and hence the corrosion velocity. The hydrogen electrode becomes more noble with increase of hydrion concentration, leading to a cathodic curve *C′*, Fig. 5 *b*, and a higher current i_2, which explains the increase of corrosion velocity with increasing hydrion concentration. Again, various cathodes have very different capacities for catalysing hydrogen discharge, a more active cathode will give a curve *C″*, Fig. 5 *c*, which again leads to a higher current i_3 and increased corrosion velocity. The ease of discharge of hydrogen from a metal when made cathode by an applied current is doubtless a measure of the effectiveness of its special cathodic points, and thus metals giving the lowest hydrogen overpotentials under such conditions are found, *ceteris paribus*, to corrode the most rapidly in acids. Any heterogeneous impurities in the metal which are effective cathodes increase corrosion velocity in this way. The effect of temperature also is to increase the ease of hydrogen discharge (i.e. to lower the overpotential) and results in a similar shifting of curve *C* to *C″*, with consequent increase in corrosion velocity. Conversely, factors which raise overpotential, e.g. the organic inhibitors discussed later, diminish the corrosion velocity.

Certain metals with amphoteric properties, e.g. zinc and aluminium, suffer general attack in *alkaline* media. The corrosion velocity increases with increasing alkalinity: this is because the effect of hydroxyl ion in removing hydrion and thus lowering the cathodic potential is outweighed by its effect in removing the metal ions as zincate and aluminate, thus lowering the anodic potential.

The increase of the velocity of acid attack often found when air or other oxidizing agents are present is due to the alternative cathodic reaction provided, for hydrogen need not be discharged as gas, but can be depolarized to form water. This process may often take place, at the corroding potential, at least as fast as the hydrogen evolution reaction: indeed, where the latter is slow, as on a metal with high hydrogen overpotential such as tin, presence of air may increase the rate of acid attack many times.

For a review of the mechanism and velocity of general attack from a slightly different standpoint, reference should be made to the work of Straumanis [68, 1933].

(*b*) **Attack at Large Well-defined Areas.** This type of attack is usually associated with oxygen absorption, and is generally much slower than attack where hydrogen evolution is the main cathodic process. It is particularly often met with in the corrosion of fairly reactive metals such as iron and zinc in more or less neutral, unbuffered salt solutions.

The corrosion velocity of iron and zinc in aerated chloride and sulphate solutions at first increases somewhat with increasing salt concentration, but passes through a maximum and eventually decreases, as shown by Friend and Barnet [38, 1915] and Bengough, Lee, and Wormwell [6, 1931]. The rate is also increased by higher temperature, and by higher partial pressures of oxygen in contact with the corroding medium. It is on the whole greater for the more electronegative zinc, but is not greatly affected by the presence of impurities.

We have seen in the section on Distribution that this kind of corrosion can be qualitatively explained in terms of the current flowing between the attacked and unattacked areas. The corrosion velocity is equivalent to the current, and therefore depends on the electrical characteristics of the corrosion cell.

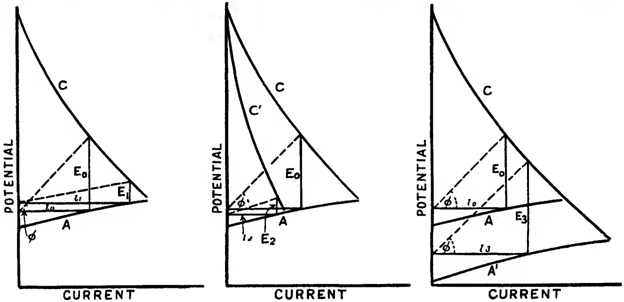
The unpolarized p.d. on open circuit of a cell whose net cathodic reaction is

$$O_2+2H_2O+4\epsilon \rightarrow 4OH^-,$$

and whose anodic reaction is of the type

$$Me \rightarrow Me^{+}+\epsilon,$$

will be, theoretically, the difference between the electrode potentials of oxygen and the metal in the corroding solution. Referring to Table II, it will be seen that the p.d. on open circuit of a cell consisting of, say, iron in normal ferrous chloride solution and a true oxygen electrode in normal alkali is theoretically about 0.84 volt. But, apart from the effect produced on this value by the (unknown) concentrations of ferrous and hydroxyl ions, the current flowing in the case of a corroding iron specimen produces polarization of both electrodes, especially the oxygen electrode. Fig. 6 *a* shows schematic cathodic and anodic curves *C* and *A*. The e.m.f. of the corrosion cell falls to the fairly small value ($<$ 0.15 volt) E_0, which is necessary to force the corrosion current i_0 through the often appreciable internal resistance of the cell, E_0/i_0, seen to be equal to tan ϕ.



(*a*) (*b*) (*c*)

Fig. 6

Clearly, then, increase of concentration of the salt solution diminishes the cell resistance, giving rise to a smaller e.m.f. E_1, and a larger current i_1, which accounts for the increased corrosion velocity observed. But great increase of the salt concentration involves a concomitant decrease in the solubility of oxygen in the solution, which shifts the cathodic curve to *C′*, Fig. 6 *b*, thus explaining the diminished corrosion velocity in strong solutions. Increasing temperature has two effects: it assists the cathodic process by speeding it up, but diminishes the solubility of oxygen, thus although moderate increase of temperature speeds up corrosion, at high temperatures the corrosion velocity of zinc diminishes. As discussed in the section on General Attack, increasing electronegative behaviour of the metal lowers the anodic polarization curve to A′, Fig. 6 *c*, thereby increasing the corrosion current to i_3 and hence the velocity. Impurities have here little effect on corrosion velocity, because the cathodic reaction

$$O_2+2H_2O+4\epsilon \rightarrow 4OH^-$$

takes place, not on them, but on the oxide-film covering the unattacked areas.

The case of iron and steel strips partially immersed in salt solutions has proved especially amenable to quantitative study, owing to the simple distribution of corrosion, shown in Fig. 7, obtained on cut strip free from rolling flaws. Evans, Bannister, and Britton [28, 1931] measured the electrode potentials of the attacked and unattacked zones, and found the attacked zone to be always anodic. The e.m.f. of the corrosion cell was about 5 mv. in 0.1 N potassium chloride solution, increasing to over 100 mv. in the most dilute solutions. Evans and Hoar [30, 1932] extended the measurements, and also, by using divided specimens cut along the line dividing the attacked and unattacked areas, directly measured the current flowing. They were finally able to calculate the corrosion velocity of

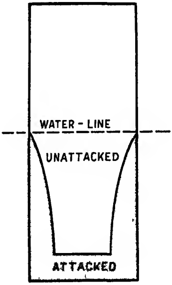


Fig. 7

ordinary uncut iron specimens from electrical measurements alone, and the results were in excellent agreement with the values observed by the loss of weight of the specimens over a considerable concentration range. The electrochemical mechanism of this type of corrosion may therefore be regarded as quantitatively established, and the velocity of corrosion is seen to be controlled by the speed at which the cathodic and anodic electrode reactions can take place at the potentials to which the two electrodes mutually polarize one another. Hoar [43, 1933] showed that the cathodic reaction

$$O_2+2H_2O+4\epsilon \rightarrow 4OH^-$$

is an especially sluggish, easily polarized process even on a platinized platinum electrode, it is still more sluggish on the oxide-film cathode of a corroding metal. It is consequently often the main factor limiting the corrosion velocity, which is then said to be under *cathodic control*.

It should be pointed out that in the series of papers by Bengough, Stuart, and Lee [8, 1927, 9, 1928, 10, 1930], Bengough, Lee, and Wormwell [5, 1931, 6, 1931], and Bengough and Wormwell [12, 1933], who made many very accurate determinations of corrosion velocity for zinc and iron, the current flowing between the attacked and unattacked areas is regarded as being of secondary importance, the depolarization by oxygen being supposed to take place at the attacked areas. This conclusion of these authors is not supported by any electrochemical measurements, until and unless these are forthcoming it seems best to maintain the theory outlined above, especially as it has been quantitatively verified in certain particular cases.

(*c*) **Attack at Isolated Points**. This kind of corrosion occurs when the conditions are such as *tend* towards film-repair, but do not give complete protection. Since the anodic parts of the metal, i.e. the points of attack, are small, the corrosion velocity may often be controlled by the rate at which the anodic process can take place; this may be greatly hindered by the partially protective effect exerted by compact corrosion-products.

An important new factor of a different kind arises in cases of isolated attack. Evans and Mears [32, 1934] pointed out that the corrosion velocity of any given point, *once it has commenced to corrode*, bears no relation to the *probability that corrosion commences*. They placed drops of 0.001 N potassium chloride on iron under a series of oxygen-nitrogen mixtures, and found that, in oxygen-rich mixtures, corrosion commenced in but few drops and then proceeded rapidly, whereas, in nitrogen-rich mixtures, corrosion commenced in nearly every drop and proceeded with small velocity. The *expected velocity* of corrosion is the product of the *actual velocity* and the *probability* that corrosion occurs at all.

Localized attack seldom gives rise to a *total* amount of metallic loss comparable with that found in cases of more general attack, but corrosion confined to a few points may there be exceedingly intense, producing pitting and perforation of the metal; thus localized attack is often more serious in practice than a more uniform corrosion. Since the addition of film-repairing agents, such as chromate and hydroxyl ions, is often resorted to in practice as a method of minimizing corrosion, it is important to emphasize that insufficient inhibitor will give only partial film-repair, and may actually make matters worse by producing intense localized attack.

(*d*) **Accelerators and Inhibitors of Corrosion.** It will now be convenient to assemble together the main types of accelerators and inhibitors of corrosion.

Accelerators act by assisting either the cathodic or anodic process or both. Cathodic accelerators are of two kinds. The first kind includes substances which can give rise to new cathodic points on the metal surface. Thus traces of ions of more noble metals having low hydrogen overpotentials, e.g. platinum, may greatly accelerate the corrosion of baser metals with high overpotentials, e.g. zinc, as shown by Centnerszwer and Straumanis [16, 1925], for the noble metal 'plates out' on the base and provides it with catalytically active spots for hydrogen discharge. The second kind of cathodic accelerator includes all oxidizing agents which can depolarize nascent hydrogen at cathodic points, or take part in any equivalent cathodic reaction, typical instances being oxygen, hydrogen peroxide, ferric salts, and permanganates. Chromates in small concentrations may act similarly, but the effect is easily masked by their powerful inhibiting action (*vide infra*) due to film-repair.

Anodic accelerators may be similarly classified. The first group consists of substances which provide new anodic points, i.e. which break down the oxide-film. Chlorides and sulphates are the most generally active bodies in this respect, and, of course, acids which directly dissolve the film exposing anodic metal. The second group consists of substances which depolarize the anodic reaction, usually by removing the metallic ions as complexes, the more stable the complex, the greater the depolarization and the accelerating effect. Cyanides, oxalates, tartrates, and citrates often act in this way. A third kind of anodic acceleration is operative in the well-known effect of traces of hydrogen sulphide on the acid attack of iron, discussed by Hoar and Havenhand [47, 1936]. Here the metal anodic reaction is a peculiarly sluggish one, showing (as is also the case with nickel and cobalt) a very much higher 'metal overpotential' than most metals, hydrogen sulphide, which is doubtless specifically adsorbed, catalyses the anodic reaction.

Inhibitors also may be either cathodic or anodic in their action, as discussed by Warner [81, 1929]. Cathodic inhibitors act by destroying the catalytic activity of cathodic points, probably by becoming selectively adsorbed there. Friend and Vallance [39, 1922] and more recently Schunkert [66, 1933] found that many colloids inhibited the acid corrosion of iron and zinc, presumably by becoming adsorbed. Proteins and many quinoline and acridine derivatives are often good inhibitors, and it is significant that these are large molecules which can exist as *positively charged* ions or colloid particles. Such bodies will migrate to the negative cathodic points on the corroding metal, and if they become adsorbed, will 'blanket' the cathodes and impair their efficiency for the discharge of hydrogen, it is the initial reaction

$$H^+ + \epsilon \rightarrow H,$$

rather than the secondary

$$H + H \rightarrow H_2,$$

which is inhibited, as shown by the work of Morris [55, 1935] on the diffusion of hydrogen through steel. Evidence for this effect was provided by Chappell, Roetheli, and McCarthy [17, 1928], who correlated the acid corrosion of iron in the presence of quinoline ethiodide with the rise in hydrogen overpotential produced by the inhibitor. Furthermore, adsorption of the inhibitor was directly demonstrated for phenylacridine on iron by Rhodes and

Kuhn [62, 1929], and for gelatin on steel by Morris [54, 1931]. Morris also showed that the adsorption, and efficiency of gelatin as an inhibitor, decreases greatly when the acidity is varied from *pH* 2.5 to *pH* 5.0, this is to be expected, since the positive charge on gelatin particles decreases with decreasing hydrion concentration, becoming zero at *pH* 4.7, the isoelectric point for gelatin. Generally, cathodic inhibitors are efficient only in fairly acid solutions. They have found extensive practical application in the acid 'pickling' of scale-covered metals.

Anodic inhibitors act by removing anodic points, i.e. by repairing or renewing the protective film. As previously discussed, alkali hydroxides, phosphates, silicates, and chromates act on most metals in this way, carbonates have a similar but less pronounced effect. Iron, and probably other metals which dissolve to oxidizable ions (e.g. ferrous), are especially well inhibited by chromate for chromate is an oxidizing agent, and moreover its reduction product, hydrated chromic oxide, seems to have specific value in healing the pores in the film. Strongly oxidizing acids, such as nitric and chromic, are often effective inhibitors if present in sufficient quantity, for they form oxide to repair or renew the film, thus iron becomes passive in very concentrated nitric acid. Oxygen itself has a small anodic inhibiting effect, the diminished number of points of attack when excess oxygen was present in the previously cited experiments of Evans and Mears [32, 1934] may be instanced. Furthermore, Bryan and Morris [15, 1932] found that the attack of stainless steel by citric acid is much less in the presence than in the absence of air. Schikorr [64, 1928, 65, 1933] emphasized the necessity of regarding oxygen either as an inhibitor or an accelerator according to circumstances.

Small amounts of ions of a metal 'nobler' than that undergoing attack, such as arsenic or antimony ions in the acid attack of iron, may sometimes plate out as a coherent film which inhibits both cathodic and anodic reactions. However, the inhibiting influence of tin ions on the acid attack of steel was shown by Hoar and Havenhand [47, 1936] to be due to the removal of traces of accelerating hydrogen sulphide, this is thus an indirect anodic inhibition.

Atmospheric Corrosion

The atmosphere ordinarily contains small amounts of moisture and acid gases, which have a profound effect on the course of metallic oxidation. The action of dry oxygen in producing oxide-films has already been described. One of the chief effects of moisture and gases such as sulphur dioxide is to give rise to different kinds of corrosion-product, which may be either protective or the reverse. In fact, the properties of the corrosion product are often the main factor in determining the course of attack, as shown in the extensive work of Vernon [74, 1924, 76, 1927, 77, 1931; 78, 1932, 79, 1932], and Hudson [48, 1929, 49, 1930; 50, 1934]. Vernon found that the rate of attack of copper by an unsaturated atmosphere containing traces of sulphur compounds fell off as the partly protective film thickened, whereas zinc under similar conditions showed an undiminished rate of attack during the thickening of the clearly unprotective film. Iron, in atmospheres sometimes reaching saturation, corroded *more* rapidly when it had become blanketed with rust, very probably because the rust retained moisture.

Vernon [77, 1931] studied the attack of copper in 'artificial' atmospheres containing regulated amounts of moisture and sulphur dioxide. He found that both must be present to produce any sensible attack, which varies greatly with the amounts present. The rate of attack first increases with increasing sulphur dioxide and then sinks to a minimum at 1% of that gas, here the corrosion product is normal copper sulphate, which appears to be more protective than the basic salts formed at lower and higher concentrations of sulphur dioxide. Moisture up to 50% relative humidity gives only slow attack even with large amounts of sulphur dioxide, but at 75% and more the attack is very rapid. This illustrates the 'Principle of Critical Humidity' developed by Vernon [77, 1931, 78, 1932] and by Patterson and Hebbs [57, 1931]. The critical humidity above which corrosion becomes rapid is probably that at which the corrosion-product can readily take up moisture from the atmosphere, since many products are markedly hygroscopic, it may be well below 100% relative humidity.

Resistant Materials

The so-called 'noble' metals, such as platinum and gold, are resistant to corrosion on account of their very positive electrode potentials—they are thermodynamically the most stable of the metals towards oxidation. Less noble metals such as silver and copper are still electropositive to hydrogen, and therefore do not dissolve in non-oxidizing acids provided air and complex-forming substances are absent. In similar circumstances, tin and lead are almost as resistant, because although they are slightly electronegative to hydrogen, they show very high hydrogen overpotentials and catalyse the discharge of hydrogen very weakly.

But the comparatively 'reactive' (thermodynamically) metals chromium, nickel, cobalt, and aluminium, and many of their alloys, are found in practice to be very resistant to many types of corrosion, a resistance due not to the nobility of the metal but to the strength of the oxide-film. The excellent resistance, even to aerated chloride solutions, of chromium, chromium-nickel alloys, and the chrome-nickel 'stainless' steels, shows that the film requires no more than dissolved oxygen to repair it even in the presence of chlorides. Aluminium is somewhat less resistant, for chlorides give localized attack, but its alloys the aluminium brasses and bronzes withstand chloride attack very well.

It should be noted, however, that this type of resistant material often fails in the absence of air, as in the work of Bryan and Morris [15, 1932] on stainless steel in citric acid, the film is not *self*-repairing, but *air*-repaired. That oxygen alone is able to keep the film in good repair shows that it is of a specially impervious nature. This was confirmed by Forrest, Roetheli, and Brown [36, 1930], who showed that the initial rate of oxygen uptake, from distilled water containing dissolved oxygen, was the same for film-free stainless and film-free mild steel, but that it fell to practically zero after a very short period for the stainless steel. clearly the oxide-film becomes sensibly impervious when still much thinner than that on mild steel. There is little doubt that this is due to the chromic oxide content of the film, it will be remembered that the Pilling and Bedworth [61, 1923] ratio, oxide volume/metal volume, is as high as 3.92 for chromium.

Detailed information on the stainless steels will be found in Monypenny's [53, 1931] book.

Protection from Corrosion

The action of inhibitors in the corroding medium in arresting corrosion, and the nature of resistant materials, have already been discussed It remains to consider the several kinds of protective coating in common use on metals, viz (1) oil and grease films, (2) non-metallic chemically applied coats, (3) metallic coats, (4) paints, varnishes, and lacquers

(1) Oil and grease films have only a limited application depending on service conditions Their action is purely mechanical, in excluding moisture and to some extent air from the metallic surface, and is not usually very efficient indeed, the organic acids and sulphur compounds contained in some oils may themselves have a pronounced corrosive effect Furthermore, patches of oil or grease forming an incomplete coat may act as oxygen screens and set up differential aeration, giving rise to considerable attack

(2) The most successful non-metallic protective coating is the oxide layer produced on aluminium by the 'anodizing' process due to Bengough and Stuart [7, 1923] Aluminium made anodic in warm dilute chromic acid becomes coated with a very tough, insulating oxide-film, which besides being protective in itself affords an excellent basis for a paint or lanoline coat Owing to its mordanting properties, it can also be coloured by immersion in suitable dyeing solutions Attempts to coat magnesium chemically have led to the development of the chromate coating of Sutton and Le Brocq [69, 1931], and the selenium oxide coating of Bengough and Whitby [11, 1932] These coatings confer moderate protection and are advocated for use under paint or lanoline

(3) Many metallic coatings are in common use, and fall into two distinct classes, reviewed by Evans [26, 1928] In the first, the coating is of a metal more noble than that to be protected coatings of silver on copper and white metal, and of copper, nickel, and chromium on iron may be instanced The protection is purely mechanical, in fact, at breaks or pores in the coating the exposed base metal may suffer anodic attack owing to the action of the cell and serious local corrosion may occur It is therefore imperative that the coating should be as impervious as possible The second class of metallic coating is *less* noble than, and therefore *anodic* to, the base metal, examples being tin on copper and zinc on iron Here the anodic dissolution of the coating at a pore produces cathodic alkali at the base metal cathode, and this is therefore *electrochemically*, as well as mechanically, protected at the expense of the coating A coating which is sometimes cathodic, sometimes anodic, is that of tin on iron Only mechanical protection is afforded against, for example, neutral salt solutions, for the tin is here cathode but if ions such as citrate which form stable tin complex ions are present, the tin becomes anodic and affords electrochemical protection as well

CATHODE		ANODE
'Noble' coating	Corroding electrolyte	'Base' metal

(4) The protection afforded by paints is partly mechanical in the exclusion of corrosive agencies, and partly chemical if the paint pigment contains corrosion inhibitors Thus ferric oxide paints protect only mechanically, while red lead and lead chromate have a marked passifying influence on iron, tending to heal the oxide-film and afford chemical protection Bituminous paints probably owe their value against acid atmospheres to the presence of inhibitors of the cathodic type (*vide supra*) which are the most effective in minimizing acid attack Protective painting has been extensively discussed in a series of papers by Evans and Britton [29, 1930], Britton and Evans [14, 1932], and Lewis and Evans [51, 1934], one of their main conclusions is that the first or priming coat should protect chemically, e g red lead, while the second coat should exclude moisture, &c , as efficiently as possible

Varnishes and lacquers give mechanical protection only, generally of a less degree than paints, but are used for protection against indoor atmospheres and other mildly corrosive circumstances

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THE MICROBIOLOGICAL ASPECT OF CORROSION

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DURING the past two or three decades the corrosion of metals has been engaging the active attention of workers in chemistry and metallurgy, and various conceptions have been put forward to explain the reactions taking place Among these theories figured for some time a biological, or rather a microbiological, explanation which, according to Speller [17, 1926] was based on the fact that certain micro-organisms thrive in water containing iron salts and decompose these salts with the precipitation of iron hydroxides—rust On the whole investigators did not take kindly to this biological theory, which was soon found to be far too restricted to explain the varied and often seemingly contradictory facts established Most workers preferred to see in corrosion an electrochemical action giving rise to the passing into solution of ions of the corroding metal at anodic areas and to the passing out of solution of hydrogen or another metal at cathodic areas, a reaction which would be greatly accelerated by electrical currents purposely or accidentally generated at or near the seat of corrosion Since the formulation of this electrochemical conception, the question of a biological aspect of corrosion has for all practical purposes been regarded as non-existent In the following pages an attempt will be made to reopen this question, since it is clear from many recent publications that conditions brought about by microbiological activity at the site of corrosion of metals, when this corrosion takes place under water or in the soil, cannot fail to have a marked effect on the rate of corrosion

In reopening the question it has not been the intention to formulate a new biological conception to replace the electrochemical theory of corrosion, but to point to a new factor which may explain certain facts which are at present not easily interpreted In doing so it should be clearly understood that it is the corrosion of metals in soil and in certain waters which are dealt with

As a general rule it may be claimed that the progress of corrosion in water or in the soil is noticeably affected by the presence of organic matter and of certain salts, notably sulphates, and that it may be independent of the supply of oxygen, anaerobic conditions being often as corrosive or even more so than aerobic conditions This is the case, for instance, in anaerobic clayey soils where the rate has frequently been reported more rapid than in aerobic sandy soils (Logan, Erving, Yeomans [14, 1928], Denison [6, 1931]) Nor does the absence of strong electrical currents which have so often been made responsible for the rapid corrosion of metals seem to render harmless either clayey soils or water polluted with organic matter or containing sulphates

A significant observation revealed by a review of the existing literature is that the corrosion products of metals destroyed in soil and in certain waters have been shown in all cases where actual determinations have been made to contain a high percentage of sulphur, in the form of sulphides. In their analyses of scale from corroded condenser tubes, for instance, Bengough and May [5, 1924] found 5% of sulphur Irvine [12, 1891] had previously recorded that an iron chain which had corroded through exposure in sea-water contained an outer casting or skin fully $\frac{1}{8}$ in thick which had a very high sulphur content Friend [8, 1922], in his interesting memoir on corrosion, records that corroded, graphitized cannon balls which had remained submerged in the sea near Brest for more than a century had an outer casing consisting of sulphide, sand, and calcareous matter And, most significant of all, Gaines [9, 1910], who analysed a large number of corrosion products from the exterior and interior of damaged iron conduit pipes, found between 1 4 and 6 5% of sulphur in these products, while rust artificially produced by connecting a gravity cell to steel plates immersed in a sodium chloride solution gave less than 0 15% of sulphur The steel used in the experiment contained no more than 0 05% sulphur Further significant evidence of a difference in sulphur content of iron corroded normally under water and iron artificially corroded and graphitized in acid was brought forward by Grzeschick [11, 1912], who analysed the product prepared by treating cast iron with hydrochloric acid until it had acquired a graphitic appearance and showed pyrophoric properties similar to those observed in cast-iron implements rescued from the sea after prolonged exposure In the artificial product prepared by Grzeschick there was considerably more carbon, phosphorus, and silica than in the original metal, but the rise in sulphur was insignificant compared with that recorded in cast iron corroded by soil or water

If it may be concluded from these observations that it is characteristic of a corrosion in soil and in certain waters that the corrosion products of a damaged metal contains considerably more sulphur than the original metal, then it would appear desirable to establish the cause for this increased sulphur content An increase of the order observed cannot have been due to the partial elimination of metal from the corroded material such as would take place where acids or electrical currents were responsible for the corrosion The work of Gaines and of Grzeschick proves this, and demonstrates that the presence of an abnormally high sulphur content in the metals must be due to the introduction of sulphur from extraneous sources In this connexion it is significant to note that the excess of sulphur is stated to be present in the form of sulphides, indicating that the extraneous source of sulphur must have been hydrogen sulphide evolved at or near the seat of corrosion

That hydrogen sulphide greatly increases the rate of corrosion was shown by Bengough and May [5, 1924], who carried out experiments with various metals, including rustless steel, immersed in sea-water to which 3 c c of hydrogen sulphide had been added per litre of water. But this participation of hydrogen sulphide in corrosion was regarded by them and by most investigators as an exceptional occurrence limited to places where putrefactive decomposition of proteins occurred That hydrogen sulphide should be found quite frequently in some soils and waters in the absence of decomposing organic matter was not generally known, though it had been demonstrated by Plauchud [16] as early as 1877 and had attracted the attention of several other writers between then and now. The source of this hydrogen sulphide was in time recognized to be sulphates present at the site of corrosion Various chemical formulae were proposed to explain the reactions by which sulphates could be reduced to sulphides In a very interesting series of publications, Bastin and his collaborators [1, 1926] gave an account of the problem of the natural reduction of sulphates, compiling many interesting observations by other writers who had shown, both that the chemical explanation of the reduction of sulphates in nature is untenable, since the drastic conditions required for such reactions do not occur there, and that certain very specific micro-organisms not only are present at the places where hydrogen sulphide is evolved by the reduction of sulphates, but actually require to carry out this reduction to maintain their normal life functions Since these organisms, the sulphate-reducing bacteria, have been found to be extremely widely distributed in soil and water, and, curiously enough, to be particularly active in such places which have empirically been found to be highly corrosive, notably clayey soils [18, 1922], estuarine waters [3, 1895], and the mud from lakes and from the sea [13, 1924], it is impossible not to suspect them of participating in the corrosion of metals in such places

No fundamental investigations have as yet been carried out to confirm this suspicion experimentally Dixon [7, 1930] suggested that the predominant cause of the corrosion of water conduit pipes in the soil was 'the action of sulphur present produced by microbes which infest the soil in question' Dixon presumably arrived at this conclusion from experiments which he carried out and in which bars of cast iron were embedded in damp clay enclosed in glass bottles to insulate it from electrical effects He found that after three months' exposure the iron showed distinct signs of blackening due to sulphur compounds

A connexion between the microbiological transformation of sulphur and the corrosion of a water-main was suggested also by Beckwith and Boward [2, 1933], and recently further evidence, which is partly of an experimental nature, has been brought forward by van Wolzogen Kühr [19, 1934] in Holland and by Bunker [5*a*, 1936–7] in Great Britain This evidence strongly supports the view expressed above that the sulphate-reducing bacteria play an important part in the anaerobic corrosion of metals As already mentioned, further work is required fully to substantiate the important relationship which appears to exist between the changes suffered by sulphates and to a much smaller extent by sulphur-containing organic substances through the action of micro-organisms and the rapid and serious corrosion of metals in soils and in water, where such sulphate reduction takes place Should this relationship finally and irrefutably be established as a result of subsequent investigations, it will be possible to predict, with much greater precision than appears possible at present, whether a certain type of soil or a certain water is likely to prove abnormally corrosive, since the isolation of sulphate-reducing bacteria, which offers little or no difficulties to the trained investigator, could be taken as clear evidence that conditions were favourable for corrosion to occur And it would then be possible also to predict that unprotected iron or steel pipelines used for conveyance of crude oils must be particularly exposed to corrosion on their internal surfaces, since the brine which accompanies most crude oils is a carrier of sulphate-reducing bacteria capable under the conditions prevailing in the brine of reducing the sulphates present to hydrogen sulphide Where, therefore, this brine, through settlement or otherwise, comes in direct contact with the metallic surface of the pipe, formation of metallic sulphides might be expected with resultant corrosion

So far attention has been paid only to a possible connexion between microbiological activity and corrosion as it concerns the metabolism of sulphur in nature Though this may well be found to be the most important aspect, the available literature refers to other substances than hydrogen sulphide which have been shown to accelerate corrosion in soil and in water, notably nitrates [10, 1913] and organic acids [15, 1922] Both of these substances are, as is well known, important products of metabolism of various micro-organisms without the activity of which they would be unlikely to be present in most soils and water To what extent either, or both, of these substances have been responsible for the remarkable observations of Bengough and Lee [4, 1932] that natural sea-water shows a greater rate of corrosion than artificially prepared sea-water of the same salt concentration, and of sea-water which has been boiled with potassium permanganate and thereby presumably rendered sterile, cannot be stated, but certainly requires further elucidation

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THE CORROSION OF REFINERY EQUIPMENT

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Sir John Cadman during the World Petroleum Congress in 1933 described corrosion as making a constant and insidious attack upon general equipment, and gave a rather startling figure as an estimate of what such attack costs the petroleum industry in the course of a year

The importance of corrosion is fully realized and the subject of general corrosion is fully dealt with in another article in this book This article is limited to a consideration of such corrosion as affects refinery equipment For an account of the work of the Committee on Corrosion of Refinery Equipment of the American Petroleum Institute reference should be made to the Proceedings of the 17th Annual Meeting of the A P I, Section III, Refining, p 71

Even in a refinery there is a certain amount of corrosion of a general character, but it differs in no way from similar corrosion in any other kind of works and therefore does not need to be dealt with in detail in this article Even the corrosion of the outside shells and of the tubes in fired oil furnaces differs very little from that met with in boiler practice The burning of acid sludges or sulphurous fuels, or overheating due to scale either from boiler water or coke, will cause undue wear and tear of steelwork exposed to the flue gases and can be met by the use of special alloy steels or doped steels, e g calorized, but is probably best met by adequate thickness of metal in the exposed parts, sufficient testing and sufficiently frequent renewals being made to minimize hazards due to this kind of corrosion The special corrosion which affects refinery equipment can be serious from two points of view, the first hazard and the second cost

Where inflammable materials such as oil are being handled, sometimes at considerable pressure, the factor of hazard has to receive very special care, and for this reason it is essential that corrosion must not be allowed to interfere with the operation of safety-valves or flame-preventing devices, and that in particular vessels at high temperature filled with oil must not be allowed to burst due to corrosion weakening the vessels

On the question of cost there is room for difference of opinion and for particular study of each problem, as will be shown in the course of the article

The kind of corrosion met with can be conveniently dealt with under several heads

1. High-temperature Corrosion.

This is probably the most hazardous of the various types of corrosion met with and results in the weakening of the walls of the heated furnace tubes or reaction vessels so that they become too thin to stand the pressures

It can be said in general that very little corrosion is to be expected from heating of even sour crudes at temperatures below 700° F, but that above this temperature very serious corrosion can occur, dependent, of course, upon the type of crude oil being processed Recent experience with high-temperature pipestills indicates that there may be an upper limit of temperature, also, beyond which corrosion is not serious

Methods of combating such corrosion can be conveniently divided into three sub-heads.

(*a*) **By limiting or preventing the corrosive influence.** The corrosion would appear to be in most cases a combination of steel with sulphur from the crude, and although there is considerable evidence that this attack is affected by the presence of traces of chlorine, there is little doubt that the severity of attack is a function of the temperature used This makes it very important to ensure that localized high temperature is not permitted to exceed greatly the general level of temperature sought Correct design with regard to turbulence within the tube and well-balanced radiation and convection intake of heat outside the tube can do a great deal to avoid the particularly bad corrosion which occurs when localized hot spots, particularly if accompanied by coking, intensify the normally present corrosive action of the crude to a dangerous extent

Another factor which is of importance at high temperature is the character of the liquid/vapour mixture passing through the tubes, it being quite a common experience to get heavy wear and tear on the inside of the tubes at a point where evaporation is only partly complete This is really very largely erosion, but the effect is the same in that the scouring action simply gives further play to corrosive tendencies, and the walls of the tubes and bends can be scooped out in a most alarming way in a quite short time

This is best avoided by allowing ample cross-section and thus reducing velocity at points where it is known that such a spray will be travelling through the heated portion of the tubes

Another method of dealing with such corrosion is to use alkali in some manner, e g by the injection of lime, caustic soda, or even ammonia, with a view to retarding or preventing the release of chlorine and/or sulphur in a form which can attack steel

(*b*) **By using non-corroding materials.** Where corrosive tendencies are so marked as to defy the methods outlined above it becomes necessary to use special metals, of which there are several now available among the various alloy steels containing molybdenum, nickel, and chromium The most resistant of these metals are relatively expensive, and furthermore a new hazard can be introduced with regard to the liability to creep stress and embrittlement which characterizes certain of these alloys

These matters are now well understood and many modern plants successfully use alloys of reasonable cost and having satisfactory properties with regard to creep stress and embrittlement

(*c*) **By using common materials and making suitable allowances in design.** Since the factor of economics must enter as setting a limit to the ways of reducing the hazard, it is often possible to use common mild steel and to meet the hazard by having an adequate thickness of metal combined with an elaborate system of examination and testing by means of measurement and the use of a hammer during shut-down periods

Where vessels of large size are concerned, liners of protective material, such as cement coatings or adherent sprays of metal, or welded liners can be used effectively to avoid the expense of making the entire vessel of corrosion-resisting material The efficacy of such devices, however, depends entirely upon the ability to cover completely the surfaces to be exposed, leaving no pin-holes or bare places where corrosive attack could get behind the lining or spray

2. Low-temperature Corrosion.

Low-temperature corrosion occurs most frequently

(*a*) In condensing equipment or in the upper portions of fractionating towers which are, in effect, part of the condensing equipment, including run-down lines and tanks
(*b*) In equipment used for treating with chemicals

Dealing with (*a*) first, the methods of dealing with such corrosion can be conveniently divided into two major divisions

(i) By limiting or preventing the corrosive influence
(ii) By using non-corroding materials

Under the first heading perhaps the best preventive of all is to avoid the presence of water in any shape or form, though this is a counsel of perfection where damp air has to be dealt with

It is usually necessary, however, to introduce some kind of neutralizing agent, the injection of lime or soda with the original crude has been used

In other cases the immediate neutralization of the vapours by the injection of soda or lime-water proved effective in protecting the condensing equipment from what had been very severe corrosion, ammonia also is used for the same purpose

In cases where the material being processed is the result of treatment with sulphuric acid, it is often possible to limit the corrosive effect of the overheads by regulating the acid treatment to prevent the formation of easily decomposed sulphonated bodies and also by limiting the temperature used in the re-running either by the use of vacuum or excessive steam Such means, however, are seldom completely effective, and the use or otherwise of such methods is determined by the reduced cost of replacement effected by their use

Under the second head, i e the use of non-corroding materials, a great deal of experimenting has been done throughout the oil industry from its earliest beginnings There is little doubt that where design permits, the use of cast iron can give very long life, and many successful applications of various coatings such as enamel or tin are to be found

In other cases a selection of suitable metal, such as bronze, solves the difficulty, though it has to be realized that bronze is readily attacked by alkali The writer's personal leaning is to adequate neutralizing of the vapours before condensation by means of an alkaline liquor such as soda or lime, followed by the use of ordinary mild-steel condensers, run-down lines, tanks, &c

Dealing with (*b*), i e corrosion of treating equipment, this is usually due to the reagents employed rather than to the oil, and is dealt with again along two main lines, i e

(1) Either preventing or limiting the corrosive influence, or
(2) Using non-corroding materials

The limiting or prevention of the corrosive influence is seldom easy where any kind of intensive agitation has been employed

In the case of the use of liquid sulphur dioxide it is of extreme importance, in fact it is essential, to exclude rigorously the entry of water in any shape or form, and it is usually necessary to provide purifying equipment to deal with even such small quantities of water as may get to the equipment from the atmosphere

In the case of sulphuric acid the sludge formed, and remaining to some extent in suspension, can never be instantaneously neutralized, and it is therefore usually necessary to provide anti-corrosive materials at the stage where neutralization begins Such materials for the vessel may be lead or regulus where no great stresses are involved, or any successful method of lining with enamel, lead, &c Phosphor bronze and stainless steels can be used for revolving parts, but care must be taken that the stainless steel has had a suitable heat treatment to render it resistant to the attack of corrosion The undersides of tanks and vessels which are not actually submerged in liquid can be protected to some extent by painting with various dressings, though few such dressings have real permanence, and it is usually better to allow sufficient metal to make replacement possible, or to provide adequate protection as above

Two forms in which low-temperature corrosion can be deadly are in the causing of safety-valves to become fixed and fail to lift as designed, and in the deterioration of gauzes placed in various flame-preventing devices

The only safe method of dealing with such subtle corrosion is to have frequent and thorough examination of such devices and to replace corroded parts where necessary

The writer has seen gauzes which were being relied upon to prevent flame propagation in such a condition as to be completely impervious to the free passage of vapours and utterly useless as conductors of heat, and yet such a condition would not have been found but for the accidental dismantling of a tank in question

Summing up, then, the corrosion problem for refineries which is special to oil can be due to

(1) High-temperature decomposition liberating corrosive acid or sulphur, and can be met by

(*a*) Limiting the corrosive influence by the use of some alkali in a preferred way, or
(*b*) Using such materials as have a greater resistance to corrosion, e g alloy steels, liners, &c , the problem being to combat the corrosion without introducing a new hazard due to the inferior general properties of the alloy used

(2) Low-temperature corrosion by acids formed during distillation which can again be dealt with by using some form of alkali injection to limit the tendency to corrode or by using protective coats or materials which are not so easily corroded

Corrosion due to chemicals introduced as treating agents can probably be dealt with only by the use of resistant materials

Hazard due to corrosion arises from

(*a*) The bursting of high-pressure equipment which may lead to fires or explosions
(*b*) The failure of the safety devices
(*c*) The release of toxic vapours or liquids without warning to operators

The economics of corrosion prevention are special to each case considered, and where hazard is absent mild steel, because of its cheapness, can often hold its own against the use of more resistant materials due to inherent low cost even when allowance is made for more frequent replacement of corroded parts

SECTION 36

INSTRUMENTS AND METERS

HYDROMETERS

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Introduction

IN the space available for this article a comprehensive treatment of the whole subject of hydrometers and hydrometry is not possible Attention has therefore been confined to some of the more important aspects of the subject, keeping in mind the particular requirements of the petroleum industry Prominence has been given to density hydrometers, because the general use of density hydrometers would lead to a much needed unification and simplification in scientific, technical, and industrial procedure not only in the petroleum but in many other industries

Details of Construction of Hydrometers

In this section the construction of hydrometers will be considered with a view to indicating various details to which attention should be paid in the manufacture, specification, or examination of hydrometers

The most generally useful type of hydrometer is a glass instrument consisting of a bulb weighted at the lower end and surmounted by a stem, small in diameter compared with the bulb, in which is enclosed a scale on which readings are taken The present article will be confined to this type of hydrometer which is the one almost universally employed in the petroleum industry

In recent years the shape of bulb shown in Fig 1, though by no means new, has come into increasing use Its merits are that it is simple to make and easy to clean

A cylindrical stem is best for hydrometers It should be co-axial with the bulb and the hydrometer should float with its stem vertical The stem should extend sufficiently, at least 20 mm , beyond the highest graduation mark on the scale, to enable the hydrometer to be manipulated by holding the top of the stem without risk of fingering the portion of the stem occupied by the scale The stem should remain uniform in diameter for several millimetres below the lowest graduation mark

FIG 1 Common form of glass hydrometer

Paper is almost universally used for the scale enclosed in the stem The paper is rolled into a cylinder smaller in diameter than the bore of the stem so that when inserted it opens and fits snugly against the inside of the stem where it is fixed in position with a spot of adhesive It is important that provision should be made whereby any accidental shift of the paper scale relative to the stem can be detected A simple means of doing this is that first given in the specification for I P T hydrometers [1, 1924] A horizontal line with a V at each end thus >—< is marked on the paper scale a few millimetres above the highest graduation mark. A horizontal line is etched on the stem of the hydrometer coincident with the above datum mark It is convenient if the line on the stem is somewhat longer than the horizontal portion of the datum mark so that the ends of the line project into the Vs at each end of the datum mark Provision of a datum mark on hydrometers is by no means general, whereas it should be universal

The paper used for the scale should be of a kind on which fine clean graduation marks can be drawn An esparto paper—65 to 75% esparto—is suitable as it fulfils this requirement and is subject to minimum changes in dimension with alterations in humidity The strips of paper for the scale should be cut with their length in the machine direction of the paper

The graduation marks should be varied in length and the scale suitably numbered to ensure ease of reading, i e to ensure that the exact significance of any graduation mark can be read at a glance Though bold figuring has obvious advantages, the position of the figures and the size of the figures relative to the spacing of the graduation marks should be carefully designed so that it is immediately clear to which graduation mark any particular number relates There should be no evident irregularity in the spacing of the graduation marks, i e no obvious differences between the lengths of adjacent subdivisions, though, of course, on all hydrometers on which the subdivisions represent equal increments in density, the graduation marks become progressively closer together from the top to the bottom of the scale Printed scales have an advantage in general appearance as regards regularity of spacing over hand-drawn scales It should be remembered, however, that printed scales are constructed on the assumption that the hydrometer stem is absolutely uniform in diameter, and the possibility of errors due to variations in stem diameter should not be overlooked

Every hydrometer should bear an inscription indicating in a manner free from all ambiguity the basis on which the scale has been constructed The inscription should include a statement of the surface tension for which the hydrometer has been adjusted, or, alternatively in special circumstances, the name of the liquid for use in which the hydrometer has been adjusted

Basis of Hydrometer Scales

The three most generally used types of hydrometer in the petroleum industry are specific gravity hydrometers, Beaume hydrometers—mainly the A P I variant—and density hydrometers

It would be an advantage to have a common basis for all hydrometers used in the petroleum industry and the one which has most to commend it is that the hydrometers used should be adjusted to indicate density—mass per unit volume—in grammes per millimetre at 20° C

Arbitrary scale hydrometers such as the Beaumé have obvious disadvantages

The specific gravity of a liquid is most simply defined by the ratio

$$\frac{\text{Density of the liquid at the temperature } t_1}{\text{Density of water at the temperature } t_2}$$

and is conveniently represented by the symbol $S\, t_1/t_2$. Clearly, by assigning different values to t_1 and t_2, innumerable specific gravities may be chosen and the position is further complicated by the use of 'specific gravity in air' in addition to specific gravity on a mass basis as defined above Although the specific gravity *S* 60° F /60° F is widely used in the petroleum industry and so to some extent there is uniformity, yet specific gravity does not afford nearly so simple a basis for hydrometry as density

A detailed consideration of the question has been given elsewhere [2, 1933], and here it must suffice to summarize briefly the advantages of the density basis These are

(1) The basis of the scale is entirely free from ambiguity and is expressed in universally recognized units
(2) The temperature corrections are exceedingly small For example, the corrections for readings taken at any temperature within the range 10 to 30° C to obtain the density of the liquid at the temperature of observation do not exceed +0 0005 g per ml
(3) The density recorded by the hydrometer is a fundamental property—mass per unit volume—of the liquid itself and provides the simplest basis for hydrometry For example, calculations of the weights of known volumes of liquids, or volumes of known weights of liquids, start from a simple logical basis and can readily be carried out (see p 2325)
(4) The basis recommended is suitable not only for the petroleum industry but could with advantage be adopted in all other industries where it is not already in use

Determination of Density by means of a Hydrometer

In this section it is assumed that a hydrometer adjusted to indicate density in g per ml at 20° C is used, and the observation of the hydrometer reading will be considered first

To obtain the density of a liquid by means of such a hydrometer, provided that it has been adjusted for a surface tension appropriate for the liquid in which it is to be used, the only observations necessary are a reading of the hydrometer in the liquid and a determination of the temperature of the liquid If the liquid is one having a low surface tension, say less than 40 dynes per cm, variations in its surface tension are not likely to occur and the hydrometer reading may be taken in a simple cylindrical hydrometer jar The liquid should be poured gently into the jar and the formation of air bubbles in the liquid avoided The hydrometer is inserted carefully into the liquid being held by the top of the stem and released when approximately in its position of equilibrium A little experience soon enables one to appreciate when the hydrometer is approaching equilibrium and to release it in such a position that it rises or falls by only a small amount when released When the hydrometer has been released the reading is noted approximately, and then, by pressing down on the top of the hydrometer stem with the finger and thumb, the hydrometer is immersed a few millimetres beyond its position of equilibrium and then allowed to come to rest If the liquid is transparent the reading is then taken at the intersection of the level liquid surface and the stem, the scale being viewed through the liquid and the eye being brought level with the liquid surface If the liquid is opaque the scale reading corresponding to the top of the meniscus is taken and an amount added to this to allow for the height of the meniscus and obtain the reading at the level surface

Liquids of high-surface tension, say above 40 dynes per cm, e g mixtures of mineral acids and water, solutions of salts, &c, are liable to exhibit considerable variations in surface tension due to surface contamination A vessel having provision whereby some of the liquid can be overflowed immediately before taking the hydrometer reading should be used for such liquids A simple and convenient vessel is shown in Fig 2 By adding sufficient liquid to the vessel to cause a small volume to overflow at the side tube *A*, immediately before placing the hydrometer into the liquid, consistent and reliable readings can be obtained

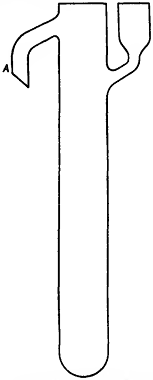

FIG 2 Overflow vessel for reading hydrometers

It is generally sufficient to observe the temperature either immediately before or immediately after taking the hydrometer reading It is safer, however, to observe the temperature both before and after taking the hydrometer reading, in order to confirm that the temperature conditions are sufficiently steady It is generally more convenient to take the hydrometer reading with the temperature of the liquid the same or nearly the same as the prevailing room temperature rather than to place the hydrometer jar in a constant temperature bath Though thermometers are often incorporated in hydrometers, it is more general, and preferable, to use a separate thermometer and a simple hydrometer

Having obtained the hydrometer reading and the temperature of the liquid, it is necessary, strictly speaking, to apply the following corrections in order to obtain the density of the liquid at the temperature of observation

(*a*) a correction for the scale error of the hydrometer at the point read,
(*b*) a correction for the change in volume of the hydrometer between 20° C and the temperature at which the reading is taken,
(*c*) a correction for the difference between the surface tension of the liquid and that for which the hydrometer is adjusted

In practice, however, the need for applying these corrections may be avoided by

(i) using a hydrometer with suitably small scale errors,
(ii) by arranging the temperature of observation to be sufficiently near to 20° C As, however, the correction under (*b*) is small, see Table I, comparatively wide departures from 20° C are possible,
(iii) by using a hydrometer adjusted for a surface tension appropriate to the liquid whose density is required

The corrections under (*a*), (*b*), and (*c*) are, however, considered in detail below in order to demonstrate their magnitude and make it possible to determine, for any required accuracy in the final result, whether or not any particular correction may safely be neglected

(*a*) Scale Errors.

The maximum permissible scale error and the length of scale equivalent to this is given below for the I P T hydrometers

	Series A	*Series B*	*Series C*	*Series D*
Maximum permissible scale error	0 0004	0 001	0 0015	0 002
Average equivalent length of scale	1 3 mm	1 5 mm	1 5 mm	1 4 mm

Thus, in each series, the maximum permissible scale error corresponds to about 1 5 mm in scale length This represents an accuracy which might well be expected without an unduly high cost of production Hydrometers, however, should not be accepted 'on trust', but their scale errors should be determined before the hydrometers are put into service In this connexion it may be mentioned that The National Physical Laboratory undertake the testing of hydrometers and it will often prove more convenient to use hydrometers which have been tested at The National Physical Laboratory rather than for the user to carry out his own verification of the hydrometers Hydrometers made to the I P T specification, for example, may be submitted to The National Physical Laboratory either simply for verification that they are accurate within the prescribed tolerances or for a certificate giving in addition the corrections actually determined, and the I P T specification itself states 'No hydrometer shall be regarded as "standard" unless it has been tested by The National Physical Laboratory for accuracy and dimensions and certified by The National Physical Laboratory monogram being etched upon the instrument'

(*b*) Temperature Corrections.

If the temperature at which the hydrometer is read is not 20° C then the correction necessary owing to the change in volume of the hydrometer between 20° C and the temperature at which the hydrometer reading is taken may be obtained from Table I

The corrections in Table I are expressed in units in the fourth place of decimals and when + are to be added to and when − subtracted from the observed reading at $t°$ C.

It will be seen that the corrections in Table I are very small For example, over the range of density 0 6 to 1 g per ml, which practically covers the requirements of the petroleum industry, the correction does not exceed one unit in the fourth place of decimals, which is negligibly small for most practical purposes, over the temperature range 15 to 25° C Again, over the whole range of density 0 6 to 2 g per ml the corrections do not exceed five units in the fourth place of decimals over the temperature range 10 to 30° C

TABLE I

Temperature Corrections for Hydrometers Adjusted to indicate Density in g per ml at 20° C

Observed hydrometer reading at t° C	*Temperature t C*								
	0° C	*5° C*	*10 C*	*15 C*	*20° C*	*25° C*	*30° C*	*35° C*	*40° C*
0 600	+3	+2	+2	+1	0	1	−2	−2	−3
0 800	+4	+3	+2	+1	0	1	−2	−3	−4
1·000	+5	+4	+3	+1	0	1	−3	−4	−5
1 200	+6	+5	+3	+2	0	−2	−3	−5	−6
1 400	+7	+5	+4	+2	0	−2	−4	−5	7
1 600	+8	+6	+4	+2	0	2	−4	−6	−8
1 800	+9	+7	+5	+2	0	−2	−5	−7	−9
2·000	+10	+8	+5	+3	0	−3	−5	−8	−10

If the density of the liquid is required at some temperature other than the temperature of observation this must be obtained by making an allowance based on the coefficient of expansion of the liquid, as the hydrometer itself can only give the density at the temperature of observation

(*c*) Surface-Tension Corrections.

The method of calculating surface-tension corrections is given in the following section, but here an indication of the magnitude of the corrections will be given Owing to the large variation in the dimensions of hydrometers at the present time it is not possible to give corrections of general application We will therefore take as an example density hydrometers agreeing in dimensions with the I P T Series A hydrometers In Table II, corrections, expressed as units in the fourth place of decimals, are given for the differences in surface tension, stated at the head of each column, between the surface tension of the liquid in which the hydrometer is read and the surface tension for which the hydrometer is adjusted When the surface tension of the liquid is *greater* than that for which the hydrometer is adjusted the correction is to be *added* to the observed reading and, when the liquid has a lower surface tension, the correction is to be *subtracted* from the observed reading

TABLE II

Example of Surface Tension Corrections

Hydrometer reading g per ml	*Difference in surface tension, dynes per cm*							
	5	*10*	*15*	*20*	*25*	*30*	*35*	*40*
0 650 to 0 700	1	2	4	5	6	7	8	9
0 700 to 0 750	1	2	3	5	6	7	8	9
0 750 to 0 800	1	2	3	4	6	7	8	9
0 800 to 0 850	1	2	3	4	5	6	8	9
0 850 to 1 100	1	2	3	4	5	6	7	8

Suppose a hydrometer, of range 1 to 1 05 g per ml and subdivided into intervals of 0 0005 g per ml, to which the corrections of Table II are applicable, i e one agreeing in dimensions with the I P T Series A hydrometer of this range, were to be adjusted to a surface tension of 35 dynes per cm—a reasonable value for heavy oils. If this hydrometer were to be used in dilute sulphuric acid solutions having a surface tension of 75 dynes per cm. then the readings in the acid would be 0·0008 g. per ml. too low, equivalent to 1·6 subdivisions or 2·6 mm. on the stem of the hydrometer. Conversely, if the hydrometer were correct in sulphuric acid it would read 0·0008 g. per ml. too high in heavy oils.

As another example, a density hydrometer of range 1 to 1·05 g. per ml. and subdivided into intervals of 0·002 g. per ml. and having the dimensions of an I.P.T. Series D hydrometer, if correct in sulphuric acid solutions would read 0·0045 g. per ml., equivalent to a length of 3·4 mm. or more than two subdivisions on the scale, too high in heavy oils.

These examples show clearly the necessity for hydrometers being adjusted for a surface tension appropriate to the liquid in which they are used, or for the application of appropriate corrections if they are not so adjusted.

Surface-Tension Factor of a Hydrometer

The term surface-tension factor is used as a convenient expression for indicating the amount by which the reading of a hydrometer changes due to 1 dyne per cm. change in surface tension.

Perhaps the simplest method of deducing the surface-tension factor of a hydrometer is as follows.

Suppose a hydrometer to indicate density correctly in a liquid at a temperature of 20° C. and having a surface tension equal to T_1 dynes per cm. Let this hydrometer be transferred to a second liquid also at 20° C. and having the same density as the first liquid but a surface tension equal to T_2 dynes per cm. Suppose T_2 to be greater than T_1. Then in the second liquid the hydrometer will float with more of its stem submerged than in the first liquid owing to the increased downward pull on the stem due to the higher surface tension. Equilibrium will be attained in the second liquid when this additional downward pull is exactly balanced by the increase in upward pressure on the hydrometer due to more stem being immersed in the liquid. The increase in downward pull is:

$$\pi \times \frac{d}{10} \times (T_2 - T_1) \text{ dynes,}$$

and the increase in upthrust is equal to the weight of the additional liquid displaced, i.e. to

$$\frac{\pi}{4} \times \left(\frac{d}{10}\right)^2 \times \frac{h}{10} \times K\rho \times g \text{ dynes,}$$

where d = diameter of hydrometer stem in mm.,
h = additional length of stem, submerged, expressed in mm., when the surface tension increases from T_1 to T_2,
ρ = density of liquid in g. per ml.,
K = factor for converting density in g. per ml. to density in g. per cm.^{3} which, for the present purpose, may be taken as unity without significant loss of accuracy,
g = acceleration due to gravity in cm. per sec.^{2}

Equating the above expressions and rewriting the equation, we have

$$h = \frac{400(T_2 - T_1)}{\rho d g} \qquad (1)$$

Now, the surface-tension factor has been defined as the change in reading due to 1 dyne per cm. change in surface tension. If λ mm. is the length of scale equivalent to a change in density of 0·001 g. per ml. the change in reading corresponding to a stem length h is $[(h/\lambda) \times 0{\cdot}001]$ g. per ml. Hence, the surface-tension factor, ϕ_ρ say, is equal to $[(h'/\lambda) \times 0{\cdot}001]$ g. per ml., where h' is the value of h given by equation (1) when $(T_2 - T_1)$ is unity. We therefore have

$$\phi_\rho = \frac{4}{10\rho\lambda dg} \text{ g. per ml.} \qquad (2)$$

It is sometimes convenient to express the surface-tension factor in terms of subdivisions on the hydrometer scale, and in this form we will denote it by ϕ_l. If l is the length of one subdivision and h' is, as before, the value of h given by equation (1) when $(T_2 - T_1)$ is unity then

$$\phi_l = \frac{h'}{l},$$

or, substituting for h' from equation (1),

$$\phi_l = \frac{400}{l\rho dg} \text{ subdivisions} \qquad (3)$$

From expression (3) for ϕ_l it is clear that the greater the value of $l \times d$, i.e. the product of the length of a subdivision and the stem diameter, the less will be the value of ϕ_l. In the design of a hydrometer, therefore, the value of the product $l \times d$ should be kept as small as compatible with other requirements. This fact is not generally recognized in the design of hydrometers.

The method of computing surface-tension corrections such as those given in Table II will now be clear. Taking the expression (2) for ϕ_ρ and applying it to a hydrometer of range 0·95 to 1 g. per ml. for which λ = 3·3 mm. and d = 6·35 mm. (I.P.T. Series A dimensions) we have

$$\phi_\rho = \frac{4}{10 \times 0{\cdot}975 \times 3{\cdot}3 \times 6{\cdot}35 \times 981},$$

$$\phi_\rho = 0{\cdot}000020 \text{ g. per ml.}$$

The change in reading for 1 dyne per cm. change in surface tension is therefore 0·00002 g. per ml., and if the hydrometer is adjusted for a surface tension T_1 the correction necessary to readings taken in a liquid having a surface tension T_2 is

$$(T_2 - T_1) \times 0{\cdot}00002 \text{ g. per ml.}$$

Hence when $T_2 - T_1$ is equal to 5 dynes per cm. the correction amounts to one unit in the fourth place of decimals, and when $T_2 - T_1$ is 40 dynes per cm. the correction amounts to 8 units in the fourth place of deimals. It will be seen that these values agree with those given in Table II.

Use of Hydrometers in determining the Weight of a Known Volume of Oil

In this section only the part played by the hydrometer in the determination of the weight of a known volume of oil or the volume of a known weight of oil will be considered. Apart from the effect of surface tension it is the density of the oil which determines the position of equilibrium of any hydrometer floating in it. Hence, whatever the scale of the hydrometer, the indication of the instrument is a function of the density of the liquid in which it is floating, and so the weight per unit volume of the liquid, at the temperature at which the hydrometer reading is taken, can be determined. This is the sole contribution of the hydrometer to the procedure of determining the weight of a known volume of oil, or vice versa, and alone need concern us here.

As an example, the weight in lb. per gal. of a liquid having a density ρ g. per ml. at t° C. will be calculated. The density ρ may be obtained most simply by reading a hydrometer, adjusted to indicate density in g. per ml. at 20° C., in the liquid at the temperature t° C. and, if the accuracy required demands it, correcting for the scale error of the hydrometer, applying the necessary temperature correction from Table I and making any necessary surface-tension corrections

Let W be the weight in air in lb of a quantity of the oil which occupies 1 gal at $t°$ C, the liquid being at the temperature $t°$ C when weighed From the equilibrium existing at the time of weighing if W is determined by direct weighing in air we have

$$W \times G\left(1-\frac{\sigma}{\Delta}\right) = K(\rho-\sigma)$$

or

$$W = \frac{K}{G} \times \frac{1}{(1-\sigma/\Delta)} \times (\rho-\sigma), \qquad (4)$$

where K = number of millilitres equivalent to 1 gal = 4545 96,
G = number of grams equivalent to 1 lb. = 453 592343,
σ = density of air in g per ml (0 0012 g per ml will be taken as an average value),
Δ = density of weights used in g per ml (8 3 g per ml will be taken as an average value for brass weights)

The coefficient of $(\rho-\sigma)$ in (4) is a constant which may be determined from the numerical values quoted and the equation is in a convenient form for calculating W for any determined value of ρ

It is not, however, necessary to carry out the computation in full for every determination as the work can be simplified considerably by means of a table constructed as follows

The value of W obtained from equation (4) will always be approximately equal to 10ρ, a result which follows directly from the definition of the gallon If, therefore, the differences between W and $10\,\rho$ are calculated by means of equation (4) for a series of values of ρ, and these differences divided by 10 are tabulated as in Table III, we obtain a simple means of converting g per ml to lb per imp gal, which is made clear by the example following the table Table III has been constructed to cover a range of density adequate for petroleum products, and it will be seen that only a small and simple table is necessary

TABLE III

Correction Table for Conversion of g per ml to lb per imp gal

Density in g per ml at t° C	*Correction for calculating weight in lb of quantity of liquid occupying 1 imp gal at t° C*
0 65	0 0003
0 70	0 0004
0 75	0 0006
0 80	0 0007
0 85	0 0008
0 90	0 0009
0 95	0 0010
1 00	0 0012
1 05	0 0013
1 10	0 0014

As an example of the use of Table III let 0 8764 g. per ml be the density of an oil at $t°$ C The appropriate correction from Table III is 0 0009 and the weight of the quantity of oil which occupies 1 gal at $t°$ C is

10 (0 8764+0 0009) = 8 773 lb.

Table III may also be used to obtain weights per U S A gal by multiplying by 8 3268 instead of by 10 Thus, in the above example the weight of the quantity of oil which occupies 1 U S A gal at $t°$ C is

8 3268 (0 8764+0 0009) = 7 305 lb

Tables I and III may be combined to obtain corrections directly applicable to the observed hydrometer reading at $t°$ C for the purpose of conversion of the readings to lb per gal This has been done in Table IV In this table the hydrometer reading in the first column is the reading on a hydrometer correctly adjusted for a surface tension appropriate to the liquid in which it is read, or an observed reading corrected for any difference between the surface tension of the liquid in which it is read and the surface tension for which it is adjusted

TABLE IV

Corrections Table for obtaining lb per gal from Readings on a Density Hydrometer adjusted to indicate Density g per ml at 20° C

Hydrometer reading at t° C	*Temperature, t° C*								
	0° C	*5° C*	*10° C*	*15° C*	*20° C*	*25° C*	*30° C*	*35° C*	*40° C*
0 65	+7	+6	+5	+4	+3	+2	+2	+1	0
0 70	+8	+7	+6	+5	+4	+4	+3	+2	+1
0 75	+9	+8	+8	+6	+6	+5	+4	+3	+2
0 80	+11	+10	+9	+8	+7	+6	+5	+4	+3
0 85	+12	+11	+10	+9	+8	+7	+6	+5	+4
0 90	+14	+13	+12	+10	+9	+8	+7	+6	+5
0 95	+15	+14	+13	+12	+10	+9	+8	+7	+5
1 00	+17	+15	+14	+13	+12	+10	+9	+8	+6
1 05	+18	+17	+15	+14	+13	+11	+10	+9	+7
1 10	+20	+18	+17	+15	+14	+12	+11	+10	+8

The corrections in Table IV are expressed as units in the fourth place of decimals

Example of use of Table IV

Observations

Hydrometer reading (R) = 0 8764 g per ml
Temperature of oil, $t°$ C = 10° C

Derivation of lb per gal

By interpolation between the values given under 10° C against 0 85 and 0 9 respectively in Table IV, the correction appropriate to a temperature 10° C and a hydrometer reading 0 8764 is +0 0011

Hydrometer reading (R)	= 0 8764
Correction from Table IV (c)	= +0 0011
($R+c$)	= 0 8775
Weight of oil which occupies 1 imp gal at 10° C = 10($R+c$)	= 8 775 lb
Weight of oil which occupies 1 U S A gal at 10° C = 8 3268($R+c$)	= 7 307 lb

The weight in air of 1 litre of oil may also be obtained readily from a reading on a density hydrometer

Let ρ g. per ml be the density of a liquid at $t°$ C determined from the reading of a density hydrometer, in the liquid at $t°$ C

Let ρ' be the apparent weight in air in grams of the quantity of oil which occupies 1 ml at $t°$ C.

Then

$$\rho'\,(1-\sigma/\Delta) = \rho-\sigma$$

or

$$\rho' = \rho-\sigma\,(1-\rho/\Delta)$$

TABLE V

Conversions of Density—g per ml at t° C—to Weight in kg per litre

Density of liquid in g per ml at t° C	Correction to give weight in air in kg of the quantity of the liquid which occupies 1 litre at t° C
0 60 to 1 03	−0 0011
1 04 to 1 72	−0 0010
1 73 to 2 00	−0 0009

Now density in g per ml is numerically equal to density in kg per litre and the weight in grams of 1 ml is numerically equivalent to the weight in kg of 1 litre and so tabulating the second term of the above equation as corrections we obtain Table V

Thus if 0 8764 g per ml is the density of an oil at $t°$ C the weight in air of the quantity of the oil which occupies 1 litre at $t°$ C is 0 8764−0 0011, i e 0 8753 kg

We have thus seen that a hydrometer adjusted to indicate in g per ml at 20° C can be used in conjunction with quite simple tables to obtain

(*a*) weight in lb of 1 imp gal ,
(*b*) weight in lb of 1 U S A gal ,
(*c*) weight in kg of 1 litre

NOTE Since the above article was written the recommended basis of adjustment for hydrometers, namely, that they should indicate density—mass per unit volume—in grams per millilitre at 20° C has been adopted by the British Standard Institution [3, 1936]

REFERENCES

1 *Standard Methods for Testing Petroleum and its Products,* 1st ed , 1924, 3 and 3rd ed , 1935, 144

2 STOTT, V Hydrometers and Hydrometry *Proc World Petr Cong , London,* **2,** 880 (1933)

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INDUSTRIAL INSTRUMENTS

By H. HARPER, S.M., B.Sc., A.I.C., A.M.I.Chem.E.

During the past decade the range of application of instruments to industry in general has been extended to such an extent that in the most highly developed and complex industries the measurement and automatic control of the major process variables has been completely adopted, with the result that all factors affecting the quantity and quality of the final products are determined and regulated from the time the raw materials are first handled.

The trend towards complete scientific and automatic control is the result of economic stress and the continually increasing demand that products should conform to more numerous and more rigorous specifications. The demand of industry for suitable equipment to achieve this closer control has been met by the development and supply of instruments which, as the result of accumulated experience, are improved upon year by year.

The use of instruments which control the process automatically, in addition to measuring it, has grown rapidly. Such instruments can be adopted only when they are at least as accurate as the manual control which they are augmenting or replacing and when their cost is offset by adequate saving in the cost of supervision of the process. This stage has been generally reached and surpassed, on the one hand owing to the improved accuracy of modern instruments, and the employment of standard parts in their construction, resulting in lower price, and, on the other hand, to the gradually increasing cost of skilled manual supervision.

Temperature

Temperature may be defined in general terms as the 'level' or potential at which heat is available. Differences in temperature between two bodies exist when heat can be caused to flow from one to the other, the direction of the transference being from the higher 'level', or temperature, to the lower.

The datum 'level' or reference potential may be arbitrarily chosen at any convenient point, such as that at which phase transition occurs in any pure element or compound. In principle, temperature may be measured by any physical property of a substance which changes with temperature and which is susceptible of easy and accurate measurement.

The absolute zero of temperature may be defined in terms of various physical phenomena. Nevertheless the principles established by Carnot's investigations in 1824 into the reversible heat engine, in which heat is converted into work, taken in conjunction with the Second Law of Thermodynamics, enable a definition of absolute zero temperature to be made in such a way that it is independent of the thermometric substance used, viz. 'Only when a temperature of absolute zero is available can the whole of a given quantity of heat be converted into work.' These principles also enable the following definition to be made of equal intervals of temperature such as are required in graduating a scale for temperature measurement, as was first established by Kelvin.

'Equal differences of temperature exist between a series of systems when equal amounts of work are done by a series of reversible engines working between them and arranged so that each engine receives the heat rejected by the preceding engine in the series.'

Just as the datum 'level' may be arbitrarily chosen, so may the temperature intervals be selected at will. The most widely used datum level is the temperature of melting ice under 1 atmosphere absolute pressure, which is taken as zero. The temperature of pure water boiling under the same pressure is taken as the other limit of the temperature interval. As this temperature difference is too large for general use it has been subdivided into 100 equal parts according to the Centigrade scale, and into 180 equal parts according to the Fahrenheit scale—these parts being Centigrade degrees and Fahrenheit degrees respectively. The zero of the Fahrenheit scale has, however, been selected at a level 32 Fahrenheit degrees below the melting-point of ice under 1 atmosphere pressure, so that the melting-point of ice is 32° F. and the boiling-point of water is 212° F. These scales of temperature may be referred back to absolute zero by the addition of 273° (or 273.09 exactly) to the Centigrade temperature and 460° to the Fahrenheit temperature. Conversely, absolute zero may be referred to alternatively as −273° Centigrade or −460° Fahrenheit.

In actual practice other well-determined points of reference may be employed in the calibration of temperature-measuring devices in addition to the melting-point of ice and the boiling-point of water, such as

	Temperature	
	°F	*°C*
Solidification-point of liquid tin	449	232
„ „ , lead	621	327
„ , zinc	787	419.4
Boiling-point of liquid sulphur	832.5	444.7
Solidification-point of liquid antimony	1,166	630
„ „ „ aluminium (97.7% pure)	1,218	659
Melting-point of solid gold	1,945.5	1,063
Solidification of liquid copper	1,981	1,083
Melting-point of solid nickel	2,646	1,452
„ „ solid palladium	2,831	1,555
„ „ platinum	3,191	1,755

The Measurement of Temperature

The properties of substances which may be conveniently utilized in the measurement of temperature are thermal expansion, vapour pressure, thermo-electric force at the junction of two different metals, the electrical resistance of metals, and the luminosity of radiating bodies. Instruments used in the measurement of temperature may therefore be classified as follows, depending upon the physical property employed:

Group (*A*) Thermometers, of the gas or liquid expansion or vapour-tension types.
„ (*B*) Resistance thermometers.
„ (*C*) Thermo-electric and optical pyrometers.

Group (*A*). Gas, Liquid, and Vapour Tension Thermometers.

The most convenient thermometer depends upon the thermal expansion of substances, especially liquids. However, it is unfortunately found that, if two thermometers partially filled with different liquids are calibrated at the melting-point of ice and the boiling-point of water, the scale intermediate between these points on each thermometer being graduated into the same number of equal parts, the thermometers do not in general indicate the same scale reading when both are at some intermediate temperature

If, instead of being filled with liquid, the thermometers are filled with different gases, the scale indications agree much more closely at all temperatures regardless of the chemical composition of the gas employed All gases, if at a constant small pressure, so that they are under ideal conditions, expand 1/2 732 of their volume between the melting-point of ice and the boiling-point of water This interval is 100° Centigrade, and therefore 1° C may be defined, in terms of an ideal gas thermometer, as the temperature change over which the volume of an ideal gas (at constant pressure) changes 1/273 2 of its volume at 0°C This temperature scale is identical with the thermodynamic temperature scale based on the Second Law of Thermodynamics

In 1887 the International Committee of Weights and Measures specified the standard thermometric scale as that of the constant volume hydrogen thermometer, the hydrogen being at an initial temperature of 0° C and at a pressure of 1,000 mm of mercury, measured at sea-level and latitude 45°

The first thermometer, invented by Galileo about 1595, was filled with air, using water or alcohol as an indicator only A few years later the first liquid expansion thermometer was developed, the filling of the bulb being wine, and by the middle of the seventeenth century hermetically sealed thermometers using mercury as the thermometric substance were in existence

While the mercury-in-glass thermometer is of extensive use in laboratory work on account of the wide range of temperature over which it may be employed, viz approximately −40° C to +550° C, and also the extreme accuracy obtainable in the measurement of small temperature differences as with the Beckmann type, nevertheless its fragility and the necessity of the scale being close to the point of temperature measurement restrict its utility in industrial practice, except for checking purposes, and for readings of an occasional nature

To fulfil the need for an instrument capable of (*a*) robust construction, (*b*) being read at a point remote from the point of measurement, and (*c*) being used for continuous recording, a thermometer has been developed comprising a metal bulb connected by a fine capillary tube to a Bourdon tube, the whole being filled with mercury or other suitable liquid, or with a gas The thermal expansion of the liquid or gas in the bulb, which is exposed to the temperature under investigation, supplies the pressure to deflect the Bourdon tube in such a way that a pointer coupled thereto is moved over a calibrated scale Alternatively the system may be only partially filled with a suitable liquid from which the vapour fills the remainder of the system In this type of instrument the vapour pressure varying with temperature actuates the pointer through the medium of the Bourdon tube, as in the case of the liquid- or gas-filled type

The liquid-filled thermometers are sometimes denominated Class I instruments, the vapour-pressure type thermometers as Class II instruments, and the gas-filled thermometers as Class III instruments

The capillary tubing used to connect the Bourdon tube to the bulb must be of exceedingly fine bore in order that its volume should be small in proportion to the volume of the bulb, otherwise changes in the ambient temperature (i e the temperature of equipment other than the bulb) may appreciably upset the accuracy of the instrument, particularly when the temperature being measured is low and large fluctuations are liable to occur in the atmospheric temperature This error which theoretically does not occur with vapour-pressure type thermometers is termed capillary error, and may be compensated for in a variety of ways

By using fine-bore tubing of internal diameters as low as 0 005 in, thereby decreasing the volume of fluid outside the bulb Further diminution of this error is obtained by the use of a flattened-type Bourdon tube and the use of

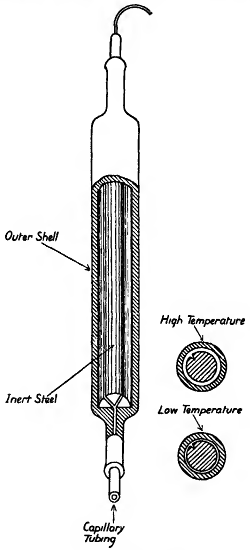

FIG 1 Compensated capillary

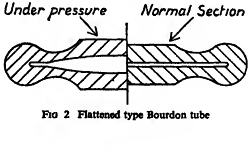

FIG 2 Flattened type Bourdon tube

'Compensated Capillaries' such as are used by Negretti and Zambra in their mercury-in-steel thermometers and illustrated in Figs 1 and 2 By this means the capillary error may be reduced, for example, to 0 2% of the scale range of 50–250° F for an 18° F change in the ambient temperature using a capillary 24 ft long

Another method of accomplishing the same end is by the use of a compensating element comprising a balancing length of capillary tubing and compensating Bourdon tube which are exposed to the same change in ambient temperature, and being without a bulb merely serve to reset the indicating or recording element and act as an automatic zero-setting device This type of compensation has been adopted by the Foxboro Company in their 'Anti-ambi' instrument Changes in the ambient temperature will also cause errors if only one Bourdon tube is employed, due to variations in the elasticity of the Bourdon tube material This error may be overcome by means of a bimetallic compensating coil forming an extension of the innermost turns of the Bourdon tube This form of compensation is generally employed when the case and tubing are at a uniform temperature

A further source of error in thermometers is thermometric lag which results in a high reading with falling temperatures and a low with rising temperatures Chief among the factors upon which this phenomenon depends are

1 The rate of heat transmission from the outside medium to the outside wall of the bulb This can be improved by the production of turbulence round the bulb and by having the largest possible outside area of contact in relation to the volume of the contents
2 Conductivity and heat capacity of the bulb material
3 Conductivity and heat capacity of the thermometric substance

Factors 2 and 3 require high conductivity for the bulb material and thermometric substance with low specific heat in both instances In addition, the size of the bulb should be as small as possible to reduce lag This is opposed, however, to the necessity for having the bulb volume large in comparison with the capacity of the capillary tubing and Bourdon tube so that a balance must be struck in design

Limitations and Comparative Merits of the Various Classes of Thermometers.

Class I. Liquid-filled Type. The liquids commonly used as thermometric substances are

Mercury	for ranges	—40°	to +	1,200° F
Alcohol	,,	−155°	,,	260° F
Ether	,, ,,	+70°	,,	195° F
Xylene	,, ,	−40°	,,	750° F
Paraffin base oil soln			,,	400° F

This class is subject to capillary error, which may be minimized as described above, also to thermometric lag in greater degree than the Class III gas-filled type owing to the higher specific heat, mass, and thermal conductivity of the thermometric substances used Mercury-filled thermometers usually have smaller thermometric lag than those filled with the other liquids because, although the specific heats are comparable, mercury has a much higher thermal conductivity than the other liquids

Owing to liquids being practically incompressible the operating force of Class I instruments is very high, so that the Bourdon tube and gauge in general may be made robust and of relatively low sensitivity

In the vapour-filled and gas-filled types of thermometers the Bourdon tube is used as a pressure gauge, whereas in the liquid-filled type it is essentially a volume-measuring device, liquids being comparatively incompressible, and any small variation in the pressure exerted on the mercury does not appreciably alter the accuracy of its deflections Consequently hysteresis error or lag, such as is exhibited by Class II and Class III instruments, whereby rising temperatures are indicated low and falling temperatures high, is likely to be a fault of comparatively negligible magnitude in Class I instruments

Class II Vapour-pressure Type. Vaporizing liquids commonly used as thermometric substances are

Alcohol	for ranges	150	to	390° F
Ether	,, ,,	50	,,	350° F
Sulphur dioxide	,, ,,	−20	,,	+250° F

Owing to the fact that the vapour pressure of a liquid is not a straight-line function of temperature, but is a curve of increasing slope with rising temperature, the gauge on this class of thermometer must be calibrated with a non-uniform scale having close intervals at the lower temperatures changing progressively to open intervals with rising temperature This restricts the range for which the scale may be calibrated since, if it is only just sensitive enough in the upper ranges, it may be too insensitive in the lower ranges

One advantage of this class of thermometer over the other two classes is that although not entirely free from capillary error, owing to the difficulty in making the vapour space absolutely air or gas free, the permissible length of capillary tubing is somewhat greater than with Class I and III instruments The thermometric lag may also be less owing to the improved thermal conductivity of a vaporizing or condensing liquid

On the other hand, the pressure changes available for operating the indicating or recording element are small, and the gauge must be of more sensitive construction than the Class I type

Furthermore, it must be calibrated for the bulb and indicator in the same relative position as in the final installation in order to obtain accurate results, although actually this correction may be comparatively small Changes in barometric pressure are liable to affect the accuracy of this class of thermometer As a class, this type of instrument is particularly suitable where the lower temperature readings are unimportant, but where close readings must be obtained at the working portion of the chart

Class III. Gas-filled Type. The gases commonly used as thermometric substances in this class of thermometer are nitrogen and hydrogen which are charged under pressure Since an 'ideal' gas at constant volume for 1° C temperature rise increases in pressure 1/273 of its pressure at 0° C, in order to obtain a greater operating force in the Bourdon tube, which in uncoiling operates the indicating mechanism, the thermometer is filled with the gas at pressures up to 100 atmospheres

As indicated above, an 'ideal' gas would give a perfectly uniform scale of calibration, and nitrogen and hydrogen approach this ideal condition reasonably closely.

With this class of thermometer the limiting factor is not the thermometric substance, but the material of which the bulb is composed At high temperatures the bulb may soften and become porous. By choosing appropriate materials for the bulb this class of thermometer may be

FIG. 4

FIG. 5

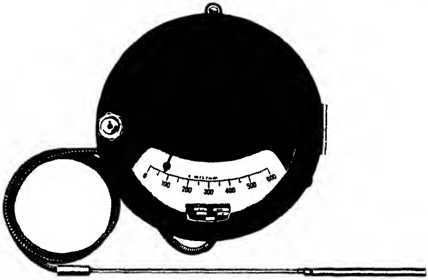

FIG. 6

used over a temperature range of -130 to 600° C As previously explained, this type of thermometer is subject to capillary error which diminishes with increasing ratio of the capacity of the bulb in relation to the capacity of the capillary tube and Bourdon tube

Owing to the high pressures at which gas-filled instruments are usually charged, changes in barometric pressure are unlikely to have any appreciable effect on the accuracy of the instrument For example, a change of $\frac{1}{2}$ in in the barometer theoretically affects the temperature indication in a Class III instrument charged at 100 atm pressure, even at the highest temperature for which this class is employed, less than $\frac{1}{2}$° C, and this error is compensated for in the design of the instrument Furthermore, as the instrument is entirely filled with the thermometric substance no appreciable error results should the position in use differ from the position at calibration

Mechanical Features of Group (*A*) Instruments

Bulbs The type of bulb selected should be suited to the particular circumstances in which it is to be used, as one standard form of bulb will not give the best results in all applications Consequently, accuracy can only be assured by giving consideration to the conditions of radiation, conduction, and convection to which it will be subjected These in turn must be correlated with the type of thermometric substance to be used Furthermore, the medium surrounding the bulb must be taken into account and special precautions taken should this be corrosive in character Bulbs may be obtained in copper, brass, lead, steel, and monel metal and may also be plated with chromium, tin, nickel, silver, &c

Plain bulbs are used where they may be directly suspended in open tanks, ventilating ducts, combustion chambers, &c Specially designed bulbs, with screw unions, are available for screwing into pipelines, tanks, and vessels under pressure or vacuum where a rigid pressure-tight coupling is desired Both these and the plain bulbs may be arranged with bendable extension necks to suit confined spaces

A particularly interesting development is the 'capillary bulb', which is designed to obtain maximum responsivity, for the measurement of atmospheric temperatures The length of the bulb is greatly increased and the diameter reduced so that the bulbs can be strung across ducts or flues to obtain a representative record covering the entire area When used as a component of a vapour-pressure type instrument capillary bulbs will measure a temperature which is above the arithmetic average along the bulb and approach the maximum or hot-spot temperature

Capillary Connecting Tubing. The capillary connecting tubing is generally fabricated of copper or steel suitably covered Examples of typical coverings available, and of the circumstances for which they are particularly suitable, are given below

Flexible Bronze Sheathing with Asbestos Packing Impervious to oil and moisture, standing comparatively high temperatures without failure Should not be handled excessively

Rubber-covered Woven Fabric Hose over Flexible Bronze Sheathing, also Moulded-rubber Covered Flexible Bronze Sheathing Suitable for corrosive fumes

Plain Copper Sheathing Suitable for repeated handling

Plain Steel Sheathing Useful where tubing will be subjected to caustic or other substances corrosive to copper

Flexible Galvanized Steel Sheathing Suitable for humid caustic conditions corrosive to copper

Plain Lead Sheathing Suitable for use in acid and other severe conditions

Aluminium Sheathing Suitable for use in refinery fumes combined with sea air

Bourdon Tube. Several modifications of the Bourdon tube are in use In general principle, however, they are alike in that, as is essential, the internal volume is reduced to a minimum by flattening the tube upon itself as in Figs 2 and 3

Certain manufacturers modify the plain section of the tube in the manner shown on Fig 2 so as to relieve the stresses set up on expansion This reduces the possibility of fracture resulting from fatigue which occurs with repeated dilation Made of bronze or steel the tube may be in a single convolution or, if of multiple convolutions, either in the form of a spiral or helix

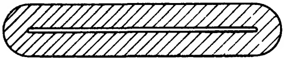

Fig 3 Plain flattened type Bourdon tube

A typical Bourdon tube, in this case of the spiral type, is shown in Fig 4 This has two continuous coils, each of several turns, both ends being situated near the centre of the coil

One end is fixed and leads to the capillary, the other end, which is closed, is attached to a small bimetallic coil which forms a continuation of the Bourdon coil and compensates for changes in its temperature This small coil is attached directly to the pointer spindle or pen arm An increase in temperature causes the pressure or volume of fluid inside the capillary and Bourdon to increase The latter undergoes an increase in its sectional area, the coil becoming to a small extent less flattened in form, which alteration in turn causes it to unwind

Owing to the special formation of the tube, the pointer would thus be caused to rotate truly about its axis even if no bearings were provided for its spindle Actually, bearings are generally provided to steady the pointer against vibration, but the friction loss involved is practically negligible

An alternative type of arrangement is shown in Fig 5 In this instance the Bourdon tube is of one convolution, although several turns forming a helix may be employed In order to obtain radial pointer deflection, the movement of the free end of the tube is transferred through a rack and pinion movement

At the free end of the tube is a trough *C* in which the ball end *D* of the segmentary rack *B* is free to move As the tube *A* uncoils it releases the ball end *D* which is forced to follow in contact with trough *C* by the tension of the hair-spring *E* on the pinion *F* which is in mesh with the segmentary rack *B* The pointer is fastened to the end of pinion *F* and is deflected a definite amount proportionate to the movement of the free end of the tube *A* As the moving power for the pointer, which is of specially light construction, is obtained from the released hair-spring there is no lost motion This ball and trough design gives uniform multiplication, and by avoiding angularity makes possible the use of duplicate standard dials

The Brown Instrument Company arrange for calibration being effected by means of a micrometer adjusting screw which varies the length of the arm through which the helical Bourdon tube rotates the pen shaft

A typical distant indicating thermometer is shown in Fig 6 In the recording instrument the dial is replaced by a graduated chart which may be of the circular or strip type The rotating chart holder, or cylinders in the case of the strip chart, may be operated by clockwork or by means of a synchronous motor The chart is divided into hourly parts with subdivisions so that the recorded temperature at any time of the day may be obtained In the recorder the indicator pointer is replaced by a pen

Specially prepared charts are available for humid tropical conditions In addition the cases can be made air and moisture proof, and the air inside the case dried by providing containers holding a supply of calcium chloride or similar hygroscopic material

Group (*B*). Resistance Thermometers.

The electrical resistance thermometer is suitable for measuring temperatures from −300° to +1,000° F This group of instruments is especially convenient for measuring temperatures below 300° F At such temperatures thermoelectric pyrometers, such as are described in Group (*C*), are not desirable because of the low electromotive force generated by the thermocouple The same instrument can be applied to measure both high and low temperatures with equal accuracy

Furthermore, the electrical resistance thermometer is capable of much wider application than the Group (*A*) instruments described above, as it may be used for the observation, recording, or controlling of temperatures at a considerably greater distance Accurate readings are obtainable at a distance of half a mile

A further advantage of this type of instrument over those in Group (*A*) is that it is particularly suitable for multipoint recording or controlling, and can be used to register on one instrument, located at a convenient position, the temperatures which exist at a large number of scattered points The accuracy of the readings is quite unaffected by the distances between the point of measurement and the indicator In addition the average of a number of temperatures, existing for example in a building, can be measured by installing, at various points, elements which are suitably coupled together

Operating Principle. In this group of thermometers the known variation of the electrical resistance of metals with changing temperature is employed as a means of measuring temperature Platinum, nickel, and copper are most generally used for this purpose Taking platinum as an example, an approximation to the relationship between the electric resistance at a temperature t_2 and a temperature t_1 is given by the equation

$$R_2 = R_1[1+\alpha(t_2-t_1)] \text{ ohms}, \qquad (1)$$

where R_2 is the resistance at temperature t_2,

R_1 " " " t_1.

α is the resistance-temperature coefficient at t_1

This equation gives only small errors at low temperatures, but the inaccuracy increases with rising temperature A truer relationship is the parabolic expression

$$R_t = R_0(1+\alpha t+\beta t^2), \qquad (2)$$

where R_t is the resistance at temperature t, R_0 the resistance at 0° C, and α and β are constants The shape of the curve representing the above relationship enables the sensitive element to be calibrated against three standard temperatures, e g melting-point of ice, boiling-point of water, and boiling-point of sulphur, all at atmospheric pressure

The sensitive element is formed of a coil of fine wire, the resistance of which depends upon the temperature being measured This coil, which is wound on a suitable former, is enclosed in a tube or casing, the material of which depends upon the temperatures at which the element is to be employed and the specific protection it requires both chemically and mechanically

The measurement of the resistance of the element is effected by means of a form of Wheatstone bridge, and in the early days the actual resistance was determined, and translated afterwards to temperature by calculation or reference to a graph In the early instruments the unknown resistance of the element was manually balanced Referring to Fig 7, a battery *B* was connected to the terminals *a* and *b* of a parallel connexion containing three known adjustable resistances R_1, R_2, and R_3, and the unknown resistance R_x, a galvanometer being connected between *c* and *d*

The galvonometer consists essentially of a light coil of fine wire suspended between the poles of a permanent magnet

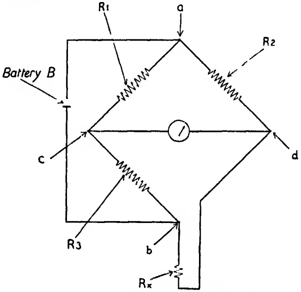

FIG 7 Circuit for resistance thermometer

The resistances R_1, R_2, and R_3 were adjusted until no current flowed through the galvanometer and R_x was calculated, from the known values of R_1, R_2, and R_3 This is known as the 'null' or balanced-bridge type of measurement

Later the Wheatstone bridge was arranged with a bridge wire upon which a contact was adjusted to vary the resistance on either side of the bridge until the galvonometer showed the point of balance The temperature was read direct upon a scale associated with the bridge wire This balanced-bridge operation still called for manual operation which proved a stumbling-block in the way of the general use of the balanced-bridge type of instrument until the advent of the automatic self-balancing type, such as the Leeds & Northrup Micromax instrument described later under Temperature Recorders.

The unbalanced-bridge method is commonly used In this the 'out of balance' current through the galvanometer is used to indicate the temperature The arrangement of the Wheatstone bridge is therefore generally as indicated in Fig 8

R_1, R_2, R_3, and R_4 are fixed resistances, of material with small change of resistance with temperature

R_5 is a variable resistance or rheostat

R_x is the element, of unknown resistance

When the bridge is in balance the deflection of the galvanometer is zero, but as the resistance of the element increases or decreases with change in temperature, current flows through the galvanometer causing it to deflect The deflection is read directly in terms of temperature The arrangement shown in Fig 7 has two limitations to its accuracy

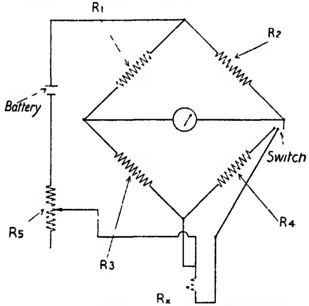

FIG 8 Circuit for resistance thermometer (unbalanced bridge type)

(a) Variations in the battery voltage which affect the galvanometer deflexion

(b) Variations in the resistance of the cable connecting the sensitive element R_x, due to changes in the ambient temperature, will affect the galvanometer deflection In Fig 8 it will be seen that a triple cable is used to connect the element into the circuit A connexion is made to both sides of the bridge, so arranged that there is an equal amount of cable resistance on each side, and consequently any change in the resistance of the cable due to atmospheric temperature change does not affect the balance of the bridge

Variations in the battery voltage may be checked from day to day in the following way R_1 and R_2 are made as coils of equal resistance Coils R_3 and R_4 are made equal to the resistance of the element R_x at the highest and lowest temperatures for which the instrument is graduated By means of a switch the sensitive element R_x is disconnected and R_4 connected. The rheostat R_5 is adjusted until the galvanometer reading is at the lowest graduation The checking or 'standardization' of the measuring instrument may be effected as in the Electroflo instruments by employing a magnetic shunt in place of the rheostat which is liable to contact troubles This shunt consists of an iron yoke, the position of which in relation to the magnet poles is varied by hand as required, thus altering the distribution of magnetic flux and the movement of the coil relative to the galvanometer scale Hand adjustment is eliminated in the arrangement of the Foster electric resistance thermometer shown in Fig 9 The galvanometer is arranged with a control coil C which functions so that the indications are independent of change in the battery voltage The force limiting the deflection of the galvanometer pointer is due to the control coil C A fall in the battery voltage would, therefore, reduce in the same proportion and at the same time the deflecting force due to the galvanometer coil and the controlling force due to coil C In order to keep the bridge in balance a small coil R_4 is added in the opposite arm of the bridge to balance the control coil C

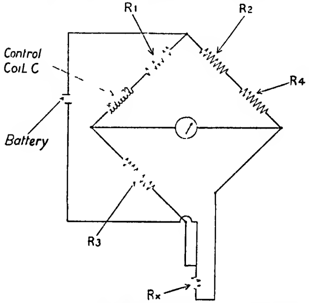

FIG 9 Circuit for resistance thermometer (with galvanometer control coil)

Resistances in the bridge are made high in comparison with the resistance of the connexions to the sensitive element, so that changes in the ambient temperature have no appreciable effect on the battery current

It is common practice for instrument makers to provide a sensitive element such that, as the temperature increases from 0 to 100° C the element resistance increases by, say, 10 ohms This is called a 10-ohm fundamental interval If closer readings are required, the fundamental interval is increased to, say, 20 ohms, in which case the scale interval is halved, but whereas with the 10-ohm fundamental interval the temperature may be read to a single degree, with the double resistance the temperature may be read to ½ degree

Sensitive Elements. The sensitive elements for normal temperatures, e g up to 360° C, usually consist of fine pure nickel wire wound on a bobbin or other support which eliminates risk of deformation in service Above 360° C platinum wire mounted on a refractory bobbin, of such material as steatite, is used. For example, the platinum wire may be wound in a thread cut on a steatite former which is reinforced or stiffened by heavy internal wires. The whole is then coated with a ceramic glaze to protect it against contamination.

Electric Current Supply. Resistance thermometers require to be provided with an external supply of low-tension current. This may be obtained either from an accumulator or from a dry cell. Where accumulators are used two are generally provided so that one may be charging while the other is in use, trickle-charging from either a.c. or d.c. mains being commonly employed for renewing the charge in the stand-by accumulator.

General Note on Resistance Thermometers. An accuracy of plus or minus 1° F., or even better, under industrial conditions, can be obtained with this type of instrument. Furthermore, although considerably more expensive as a single point indicator than a corresponding liquid filled instrument, for reading a multiplicity of temperatures it may be eventually cheaper to employ this type of thermometer. For example, should it be necessary to obtain readings of temperatures at a dozen points, this may be easily and simply effected by switching the connexions from the sensitive elements, one after another, to a single indicator or recorder. This system, which can be made automatic, is limited only by the frequency with which the temperature at each point must be read, and is considerably cheaper than a series of single, double, treble, or quadruple point liquid-filled thermometers to give an equal number of readings.

Moreover, this type of instrument has the great advantage that the indicator or recorder may be located up to eight or nine hundred yards from the sensitive element without impairing the accuracy of the temperature measurement. The advantages of this type of instrument for the measurement of temperatures may be summarized as follows:

1. It is capable of measuring distant temperatures.
2. It can measure temperatures at a large number of points, or the average thereof.
3. No cold junctions are required.
4. The bulbs are small and extremely sensitive.
5. High resistance ensures accuracy under varying ambient conditions.
6. No trouble from gas or liquid leaks.
7. Battery deterioration cannot detract from accuracy.

Mechanical Arrangement of Moving Coils in Indicating or Recording Instruments. It is obvious that the mechanical arrangement of the moving coil is of great importance as far as the suitability of the instrument to industrial conditions is concerned. It must be so mounted that it is sensitive to extremely small changes in the current flowing through it. The coil is generally fitted with finely pointed pivots operating in jewelled bearings. Should the instrument, as may often occur in transit or in industrial use, be subjected to vibration or jarring, unless carefully designed the pivots and bearings may be momentarily separated and in returning into position strike one against another. This would blunt the needle-fine pivot points causing them to acquire a greatly increased bearing surface with consequent loss in sensitivity, or would damage the highly polished jewel surfaces. Various methods are used to prevent this such as supporting the two jewel bearings resiliently on springs from the main body of the instrument but rigidly mounted with respect to each other. Alternatively the magnetic field of the permanent magnet is used instead of springs by supporting the jewel bearings on light iron armatures.

In one design the magnetic field in which the coil moves is established between poles of a permanent magnet and a cylindrical iron core. The coil carrying the current, by means of which the measurement is made, swings in annular space round the core and between it and the magnet poles. The coil is fitted usually with two opposed inturned pivots which rest in two conical jewels mounted at either end of a very light staff. This staff is passed through the axis of the cylindrical core and is held in position relative thereto by means of light springs. Any jolt of the instrument will, therefore, move the whole system of coil, pivots, jewels, and staff so that the possible separation of the jewels and pivots is obviated. In this design the weight of the pointer, which is attached to the coil and moves over the calibrated temperature scale, is counterbalanced by mounting the coil in a slightly eccentric position relative to the axis of the staff, final adjustment of balance being obtained by means of a small sliding weight on the pointer arm. This construction avoids the use of a counterweight tail and counterweight, thus enabling the weight of the whole moving system to be so reduced that the instrument may still preserve sensitivity although the controlling forces may be small.

Sensitivity to extremely small controlling forces is especially necessary in the case of thermo-electric pyrometers such as are described below.

Group (*C*). Thermo-electric Pyrometers.

The basic principle underlying thermo-electric pyrometry was discovered by Seebeck in 1821, when he found that if in a closed circuit consisting of two dissimilar metals the two junctions are at different temperatures an electric current will flow in the circuit, the electromotive force of which depends upon the difference in temperature of the junctions.

The e.m.f. developed is very small, usually of the order of tens of millivolts. Thus it is possible to calibrate a millivoltmeter in terms of this temperature difference. Essentially the meter measures, not the temperature of the hot junction located at the point where the unknown temperature exists, but the difference of temperature between the two junctions. Should, therefore, the cold junction temperature be known (generally it is kept constant) the system provides a means of determining the temperature of a heated object by reckoning upwards from the cold junction temperature by a temperature interval equivalent to the generated e.m.f. In practice, therefore, an industrial pyrometer of this group consists essentially of:

1. A thermocouple consisting of two wires of dissimilar metals, either pure or alloys, fused together at one end, the hot junction.
2. A millivoltmeter or potentiometer.
3. Cables or wires to connect the other ends of the two wires, or cold junction, of the thermocouple to the millivoltmeter or potentiometer.
4. Means of measuring the cold junction temperature, or of maintaining it manually or automatically at a predetermined value.

Thermocouples. An ideal thermocouple possesses the following properties:

(*a*) A large electromotive force for unit-temperature difference.
(*b*) Strength and ruggedness consistent with economy in cost.
(*c*) Constant electro-potential characteristics.

(*d*) Electromotive force generated in direct proportion to the difference of the terminal temperatures

The wires used in thermocouples may be composed either of noble or base metals or their alloys, and the following table summarizes the characteristics of those most commonly employed

Type	*Metals used* *Positive*	 *Negative*	*Maximum operating temperature ° C*	*Approx e m f at maximum operating temperature*
Base metal	iron	constantan	760	41 7 millivolts
,,	nichrome	constantan	760	57 2
,	,,	nickel-aluminium	1 000	39 7
Noble metal	platinum-rhodium	pure platinum	1,600	18 0
,	platinum-iridium	pure platinum	*1 000	22 75 (at 1 400° C)

* Tendency to volatilize at higher temperatures

Generated e m f s may be converted to temperature by various formulae, but each of these is only accurate over a limited temperature range A typical formula is

$$E = a+bt+ct^2, \tag{3}$$

where E is the e m f measured in millivolts,

t the temperature of the hot junction in ° C, the cold junction being at 0° C,

a, b, and c are constants the values of which depend upon the metals which form the thermocouple

Tables are available which give the e m f for every degree over the working temperature range for all the well-recognized pairs of metals used for thermocouples, and these tables are more satisfactory for practical use than empirical formulae It will be noted from the above table that, although the noble metal thermocouples are the only ones which may be used for very high temperatures, the e m f generated is considerably lower than is given by the base metal thermocouples The most sensitive type of millivoltmeter or potentiometer is therefore required for the former On account of expense the noble metal thermocouples are made up of fine wire which involves high resistance and consequent low current carrying capacity The use of high internal resistance in the meters in order to minimize the effect of changing temperature along the conducting wires increases the necessity for employing a moving-coil system in the meter of the lightest and most sensitive type obtainable Base metal pyrometers, on the other hand, being relatively cheap may be made up in thicker low-resistance wire, and are capable of generating a considerably more powerful operating force They may, therefore, be used in conjunction with a relatively heavy moving-coil system

All thermocouples must be calibrated before use, but even so, depending upon their composition and the conditions under which they are used, they depart more or less rapidly from their original calibration and must be checked periodically against a standard If base metal couples are used at high temperatures, the necessity will arise for frequent recalibration This is due to changes in the metal structure and to the development of heterogenicity

For moderate temperatures, below the upper limit for base metal thermocouples, the choice between noble metal and base metal thermocouples will be decided by the following factors

(*a*) The importance of continued accuracy

(*b*) The nature of the medium surrounding the thermocouple

(*c*) The cost

Noble metal couples are liable to contamination in reducing atmospheres, and iron/constantan couples in oxidizing atmospheres

Mechanical Design of Thermocouples In order to protect thermocouples against contamination, they are fitted, except for low temperatures, with protective coverings The wires are first insulated by means of single or double hole silica or porcelain tubes Over this is fitted a silica or porcelain tube closed at the hot junction end which protects the couple against contamination Covering this is an additional outer sheath, frequently of metal This outer sheath is to protect the inner one mechanically against breakage In the case of high temperatures or particularly corrosive atmospheres it may be necessary to have the outer sheath also of porcelain or silica The inner and outer sheaths are usually fitted into a gas-tight terminal head to which the leads or connecting wires are attached This head is really the cold junction

Cold Junction Temperature Correction As the magnitude of the e m f developed by a thermocouple is determined by the difference of the terminal temperatures the cold end is generally maintained at a known temperature Alternatively the necessary correction must be made manually, automatically, or calculated from accurate temperature readings taken at the cold end of the thermocouple

In the case of base metal couples this correction amounts to practically the same number of degrees as the cold junction temperature differs from the zero, and approximately one-half of this value in the case of noble metal thermocouples

Many pyrometers are equipped with zero adjusters for the manual correction of the pointer position to compensate for the cold end change but, as this is usually constantly varying, this adjustment is not of great use To overcome this difficulty some form of automatic adjustment is generally fitted This, in certain cases, takes the form of a thermostatic bimetallic spiral or helix, the deflection of which is directly proportional to the change in temperature of the surrounding medium It is, therefore, very suitable for moving the control spring, thereby correcting the pointer position A bimetallic spiral is used in this way by the Brown Instrument Company If the temperature of the instrument, which is that of the cold junction when compensating leads are used, rises from, say, 75 to 100° F, the spiral uncoils sufficiently to move the pointer upscale the equivalent of 25° F

Compensating Leads. Such a device as the bimetallic spiral referred to above provides a compensation within the instrument for the difference between the temperature of the atmosphere surrounding the instrument and 0° C at which the millivoltmeter is calibrated By connecting the head of the thermocouple to the instrument with compensating leads formed of the same metals as the thermocouple, or of metals having the same thermo-electric characteristics, the cold junction is in effect transferred to the point where the leads join the instrument The combination of such leads with a thermostatic compensator provides complete automatic cold junction compensation

In cases where a considerable number of thermocouples are in use, and it is important for accurate temperature readings to be obtained, it has been found advantageous to extend all thermocouples by means of compensating leads to a common centrally located thermostat which maintains all the cold junctions at a constant temperature, thus enabling a constant correction to be made and reducing cost by permitting all leads from the thermostat to the recorders to be of ordinary copper wire This arrangement obviates the need for automatic compensation in the instrument itself

This scheme is capable of several modifications, for example, the thermocouples may be extended by means of compensating leads to a junction box Also connected into this junction box is a couple made up of one set of additional compensating leads—the junction of which is buried at a sufficient depth underground to give a reasonably constant (within 5° F) cold junction temperature throughout the year This becomes a compensating couple, the hot junction temperature of which corresponds to the cold junction of the thermocouples The compensating couple is arranged in series between the instrument and the selector switch (if such is used), and sets up in opposition to that of the thermocouple a back e m f which varies with the cold junction temperature of the thermocouple This method may be used where the cost of running compensating leads to a central instrument is too expensive, since all leads from the junction box to the instrument may be of ordinary copper wire

In the Wilson-Meulan potentiometer pyrometers made by the Foxboro Company the resistances in the Wheatstone bridge of the instrument are made of metals having a negligible thermo-electric coefficient The fourth resistance, which is located at the cold junction (compensating leads being brought from the thermocouple to the instrument), is constructed as a nickel coil having a high thermo-electric coefficient The electrical resistance of this coil, therefore, varies with the cold junction temperature, and permits a varying and compensating current to flow from the bridge battery to the galvanometer to correct the couple e m f In the Leeds & Northrup potentiometer pyrometer a nickel coil is also used for the same purpose This may be located at the instrument when compensating leads are used, or alternatively at the cold junction should this be some distance from the measuring instrument

Meters. For measuring the e m f set up by a thermocouple two types of meters are available, viz

(*a*) Millivoltmeters
(*b*) Potentiometers

Millivoltmeters Potentiometers measure only the e m f existing at the point of reference or cold junction, whereas millivoltmeters are affected by line resistance and must be calibrated for a definite value Millivoltmeters are therefore liable to inaccuracies arising from such factors as corrosion, loose contacts, or temperature change This objection is overcome, however, by using millivoltmeters with high internal resistance so that the error arising from changes in line resistance are reduced to a minimum

Potentiometers This type of instrument is generally considered the most accurate which is available for measuring the electromotive force set up by a thermocouple It provides a means for obtaining a known variable potential, and suitable electrical connexions for connecting it in opposition to the unknown electromotive force of the thermocouple So long as one is stronger than the other a current will flow through the thermocouple, when they are equal no current will flow

Fig. 10 shows a simple potentiometer circuit A dry cell B supplies a constant flow of current through the slide-wire resistance C–D For each position of the slider F there exists a definite difference of potential between the points C and F The circuit, containing a galvanometer G and a thermocouple M, is connected to the points C and F In this circuit the potential difference between C and F is opposed by the e m f of the thermocouple By moving the slider F the potential difference between C and F can be so adjusted that it will exactly balance the e m f of the thermocouple and the galvanometer will be undeflected This is known as the zero balance or null method In practice a scale is associated with the slide wire which is calibrated to indicate in terms of e m f the position of the slider Alternatively it may be calibrated to read, with suitable compensation, directly in terms of the temperature of the hot junction of the thermocouple The null method employs the galvanometer merely as a current detector The galvanometer is therefore uncalibrated, and as it does not require to be confined to the limits of any temperature scale it can be given the greatest possible sensitivity and greatest deflection per degree of temperature This feature of the potentiometer method of temperature measurement is distinctly advantageous for automatic control where detection and reaction with the slightest temperature change is essential for close control Furthermore, the galvanometer, being uncalibrated, may be replaced without upsetting the accuracy of temperature measurement

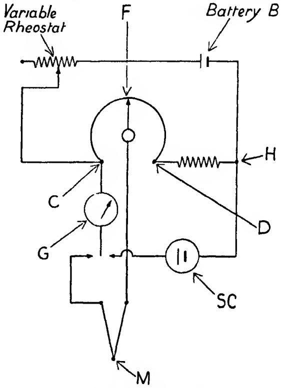

FIG 10 Simple potentiometer circuit

In Fig 10 SC is a standard cell whose voltage is constant. It is connected to the potentiometer circuit at points C and H by closing the contact (shown between SC and the galvanometer) whenever the potentiometer current is to be standardized The galvanometer is then in series with SC The variable rheostat A is then adjusted until the galvanometer is balanced, and in this way the current flowing in the slide wire CD is standardized.

Instead of employing the null method, in certain instruments the galvanometer deflection is used to indicate the extent to which the potentiometer is unbalanced

Switches. Switches are employed to connect thermocouples in rotation to a single indicator or multi-point recorder For indicating purposes a switchboard of the plug-in type similar to a manual telephone switchboard is used, or alternatively a rotary switch in which the contactor arm is moved from one contact stud to another For use with a multi-point recorder electrically driven commutator type switches are commonly employed

The number of pyrometers which may be coupled by means of a mechanical selector switch to a recorder depends largely upon the stability of the temperatures being measured and the necessity or otherwise of a short interval record Under favourable circumstances, mechanical switching of this type may be used for the recording of 16 to 20 temperatures

It is essential that such rotary switches be moisture and dust proof, particularly when used in conjunction with a millivoltmeter instrument Where parallel operation of a recorder and indicator is adopted it is advisable to install cut-out switches which interrupt the moving-coil circuit of the recorder and incidentally all records of the thermocouples while the indicator is being read This is particularly useful to eliminate errors due to parallel operation when high-resistance noble metal couples are used

Optical Pyrometers This type of instrument is used for the measurement of instantaneous temperatures above 750° C (1,382° F), and is particularly suited for the investigation of the temperatures of small hot bodies at a comparatively long working distance dictated by the relative inaccessibility of the hot body Its operation involves the comparison of the intensity of light radiated by the hot body with that emitted by a calibrated filament This instrument is known as the 'disappearing filament' pyrometer

The optical pyrometer consists in its essentials of the following items

(*a*) A telescope through which the heated object is viewed

(*b*) A lamp bulb, having a heated filament to emit light the intensity of which can be compared with that emitted from the heated object

(*c*) A rheostat to vary the current passing to the lamp bulb

(*d*) A milliammeter or millivoltmeter to measure the current passing to the lamp bulb, complete with an indicator, the scale of which is generally graduated directly in terms of temperature

(*e*) An electrical accumulator to supply the current

For work of moderate accuracy the voltage drop across the lamp is used as a measure of the temperature

For more accurate work the Wheatstone bridge principle is resorted to, using a milliammeter as the bridge galvanometer The circuit in this instance is shown in Fig 11

The resistances *A*, *C*, and *D* are so arranged that no current flows through the milliammeter when the current flowing through the lamp filament is that required to heat the filament to a temperature corresponding to the lowest end of the scale. For measuring higher temperatures over the range of the scale the rheostat is adjusted so that the current flowing through the lamp filament is progressively greater As the temperature of the filament rises its resistance increases, and the other resistances *A*, *C*, and *D* being made of material which does not alter its resistance with change in the amount of current flowing, the bridge is thrown out of balance, with the result that as more current flows through the filament a corresponding increase takes place in the flow through the milliammeter, the pointer of which deflects to readings up the scale

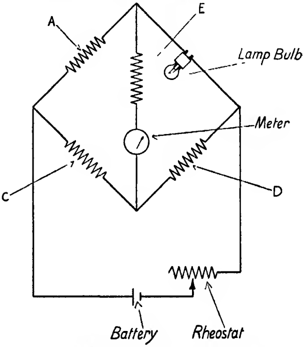

FIG 11 Lamp bridge circuit for optical pyrometers.

In order to avoid the calibration of the instrument being upset by changes in the temperature of its surroundings a slump resistance is included at *E* and the instrument calibrated with this in position This slump resistance is of sufficient magnitude to ensure that changes in the temperature of the instrument do not appreciably affect its readings The arrangement described above is typical of that employed in the Foster Instrument Company's 'Lamp-bridge Unit'

As previously stated, a telescopic arrangement is adopted in this type of instrument, the optical system being as illustrated in Fig 12

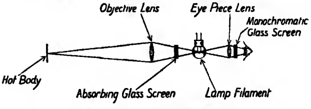

FIG 12 Optical system of hot filament pyrometers

The lamp filament is viewed through the eyepiece which is adjusted so that the filament is sharply focused The objective lens is moved until the hot body is seen in the same field of view with the filament superimposed on it. The rheostat is then adjusted until the filament just fades out against the hot body (i e is neither more brilliant nor darker in appearance, but merges completely), and the milliammeter or millivoltmeter is read directly in temperature A monochromatic red glass screen inserted in front of the eyepiece lens prevents dazzle at temperatures above

1,500° F, and also obviates colour differences For exceedingly high temperatures, above 2,600° F at which the life of the filament would be reduced, or its calibration be impaired, an absorbing glass screen is inserted between the filament and the objective lens so that the filament is compared with a reduced intensity of light emitted by the hot body Thus the highest temperatures can be measured with a suitably calibrated instrument without danger of overheating the filament A special high-temperature scale is provided for use when the absorbent screen is in use An accuracy within 5° C at a temperature of 1,200° C may be expected of an instrument of this class when dealing with black body radiation, as, for example, when a surface inside a furnace is viewed through a comparatively small aperture In the open, where the surface may be illuminated from outside, correction factors are necessary In the case of a stream of molten steel at approximately 1,400° C so flowing that any oxide formed is rapidly broken up and does not affect the reading, positive correction of approximately 7% is found necessary to give an accurate result, similarly a stream of molten copper at approximately 1,200° C in the open will give a pyrometer reading about 16% low

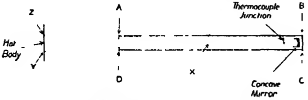

Fig 13 Diagrammatic arrangement of radiation pyrometer

Radiation Pyrometers This class of instrument may be used either to read or record the temperatures of hot bodies from about 950° F upwards Compared with an optical pyrometer it has a shorter working distance and is not so suitable for taking the temperatures of small hot surfaces It requires, however, a shorter time to take a reading, about 15 sec instead of 30, and has the advantage of being suitable for continuous reading or automatic recording

In principle a proportion of the radiant heat emitted from the hot body is allowed to fall upon a mirror which focuses it on the hot junction of a very small thermocouple, thus generating an electromotive force which is detected in a similar way to that employed in the thermo-electric pyrometers described above

The Stefan-Boltzmann law is an expression of the fact that the total energy radiated per unit area from any hot body which behaves as if it were one hundred per cent 'black' is directly proportional to the fourth power of the absolute temperature of the body, i e

$$q = kT_1^4, \tag{4}$$

where q = energy radiated per unit of time per unit area of body,

T_1 = absolute temperature of hot body

Actually, in determining the net energy received by the pyrometer the above equation should also be applied to the instrument which is simultaneously radiating energy

The net radiation received by the instrument may be expressed as

$$q = k(T_1^4 - T_0^4), \tag{5}$$

where T_0 is the absolute temperature of the receiving instrument However, as T_0^4 is negligible compared with T_1^4 the former term may be dropped in practice Then comparing the energy received by the radiation pyrometer at two temperatures T_1 and T_2 we get

$$\frac{Q_1}{Q_2} = \left(\frac{T_1}{T_2}\right)^4, \tag{6}$$

and in accordance with this relationship radiation pyrometers are calibrated This results in a very open scale at the higher temperatures, since the energy received rises very rapidly with increase in temperature of the hot body

In the same way as light radiations can be focused by a concave mirror or convex lens, so can invisible heat radiations be focused, as, for example in the use of the 'burning glass' to concentrate the heat rays from the sun This method of concentrating heat rays enables a radiation pyrometer of convenient size to be made

The radiation pyrometer, therefore, consists of such an arrangement as is shown in Fig 13

ABCD is a tube having a fixed aperture *AD* at one end The heat rays, from the surface of the hot body delimited in elevation by *ZY*, are allowed to pass into the tube by pointing the aperture at the hot surface The heat rays pass to the closed end of the tube where they are intercepted by a concave mirror and concentrated on a thermocouple placed at the focus of the mirror

So long as the hot body fills the extended cone of vision *AXD* the operation of the instrument is independent of the distance between the hot body and the instrument In practice this is ensured by the stipulation of a maximum working distance which is a fixed multiple (usually 10 or 12) of the smallest cross-sectional dimension of the hot body For working distances less than this the cone of vision is completely filled Alternatively, with certain instruments the object may be focused to ensure that the cone of vision is filled

The thermocouple cold junction ends are attached to an electric circuit comprising a connecting cable and millivoltmeter

As noted above, the Stefan-Boltzmann law is only strictly applicable to true 'black' body radiation, i e from a body devoid of reflecting power Any hot body in a recess deeper than 1½ times the width of the opening is essentially under these conditions, and readings taken under such conditions will not be more than ½% out at 1,000° C This condition generally holds in the case of a furnace viewed through an inspection door In the open the error may be very much greater, but as the heat given out from a hot body bears a definite relation to its temperature a correction factor can be arrived at for any set of constant conditions which will enable the process temperature to be checked accurately at intervals as required for control of the process

The Measurement of Pressure

The measurement of the static pressure of fluids may be carried out by means of a variety of instruments and can be expressed in a great variety of units All units, however, basically refer to the height of a column of liquid which would produce at its base the pressure in question For example, the pressure of the atmosphere is most commonly measured in terms of the height of the mercury column which it will maintain against a Torricellian vacuum The density of mercury being known, the standard atmospheric pressure, chosen as 760 mm of mercury column, may be expressed as 14 7 lb per sq in In industrial work pressures above this value are commonly measured upwards from this standard pressure as datum line, and are known as gauge pressures, although for scientific work it is often more convenient to refer to the absolute pressure which includes the standard atmospheric pressure and which in effect actually refers back to the mercury column which can be supported by the pressure against a vacuum For sub-atmospheric pressures the absolute system of measurement is also preferable

Pressure and Vacuum Gauges.

Barometric Type For the measurement of pressures above or below atmospheric pressure the most accurate instrument is of the barometric type Generally in industrial practice it is found advisable to sacrifice the high accuracy of this type of instrument which is of a fragile nature (usually mercury-in-glass) for the greater ruggedness and strength of the Bourdon tube type of gauge Under certain circumstances, however, the advisability of having an instrument which does not age or require frequent checking to ensure close accuracy results in the barometric type holding its own Such circumstances arise, for example, in the case of a vacuum-distilling unit where even if Bourdon tube type vacuum gauges are employed it is advisable to have a reference instrument of the barometric type The Kenetometer as illustrated in Fig 14 and made by Brady & Martin Ltd is typical of the class of instrument available for industrial use

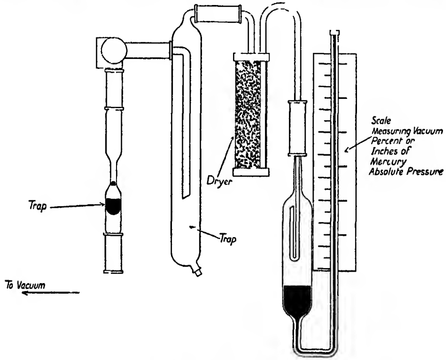

FIG 14 Kenetometer vacuum gauge

Mechanical Type of Pressure Gauge. The Bourdon tube type of instrument consists essentially of a tube wound in the form of a coil having a fixed open end and movable closed end, which with increase in internal pressure tends to uncoil or expand, and with decrease in internal pressure tends to coil or contract, the movement of the closed end being used to operate a pointer moving over a calibrated scale Such gauges may be used to measure all ranges of pressure. The coils may be made of bronze or steel, depending upon the corrosive characteristics of the liquid, vapour, or gas with which the coil is in contact, and also depending upon the pressure range

In order to avoid possible binding of the coils a helical arrangement of the tube is frequently adopted, the tube being formed in a flat cross-section similar to that described above as used with liquid-filled thermometers

For low pressure or vacuum conditions a bellows arrangement, such as is used in an aneroid barometer, is sometimes adopted The actuating movement consists of a series of metal diaphragms built up in the form of a bellows The straight-line movement of the free side of the bellows, with varying pressure, is converted into rotary movement and transmitted by levers to the shaft carrying the pointer or pen For the measurement of absolute pressure two bellows are arranged in opposition to provide a compensating action for varying atmospheric pressure One bellows is connected to the pressure to be measured, the other is evacuated and sealed If the absolute pressure in the measuring bellows remains constant and the barometric pressure increases, this bellows will tend to contract The sealed bellows will also contract, however, and, acting in opposition to the measuring bellows, will maintain the indicator stationary Mechanical gauges of these types should be periodically checked and calibrated, as owing to fatigue of metals, &c , they tend to lose calibration

Differential Manometers.

It is frequently necessary to measure the difference between two pressures This may be done, of course, by employing two gauges as described above, one for each pressure, and subtracting the readings, after correction if necessary

However, for very small differences in pressure resort is made to liquid-filled manometers of the U-tube type For example, the liquid-filled U-tube is widely adopted for measuring the differential pressure across the orifice of a flow meter

The difference in pressure between the two limbs of the U-tube causes a rise of liquid in one and fall in the other, the difference in level representing the difference in pressure

Multiplying Gauges.

A variation of the ordinary manometer is the inclined tube pressure gauge used for measuring furnace draught which is sub-atmospheric The draught draws the liquid (water, kerosine, or other light liquid) upwards through an inclined glass tube from a reservoir The inclination of the tube at 5 to 10° from the horizontal gives a multiplying effect, so that for an inch change in the water pressure the movement of liquid in the tube may be 7 or 10 inches Such instruments in industrial use are fitted with zero-adjusting screws for the scale or reservoir, drain-plugs and other facilities

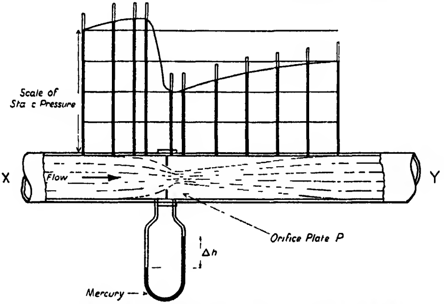

Fig 16 Diagrammatic arrangement of orifice plate and differential manometer

Another type of draught gauge consists essentially of an arm operating over a fulcrum, having at one end a bell inverted over and dipping into a trough of water At the other end a counterweight is also suspended partially submerged in the water Weighted pendulums are arranged on either side of the fulcrum Extending into the air space of the bell and reaching above the surface of the water is the draught tube. An increase of draught causes the air inside the bell to diminish, the water to rise, and the bell to sink until the pull is counterbalanced by the pull of the pendulum weights A pointer attached to the end of the arm moves over a calibrated scale from which the draught may be read The Bailey draught gauge shown in Fig. 15 is of this type

The Measurement of the Flow of Fluids

Two very important classes of instruments for the measurement of the flow of liquids and gases depend upon the conversion of static or pressure head to velocity head These are (*a*) orifice meters and flow nozzles, (*b*) Venturi meters

Orifice meters employ an orifice plate inserted in the conduit to bring about this conversion of heads A diagrammatic arrangement of this device is shown in Fig 16

In a section of the pipe *XY* an orifice plate *P* is inserted having an orifice area considerably smaller than the cross-sectional area of the pipe At a distance approximately 0 8 pipe diameters on the upstream side of the plate the lines of flow of the liquid flowing through the pipe just start to converge, and the velocity of the fluid starts to rise This convergence of lines of flow, and rise in velocity, continues until the fluid has passed through the orifice. The increase in velocity and velocity head is accompanied by a corresponding fall in static head as shown in the graph above the pipe In this graph the ordinates may be taken to represent the heights of the columns of fluid representing the static heads at various points in the path of the fluid After passing through the orifice the lines of flow continue to converge, reaching greatest contraction at a point about 0 4 pipe diameters downstream from the orifice plate Thereafter they diverge, but more gradually than in the corresponding convergence on the upstream side These distances are based on the pipe above and below the orifice being straight for at least 5 times the diameter of the orifice

The velocity head is the pressure difference, expressed in head of the flowing fluid, which is required to accelerate the fluid to the given velocity from rest The principle governing the measurement of flow in this way is given by Bernoulli's theorem which is a mathematical expression of the principle of the conservation of energy By equating the kinetic energy of the fluid at the given velocity to the fall in potential energy due to the drop in pressure necessary to give it this velocity the expression for the velocity head is simply derived, namely,

$$\Delta h = \frac{U^2}{2g}, \qquad (7)$$

where U is the linear velocity and g is the acceleration due to gravity

In the practical measurement of flow the velocity is calculated on the area of the orifice or the throat of the nozzle or Venturi meter In the case of an orifice meter the pressure difference actually measured corresponds more nearly to the velocity head at the point of minimum cross-section of the stream which is considerably smaller than the orifice itself In the case of nozzles and Venturi meters the effect of frictional losses have to be allowed for, and in all cases when the area of the constriction is not very much smaller than the area of the pipe the effect of the initial velocity of the fluid in the pipe has to be allowed for also

This is done by means of an empirical coefficient C, introduced into equation (7) which is usually rearranged as follows

$$U = C\sqrt{(2g\Delta h)} \qquad (8)$$

For a sharp-edged orifice in a thin plate fitted into a pipe more than about 5 times the diameter of the orifice the value of this coefficient is approximately 0 60, but the exact value depends on many circumstances which are more fully discussed elsewhere (See articles on 'Metering of Gases' by H S Bean, the 'Principles of Practical Orifice Metering' by E S L Beale, also the 'Principles and Practice of Flowmeter Engineering' by L K Spink) For a smoothly rounded orifice or nozzle, or a Venturi meter, the value is very nearly 1 0, usually about 0 98

Flow Meters (Orifice Type).

An industrial orifice type flow meter consists essentially of the following components

- (*a*) An orifice plate inserted in the pipe conveying the fluid
- (*b*) A differential gauge complete with indicating or recording device, to read or record on a calibrated scale or chart the flow as derived from the differential static pressure set up by the orifice plate
- (*c*) Piping to couple the differential gauge to the pressure tappings on the pipe

The orifice plate is inserted between flanges in the pipe and is very accurately drilled to give a sharp-edged orifice, generally of such diameter that the differential pressure in inches of water does not exceed twice the absolute static pressure expressed in pounds per square inch

The differential gauge is usually of the simple U-tube type with certain elaborations Typical of the normal U-tube design is the Foxboro instrument, the operation of which is illustrated in Fig 17

The differential pressure created in the pipe by the orifice is transmitted by a column of fluid to the differential chambers, sediment and/or, vapour traps in the connecting piping being employed to keep the meter free from dirt or vapours

A steel float rests on the surface of the mercury in the upstream chamber, and its motion is transmitted to the segmental lever which operates the pointer or pen arm through a pressure-tight bearing Check floats, located in each of the legs of the piping coupling the bases of the differential chambers, prevent the mercury being blown from the instrument by a sudden surge in flow, or overloading of the instrument For comparatively low static pressures the chambers are usually made of seamless mild steel, while for pressure above 1,000 lb per sq in static pressure forged-steel chambers are used The design of the pressure-tight bearing in which the spindle operating the pointer or pen works is of importance as it must be sufficiently tight to ensure no loss of pressure and yet free enough to avoid interference with the sensitivity of the instrument It is further important that there be no lost motion in the mechanism transferring the motion of the float, and advantageous that equal displacements of the float throughout the ranges of operation result in equal movements of the pointer or pen in order that the graduations on the scale or chart be uniform

The American Meter Company and Geo Kent Ltd employ a similar design of manometer, but the motion of the float is transmitted to the pointer or pen spindle direct by a hinged lever arm connecting the float to the spindle of the pen

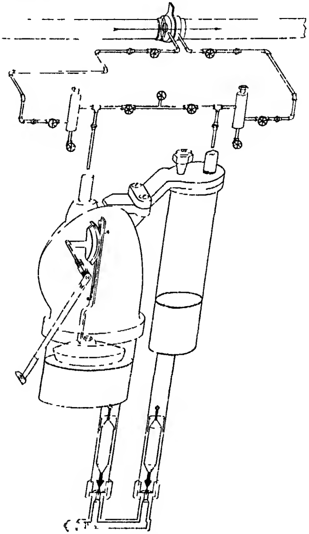

FIG 17

The Brown Electric Flowmeter employs a similar form of manometer, but instead of the motion of the float on the surface of the mercury in the upstream chamber being transmitted mechanically to the pointer or pen, it is transmitted by an electro-magnetic relay system as illustrated in Fig 18 As in the Foxboro instrument described above, the float carries a spindle In this case, however, the spindle takes the form of a magnetic armature which, as the float is displaced, moves up or down within a non-magnetic tube Located around this tube is a divided inductance coil which is supplied with a c current, and the ratio of the voltages across the two sections of the coil is governed by the position of the float and the armature attached thereto

Inside the indicating or recording section of the instrument is a counterbalanced armature suspended within a similar divided coil This armature is controlled by the electro-magnetic forces imposed upon it by the coils which are connected in the same electrical circuit as the manometer coils The manometer armature is held in position by the mercury-operated float, and the instrument armature moves in synchronism with it so that the ratio of voltage across the two sections of the two divided coils are equalized, and the electro-magnetic forces in the indicator or recording section are balanced The movement of a counterweight arm in sympathy with the instrument armature operates a geared section which in turn engages with a gear wheel on the pointer or pen spindle

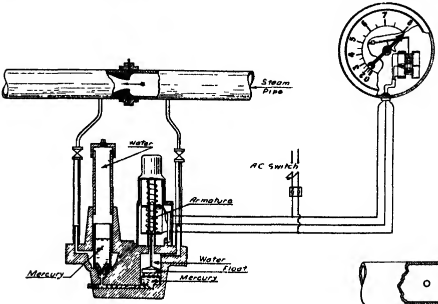

FIG 18

Another system, while employing a simple U-tube type manometer, discards the use of a float on top of the mercury The method of operation is shown in Figs 19 and 20

The low-pressure leg of the mercury U-tube contains a resistance-element chamber and oil-cooled internal resistance element When there is flow in the pipe the mercury level is depressed in the high-pressure chamber and raised in the resistance-element chamber

The rise of the mercury in the contact chamber makes contact with the ends of a series of rods of varying length, which at the other end are connected to the electrical circuit at points intermediate between a corresponding number of resistances arranged in series In establishing or breaking contact these resistances are cut out of or into the circuit, thus regulating the flow of current through the circuit which includes the annular mercury container and the mercury itself The resistance element is so made that the variation in conductance is always directly proportional to the flow of fluid in the pipe The current is suitably indicated or recorded by an instrument of the ammeter type which may be calibrated directly in terms of the flow By proper proportioning of the lengths of the rods the necessary allowance for the square root relationship between differential pressure and rate of flow may be made, so that the recorder or indicator scale is uniform

An example of direct magnetic coupling between the manometer and the indicating device is the Bailey Indicating Flow Meter illustrated in Fig 21

The differential manometer consists of a mercury-filled U-tube in which the differential pressure produced by the orifice is balanced by the fall of the mercury in the centre tube and the rise in the two side legs An iron ball, which floats on the surface of the mercury, varies in position with the differential pressure Around the tubes, which are made of non-magnetic material, is a U-shaped magnet which follows the ball The magnet is carried at one end of a beam supported on knife edges, and thus actuates a pointer which travels over a scale graduated in terms of the rate of flow of the fluid The Kent mer-

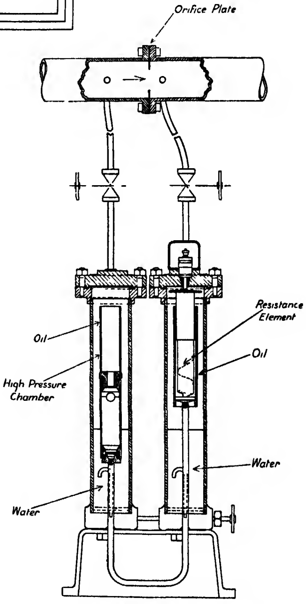

FIG 19 Electrical resistance type flow meter

curial magnetic manometer operates on the same principle and is similar in arrangement

Floating Bell Type Differential Manometer.

The floating bell design involves in effect a U-tube in which the two legs are concentric, the inner leg being sealed at the top to form a bell which with varying differential pressure floats higher or lower in the outer leg, thus replacing the float used in the plain U-tube design

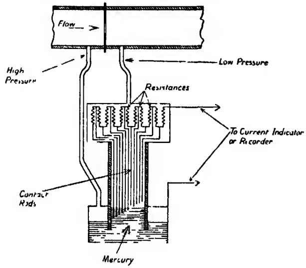

Fig 20 Diagrammatic arrangement of electrical resistance type flow meter

As employed in the Bailey fluid meter it takes the form shown in Fig 22

The upstream pressure is connected to the interior of the inner mercury-sealed leg known as the Ledoux bell, and the lower downstream pressure to the outer chamber The movement of the bell upwards or downwards in response to changes in the differential pressure is transmitted directly to the pen spindle by means of a forked lever hinged directly to the top of the bell Fig 23 illustrates the theory underlying the specially designed shape of the bell which is weighted and is of large diameter at the top and narrows towards the bottom Owing to the square root relationship between the velocity and the differential pressure the head available to operate the bell at 10% of the normal flow is only about 1% of the head at normal flow In order to produce a motion of the bell directly proportional to the rate of flow the bell in addition to being specially shaped as regards cross-section has thin walls at the bottom and thick at the top In zero position the bell is held almost completely submerged so that the large effective area and thin wall are at the surface of the mercury The increment of differential pressure corresponding to the first appreciable rate of flow is very small, but is brought to bear over the maximum area of the bell, forcing it upwards As the bell rises its walls emerge from the mercury, changing the buoyant force until this exactly counterbalances the upward force due to differential pressure This design ensures power at low rates of flow, and permits the use of a uniform chart

Of a somewhat similar design is the Foxboro Bell Type Meter for low-pressure gas-flow measurement In this case a large diameter bell is suspended inside the outer chamber by means of a calibrated spring The low-pressure side of the orifice is connected to the inner bell compartment, the higher upstream pressure being connected to the outer chamber The motion of the bell is transmitted to the pen spindle by means of a segmental lever as in the Foxboro flow meter previously described

In the Brown Low Range Manometer, which is used for the measurement of the flow of gases only, a bell design is adopted The interior of the bell is connected to the upstream pressure and the chamber to the downstream The top of the bell carries a vertical non-magnetic rod, at the top of which is an armature surrounded by a split inductance coil forming part of an electro-magnetic relay system

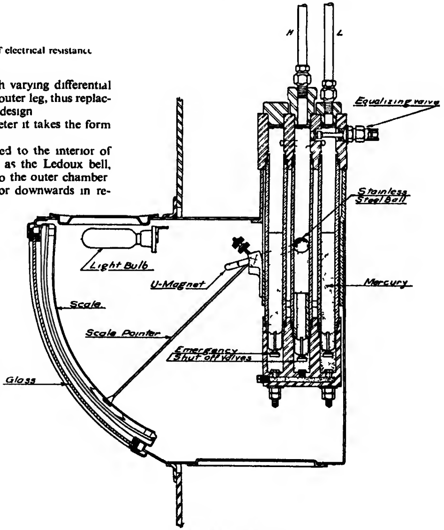

Fig 21 Bailey indicating flow meter

to the indicating or recording section of the instrument similar to that described above in the Brown Electric Flow Meter

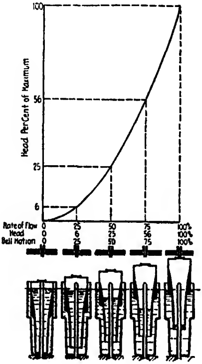

FIG 23

Flow Nozzles.

For very high rates of flow which would require an orifice greater than three-quarters the diameter of the pipe, flow nozzles are used in place of orifice plates on account of inaccuracies which would arise due to irregularities in the pipe Fig 24 shows diagrammatically a flow nozzle installed in a pipeline The nozzle is in effect a carefully machined throat

Straightening Vanes.

To obtain the most accurate results when using an orifice meter it is necessary that the lines of flow of the fluid be parallel as they approach the orifice To bring about this condition a straightening vane is used, generally consisting of a nest of small-diameter tubes fitted inside the pipe and located in a pipe nipple at a distance of about 6 pipe diameters on the upstream side of the orifice

Venturi Meters.

In the standard orifice the velocity head which has been created by the orifice from an equivalent static head is largely lost as internal friction and impact owing to the sudden enlargement in the cross-section of flow This means a permanent loss of much of the observed differential pressure, which is in some cases a serious disadvantage to the use of an orifice meter In such cases recourse is frequently had to a Venturi tube which has the great advantage that the permanent reduction in the static pressure is only about 12% of the manometer reading

Fig 25 shows a Kent Venturi tube The outstanding difference between this type of device and an orifice plate is that the contraction and enlargement of the cross-section of flow is effected gradually Usually the throat is lined with bronze and is very accurately bored and finely finished to a calculated diameter generally between $\frac{1}{2}$ to $\frac{1}{4}$ the upstream diameter For very high pressure recoveries the length of the throat should not exceed 1 throat diameter, and the total divergence of the tapered sides should not exceed an angle of 25° on the upstream side and 7° on the downstream side

The basic equation for the Venturi tube, derived from Bernoulli's theorem, is

$$\sqrt{(U_2^2 - U_1^2)} - c\sqrt{\{2g\Delta h\}}$$

Although very successful when measuring water and gas flow, the Venturi tube is unsatisfactory for viscous liquids

The Pitot Tube

The Pitot tube measures the velocity head of the fluid at one particular point in the cross-section of the pipeline, and if the velocity distribution is known the rate of flow can then be calculated The arrangement consists of a small bore tube inserted into the pipeline with its open end facing directly upstream to measure the impact pressure while the static pressure at the same point is measured by an opening in the wall of the pipe in the same plane The Pitot tube measures the velocity head as defined above and U actual $= \sqrt{\{2g\Delta h\}}$, where Δh is expressed in terms of head of the fluid being measured

There are various practical modifications to this arrangement, one of which is shown diagrammatically in Fig 26 in which two tubes are inserted into the pipe pointing up- and downstream, thus increasing the pressure difference above the theoretical velocity head In such cases the particular arrangement has to be calibrated

The Pitot tube is of advantage where the velocity is high and the static pressure low, since it involves no appreciable loss in static head It is useful for exploration purposes in plant already installed, but in view of the variation in velocity from the wall to the centre of a pipe it is advisable in such work to average the readings from a large number of observations taken across the full pipe diameter The instrument itself causes deflexion of the fluid stream which tends to interfere with the accurate determination of the static pressure For this purpose it is of advantage to employ a Piezometer ring, which averages the pressures from four static openings equally spaced round the pipe in perpendicular plane Pitot tubes are not recommended for use with liquids containing foreign material or dirt, as the openings are small and easily choked

Piping and Accessories to Manometers.

An orifice should, if possible, be installed in the pipeline with a straight unobstructed upstream length of pipe equal at least to 8 times the pipe diameter and a straight unobstructed downstream length of pipe equivalent to 6 times the pipe diameter For gas measurement the American Gas Association specifies an average of 12 pipe diameters on the upstream and 8 on the downstream, of straight unobstructed pipe The following desirable conditions should be considered in locating a manometer equable temperature, not below freezing and not above 100° F, freedom from vibration and reasonable accessibility The best level of the manometer with reference to the pipe varies with the fluid being measured. For example, when measuring steam or water, any air which enters the connecting tubing will return to the flow pipe if the manometer is

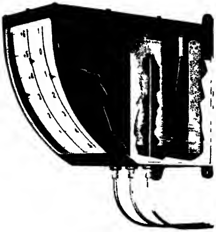

Fig. 15

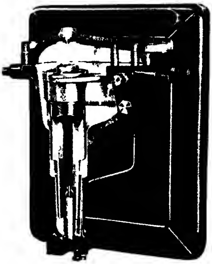

Fig. 22

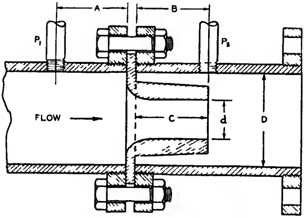

Fig. 24

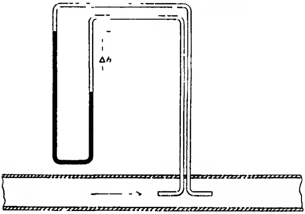

Fig. 26 Diagrammatic arrangement of Pitot tube

Fig. 25

installed below the level of the line On the other hand, if the manometer is installed above the pipe when measuring a moisture-laden gas or air, any condensate in the connecting tubing will run back into the flow pipe In general, precautions must be taken to avoid air or gas locks in the connecting tubing when measuring liquids, and liquid locks when measuring gas or air Arrangements must also be made to prevent corrosive liquids or gases from coming into contact with the mercury by using a buffer liquid, and to prevent congealable liquids from entering the connecting tubing by using an immiscible buffer liquid

For the above purposes vapour and sediment traps, and also seal chambers, are inserted in the connecting tubing where necessary

It is impossible here to go into the many arrangements of tubing, traps, and seal chambers devised to meet wide variation in conditions, but a number of standard installations are shown in the A S M E research publication entitled *Fluid Meters, their Selection and Installation*, 1933

Other Types of Flow-measuring Instruments.

Float Meters In the Kent flow indicator the fluid enters an outer chamber, passes downwards to the inlet of a concentric flow tube which is conical in shape, and presents an increasing cross-section to the fluid rising through it The fluid is discharged into the outlet chamber at the top

Inside the flow tube is a float which rises to a position such that the upward forces acting upon it due to the flow of fluid between it and the wall of the flow tube are balanced by the weight of the moving parts A spindle extends downwards from the float into a transparent tube filled with a suitable fluid to damp the movement The end of the spindle forms an indicator which registers on a scale calibrated in terms of the flow When glass is unsuitable for the indicator tube this may be made of a non-magnetic metal and the movement of an iron indicator inside the instrument followed by a magnet in a similar manner to the magnetic indicator coupling previously described for certain flow meters The float is so shaped that the flow of fluid keeps it in the centre of the tube This is accomplished in some designs by grooving the float in such a way that the flow of fluid keeps it spinning This type of instrument is reasonably accurate, provided the viscosity of the fluid is not subject to appreciable variation Under favourable conditions it may be accurate to within plus or minus 2% for flows down to 1/10 of the maximum flow The maximum fluid viscosity for which it is recommended is 10 times that of water

Thermal Flow Meters. This type of instrument is based on the principle of adding by electrical heating to a fluid of known specific heat a known amount of energy, which is measured by a wattmeter The temperature of the fluid is measured before and after the addition of the heat and its quantity thus determined The Thomas meter which is representative of this class actually maintains a constant temperature rise between upstream and downstream thermometers so that the varying current input required to maintain this temperature difference is a measure of the flow, in terms of which the wattmeter can, therefore, be calibrated In order that the electrical energy consumed should not be uneconomic, the two resistance thermometers which are used to determine the inlet and outlet temperatures are connected to two sides of a Wheatstone bridge so adjusted that the galvanometer shows no deflexion for a 2° F. temperature difference The heating current is controlled by a balancing device which increases the current when the galvanometer deflects due to too low a temperature difference, and decreases it for the opposite deflexion For the measurement of large volumes of gas of practically unvarying composition this type of meter is particularly applicable

Positive Displacement Meters. As used for liquids, displacement meters usually consist of a body casing with a moving element in the form of a disk, or piston which in completing a cycle of motion sweeps through a definite calibrated volume Usually the moving element is made to trip a counting device of the tachometer type each time a cycle of motion is completed, and the volume of liquid passed through the instrument is thus integrated Such instruments are, therefore, generally suitable for measuring quantities, but not rates of flow

In the Kent oil meter the moving element is a rotating cylindrical or elliptical piston which operates in a cylindrical working chamber The piston in rotating, alternatively covers and uncovers inlet and outlet ports, passing a definite volume of liquid at each revolution For the measurement of oil such meters are available in standard sizes to handle up to 15,000 gal per hr

Rotary disk meters have the working chamber in the form of a truncated sphere, the top and bottom of which are conical surfaces each having its apex towards the centre of the sphere A disk of rubber or other suitable material is fitted diametrically across the chamber in such a manner that the upper surface moves over the upper conical face and the lower surface over the lower conical face The disk is pivoted above and below on a hemisphere which fits into hemispherical bearings in the apex of each cone, the top hemisphere carrying a shaft which rotates in a circle and operates the counting device The liquid enters from one side of the chamber under pressure, causes the disk to gyrate, and is discharged from the opposite side of the chamber

Helix, Vane, and Turbine Type Meters In the 'Helix' or 'Spiral' meter originally developed for boiler-feed service and recently successfully adapted for the measurement of Diesel oil and light lubricating oils, the flow of liquid through the meter drives a set of helically arranged vanes fitted to a shaft running parallel to the line of flow The rotation of the shaft is transmitted by a worm drive to a vertical shaft and then through a train of gear wheels to a counting mechanism Fixed straightening vanes running parallel with the axis of the pipe are interposed between the inlet and the rotating helical vanes to help to reduce eddy currents which might upset the accuracy of the instrument This instrument operates with a low-pressure loss only of the order of ¾ lb per sq in when delivering at the rate of 1,000 gal per min of water With pressure losses up to 10 ft head of water, meters of this type are available for capacities up to 20,000 gal per hr For small flows to be measured down to 2 gal per hr within an accuracy of ±2% a modification of the above is available in the form of a rotary meter (fan type) having plain flat vanes rotating round a vertical shaft, the vanes being rotated simply by the flow of fluid past them The pressure loss is, however, considerably higher than with the helix meter It should be noted that in the vane type of instrument the casing does not fit closely round the vanes This class of instrument must be calibrated separately for all fluids to be handled

For the measurement of volumes of water up to 500,000 gal per hr turbine type meters are also available In a successful design of this type of meter the turbine-bladed 'impeller' rotates in a horizontal plane carrying a vertical shaft which operates the counting mechanism The water enters the 'impeller' flowing axially downwards and, leaving the blades radially, drives the mechanism The pressure loss in this type of instrument may be, however, 10 times higher than when using the 'helix' or 'spiral' type

Wet and Dry Gas Meters As used for the measurement of gas a number of types of positive displacement meters are available In the 'wet' gas meter a water seal is used, the meter being in the form of a cylindrical metal casing in which a number of paddles rotate on a horizontal axis These paddles are specially shaped to trap a specified volume of gas when the water seal is maintained at a predetermined level The gas enters the meter through passages at the centre, which are caused by the water seal to function as valves It is discharged from these passages into the compartments formed by the paddles extending above water-level and, on these in turn being submerged, is forced out by the water seal through the opening between the tip of one paddle and the next, thus leaving the meter via the space between the casing and the paddles This type of gas meter is accurate for the smallest rates of flow, and only becomes inaccurate if the flow fluctuates to such an extent as to cause surging of the water-level It is, of course, essential that the level of the water seal be maintained constant at the standard height This type of meter is generally of the integrating type, the revolutions of the paddles being transferred to a counting mechanism

In the Westinghouse fluid gas meter a liquid-level is again maintained in an essentially cylindrical vessel A compartmented chamber in the form of an inverted cup dips into the sealing liquid and rotates about a vertical axis The gas enters at the base and is distributed to various compartments which in rotating are registered alternatively with inlet and outlet ports The differential pressure between the inlet and outlet of the meter causes the chamber to rotate, and after leaving the compartments the gas flows upwards and out of the top of the meter casing The revolutions of the chamber are transferred to counting mechanism which records the integrated flow

'Dry' gas meters, such as are generally used for domestic purposes, require no liquid for their operation and less supervision than the 'wet' type They are, however, appreciably less accurate

The meter is actuated by the differential pressure of the gas across it For example, if in a gas-supply line in which a 'dry' gas meter is installed the gas is available at a given pressure on the inlet side of the meter, the opening of a burner valve on the outlet side causes a lower downstream pressure The difference in pressure moves a double-acting piston, and when the limit of travel of the piston is reached, the inlet port is closed by a sliding valve and the outlet port is opened Similarly, the outlet port of the other end of the cylinder is closed and the inlet valve opened, the piston then reverses its motion The valves are operated from the piston by means of a series of cranks, shafts, and arms

In actual practice the American Meter Company's meter has four chambers instead of two, and the pistons are flexible leather diaphragms attached to a central partition This meter is made in sheet steel or cast iron for pressure up to 250 lb per sq in and capacities up to 17,500 cu ft per hr

Weir Meters. For the measurement of water in pipelines under pressure the orifice meter or Venturi meter gives very accurate results when the minimum flow does not drop below 10 to 15% of the normal for any appreciable duration of time Where the flow may decrease to 3 or 5% of the maximum, however, the V-notch weir meter is particularly suitable, especially when the fluid is under very little or no pressure Typical of this type of meter is the Bailey weir meter The arrangement for indicating or recording the flow over the weir is particularly interesting The pen spindle is actuated by a beam resting on a knife edge At either end of the beam is a weighted displacer These displacers are exactly balanced and just touch the surface of the water at zero-level They have equal base areas, but one is conical and the other cylindrical As the water-level rises the submerged volumes adjust themselves so that the members are balanced In order to do so the cylinder rises and the cone sinks This action displaces the beam which rotates the pen spindle, the pen or pointer moving over a calibrated scale The relative shapes of the displacers are also designed that the pen or pointer movement is directly proportional to the rate of flow over the weir

Bulk Measurement of Fluids

The measurement of gases or liquids in bulk is generally carried out in calibrated gas holders or tanks The volumes are usually determined by mathematical calculation from the shape of the vessel, taking into account, where high accuracy is necessary, the deviation of the vessel from the basic shape due to structural features such as beams, angles, &c , also having regard to the deflexion of the vessel under pressure In very large quantities the determination of mass is a matter of serious difficulty owing to the differences in temperature, pressure, and consequently density which may occur simultaneously in huge volumes of fluid The average specific gravity or density is generally determined by averaging samples from various points in the vessel

The Measurement of Liquid-level.

In the petroleum industry the measurement of liquid-level is generally accomplished by the use of a float-type mechanism, or alternatively by the measurement of the correlated hydrostatic pressure, or the differential pressure existing between the top level and the bottom of the liquid

Float Type This type of instrument is seen in its crudest form in storage-tank service, when it may consist merely of a float connected, by means of a cable passing over a pulley, to a counterweight and indicator registering on a calibrated scale The rotation of the pulley may be employed to rotate a pointer spindle in an indicator or pen spindle in a recorder Alternatively for distant recording the movement of the float may be transmitted by an electrical relay system to a recorder actuated by electrical impulses set up in the relay system by the float movement

The required rate of discharge of liquid from a system frequently depends upon the rate at which the liquid flows into a closed receiver For this purpose it is necessary to maintain the liquid-level in the receiver within comparatively restricted limits The float-operated indicator is widely used for this purpose When there is danger of connecting lines being 'frozen', as, for example, when handling very viscous oils or asphalt, the float is preferably located inside the tank, its movement being transmitted to the outside pointer by the rotation of a spindle in a pressure-tight bearing A rugged construction is desirable as it may sometimes be advantageous, when in doubt, actually to 'feel 'the position of the float by means of the e control or indicator arm For less viscous oils the external type of float mechanism is employed The float cage is located externally at the average liquid-level to be maintained and is coupled to the receiver by two pipes, one entering the receiver below the desired minimum liquid-level and the other above the maximum An external arm may be fitted with electric switches to operate different coloured lights for high, average, and low levels and/or may be used to operate a control mechanism Liquid-level meters of the float type are also suitable for either indicating, recording, or controlling the interface surface between two liquids such as oil and water These 'Duogravity' instruments use a specially weighted float, the buoyancy of which is adjusted (usually by means of lead shot) to that required for interface operation

Hydrostatic-pressure Liquid-level Meters As shown in the section on flow meters, the pressure of a liquid due to its level above a datum-line may be expressed in weight per unit area or in height of the column of liquid above the datum-level In suitable locations, therefore, a simple Bourdon pressure-gauge type instrument fitted to the receiver at the datum-level may be used However, it is usually desirable to locate the gauge at some distance from the point of measurement and at different elevation It is, therefore, more convenient to convert the liquid head into equivalent air pressure and transmit this pressure to the gauge movement In this case the indicator or recorder may be located at any convenient position and connected by pneumatic piping to a diaphragm box The hydrostatic pressure is transferred by the liquid column to a sealing liquid which in turn compresses a volume of trapped air on the lower side of a diaphragm The diaphragm transmits in turn the hydrostatic pressure to the air in the pneumatic connexion to the gauge The seal chamber and liquid are only necessary if the liquid in the receiver attacks either rubber or bronze

An alternative arrangement operating on the same principle but employing a submerged bell may be employed when the rubber diaphragm must be protected from chemical action or high liquid temperature

The transmission of the effect of hydrostatic pressure may be also accomplished electrically as in the Electroflo instrument in which the piping from the datum-level is brought to one side of a bellows which, in moving, alters the position of an arm on a contact type of resistance, thereby altering the conductance of the electric reading instrument circuit

Back-pressure Liquid-level Meters. Back-pressure liquid-level meters may be of the continuous or intermittent type depending upon whether they are for recording or indicating Both types involve the injection at datum-level of air, gas, or liquid into the liquid whose level is to be measured—the back-pressure on the injection system when flow is established being a measure of the liquid-level In practice air is most commonly used for gauging acids, chemicals, oils, &c An open-ended pipe is set with the open end at datum-level and air injected A gauge on the air-supply line measures the back-pressure exerted by the liquid and hence the liquid-level

Differential-pressure Liquid-level Meters By connecting piping from the datum-level in the receiver to the high-pressure side of any differential manometer of the types described above for flow-meter use, and the gas space above the highest liquid-level to the low-pressure side, the usual flow-meter mechanism can be used for the indicating, recording, or controlling of liquid-level

The Measurement of Specific Gravity

Gravitometers.

For Gases For the measurement of the density of gases the gravitometer is generally used The principle upon which this instrument works is the U-tube principle of measuring weights or pressures In a uniform bore U-tube having legs of equal length, one of which is filled with the gas and the other with air, it is obvious that the force acting on a diaphragm placed between the gas and the air is

$$haw - hawd,$$

in which h is the height of each leg of the U-tube,
a is the area of the U-tube cross-section,
w is the weight of a unit volume of air,
d is the density of the gas relative to air

Hence the force $= haw(1-d) = k(1-d)$, where $k = haw$

Thus, provided haw is constant, equal increments of gas density will produce equal decrements of force In practice a is kept constant, but as w varies with barometric pressure, temperature, humidity, &c, it is necessary to make h vary inversely with w As w varies inversely with the volume of air due to temperature and pressure, h varies directly with the same factor

In the Simmance Gravitometer as made by Alexander Wright & Co, the variation in volume of an enclosed quantity of air raises or lowers the tubes which regulate the height h This industrial indicator and recorder employs what is in effect the Bell type manometer described in the flow-meter section above It consists essentially of

A balance supporting at one end an aluminium bell which forms a gas chamber over the surface of oil in a tank, the bell being counterbalanced by a weight at the other end of the balance beam The exit standpipe is extended upwards to form a tall ascension pipe through which the gas passes to a burner The movement of the bell is indicated by the pointer on a calibrated scale, and recorded This instrument is provided with a barometric compensator which automatically corrects the height of the ascension pipe to allow for changes in density due to barometric pressure changes

Gas enters the instrument at negligible pressure produced by a governor, flows through the bell and up the ascension tube to the burner The displacement of the air originally in the bell causes the balance to tilt more or less according to the difference in weight between the column of air on the outside of the bell and the column of gas in the ascension pipe The barometric compensator consists of an air chamber of fixed volume, which is connected by a standpipe to a separate counterbalanced bell suspended in a water tank The ascension pipe passes through this tank, and being telescoped and attached to the bell is raised or lowered by the expansion or contraction of the air in the chamber operating on this bell

The Ranarex Gas Density Meter If two fans of equal size run at the same speed but in opposite directions, one operating on air and the other on a gas of different density, the torques exerted by the resulting streams of air and gas upon two similarly located paddles of equal size will be proportional to the relative densities of the air and gas This principle is adopted in an instrument made by the Permutit Company The paddles are mechanically linked and the resultant torque transmitted to an indicator pointer or recorder pen

For Liquids. As applied to liquids the gravitometer becomes essentially an automatic hydrometer In the

Bailey gravity meter a similar arrangement is adopted to the Bailey draught meter described above, except that the movement is 'drowned' in a sealed container and the bell is replaced by displacers of equal weight but greater volume than the counterweights, and the pendulum is located at the fulcrum

For the purpose of illustration, assume the volume of the displacers to be x cu cm and that of the counterweights to be y cu cm, also that they are located equidistant from the fulcrum In water the displacing force is due to x gm minus y gm, and the beam is tilted until this force is counterbalanced by the potential force of the tilted pendulum weight In gasoline of specific gravity, say, 0 75, the displacing force will only be due to a difference of 0 75 $(x-y)$ gm, hence a smaller tilting of the beam is produced by the necessary counterbalancing potential force in the pendulum weight

The pendulum is fitted with an adjustable weight by means of which the instrument is calibrated The displacers are made of flexible material and are filled with a liquid having the same coefficient of thermal expansion as the liquid being measured They, therefore, expand or contract in sympathy with the liquid passing through the meter, thereby automatically compensating for temperature changes and making the readings independent of temperature The pendulum is fitted with a magnet which moves in an arc in front of a non-magnetic plate On the other side of the casing, which may thus be completely sealed, an armature supported from a pivoted beam having its axis in line with the displacer beam, follows the magnet in a corresponding arc and actuates the pointer or pen arm

Continuous Gas Analysers.

Continuous gas analysers are generally used in industry for the determination of the composition of flue gases, particularly in terms of CO_2 and occasionally of CO and hydrogen They may be either of the chemical absorption type or depend upon the thermal conductivity of the gas

Chemical Type. A typical CO_2 recorder of this type operates as follows The CO_2 in a measured volume of the gas is absorbed in a solution of caustic potash or soda and the residual gas is measured in a floating bell A stream of water passing through an injector causes a continuous supply of gas to be withdrawn from the flue connecting-pipe The water then passes to a tank containing a gas-sampling chamber

As soon as the tank is filled the water syphons away and in so doing induces a supply of gas to replace the water When the water again rises it forces most of the gas through a sealed outlet, but traps a definite volume in the gas-sampling chamber and sweeps it through to a potash tank in which the CO_2 is absorbed and the volume of gas proportionally diminished From the potash tank the residual gas passes via a standpipe to a water-sealed measuring bell which is of the same volume as that of the originally entrapped flue gas If no gas were absorbed in the potash tank, the bell would rise to its full height Residual gas of smaller volume raises the bell less, so that the height to which the bell rises is a direct indication of the volume percentage content of CO_2 in the sample This height is indicated or recorded by a simple pen movement, and on the syphon again discharging the old sample in the bell is exhausted The various water seals are kept replenished by a constant small stream of water The cycle of operations takes 2 to 3 min to complete In a similar meter designed to measure carbon monoxide content suitable reagents are incorporated to change the monoxide to dioxide, the latter being determined as described above, the original volume of CO being changed to an equal volume of CO_2

Thermal Conductivity Type The thermal conductivity type of instrument depends upon the fact that the thermal conductivity of carbon dioxide is approximately 40% less than that of the various gases such as oxygen, nitrogen, methane, and carbon monoxide in admixture with which it is generally found, for example, in flue-gas analysis Kaye and Laby in their *Physical and Chemical Constants* give the following values, in metric units, for the thermal conductivity of these gases

Hydrogen at	0° C	$31\ 90 \times 10^{-5}$
Nitrogen	7 C	$5\ 24 \times 10^{-5}$
Oxygen	7° C	$5\ 63 \times 10^{-5}$
Air	0 C	$5\ 22 \times 10^{-5}$
Methane	8° C	$6\ 47 \times 10^{-5}$
CO ,	7° C	$5\ 10 \times 10^{-5}$
CO_2 ,	0° C	$\left.\begin{matrix}3\ 07\\3\ 27\end{matrix}\right\} \times 10^{-5}$

The application of this principle is generally the following a wire heated by an electric current is placed in a metal chamber so designed that all heat losses from the wire are rendered negligible with the exception of that conducted by the gas between the wire and the walls of the chamber The temperature of the gas rises until the heat supplied by the current is just balanced by the heat losses from the chamber walls, substantially all of which is conducted by the gas If the wire used has a high-temperature coefficient of electrical resistance, this resistance will have a value dependent on the thermal conductivity and, therefore, on the composition of the surrounding gas By comparing the resistance of two such wires, one of which is surrounded by a reference gas and the other by a gas of known composition, the instrument can be calibrated In this type of instrument one chamber contains a sealed or flowing reference gas such as air, whilst through the other is passed the gas of which the CO_2 content is to be measured

A Wheatstone bridge circuit is employed consisting of four platinum filaments of equal resistance which are heated by the current from an electrical accumulator This current is controlled to a constant value by the rheostat, and indicated on the ammeter Two of the platinum filaments connected on opposite sides of the bridge are mounted in a chamber containing sealed reference gas and the other two in the chamber through which is passed the gas to be analysed If the gases in both chambers are alike, the gaseous conductivity to the walls of the chambers are equal, the temperature of the filaments reach the same value, and the bridge remains in balance If the gases differ in CO_2 content, the conductivities differ, the filaments attain different temperatures, the resistances change, and the bridge becomes unbalanced A current, therefore, flows through the meter which is calibrated in terms of percentage of CO_2 and may be either an indicator or recorder.

Hydrogen is frequently found in flue gas as the result of the incomplete combustion of natural gas or of the burning of wet coal This may be removed by passing the flue gas over heated copper oxide, when an Orsat determination will show the same percentage of CO_2 as is shown by the thermal conductivity CO_2 meter Owing to the conductivity of hydrogen being approximately 6 times greater than air, while that of CO_2 is only approximately 40% less than air, 1% of hydrogen in flue gas will completely neutralize in a thermal conductivity type meter the effect of approximately 10 to 12% of CO_2 Unusual behaviour of an electric CO_2 meter may, therefore, be a reliable guide to abnormal combustion conditions Before the gas passes to the electric CO_2 meter the entrained moisture and condensate is drained off after the removal of soot and other suspended matter by a filter It is then dried over calcium chloride and finally filtered, for mist or dust removal, before passing to the analysis cell On leaving the analysis cell the gas passes through an exit water seal, which also serves as indication of flow, and thence to a water aspirator which draws the gases through the instrument

Indicating Instruments.

An indicating instrument consists essentially of the following parts a detector, mechanism for transferring movement in the detector to a pointer, the pointer itself, and a graduated calibrated scale over which the pointer moves The position of the pointer with reference to the scale determines the value of the variable under investigation

In the foregoing sections the detectors are described and also the mechanism for transferring the movement to the pointer The remainder of an indicating instrument is comparable with the hands and dial of a clock

Recording Instruments.

Recording instruments differ from indicators in that the factor of time is introduced and the value of the variable is mechanically and automatically graphed against it This is exceedingly valuable in plant control, and it is rare that the additional cost over an indicator is not justified, particularly if the variable is of sufficient importance to be periodically observed and manually recorded In the recorder the scale instead of being a permanent fixture is marked on a removable chart and the pointer is replaced by a pen which records its position automatically on the chart

When the mechanism which actuates the pen is of a powerful character, as, for example, a Bourdon tube, the pen may be forced by a spring to rest lightly but continuously on the chart and produce an uninterrupted record The chart may be of the circular type, of the strip type, or of the single drum type

The mechanism driving the disk, rollers, or drum carrying the chart may either be of the clockwork or of the synchronous electric type for use with alternating current Alternatively using direct current, an impulse type of clock may be incorporated operating in synchronism with a master clock Circular charts are marked with equally spaced radial arcs representing periods of time, the period length depending upon whether the chart is for 24 hours' or 7 days' operation The former is the more usual Concentric circles represent values of the variable spaced over a diameter of 6 to 12 in Strip charts and drum charts have longitudinal lines representing the values of the variable and transverse lines representing time In order to provide open, easily read scales standard charts are available up to 12 in wide

The pens used in recorders are generally of the capillary type with a reservoir for the ink supply The pen itself may be of glass or pointed with nickel silver, platinum, or other corrosion-resisting material The ink is generally composed of water, a dye, and alcohol or glycerine

As paper charts may contract or expand with varying humidity of the atmosphere, provision is frequently necessary to avoid errors arising from this source In the Brown instruments, for example, this takes the form of a humidity compensator A strip of paper of the same composition as the chart (preferably cut therefrom) is held under tension by a spring When the length of the compensator strip changes due to variation in humidity the movement is transmitted by mechanical linkage to the pen or print hammer, the linkages being so designed that the movement of the pen position is equal to the change in width of the chart up to the point at which the pen is recording In exceedingly humid tropical atmosphere it may be necessary to enclose the instrument in an air-tight case to avoid the excessive friction of the pen on a damp chart In the air-tight case may be fitted containers holding hygroscopic material

Where the pen is directly actuated by a galvanometer it is frequently impracticable, on account of the slight operating forces involved, to maintain the pen in constant contact with the chart To obviate this difficulty the pen is depressed every few seconds by a motor-operated depressor bar to give a dotted record line, the depressions being at sufficiently short intervals to show a substantially continuous record In this type of instrument the pen is usually replaced by a print hammer, which, as in a typewriter, prints the record through an inked ribbon

Mechanism of Self-balancing Null Type Potentiometer Recorders. In the Brown Null Type Potentiometer Recorder a galvanometer is used to direct the operation of the mechanism to rebalance the circuit for each change in e m f that is measured There is a motor-driven shaft on which are mounted two kidney-shaped cams As these cams rotate they cause a selector table to rise into gentle contact with the galvanometer pointer On touching the pointer the selector table stops and through a shaft, which moves with it, gives a definite position to a robust secondary pointer This pointer carries an extension which registers with the steps in a step lever After the secondary pointer is positioned, further rotation of the motor-driven shaft allows the step lever to drop into contact with the extension of the secondary pointer The pointer extension registers with one of three notches on the upper or lower side of the step lever, depending upon the position of the secondary pointer The actual notch engaged determines the amount of rotation of a gear which readjusts the slide wire contact, and simultaneously the pen is moved to the position corresponding to that of the galvanometer pointer

In the Leeds & Northrup Micromax balancing device the galvanometer pointer is periodically clamped by a motor-driven chopper bar Two vertical sensing fingers move inwards to determine the pointer location If the pointer is displaced from zero centre, one of the fingers stops before reaching centre position and the other after The position and distances of the fingers off-centre are dependent on and proportional to the deflexion of the pointer By mechanical linkage the fingers in locating the pointer turn a pivoted clutch lever On moving this lever, cork pads thereon are forced by a cam into contact with a disk which turns in sympathy, the rotation being proportional to the displacement of the clutch lever and incidentally of the galvanometer pointer The disk drives two drums carrying the two slide wires, the rotation of the drums causing the slide wires to move in relation to two fixed contracts This takes the place of the hand operation of movable contacts in the manually controlled instrument, and the bridge is thus brought into balance The disk also drives the pen-operating mechanism and determines the position of the pen on the recording chart When the chopper bar is released by the operation of the motor the galvanometer pointer takes up a new position and at the same time the clutch mechanism is released from the disk

Controllers and Control Systems

In the foregoing sections have been described the sensitive elements, and associated mechanisms used in instruments for indicating and recording the values of various process variables such as temperature, pressure, fluid flow, &c The object of automatic control equipment is to maintain constant such variables as affect the results of the process In most cases suitable automatic control instruments will accomplish this result with greater accuracy than can be achieved by manual control, thus reducing the amount of attention required of the operators so that other duties may be attended to by them and their number reduced Nevertheless, such control equipment must only be looked upon as a mechanical assistant to the operator It cannot think nor always take into account unusual conditions which may arise from factors outside its control The operator must, therefore, remain fully responsible and, if necessary, make one or two simple adjustments to the control equipment to enable it to cope with very unusual conditions

The control of temperature, pressure, liquid-level, &c , usually involves the control of flow of solids, liquids, gases, or electric current The control of such flows necessitates the use of valves, dampers, &c , located in the stream to be controlled Such mechanical devices require power for their operation which it is usually beyond the capacity of the sensitive detecting element to provide Exceptions, however, are the direct-acting controllers which are of a comparatively crude and rugged type, as, for example, mechanically linked float-operated liquid-level controllers In general it is found necessary to interpose between the detecting element and the valve a transmission system which is capable of control by the detecting element and which is able to transfer this control with augmented power to the valve or damper Such intermediate transmission systems may either be of a pneumatic type employing as transmitting fluid either compressed air or steam, or alternatively hydraulic in character employing as fluid water, oil, alcohol, or similar liquid Again, the intermediate system may be electrical Generally, potentiometer type instruments employ an electrical intermediate system in the controller mechanism, although they may occasionally be associated with an air-operated pilot system Bourdon tube type instruments, on the other hand, usually employ the latter type of pilot system

In setting out to control a variable it is necessary at first to determine the extent to which deviation from the predetermined value of the variable may be allowed The ideal controller would, of course, detect and correct, in the variable, any tendency to change, so rapidly that it would not depart appreciably from the desired value Such absolute perfection of control is almost impossible and seldom required Generally it is satisfactory if the variable is maintained within upper and lower limits on either side of the desired valve, these limits depending upon the magnitude of the effect of the variable upon the process results Close limits require complicated and expensive instruments

Controllers fall into two general classifications, viz

(*a*) 'Open and shut', or 'On and off', Action,
(*b*) Floating or Throttling Action

'On and Off' Action.

The simple laboratory electrical thermostat is an example of the 'On and Off' action It is used to maintain a bath, say, at a predetermined temperature When the temperature of the bath falls below a certain fixed value for which it is set by means of a thermometer, the heating current is switched on, and when it rises above a certain fixed value the heating current is shut off Similarly, if the bath is heated by means of steam, the controlling valve of the steam-supply line will be opened and shut respectively at the lower and higher temperature limits The temperature of the bath is therefore never constant but falls below and rises above the desired value within certain fixed and permissible limits and in such a way that the average temperature is that required This type of control is frequently suitable for a simple process of the batch type in which the process lag is small, the reason being that the sensitive element very quickly receives back through the process the result of its action in opening or closing the valve

This action however, involves a sudden change or surge in the controlled medium which obviously would be undesirable, for example, in the control of the supply of fuel to a furnace In order to avoid large fluctuations in temperature the limit switches might be adjusted so that the movement of the controlling valve from one position to the other would result in only a small change in the flow of fuel to the burners, but the change of valve position from open to shut would occur frequently If a sudden change occurred in the fuel-supply pressure or in the furnace load, the valve positions corresponding to the limit switches would probably require readjustment

If the variable controlled by an 'On and Off' action mechanism is recorded against time, the result is a sinuous line which rises and falls regularly above and below the straight line representing the desired value of the variable

Floating or Throttling Action.

Many control problems involve large thermal capacities and considerable time lags in the process A time lag causes the instrument to be 'out of step', as it only detects the result of its action after an interval during which the variable tends to swing in one direction or other away from the control-point This gives rise to the phenomenon known as 'hunting' In such cases 'Floating or Throttling Action' controllers are employed The valves are always partially open in operation, but are adjusted when necessary by the reaction of the sensitive element to compensate for variation in the effective conditions or change in demand

A throttling or floating action controller settles down to an average setting which will meet the demand without change in valve position so long as the demand does not fluctuate With change in demand, however, the new setting will tend to be slightly different from the original control-point A control instrument operating in conjunction with a floating or throttling valve should, therefore, have a stabilizing element which acts to oppose any change in the variable and a compensating element which readjusts the position of the stabilizing element to maintain the variable at the exact desired value Such instruments are classed as Compensating, Trend-analysing, or Anticipating controllers

Liquid-level Controllers.

When the valve controlling the flow of liquid from the vessel in which the predetermined level is to be maintained is located near the float mechanism, the lever operated by the float may be directly connected by mechanical linkage to the controlling valve When the control valve is located at a distance, a pneumatic or hydraulic transmission system is interposed between the float lever and the valve, similar to that described below for the temperature and flow controllers

Alternatively mercury contact switches may be fitted to the float lever to operate a motor-driven control valve

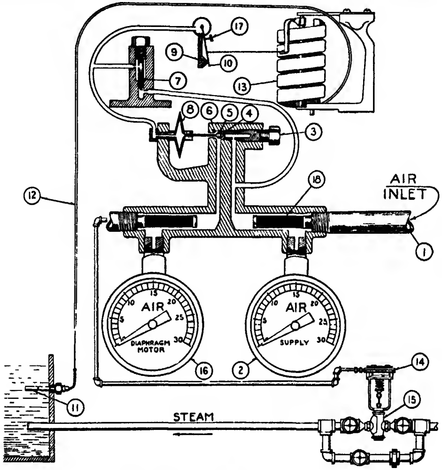

Fig 27 Diagram of operation of single-action temperature controller

Pneumatic or Hydraulic Pilot-operated Controllers for Temperature and Pressure.

Compressed air at a pressure of 15 to 20 lb per sq in gauge pressure is generally used in pilot systems on account of its being widely available, easily cleaned and dried, and easily disposed of when used by venting to atmosphere Temperature and pressure controllers operate by controlling the flow of a fluid, be it liquid, gas, fuel, or electricity In essentials the operating principle is illustrated in Fig 27 which shows a simple single-action Foxboro temperature controller

The operating air for the pilot system enters through a filter 18 and flows through a port in an adjustable pilot-valve seat 3 and thence, the valve being open, to the diaphragm head 14 of the control valve 15, which is open to admit heating steam to the process The air supply also passes simultaneously through a pressure-reducing valve 7 and escapes to atmosphere through a leak valve 9, which is open

Should the temperature rise beyond the control-point a sensitive bulb 11 operating on a helical tube 13 closes the flapper arm 10 of the leak valve The pressure in the system rises, bellows 8 expands, and being fixed at one side forces against the pilot-valve seat at 4 the valve 5 attached to a spindle carried by the free side of the bellows The high-pressure system is thus closed to the diaphragm head of the control valve which consequently closes

When the temperature drops the helical tube 13 winds up, and the flapper arm 10 is moved away from the nozzle of the leak valve 9 The pilot-system pressure drops, causing the bellows to contract and close the pilot-valve head 5 against its seat at 6 The high pressure is now open to the control valve, which is thus caused to open admitting the heating steam again to maintain the temperature

The pilot system, as described above, operates on the 'on and off' principle If, however, 'throttling action is required, an adjustable flapper valve is used which begins to close the nozzle before the control-point is reached Varying temperature thus varies the amount of 'winding' of the helical tube, alters the position of the flapper arm relative to the leak-valve nozzle, and hence the amount of air escaping therefrom The resultant variation in the air pressure on the diaphragm head of the control valve causes it partially to open or close in response, thus controlling the flow of heating medium in a continuous manner as opposed to the spasmodic control of the 'on and off' action

The typical operating principles governing the introduction of compensation to prevent over controlling of the control valve are shown in Fig 28, which illustrates the operation of the Mason-Neilan compensated temperature controller

The operating air enters the system through a reducing valve which vents any excess air pressure, bringing this down to 15 lb per sq in After the removal of dirt and moisture in a filter 3 the air passes through a fixed orifice 7 The flapper arm 12 partially closes the outlet of the leak valve 8, and the pressure from 7 builds up in bellows 13 The increasing pressure in the bellows closes valve 15 and opens valve 14, allowing air to enter chamber 16, flow through 17, and equalize the pressure in 16 and 18 When the pressures inside and outside the bellows 13 equalize, valve 14 closes and prevents the pressure in 16 from increasing further This pressure exerts a downward force on the diaphragm head 20 of the control valve 21, which partially closes and reduces the supply of heating medium

As the temperature falls the Bourdon tube or helical coil 11 winds (counter-clockwise) and lowers the flapper arm 12, point 25 acting as the fulcrum This partially opens leak valve 8 which reduces the pressure on the diaphragm head 20, and allows the valve 21 partially to open and more heating medium to flow, thus preventing further temperature drop

To compensate for changes in the pressure of the heating medium which might precede changes in the controlled temperature, the downstream pressure is carried to the 'thermo-pressure compensator' expansion element 23 If the pressure drops this element contracts, lowering arm 30 acting on 27 as a fulcrum This lowers flapper arm 12 and partially opens the air-leak valve The pressure on the diaphragm head drops, and the valve opens partially to allow the heating-medium pressure to build up to the required value, thus compensating for pressure change before it affects the controlled temperature

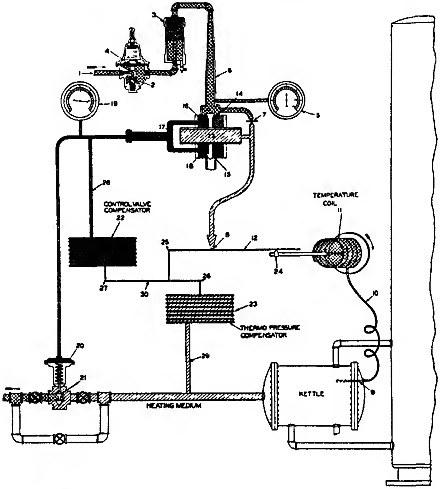

FIG 28 Diagrammatic sketch of operating principle of Mason-Neilan temperature controller with thermo-pressure compensator

The control-valve compensator operates in the following manner to prevent overcontrolling

As the pressure which actuates diaphragm head 20 tends to increase, it is transmitted to an expansion element 22 This expands, forces arm 30 downwards, acting on 26 as fulcrum, and lowers flapper arm 12 slightly away from the leak valve, as the result of which the increase in pressure on the diaphragm head is checked For any tendency of pressure on the diaphragm head to be reduced the action is reversed

The drift compensator which compensates for load change and lag in heating medium operates in a similar manner to the thermo-pressure compensator

Although the description given above is that of a temperature controller, the same principles are obviously equally applicable to the control of pressure using a Bourdon tube or helical coil type sensitive element

Where the lags in the process are large the throttling or floating-action control valve is used The range between the closed and open positions of the control valve is known as the 'throttling range', and is usually expressed as a percentage of the total range of the instrument, e g if it requires a 40° change in temperature to open the valve fully and the instrument has a range of 200°, the throttling range is 20%

In an air-operated single-response type of controller there exists only one position of the control valve corresponding to the position of the free end of the Bourdon tube which results from the variable in question Therefore only one control-valve position exists for each value of the process variable, be it temperature or pressure, &c, irrespective of change in the process load or demand

Considering the situation from the point of view of the control valve, it is obvious that if the conditions of the process permanently change, the control-point will also change, that is to say, the position of the control valve required to keep the controlled variable constant For example, if the throughput of a fractionating tower is permanently changed or the analysis of the charging stock varied, the temperature at the top of the tower will change unless such permanent change is made in the amount of reflux returned to the top of the tower as will compensate for the increase or decrease in the overhead fraction The reflux control valve will therefore require to be reset at a control-point within the 'throttling range' differing from the original control-point, i e a different control-valve opening will correspond with the desired value of the variable This involves a correspondingly different pressure of the fluid in the pilot system Using a simple single-action control valve operating as in Fig 27 a smaller valve opening for the same temperature will require a greater pilot-fluid pressure This may be brought about by bringing the leak valve closer to the flapper arm for the arm position corresponding to the desired temperature In this way the location of the throttling range can be varied with change in demand and the resetting accomplished either manually or automatically

In the single-response type of controller the resetting must be done manually, but in the double-response type of instrument with follow-up action the resetting is accomplished automatically

In the *Foxboro Stabilog Controller* this is effected by means of a differential-pressure 'motor' which is mechanically 'linked' to the leak valve The 'motor' consists of two bronze bellows with a separating diaphragm, the bellows being fixed at both ends with the dividing diaphragm free to move in the centre The reset action is linked to the centre diaphragm One compartment of the bellows is connected directly to the line by means of which the operating air is supplied to the control-valve motor The other compartment is connected to the same line through 'resistance spools' consisting essentially of fine capillary tubing A sudden change in operating conditions will influence the directly connected side more rapidly than through the 'spools' and so bring about a quantitative delayed effect which temporarily resets the control-point and through the medium of the 'resistance spools' ultimately returns this to its original setting This is an asymptotic approach which prevents crossing of the control-point and hence obviates 'hunting'

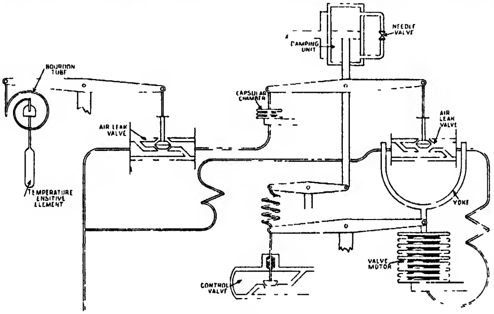

Fig 29

The action of the Taylor 'Dubl-Response' control system is illustrated diagrammatically in Fig 29 The action may best be explained by assuming a sudden decrease in the process load This brings about a rapid temperature increase of the temperature-sensitive element which causes a Bourdon tube to unwind, thereby raising the left side of a balanced lever and lowering the right side The supply of air to the capsular chamber is decreased and the air leak increased The capsular chamber contracts, and by means of the second balanced lever restricts the air leak from a second leak valve The motor valve is caused to expand by the resulting increase in air pressure and continues to do so until, by means of a yoke, it raises the second leak valve just sufficiently to balance the incoming air from the air supply, against the air leaking from this section of the system Simultaneously the disk of the control valve is pushed a proportional amount towards its seating (This is the normal response in a single-response controller) Meanwhile the second response or follow-up action is starting The spring above the control valve is extended by the downward movement of the control-valve disk, and through a further balanced lever the tension of the spring pushes up the piston in the fluid-filled damping unit, the rate of movement of the piston or follow-up action being adjustable at will by controlling the rate of leakage of fluid from one side of the piston to the other The rising piston carries with it the second balanced lever and restricts still further the escape of air from the second air-leak valve, resulting in the motor valve slowly moving the control-valve disk still nearer its seating

This gradual closing continues until the temperature begins to return to its control-point At this time the Bourdon tube begins to wind up again and raises the disk in the first air-leak valve by means of the first balanced lever The increased pressure in the capsular chamber lowers the valve disk in the second air-leak valve This increase in pressure in the capsular chamber takes place when the piston is still moving slowly upwards As the temperature reaches the control-point the capsular chamber has expanded just sufficiently to prevent further lifting of the second air-leak valve disk and consequently further lifting of the piston When the control-point is regained under the new conditions of process load the temperature is as required, but the second air-leak valve disk, the valve motor, the piston, and the control-valve disk are in the necessary new positions

Potentiometer Temperature Controllers with Fluid-operated Pilot System.

Falling midway between the class of controllers described above which employs a Bourdon or helical tube sensitive element coupled with a fluid-operated pilot system and the potentiometer all-electric class of controller described below, are the potentiometer controllers having fluid-operated pilot systems Of this class is the Foxboro Potentiometer Stabilog, the principles of which may be readily gathered from the preceding descriptions of potentiometers and of the Stabilog air-operated pilot system of control The method employed in combining these components is shown in Fig 30 The changes in the position of the galvanometer pointer are sensed by a calibrated detector arm which is periodically raised from and lowered to the pointer by a lifter arm This lifter arm is operated by means of a motor-driven cam, the pointer being free to deflect in either a high or low direction when the detector arm is raised A rising temperature will deflect the galvanometer pointer to the high side of the scale, allowing the detector arm to be lowered farther than during the previous cycle As the arm descends it engages a rocker which turns the flapper shaft, thus adjusting the flapper valve which in turn readjusts the controlled valve opening sufficiently to maintain the desired temperature A falling temperature results in the detector arm falling to a smaller extent than before In this case the lifter arm engages the other side of the rocker which is turned until stopped by the detector arm The flapper valve is thus adjusted and the controlled valve closed the correct amount

Bourdon Tube—Electrical Relay Type Controllers.

Also in the midway class is the type of instrument which employs a Bourdon or helical tube detecting device incorporated with an electrical relay type of coupling to a motor-driven control valve In this type an arm attached to the axis of the tubular detector is arranged to engage with a stud on a tilting plate carrying a mercury type switch At the required temperature the mercury tube is caused to tilt, thus making or breaking an electric circuit which includes the motor operating the control valve Alternatively the arm may be arranged to make contact with stud terminals with the same effect

All-electric Controllers.

In electrical controllers, incorporating potentiometers for temperature measurement or utilizing electrical relay systems to the indicating or recording instrument, the depressor bar in periodically depressing the pointer on the chart simultaneously completes the circuit energizing the control mechanism

Various modifications of this are in use For example, in the case of the Leeds and Northrup controller the control contacts are operated by two concentric disks If the temperature does not change, the disks do not move, but, when the temperature rises or falls from the control temperature, rotation of the disks occurs similar to the rotation of the clutch mechanism in the same make of self-balancing potentiometer

A controller having two switches only—a high-limit switch and a low—can never allow the control valve to settle down, but must result in it periodically moving backwards and forwards The addition of an intermediate or third switch, which corresponds substantially to that necessary to provide the correct flow at the desired operating temperature, produces a 'backing-off' effect when the control valve is moved to its centre position from either the high or low settings

Where time lags in the process are appreciable, compensating devices are incorporated in the all-electric controllers to achieve the same effect as is obtained in the compensated air-operated systems By adding auxiliary contacts the control mechanism may be caused to take very small steps with each depression or cycle of the control instrument Also by suitable arrangement of auxiliary contacts it may be arranged to produce a large correction if the temperature should depart beyond a certain fixed limit

Anticipating or Trend-analysing Controllers (All-electric Type)

This type of controller has been evolved to handle difficult or complicated control conditions in which there may arise sudden changes in demand or a general tendency towards sudden fluctuations in conditions It has to take into account the direction and rate of change of the variable and also the degree of deviation from the control setting

The principles adopted in the Brown Trend-Analysing Controller are illustrative of how this may be accomplished It is obvious that a differential type of mechanism must be employed to interpret the rate of change of the variable Consequently the valve must be controlled in very small steps to follow what is mathematically the first differential function of the variable

The desired result is accomplished by shifting the selector table with each movement of the depressor bar in such a way as to bring the neutral to the exact location which the pointer occupied previous to the last adjustment The effect is to maintain the valve in a definite position as long as the temperature is constant and to change its position only with temperature change The movement of the selector table is brought about by a reversible motor operating through a chain and sprocket drive This motor is connected in parallel with the motor in the valve-motor mechanism and runs simultaneously with it except when the pointer selects the centre or neutral contact When this happens, the motor in the valve mechanism is temporarily disconnected and the circuit completed to the other fields of the reversible motor which, driving through a spiral shaft, moves the selector table one step backwards to the true control setting In this way the control instrument rapidly follows the pointer when rapid changes are taking place, thus enabling the control valve to counteract the change in the variable, but immediately the valve position is adequate to halt the variable, so that the pointer remains in the same position for two consecutive cycles, the instrument starts to move back in conjunction with the control valve towards the true setting This type of instrument is, of course designed primarily for use in conjunction with throttling type mechanism Temperature controllers are commercially available which will maintain the desired temperature within 1 5 in a 600 range or within 2 5° in a 1,000° range

Motor Mechanisms The simplest type of drive for an electrically operated control valve is a *single-motor mechanism* which through gearing, moves the valve stem either directly or by means of a lever This is suitable for applications where the time lag is not great and where the control is effective when accomplished by very gradual changes in the control-valve position

The *two-motor mechanism* is a refinement which enables the valve to cope with sudden fluctuations and changes in demand The primary, or initial-stroke motor, is geared to produce comparatively large changes in the valve position The secondary, or balancing, motor corrects for permanent changes or assists when the initial stroke is not sufficient to return the temperature to normal It generally functions by enabling the lever arm to take any position throughout its entire range of movement to correspond to the middle or normal position of the initial-stroke motor

Where a moderate time lag exists it may be advisable to make provision for delaying the operation of the floating or balancing motor until after the instrument has had an opportunity of sensing the effect of the movement of the initial-stroke motor This is done by the interposition of a time-lag clutch between the balancing motor and the lever which operates the valve so that the balancing motor may function during a number of cycles of the control instrument before the clutch engages and moves the lever

Electric Relays When the current, which can be carried by the control instrument contacts, is insufficient to operate the control valve, electrical relays are used The current capacity of mercury-tube switches used in control instruments varies naturally with the type of circuit employed, &c , but in simple designs may be up to 25 amp at 125 volts, or, in switches made of refractory glass, up to 60 amp

Flow Controllers The differential manometer type of instrument may be employed as a flow controller by arranging for the float to operate the air-leak valve of an air-operated pilot system Of this type is the Foxboro flow controller As described previously, the differential manometer may be employed to indicate liquid-level, and as a liquid-level controller is in reality a flow controller, essentially the same instrument may be employed

In industry it is frequently found necessary to arrange that the rate of flow of one stream should bear a constant ratio to that of another For this purpose *ratio-flow controllers* are used This controller is in reality two interlocked instruments When of the manometric type it is constructed with two sets of differential-pressure chambers, one set connected to an orifice in the primary line and the other set to an orifice in the secondary line The differential pressure resulting from the flow of the primary fluid operates the setting device of the secondary instrument controlling mechanism in such a way that if the ranges of the instruments are equal, the differential pressures are equal or, if different, in such a way that the differential pressures are maintained in proportion to the scales

Valves.

Control Valves In selecting the most suitable type of control valve the following characteristics of the controlled medium must be considered

(*a*) Its chemical properties, also whether abrasive or non-abrasive in character If the fluid is corrosive, the necessary precautions must be taken in selecting the materials of which the valve body, stem, seating, and gland are to be fabricated

(*b*) Its normal and maximum temperatures and pressures These affect the material and design of the body and seats, also the size of the diaphragm in an air-operated type

(*c*) Its normal and maximum flows and possible fluctuations upon which depends the size of the valve and arrangement of the seats, ports, &c

Fluid-operated Type These are divided into two classes both employing a diaphragm or bellows to operate the valve In the *direct-acting type* the valve tends to close with increase of pilot-fluid pressure on the diaphragm In the *reverse-acting type* the increase of pilot-fluid pressure tends to open the valve A further division of types takes into account the arrangement of valve seats, &c

Generally the types employed are

(*a*) Butterfly valves for low-pressure gas or air

(*b*) Globe valves for medium-pressure fluids

(*c*) Balanced valves of the double-seating globe or ported type for high-pressure fluids

Gate valves are not commonly used

Globe Valves can be made suitable either for direct-acting diaphragm control, or by reversing the seat so that the valve disk closes upwards against it, suitable for reverse-acting diaphragm control The same result can be achieved by reversing the action of the motor Normally globe valves are used for pressures up to 150 lb per sq in , but they should also be used on any application where a tight-closing valve is necessary

Balanced Valves can be made suitable for direct-acting diaphragm control on fluid pressures up to 250 lb per sq in Such valves are quick opening and suitable for applications involving open and shut control They should not be used on applications requiring a tight-closing valve By reversing the seat so that the valve disk closes upwards on to it, the valve is made suitable for reverse-acting diaphragm control

The flow through a perfect throttling valve should be a straight-line function of the valve lift This is very closely approached in the Mason-Neilan parabolic design in which the area for the passage of fluid through the valve as it rises off its seating is regulated by suitably shaping the valve stem

The balanced and globe type valves may be operated to give 'On and Off' control by using a controller incorporating a non-throttling leak valve

V-port Valves are suitable for fluid pressures from 250 to 1,350 lb per sq in They are used on high-temperature high-pressure service, and are of the balanced gradual opening type They are not suitable for applications requiring a tight-closing valve, but are especially valuable where full-floating valve action is desirable The Foxboro Stabilflo valve is a modification of the V-port design which gives equal percentage increase of flow for equal increments of lift and has an effective rangeability of 2%–100%

Single-seated Needle Valves are suitable for pressures up to 3,000 lb per sq in and are available in designs which may be employed where full-floating action is required For high-pressure work the body is generally of drop-forged steel The plunger is of the needle type with bevel seat

Pilot Valves. The action of a typical pilot-valve system is illustrated in Fig 31 Air at constant pressure is supplied through line 1 to the pilot valve 2 So long as the pressure in the line 3 remains constant, no movement takes place in the control equipment If the pressure rises, the Bourdon tube tends to unwind, raises pilot-valve stem 5, and admits more air to the diaphragm head and closes the control valve sufficiently to lower the pressure to the control valve Reverse action occurs with a drop in pressure in the line The control valve is adjusted so that it moves over the entire range between the fully open and fully closed positions between certain limits of air pressure on the diaphragm head Intermediate air pressures result in intermediate positioning of the control valve The pilot-valve stem assumes a slightly different pressure for each different position of the Bourdon tube, and a movement of a few thousandths of an inch is sufficient to enable the pilot valve to accomplish the full change in the range of air supply

For operating butterfly valves, dampers, &c, a double pilot arrangement is very suitable Taking as an example an installation designed to maintain a certain gas pressure by regulation of the rate of flow

Rising pressure in the gas main raises the level of the mercury in a reservoir which in turn lifts a float This depresses the pilot-valve stem allowing increased air pressure to act on a bellows which expands and depresses the relay pilot-valve stem, admitting increased air pressure beneath the piston which operates a butterfly valve in the gas main The piston rises and partially closes the butterfly valve, simultaneously increasing the tension in a spring which tends to contract the bellows When the force of the air below the piston balances the tension of the spring, the relay pilot valve is in its neutral position and further motion of the piston and butterfly valve ceases, the gas flow having been decreased to give the required lower control pressure This type of valve is suitable for floating control

Employing the same principles, but utilizing high-pressure oil as the operating fluid in place of air, is the *Electroflo 'Straitline' Regulator* This is available for controlling temperature, pressure, or flow The pilot valve in this design carries a small impeller which rotates it continuously by reaction to the impulse of a jet of high-pressure oil This reduces friction in, and increases the sensitivity of, the pilot valve The action of the flapper type leak valve and bellows-operated pilot valve used by the Foxboro Company has already been described in the section dealing with Temperature and Pressure Controllers, and, as previously explained, it may be arranged for either 'On and Off' or floating control In the Kent and Bristol air-operated pilot systems the air leak is controlled by a chopper or vane which passes between two nozzles discharging opposing jets of air The resulting action of the chopper or vane on the pilot system is similar to that achieved by the flapper in the designs previously described

Electrically Operated Control Valves. *Solenoid Type* Control valves, generally of the 'On and Off' action type, may be operated by a solenoid arranged round an extension of the valve spindle which forms the armature The valve, which may be of the globe, balanced, or needle type, is held either in the open or shut position by a spring, and the energizing of the solenoid causes the spindle to move to the other limit of its travel in opposition to the spring

Motor Type The action of this type of control valve has been generally described in the section above dealing with All-electric Controllers With this type of valve the stem is usually connected to the motor (the drive of which is geared down) by means of a crank so arranged that the full range of operation of the valve is covered by the rotation of the stem through half a revolution As already explained, the motor control may be arranged to give either throttling or 'On and Off' action

Pressure-reducing Valves and Back-pressure Control Valves Such valves are usually of the self-operating type depending for their action on the pull or thrust of a weighted lever or spring In order to increase the sensitivity the pressure to be controlled is brought to bear on a large metal diaphragm, on the opposite side of which the force of the weighted lever or spring is exerted

For example, a diaphragm control valve may be employed as a back-pressure regulator The inlet pressure acts on the diaphragm The springs opposing this action are set for the desired pressure by means of an adjusting screw When the inlet pressure has increased sufficiently to overcome the resistance of the springs the valve stem is forced down and the valve opens, thus relieving the inlet pressure and permitting the springs to force the valve disk back on to its seat

By reversing the action of the valve so that it seats on the downward motion of the stem and by connecting the downstream pressure to the diaphragm head, this type of valve becomes a pressure-reducing valve Such valves may be obtained for use up to 400 lb pressure at 750° F or 750 lb pressure at 100° F

For the action of the compressed spring used in these valves may be substituted that of a weighted lever

For conditions which impose an onerous duty on the valve, a pilot operated design may be employed similar to that shown in Fig 32 In this instance the arrangement is adapted for pressure-reducing service The diaphragm is balanced between the action of the downstream pressure and the reaction of the main spring *B* If the downstream pressure falls, spring *B* forces open pilot valve *C* against the action of pilot spring *D* which normally keeps the pilot valve closed The opening of the pilot valve admits the upstream pressure below piston *F*, which rises and opens the main valve to allow fluid to flow through, thus raising the downstream pressure When this pressure increases to the desired value, as determined by the setting of the main spring, the diaphragm is forced back by the downstream pressure, the pilot is closed by its spring, and the flow is stopped Actually in operation the main valve floats with small variations in downstream pressure

Remote Indicating, Recording, and Control Devices

For the indication, recording, and control of liquid levels, rates of flow, pressures, draughts, temperatures, and positions of valves, &c, at long distances up to several miles, electrical devices incorporating self-synchronous motors are widely used Typical of this class of device is that adopted by the General Electric Company under the trade name of 'Selsyn' The devices are essentially small motors which when interconnected, operate so that one motor reproduces any motion imparted to the other In operation the motors are similar to synchronous motors They are shuttle wound, have definite poles, and are both connected through slip rings preferably to the same source of excitation which supplies single-phase alternating current

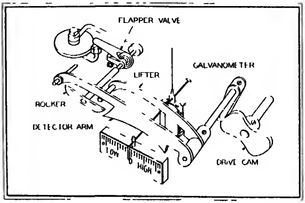

FIG. 30

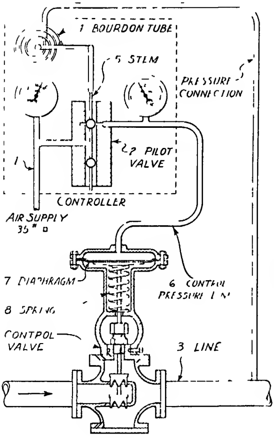

FIG. 31

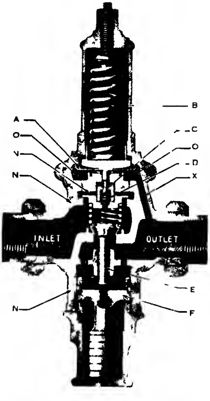

FIG. 32

The principle of operation is as follows When the receiving rotor is acted upon by the alternating current supply, as it is free to move, it will take up a position corresponding to that of the transmitter rotor In this relative position of the rotors, the voltages induced in the receiver stator equal and balance those induced in the transmitter stator, so that no currents flow in the stators and the torque is zero Should the transmitter rotor be turned to a new position, the voltages induced in the transmitter and receiver stators will no longer be equal, and as a result current flowing in the receiver stator circuit will set up a torque which tends to cause the receiver rotor to follow in the same direction as the transmitter rotor The transmitter rotor is held mechanically by its actuating mechanism, and the torque reacts against any force which may be restraining the rotor in the receiver The receiving rotor always tends therefore to seek a position which will result in it being in synchronism with the transmitter, and it will resist any effort tending to force it from that position.

The sympathetic torque which builds up in the transmitter against any force tending to restrain the receiver rotor is made use of in the de Florez system for the remote manual control of valves The motor operating the valve to be controlled functions in synchronism, as described above, with the motor which is manually operated at a distance from the control-point The distant operator in turning the rotor of the transmitter, however, can actually feel the sympathetic torque which is generated, and should this rise to an abnormal value he is aware of it and can order an investigation in case the valve has seized or is blocked by some foreign body In this way the straining of the receiver motor against undue load and possible blowing of fuses, or burning out of motors, or breakage, is obviated

It will be readily appreciated that the actuating movement of the indicating, recording, or controlling mechanism of an instrument can be easily transmitted by mechanical linkage or gearing to one Selsyn motor and thence through the self-synchronous system to another motor operating by similar linkage the final device in a distant indicator, recorder, or controller

The Application of Instruments

Process Control.

The value and use of the devices described in the foregoing sections can be illustrated well by reference to their use in the petroleum refining industry, which is typical of those in which keen competition for markets, and developments in allied fields such as engine design, has resulted in a necessity for the production of cheaper and more rigorously specified products In almost all branches the industry has incidentally passed from batch to continuous operation, which, involving, as it does, the handling in the plant of smaller instantaneous quantities, requires closer and more accurate control of the process variables

In order to achieve such control an accurate knowledge is essential of the values of the process variables, either continuously or at regular intervals This information may be obtained by judicious use of the indicating or recording instruments already described It will, however, be readily appreciated that while it is generally possible with adequate and sufficiently skilled supervision to control the process manually, more effective, and in most cases cheaper, control may be obtained by the use of controllers to regulate the more predictable or less involved variables, thus reducing the operating staff required to a number adequate to cope with only such indeterminate factors as demand human judgement

In recent times the necessary supervision has involved so little personnel that the small staff to be seen, for example, controlling large modern distilling units is a constant source of surprise and comment, their presence being generally necessary only to help the control instruments over a difficult period by resetting them to handle disturbed process variables, which may only have arisen from unusual conditions external to the plant itself

In most processes it is impossible to rely entirely upon automatic control by instruments, however well they may be selected and located, unless the process is very simple in character The best of instruments cannot handle, without readjustment, conditions outside the scope of those for which they are designed

Satisfactory results can be obtained from automatic control instruments only by a careful study of the process conditions and the selection of the appropriate instruments Consider, for example, the simple case of the automatic temperature control of the liquid in a vessel such as a reboiler heated by means of closed steam Under optimum conditions the controller should vary the position of the control valve on the steam line only when the heat load on the reboiler changes Unfortunately the pressure of the heating steam may fluctuate, resulting in unsatisfactory temperature control if a simple control instrument has been installed To counteract the varying steam pressure a more complicated instrument of the compensated type would be required, such as, for example, the Mason-Neilan Compensated Temperature Controller, the Foxboro Stabilog, or the Taylor Dubl-Response Temperature Controller On the other hand, the obvious auxiliary for a simple controller under such conditions would be a pressure controller on the steam-supply line, provided this is of adequate capacity Particularly if a number of controllers on several vessels are operating on steam from a single source, the installation of a separate steam-pressure controller will be the cheaper solution to the problem

It is frequently found advantageous to control such outside variables independently, thus permitting the use of simpler control instruments which under the more ideal conditions resulting therefrom give results as good as, or even better than, are obtainable from a complicated installation operating under the less favourable conditions

Another very important consideration in the satisfactory automatic control of a process is the location of the sensitive elements These should be so located that the process lag between the control-point and the detection-point is as small as possible Unsatisfactory results are frequently obtained because the control device is required to make changes long after the variables have affected the condition to be controlled It is natural that, where possible, an endeavour should be made in the interests of economy to take advantage of the relative cheapness of a combined recorder and controller It should, however, be borne in mind that best location of the sensitive element or detector is not always where the final result can be measured and recorded In such cases it is preferable to use a simple non-recording controller having the sensitive element and control device located in the best positions to give a simple control, and to locate a separate recorder at the position where the final result can be measured

In a typical modern atmospheric crude-oil topping unit, the following variables are automatically controlled

(*a*) The pressure of the steam supply to the pumps (if these be steam driven) (*b*) The rate at which the crude oil is charged to the unit

(*c*) The temperature at the top of the fractionating tower

(*d*) The tube still outlet temperature

(*e*) The level of liquid residue in the base of the tower

In addition it is necessary to regulate the rate at which reflux is returned to the various sections of the tower to control the specifications of the side-stream products If this regulation is effected manually, direct or remote control of the valves will be selected according to the height of the tower and the frequency of change in the side-stream product specifications Alternatively automatic control may be adopted

The steam supply to the unit will be regulated by a pressure-control valve located on the main from which are derived the branch lines to the various pumps on the unit This control valve will be set to give a supply pressure slightly below the minimum likely to occur at that point on the main, whatever may be the boiler load or the demands on the main between the boilers and the control-point

To obtain a steady rate of crude-oil supply to the unit a flow controller will be installed having the orifice located in the discharge line from the charging pump, and the control mechanism will operate a control valve on the steam line to the charging pump If the charging pump is of the centrifugal type, either motor or steam-turbine driven, the mechanism will control the discharge valve on the pump

The specifications of the overhead product obtained from the top of the fractionating tower depend upon the top-tower temperature, which in turn, other factors being constant, depends upon the rate at which reflux is pumped back over the top tray in the tower In crude-oil distillation other conditions are generally sufficiently steady to permit adequate control to be obtained by means of a temperature controller having the bulb located in the top vapour-dome of the tower, the instrument operating a control valve on the steam-supply line to the reflux pump If this is of the centrifugal type, the instrument will, of course, control the discharge valve on the pump Under conditions of steady load on the tower and steady pressure of the reflux supply to the control valves, a simple two-position electric control mechanism will generally give good results On the other hand, the greater range of valve movement inherent in a three-position controller would enable this type of instrument to cope more easily with changes required in the operating temperature without the necessity for the operator to reset the throttling range Such greater flexibility may warrant the small additional expense of the three-position mechanism

When conditions are variable, occasionally requiring a slow adjustment and at other times a quick adjustment to counteract a sudden surge in temperature, a more elaborate type of instrument is necessary These requirements would be met by a two-motor mechanism in combination with a trend-analysing instrument, or alternatively by a compensating or Stabilog type of controller

Because of the comparatively low operating temperatures which prevail at the top of a stabilizing column they are advantageously controlled by the installation of a flow controller in the reflux-supply line in place of using a top-tower temperature controller

The control of the temperature of the heated oil leaving the tube still is complicated by the possible intrusion of many variables such as heat losses from the outside of the tube still, percentage of excess air, draught, conditions of fuel supply, and charging rate Although the heat losses by radiation and convection from the setting are normally a small percentage of the heat input, a violent change in wind conditions may appreciably affect the operation of a very small tube still On the other hand, very large tube stills have their own particular problems which centre mainly round fuel and heat distribution However, if the charging rate is closely controlled, the hot-oil outlet temperature may be maintained within the required temperature limits by means of a carefully installed controller on the fuel-supply line to the burners Particularly important is the location of the sensitive element, which will vary from one tube still to another, depending upon the design It is usually desired to record the oil-outlet temperature, and in certain cases the temperature sensitive element may be satisfactorily located at the final outlet to serve a combined controller and recorder With other tube-still designs some intermediate position in the path of flow of oil through the tube still will give better control In general it should be located at a point where the oil has undergone the most rapid temperature rise In this position it is particularly sensitive to changes in the fuel supply, and changes made by the instrument in the position of the control valve in the fuel-supply line are most rapidly detected In a tube still which transmits heat mainly by radiation satisfactory results may be obtained by running the sensitive element or elements down between the roof tubes where they are particularly affected by radiant heat and can correct the fuel supply as necessary before the effect has been shown up in the hot-oil outlet temperature Some of the major variables are relatively steady, furthermore, slow gradual changes are required in the supply of fuel A floating or throttling type control is therefore suitable, and in view of the time lag in the furnace itself and the delay before changes in fuel supply affect the temperature of the oil in the tubes, a trend-analysing, compensated, or Stabilog type of instrument is desirable This great time lag makes it advantageous in many cases for the temperature controller to be operated in conjunction with a flow controller on the liquid fuel supply line or pressure controller on the gaseous fuel supply line The temperature controller resets the control point of the other instrument as may be required by the outlet temperature

The level of the liquid residue in the base of the tower is controlled by a liquid-level controller either of the float or differential manometer type operating a control valve on the steam-supply line to the residue pump, if this is of the steam-driven reciprocating type, or on the discharge branch of the pump if this is of the centrifugal type either motor or steam driven

Automatic control of the side-stream products may be accomplished by the use of flow controllers on the side-stream product lines If the quantity of internal reflux from the section of the tower above the side-stream offtake is constant and the net flow of the product is maintained constant, the spill-over reflux to the section of the tower below the offtake will be constant This assumes a constant rate of flow of charge to the tower An interesting recent development obviates even this assumption by the use of ratio-flow controllers to regulate the flow of side-stream products as a constant percentage of the charging rate The percentages of the various products present in a crude oil may be determined by laboratory analysis, and the ratio-flow controllers on the charging line and products lines set to obtain these percentages In operation the required products will be automatically secured regardless of changes in throughput, provided the composition of the charging stock does not vary

THE USE OF INSTRUMENTS IN PETROLEUM REFINING

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THE word 'instrument' really ought to cover any kind of apparatus, other than the hands, used in getting information during the process of refining, and of course a watch is such an instrument and also measuring vessels used in laboratory

The more restricted use of the term, however, is made to cover robust measuring devices which become an integral part of an operating plant

The actual principles of operation of the various instruments available are described elsewhere in this section, but there are one or two points which experience teaches in the use of such instruments which it may be worth while setting forward for the benefit of those who desire to acquire a knowledge of this particular aspect of petroleum refining

As a rule we are concerned with getting intermittent or continuous knowledge of a state of temperature or pressure or of quantity, and in an increasing number of cases with an attempt to apply controlling mechanism to make the necessary adjustment without further human intervention whenever the condition being measured tends to depart from the set or desired level Thus we have level controllers, flow controllers, temperature controllers, pressure controllers, &c , all of which can now be obtained as reliable and accurate instruments for the use of the oil refiner

It may be said, in fact, that in general, the instrument-maker has tackled his part of the work of providing the means of measuring or controlling in a very satisfactory manner, but it is still necessary to use intelligence in the setting and in using of the results which can be obtained by the use of such instruments

To take an apparently very simple case—the measurement of temperature The various types of indicators, such as mercury-in-Steel thermometers, galvanometers or potentiometers used in conjunction with thermocouples or resistance-thermometers, are each capable of recording with fair exactness the temperature at the point from which the record is taken, i e the thermometer pocket, but quite a lot of consideration needs to be given to the positioning of such a pocket before one can be satisfied that it really does represent the temperature which we are aiming to indicate, record, or control

The fitting of a pocket in a non-representative portion of a stream of gas, or the lack of care to prevent radiation from or to the pocket may easily give a very misleading reading on the instrument, however accurately the instrument is calibrated

A good deal of prejudice against flow meters has probably arisen from the fact that a type designed to count pockets full of liquid, or alternatively to record accurately a differential head due to flow through an orifice, may be entirely accurate mechanically, but unable to take account of varying temperature conditions or varying specific gravity of the fluid which were not bargained for when the instrument was fitted

It is probably useful to remind ourselves in this connexion also that a watch that keeps slightly incorrect time can be a bigger nuisance than one that stops.

A point of interest is always the decision as to which condition of a number is best measured in order to keep proper control of unit In the case of a distillation unit, for instance, for a given type of material, a certain degree of evaporation will have been achieved when equilibrium has been established at any fixed temperature and pressure It might seem a simple matter to measure the temperature at the outlet of the pipe-still when the flow of oil is constant

This is obviously true provided it may be assumed that the pressure at that point remains constant, but such an assumption is precisely the kind of assumption which tends to be increasingly falsified as a unit continues to run, the most common case being a slight but steady increase in pressure as the pipestill cokes up, which may or may not be accompanied by an increasing falsification of the temperature reading itself, due to coke deposition on the thermometer pocket,

As the pressure rises then, a bigger proportion of the heat will go into sensible heat, i e showing an increase in temperature instead of evaporation, which will cause the instrument quite wrongly to cut back the fires, if a controller has been fitted to do nothing else but maintain a constant temperature in the pipestill outlet without regard to changes in pressure

In running a cracking plant fitted with a controller to maintain a constant gas or spirit make, an unforeseen change in condensing conditions, not allowed for, would give a false apparent make of gas and thus upset conditions if an instrument had been set to control the fires to maintain a constant gas make without due regard to the effect of changing condenser conditions

In the case of orifices used to measure the flow of liquid or gas, it is necessary to assume a constancy of size and shape, but this constancy can be, and frequently is, steadily interfered with either by corrosion or by some silting up of one side, which changes the shape of the pipe, and therefore the discharge coefficient of the orifice

These are matters well known to people of practical experience, but they can be quite annoying factors in undermining people's confidence in the use of instruments if care is not taken to inspect at sufficiently short intervals and check up on these apparently simple assumptions which were made when the instrument was fitted, to make sure that they have not changed from their original setting

In connexion with control instruments, it is necessary to guard against getting a series of controls which are not mutually independent, otherwise there is a danger of setting up waves of hunting which can actually be a cause of unsteadiness in a plant, when they were in fact fitted to improve steadiness

The correct action to be taken by a control as a result of a condition moving from a pre-arranged setting has also to be considered very carefully in order to get proper steady running of the plant

In the case of a pressure controller, furthermore, the results of a collapse of the controlling mechanism should be given careful thought A quite common method of controlling pressure is to have a valve so fitted that its position is maintained by the delicate balance of a fixed spring against a diaphragm, pressure being maintained or altered in the diaphragm chamber by the changes in the condition of pressure to be maintained This is often carried out by making the temperature or pressure change, which it is sought to correct, cause alterations in the air supply to the diaphragm chamber and thus move the valve to some new position If such a pressure controller is used on a supply of gas to a furnace, for instance, it is very important that in the event of any interference with the air supply the valve shall close, thus cutting off gas completely from the furnace rather than collapse to 'full open' and thus deluge a furnace with gas with the consequent danger of a serious fire

Similarly, if a controller is used to maintain a fixed pressure in a vessel, it is important to study which is the most serious, the boxing-in of the pressure by a collapsing of the valve into the shut position, which could obviously be dealt with by some form of relieving valve, or, alternatively, the complete loss of pressure which would result from the collapsing of the valve into the open position

Summing up this brief survey it can be said

1 Instruments to-day are reliable as such and very good servants, properly used they save labour and improve products

2 Care is needed in selection of data to be observed or controlled, and in fitting instruments to really give the information required

3 Care is needed to arrange for safe behaviour in the event of unforeseen collapse of the instrument

4 Particular care is needed to guard against insidious small, but growing, errors due to changes in conditions of measurement not legislated for, e g coking of thermometer pockets, unrecorded pressure changes, silting of orifices, &c

5 In short, take care of the instrument and the instrument will take care of the plant

SECTION 37

ELECTRIFICATION OF REFINERIES

General Electrification of Refineries	D H McLACHLAN

GENERAL ELECTRIFICATION OF REFINERIES

By D. H. McLACHLAN, M.I.E.E., A.M.I.Mech E.

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ELECTRICITY makes possible the centralization of power production with the decentralization of application, and is therefore a convenient medium for the efficient utilization of various forms of energy

The conditions governing the design of power-generation plants for oilfields and refineries differ essentially from those relating to a public electricity supply station In many cases surplus fuel is available, and as a result efficiency may not be considered the most important factor

The electrical requirements are wide and varied, since almost every operation known in industry is found in one plant or another

Continuity of electrical power supply is important in order that stoppages of the various processes is reduced to a minimum

There are four ways of obtaining electrical power

1 Purchase all power
2 Purchase all power, but maintain stand-by generating equipment
3 Purchase part of power and generate the remainder
4 Generate sufficient power in the refinery for all its requirements

With the first method it is essential that power be available from at least two incoming power lines, with proper protection on each to ensure an uninterrupted power supply

The second method differs from the first, in that the stand-by generating equipment is the alternative source of power supply and is tied in and floating on the line ready to supply power in case the purchased power fails

Refining processes require considerable amounts of steam, often making by-product electric power advantageous For this reason the third and fourth methods are recommended In the third case the quantity of process steam required produces only part of the necessary electric power, whereas the fourth produces all necessary electric power as a by-product

A cessation of electrical power supply not only causes loss of output, but disorganizes the steady conditions of temperature and pressures of complicated processes, and therefore for all such plants an alternative supply should be provided The two supplies should be operated in parallel, but in cases where this is not possible arrangements should be made for automatically changing over from one supply to the other in the event of failure of the supply in use The automatic change-over should be carried out within a minimum period in order to prevent the stoppage of the electric motors In this connexion any no-volt coils used with the motor-control gear should be fitted with delayed-action devices to ensure that the control switch is not operated during the change-over

Distribution network design involves a balancing of security and economy This is most evident when the two chief types of lay-out are considered, namely, the radial and the interconnected On a large system maximum security is undoubtedly obtained by an individual transmission from the generating station to every distribution centre of a certain magnitude With such a lay-out any failure of main, switch gear, or transformer is not likely to affect more than the supply to the one distribution centre, and it is advisable to make the duplicate supply to each distribution centre automatic The objection to this arrangement is the number of feeders required Assuming that spare feeders are necessary, from 50 to 100% spare feeder capacity is involved, whereas if groups of distribution centres are fed from a common interconnected network a single spare feeder may act as spare to several other feeders In the event of a failure of protective gear, a break-down on any part of an interconnected system may affect every other part Modern system design has largely been occupied with seeking means for minimizing these disadvantages of the interconnected system In general the radial system is to be preferred with provision for mutual assistance in case of serious emergency and for ease in carrying out maintenance without having to shut down plant

An electrical power system is made up of many parts, and all of these parts must be properly designed and coordinated with each other if satisfactory and economical operation is to be achieved

The proper development includes the working out of the system problems such as limiting short circuits and abnormal voltages, system stability, selective relaying or isolation of faults, voltage control and regulation

The question of reserve capacity and multiple sources of supply to the various plants is important for facilitating easy maintenance and ensuring continuity of supply

The network should be such that the reserve parts and feeders are fitted into a unified system in such a manner that they can be used to best advantage so that the amount of spare capacity is reduced to a minimum Pyramiding should be avoided

The constant growth in the power demands to be dealt with in distribution systems has led to the adoption of generating units of increasing capacity For large units the capital outlay per unit of power is smaller The larger plant has also a better efficiency, so that the service is more economical The number of machines required for a given output is smaller with such large units, with the result that there is considerable saving in switch gear, &c, and simplification with regard to operation and maintenance

Increasing attention is now being made to the protection of plant The best safeguard for any electric machine is to adopt a substantial design Faults, however, occur, and some means of protection against them must be provided The protective relay should be arranged not only to take over the protection of the machine or parts of an installation, but also to cause the faulty parts to be cut out as soon as possible, so that the remaining parts of the system are able to continue to work undisturbed under all conditions.

Where alternating current is used for electric power distribution, the standardization of frequency is important In Great Britain, France, and other European countries 50 cycles has been adopted as standard, and 60 cycles in America and elsewhere

Voltages should be selected after a study of the economic conditions as determined by a contrast of operating losses and interest on the investment in copper conductors and apparatus when operating at the lower voltages against the lower operating losses and reduced interest payments on less copper in conductors, but increased high-voltage apparatus costs. The economic voltage will in a general way vary as the load factor, the capacity of the plant, and the distance between the generating station and the load centre.

It is of great importance to adopt or use standard voltages, as this promotes interchangeability of plant and apparatus. In Great Britain the standard high-tension distribution voltages are 3,300, 6,600, and 11,000 volts. For transmission 33,000 and 66,000 volts are standardized, with 132,000 volts for main lines, linking power stations, &c.

Standardization of high voltages is more advanced than that of low voltages. A three-phase distribution voltage of 400 volts giving 230 volts between phases and neutral for small motors and general electric lighting is now in general use. In America a voltage of 115 is favoured for general lighting and similar applications.

Frequency control is of major importance, since service to many classes of load is involved.

The increasing use of commercial synchronous time clocks requires some method of compensating for accumulated frequency error. To meet this requirement master clocks are installed in the generating stations. The master clocks offer a means of comparing the 50- or 60-cycle synchronous time to that of a standard timepiece, and thus permit periodic corrections by slight changes in frequency. The master clocks should be checked for accuracy daily against radio time signals. This method of controlling frequency error is very effective.

Choice as to whether direct-current or alternating-current generators should be installed will depend on the following:

(*a*) Capacity of plant involved.
(*b*) Distance of transmission.
(*c*) The size of loads and applications.

In general where the installation is of reasonable size alternating-current generators are employed, due to simplicity of operation and the ease with which static transformation can be carried out and thus facilitate transmission and distribution.

Direct-current machines are seldom wound for a voltage above 600, but alternating-current generators may be wound as high as 33,000 volts and for frequencies 25 to 100 cycles per sec. As a general rule where overhead transmission is adopted it is well not to use an extremely high voltage for the generators themselves, but to use step-up transformers, in cases where extra high transmission voltage is necessary. Machines wound for high potential are more expensive for the same capacity and efficiency, but the cost of step-up transformers and the losses in these transformers are saved by using such machines, so that there is a slight gain in efficiency which may be used in better regulation of the system. On the other hand, lightning troubles are liable to be aggravated when transformers are not used, as the transformers act as additional protection to the machines, and if the transformers are injured they may be more readily repaired or replaced.

Modern alternating-current generators of the revolving field type meet the general requirements of generation for industrial works.

The standard type comprises revolving field machines with direct-coupled exciters.

Ventilation is important, and special consideration should be given to the importance of ensuring steady and uniform distribution of air throughout the stator, thereby totally eliminating local heating or air pockets, which might lead to deterioration of the insulation.

The parallel operation of alternators is a subject which is exceedingly complex, and a full knowledge of the type of prime mover, its special characteristics, and the local conditions are essential in order that satisfactory service may be assured.

The inherent regulation of alternators varies over wide limits. The regulation is calculated as a percentage rise in voltage from full load to no load, assuming constant speed and excitation. There are at times certain disadvantages to be met with in alternators with close regulation when required to operate in parallel, and alternators with a wide regulation are often specified for operation in conjunction with automatic voltage regulators.

For general distribution 11,000-volt three-phase lines meet most requirements, as the erection costs are not appreciably higher than those of 3,300-volt or 6,600-volt lines, whereas the carrying capacity is considerably greater.

In certain countries types of supports, such as ferro-concrete, tubular steel, fabricated steel, &c., must be used, but apart from very high voltage transmission, the earliest form of support—a creosoted wood pole—is still in favour where these are suitable and available.

Various types of conductors have been in general use, and although it is difficult to justify any type of conductor other than copper on account of its well-known reliability and high conductivity, steel-covered aluminium may be suitable in certain cases on account of higher tensile strength, resulting in longer span construction and cheaper lines with less insulators, and consequently greater immunity from insular failures and lightning disturbances.

The question whether an earth wire should be erected is a controversial one. By its elimination a saving can be effected owing to reduction in size of poles and in cost of conductor and supporting fittings, but against this must be considered the installation of separate earth plates at each support, the resistance of which may be of a high value. This high resistance may affect the correct operation of automatic switch gear and give rise to possible danger to human life and property should a fault occur at that point. An earth wire is recommended for distribution and transmission lines, as apart from advantages indicated above the earth wire is undoubtedly of use as a protection against lightning.

With a view to reducing the duration of interruptions to a minimum, section switches should be inserted in the lines at accessible positions and at regular intervals. These enable the line to be sectionalized rapidly in the event of a fault, and also are useful when carrying out repairs and connecting up of new plant.

For the protection of branch lines, a suitable type of pull-down switch gear having a movable portion of the fuse gear which can be brought down to the ground level to enable the fuses to be inserted should be adapted. With this type of switch gear it is not necessary for the linesman to climb the pole to replace fuses.

As an alternative to pull-down fuse gear, pole-mounting automatic circuit breakers provided with reclosing devices may be used. The disadvantage of oil switches is that inspection, maintenance, &c., is difficult unless air-break isolators are provided on either side, which, of course, adds to the cost. At more important control points, however, there is ample scope for the use of this type of switch.

The reclosing devices ensure that a circuit breaker is not permanently 'opened' because of a momentary fault

The installation of lightning arresters or surge absorbers should only be fitted to important lines in exposed positions On apparatus where a failure would be of serious consequence, i e transformer, dividing box, and switch-gear insulators, &c , the flash-over value should be increased

In general, lightning arresters are not favoured in compact networks such as met with in refineries In oilfields where the network is generally scattered lightning arresters and surge absorbers may be used with advantage

In large refineries it is desirable to run both high- and low-pressure mains underground The use of a cable consisting of impregnated paper insulation with a lead sheath and steel armouring laid direct in the ground is now general

The cost of an underground system is greater than an overhead system, but as a general rule the additional capital cost is justified on the ground of less stoppages of plant, freedom from lightning troubles, and considerably less obstruction in the refinery due to the elimination of poles and other overhead structures

In general, all transformers should be of the three-phase type and be provided with natural cooling, except in sizes above 10,000 k v a where air-blast or other form of cooling may be employed above approximately half-load

On-load ratio-changing equipment should be fitted to all transformers in important sub-stations The range of ratio change to be provided depends on the conditions under which the transformers operate In general this equipment should be arranged for automatic operation

When low-voltage auxiliary supplies are required a small transformer can be directly connected to the lower voltage terminals of the power transformer These auxiliary transformers are treated as an integral part of the main transformers with which they are associated Each main transformer should be fitted with a temperature-indicating device, which registers the temperature of the oil near the top of the transformer The indicator can be used to operate an alarm or to trip a circuit breaker if required

In the early days of the application of alternating currents to electrical distribution, the question of voltage regulation was predominant and transformers even up to comparatively large sizes were built with reactance values as low as 2% or even less. This practice was quite natural, for it was realized that good voltage regulation was desirable, but little experience had been gained as to the effects of short circuits on the system and connected apparatus Practice has changed radically, until to-day the values of reactance for transformers are chosen on the basis of the minimum value that will allow the transformer to withstand the mechanical stresses due to short circuit, and these values are as high as 10% or even 12% In these cases the voltage drop that results is compensated for by on-load tap-charging equipment on the transformers, or by some other form of separate voltage regulator In spite of the increased circuit reactance which is now usual, the insertion of additional reactance is quite often necessary

The most usual application of a current-limiting reactor is where the conditions on the system result in a short-circuit k v a beyond the rupturing capacity of the installed switch gear Much knowledge has been gained in recent years as to the capability of a switch of rupturing a short-circuit current, and in many cases it has been found that existing switches do not have the rupturing capacity originally expected Systems have been extended and more generating plant installed, thus increasing the possible short-circuit k v a Hence it has been necessary to carry out careful investigations into the characteristics of the system to determine the relation between the worst possible fault condition and the capacity of the switch gear to deal with it

To replace the existing switch gear with new equipment of greater rupturing capacity is often an expensive matter, though there may be circumstances when this course is justified It may be possible in some cases to increase the rupturing capacity of the switches by making some modifications, such as the replacement of existing contacts with contacts of a later design The usual procedure, however, is to install current-limiting reactors, the effect of which is to limit the short-circuit current to a value that can be safely ruptured by the switch gear

For general distribution only the main sub-stations should be constructed of brick or stone and equipped with oil circuit breakers

The question of whether outdoor or indoor switch gear should be used depends on cost It has been found in some cases that the additional expenses incurred in making switch gear suitable for outdoor use is greater than the cost of a building

For situations where a small demand only is anticipated, the steel kiosk sub-station will be found to be an economical proposition As a general rule, with this type the high-tension compartment should consist of oil-break or air-break switch gear for controlling the incoming and outgoing feeders in the case of ring mains, and air-break isolators and fuses for local transformer protection Ample accommodation should be provided for the transformer, and provisions made for at least a 250-k v a transformer, although in the initial stage a 100-k v a transformer may only be necessary For the protection of the outgoing low-tension feeders, distribution fuse units will meet the requirements

The ventilation of the kiosk should be given consideration, and arrangements must be made to avoid the ingress of moisture or dust by providing suitable baffles

The low cost of installing pole-mounting transformers has resulted in their extensive use for the provision of electrical supplies where the demand does not exceed 100–200 k v a

The sizes and types of transformers should be standardized, as this permits of transformers being moved to other locations to meet load demands which may have increased or decreased

The transformers should be of robust design, capable of withstanding surges due to switching operations and lightning disturbances, and the insulators should have a higher flash-over value than the remainder of the insulators on the line

Terminals are fitted either on the cover or on the side of the tank, but the latter position is preferable for the inspection of the transformer or changing of tappings

In deciding the system of connexions to be adopted, the fundamental and principal factor is to keep the number of switch units to a minimum In large sub-stations which are interconnected, double bus-bars with bus-bar coupling and sectionalizing circuit breakers may be required

High-voltage switch gear of the open and metal-clad types for both indoor and outdoor services is now in general use In the most important sub-stations circuit breakers may be remote electrically controlled, the source of power being a 110-volt accumulator battery for both opening and closing the breakers. The battery capacity required for breaker operation, emergency lighting, and indicating purposes is approximately 250 amp hr at the 10-hour rate Trickle charging of batteries is now used to a great extent

Hand-operated circuit breakers are used in less important unattended sub-stations where the rupturing and current-carrying capacity of the switch is sufficiently small to make hand-closing reasonably easy In such cases the switches are tripped by means of small 30-volt accumulator batteries

Portable oil-drying and filtration equipments should be used for reconditioning the circuit breaker and transformer oils

In power stations the most important condition to be fulfilled is absolute reliability—this is best attained by making switch gear and station lay-out as simple and easy to supervise as possible, and also by not attempting to crowd the plant into too small a space Only that apparatus which is necessary to satisfy the above requirements should be installed A plant laid out on these lines is easier to supervise, and not only is the number of mistakes likely to be made in operation reduced, but the number of possible sources of error is diminished as well

It is important to provide the power station with two sets of bus-bars which give flexibility to power-station operations and constitutes a desirable reserve

In power stations supplying heavy current at low pressures, the instantaneous and steady short-circuit currents reach very high values, and the switch gear must be designed to withstand these mechanical and electrical stresses Although apparatus design and construction have reached a high standard, it is nevertheless often necessary to reduce the values which short-circuit currents would reach by subdividing the bus-bars and in some cases by adding reactors to the equipment

When current-limiting reactors are introduced between generators or bus-bar sections under normal conditions, practically no current will flow through the reactors, and as a consequence their presence will in no way affect operation However, should a short circuit occur, they will prove effective in limiting the current that might flow as a result

In plants for higher pressures with step-up transformers, the working of the generators direct on the low-tension bars should be avoided, and the output of the transformers should be made the same as that of the generators, so that a generator and a transformer can form one unit operating on the high-tension bus-bars In this way oil switches on the low-tension side can be dispensed with The power required for the needs of the station itself is in these cases tapped from one of the generators, or supplied by an auxiliary generator or small step-down transformer connected to the high-tension bus-bars

Automatic voltage regulation of all the generators should be provided

Generators of small outputs are protected by over-current time-limit relays Units for large outputs and units working in parallel should be equipped both with over-current time-limit relays and with reverse power relays, so that if a fault occurs in the generator itself the latter may be cut out quickly Differential relays form an excellent kind of protection on account of their very rapid action To prevent a defective generator from supplying its own fault, the excitation must be cut off immediately, either by the over-current relay, the reverse power relay, or the differential relay. For this purpose automatic exciter field switches are used.

For pressures up to and including 33,000 volts metal-clad switch gear is established practice, and outdoor open type is generally used for higher voltages On metal-clad gear all live connexions and all insulation are enclosed in earthed metal For the purpose of isolation and maintenance, the circuit breakers are made to withdraw from the bus-bars and circuit connexions In all designs of metal-clad gear the designer aims to make it impossible to touch or even see a live connexion, by this means he reduces the risks of short circuit, prevents danger from shock, and also reduces to a minimum the maintenance necessary to keep the switch gear in condition

The great advantages of metal-clad gear is its compactness, which not only saves space, but allows for easy and efficient interlocking, the saving of space being due to the possibility of reducing the spacing and clearances required with air insulation

The bus-bars on metal-clad switch gear are enclosed in metal containers The copper conductors are usually wrapped with fibrous insulation and submerged in either compound or oil Compound has been mainly used for this purpose for a number of years, but there is now a tendency towards the use of oil, particularly at higher voltages Oil has the advantage that it is a better transmitter of heat than compound, and where bus-bars carry heavy currents it allows an appreciable reduction in the area of conductor It is usual to keep the oil under a small pressure by means of conservator tanks as used on transformers

Cellular type gear is switch gear in which the main connexions and bus-bars are bare conductors mounted on porcelain insulators The whole gear is enclosed in brickwork or concrete cells or equivalent, designed to separate adjacent switch units The use of complete phase isolation by means of walls and floors as followed in cellular construction does not provide any advantage over the metal-clad type of gear mentioned above

On account of space required and cost of buildings, outdoor switch gear is generally used for all extra high voltage work Open type outdoor switch gear has the advantage that above certain voltages there is a saving in cost over other types With this type of equipment it is possible to space the gear and conductors widely without undue cost, and so get security and prevent the spreading of arcs and fires

There are, however, objections to outdoor gear It is exposed to danger from lightning and to danger of short circuits from birds, &c It is also more accessible to malicious damage than indoor gear Maintenance is difficult in bad weather, and the cost is relatively high In dirty districts it is necessary to maintain the insulation by frequent cleaning of insulators

The following principles should be followed in laying out cellular switch gear

(1) Individual units and equipments should be so designed that the risks of break-down are reduced to a minimum
(2) Separation of equipments by barriers and partitions so that the failure of one switch unit does not damage its neighbour
(3) The arrangement of switch units and system connexions so that one whole group can be put out of commission without seriously affecting service
(4) To provide means of fighting fire, draining, and handling oil, &c
(5) To provide for easy and safe maintenance
(6) Where necessary to section the switch gear with reactors to keep the breaking duty inside the capacity

of the circuit breakers and to maintain the voltage of the system under fault conditions

(7) To eliminate as far as possible all external inflammable materials

The principles governing the lay-out of metal-clad gear do not differ from those applying to cellular type gear, except that since metal-clad gear has been shown in practice to possess a considerable degree of fire resistance, is effectively phase isolated, and offers a much reduced risk in operation, a certain amount of latitude is permissible in applying the principles

Usually the control boards, either of the vertical or desk type for remote operation of the main switches, are provided with panels of sheet steel painted with mat finish, whilst the instruments, and as far as possible, the apparatus, should be of flush type and finished in black with nickel-plated edges and surrounds The boards can also be made of marble or slate slabs, but the sheet-steel panels are preferred

Closing by hand of large oil breakers for high voltages or current is only possible at considerable expenditure of energy, and it often happens that one attendant is not strong enough for the purpose In the case of breakers employed for synchronizing operations, rapid switching is an important condition, and the application of solenoid or motor switching-in apparatus is necessary

As a general rule it is recommended that all high-voltage sub-station and power station switch units should be remotely operated

The protection of electrical installations has now reached a high standard Large financial losses can be prevented if the instantaneous clearance of faulty sections and the stability of healthy sections is assured by means of proper protective devices The total cost of a protective system when expressed as a percentage of the cost of the equipment protected is usually very small and ought to be considered as an insurance premium

Protective systems should be designed so that they will operate with reasonable fault settings Under average conditions with good equipment a fault can be cleared in under 0 3 sec, counting from the time when the fault current becomes great enough to operate the relays until the circuit breakers have opened The rate of rise of fault current during this period is so rapid that no relay-tripping scheme can conceivably cause the circuit breakers to open in time to limit the fault current

The relay settings should therefore be adjusted to a value that will allow a high stability factor, and unduly low fault settings should not be aimed at

With the growth of electrical systems both their routine operation and their operation under emergency conditions are becoming more complex On large systems it is usual to centralize the control in the hands of a control engineer Such control deals with the most efficient generation and distribution of load and with all important routine or emergency switching System control is in the process of active development in so far as giving the control engineer more direct supervision of the system than is obtainable by telephone methods, and in the control room visual indication of the position of the more important circuit breakers on the system is being provided

Improved means of electrical communication, more stable and efficient methods of feeder protection, reliable devices for the indication at any distance of switch conditions, meter readings, and the like have resulted in the establishment of remote control systems, which are not only available at a cost which can be balanced actuarially to advantage against saving in labour and other charges, but they provide incalculable advantages in the improved reliability of the system

The improved control systems now available are the result of development work partly on power networks, but mostly in the field of communication engineering, and employ well-known basic methods of signal transmission and apparatus well proved in telephony and telegraphy, modified and adapted to suit the particular requirements of power networks

In respect of communication and supervisory control, the requirements may be summarized as follows

1 The passage of instructions between the control and subordinate personnel This may be accomplished by.
   (*a*) Telephone
   (*b*) Teleprinter
2 Facilities enabling the control operator to open and close switches at distant sub-stations or to bring in and cut out generating plant
3 Automatic indication to the control operator of the position or condition of any piece of apparatus at a distant sub-station or generating station
4 Facilities enabling the control operator to read meters at distant stations

Each of the foregoing services requires a channel of communication The channels available employing pilot wires may be summarized as follows

1 A buried armoured cable
2 Aerial wires erected on the same supports as the power conductors, or on a separate pole line
3 An aerial cable suspended from a wire attached to the overhead transmission-line supports, or on a separate pole line
4 Lines forming part of the telephone administration

In addition to the above, two further means of communication are available not requiring the use of pilot wires, &c, i e carrier currents superimposed in overhead lines and radio

The consideration of traffic requirements is important One channel may be used for several services arranging that each service occupies the channel as required Given a channel of communication, the character of which will permit of its use for telephone or telegraph, remote control, supervision, and remote metering, these four services may be operated over the single channel, the technical arrangements being sufficiently flexible to give any priority required

The simplest method of obtaining a measure of centralized control of a number of generating stations and sub-stations forming an interconnected network is to employ only a straightforward telephone system, and to arrange for all operations to be performed manually in accordance with instructions telephoned from the control point While this procedure may adequately meet the requirements of certain networks, it does not provide the advantages offered by the more comprehensive systems which can be applied to modern plant Further, it involves the provision of staff at each station to carry out the necessary operations, whereas by the addition of other facilities to the system it would be possible to leave many of the stations entirely unattended. For instance, the usual operations effected by sub-station attendants, such as opening and closing of switches, the starting and stopping of all kinds of converter plant, and the regulation of voltage on both alternating-current and direct-current distribution systems, can readily be brought under the direct control of a central station

It is now possible to control a switching station or a group of remote unattended sub-stations over one pair of pilot wires, but in this case the amount of selective equipment necessary may be such as so far to increase the total cost of the system that it would be more economical to provide an additional communication channel and employ less complicated apparatus

The principles upon which selective systems are based are those commonly employed in automatic telephony, the signals transmitted over the channel consisting of trains of impulses, by means of which standard telephone type relays are operated, which in turn control multi-point automatic selectors Thus, by combinations any particular control gear can be selected and subsequently operated by the transmission of a further signal or signals

Apart from exceptional circumstances, it is impracticable to carry out operations at a distant point without the aid of facilities whereby the actual condition of the plant could be ascertained It is therefore usual to consider remote control and remote indication together under the title of 'Supervisory Control'

By means of the same selective equipment, central indication can be obtained, either continuously or on demand, of the condition of almost any kind of plant Provision can be made for the remote indication of the positions of oil switches, field regulators, induction regulators, and transformer tap-changing gear and similar equipment, and conditions obtaining in generating stations and sub-stations

The flexibility of modern systems of supervisory control is such that their use is being extended to the remote control of pumping stations, all kinds of valves, level indicators, and in many other directions

In the majority of cases, remote metering is combined with remote control and indication, and can be introduced so that all three services may share one or more channels

The meter readings are transmitted by trains of impulses indicative of the deflexion of the originating meters either continuously or on demand, as with remote indication of switch positions and the like

The equipment on the control board consists of a diagram of connexions of the power station and sub-stations with linking-up network Coloured lamps show whether circuit breakers are 'on' or 'off', and instruments provide all necessary readings

For the purpose of considering alternative systems of drive, the plant units in an oil refinery or oilfield may best be grouped according to the length of time during which they may be shut down without causing serious inconvenience and/or damage

It may be taken that in large pipe stills loss of circulating pumps should be avoided, not only because of loss of output, but more important is the danger to the distillation unit through loss of circulating oil, and also because of the extended time required for restarting

The various units may be divided into four types

(*a*) Those which must not on any account stop
(*b*) Those which must not stop more than 5 sec
(*c*) Those which may stop up to 5 min, but not longer
(*d*) Those which may stop for a period of some hours without interfering with operations or throughput.

(*a*) The only way to ensure continuity of supply for these duties is to have the pumps in duplicate, each of sufficient size to carry the load and drive each pump of the pair from a totally different electrical supply As an alternative, one pump steam driven and the other driven by an electric motor with automatic change-over would satisfy the requirements

(*b*) These units should be arranged so that in the event of a failure of the electricity supply an alternative electrical supply is automatically switched on after disconnexion has been made with the faulty feeder The alternative supply should be available from an independent source in preference to being taken from another sub-station group

(*c*) This should be as (*b*), but with hand change-over of electrical supply, or with using as a stand-by, always kept ready for immediate use, a steam-driven pump

(*d*) In this case the usual practice is to provide no stand-by or alternative supply, but to carry spares for such parts as are likely to cause trouble, i e spare coils, &c These can be installed without entailing a shut-down of the unit for more than a few hours

The pumps most commonly used with electric drive are of the reciprocating, centrifugal, and rotary types

Both motor and pump characteristics must be examined before selection of the proper drive can be made Where constant-speed operation is required, the squirrel-cage induction motor or the synchronous motor may be used For some constant-speed applications the wound-rotor induction motor must be used on account of starting conditions, power-line requirements, or motor size Adjustable-speed operation requires a wound-rotor induction motor with secondary resistance, a brush-shifting commutator motor or a direct-current motor

Reciprocating pumps are of slow speed and are preferably coupled to the motors through gearing If the pump must be started against full head, the starting torque must be great enough to overcome the load By-pass valves can be used to reduce the load until full speed is reached, cutting down the torque considerably Varied capacity and pressure require an adjustable-speed motor

The squirrel-cage motor is generally used for constant-speed operation This motor is manufactured in a number of types with starting torques to suit various starting conditions

Wound-rotor induction motors may be necessary for driving reciprocating pumps where it is desired to limit the starting current

If the source of power is direct current, a compound or shunt-wound motor will operate satisfactorily at constant speed

For centrifugal pumps two methods are in common use to secure variable discharge or head—throttling of the discharge valve or variable-speed motor For constant-speed constant-head service the squirrel-cage motor provides the simplest drive

The wound-rotor motor takes less starting current than the squirrel-cage type, hence it is used for larger drives It causes a minimum voltage disturbance, which is desirable where the source of power is not large

In cases where sufficient generating-station capacity is available, or where permitted by a supply authority, squirrel-cage motors should be used for all centrifugal pumps, even up to the largest size, direct-across-the-line starters of the hand-operated or automatic type being used.

The synchronous motor is satisfactory for centrifugal pump drives, particularly for slow-speed large-capacity units, and their high efficiency and leading power factor make them desirable where power-factor improvement is necessary

Brush-shifting alternating-current motors have been found quite successful for adjustable-speed service They require some form of line switch and a means of shifting the brushes mechanically by a hand wheel, or a small pilot motor actuated by remote push buttons

In the case of rotary pumps the selection of suitable motors follows the lines laid down for centrifugal pumps

In order to increase the life and considerably reduce maintenance costs, all electric motors for operation in dusty or dirty locations should be of the totally enclosed self-cooled type, having two shells with fan circulation of air between them The design should be simple, and such as will allow of easily cleaning the ventilating channels

Motors required to operate in the vicinity of inflammable gas need special protective features to minimize the possibility of a fire or explosion caused by a spark or arc, and therefore must be of the flameproof and explosion-proof type

As a precaution against fire, pump houses are sometimes provided with a fire-wall, with the motors and control gear on one side and the pump handling dangerous products on the other side (Fig 1) Whilst this arrangement is more satisfactory than having standard non-flameproof motors and control gear in the same house as the pumps, it is recommended that all pumping units should be placed in the open, and only flameproof electric motors and flameproof control gear used The motors and pumps may be given sun protection by fitting a light roof In some cases it may be desirable to place the flameproof switch gear in a separate switch house

A totally enclosed motor, designed particularly for use in explosive gases, generally embodies 'wide-flange' manufacture This construction involves the use of enclosing parts heavy enough to withstand the pressures of internal explosions and the use of carefully machined flanged joints sufficiently wide to cool the flame of an internal explosion to a point where it will not ignite the surrounding gas Bolt holes are bottomed in metal No gaskets may be used, as these might be damaged or even omitted during reassembling of such apparatus The joints must be fitted with a sufficient number of bolts to prevent working or buckling of the flanges between bolts during an explosion

Units requiring large electric motors are supplied more satisfactorily at high voltage, thus relieving the low-tension distribution system of load which can be taken by the high-tension system

It is difficult to give a definite economic lower limit of load for supply at high voltage which would be applicable to all systems, but in the case of 3,300-volt distribution individual loads of 60 h p and over should generally be supplied direct

Electric motors should be protected by control gear having overload releases, which are adjustable and able to act in a reliable manner at less than 25% overload This is very important where motors are used in dangerous areas, as failure immediately to trip the motor on overload will result in motor burn-outs with possibility of fire

The proper type of overload release when accurately adjusted to suit the particular conditions will not only prevent a complete burn-out of the motor, but by opening the circuit breaker give warning that an overload exists.

There are three types of protective devices for preventing overloading—fuses, thermal devices, and solenoid or magnetic types of overload releases

Fuses are quite satisfactory for protecting small unimportant motors in a safe area for lighting or heating circuits, but for general motor protection they are not advisable

Thermal devices are extensively used as a method of overload protection for small motors These types depend for their action on a bimetallic strip, which is heated by the current flowing

The solenoid or magnetic type of overload protection is entirely satisfactory, and can be arranged with settings ranging from full-load current upwards, which enables the circuit breaker to be tripped at any predetermined overload A retarder or time lag is fitted to avoid tripping due to momentary overloads

All automatic starters should be of the simple direct-starting type, and the double-throw auto-transformer starter or star-delta type should, if possible, be avoided, as apart from high capital cost much less trouble and maintenance charges is experienced with the automatic direct-starting starters

In cases where remote operation is not desired and a fire-wall with look-out windows is used for separating pumps and motors, ordinary hand-operated control can be used

The following starting methods are in general use where for some reason or other universal direct starting is not possible

1 By connecting directly to the line This method is ordinarily used only for small motors—those of less than 7½ h p output—because in starting the motor takes an excessive current, and the voltage regulation will be disturbed unless there is ample generating capacity
2 The delta-star method of starting motors between 7½ h p and 30 h p In this case the stator-coil terminals are brought out from the frame and connected to the double-throw delta-star control switch In starting the coils are connected in star After the rotor has attained full speed the switch is thrown over to the running position which connects the coils in delta, and normal voltage is thereby impressed on them
3 By using an auto-transformer starter With this type of starter a low voltage can be impressed on the motor at starting by connecting with a suitable switch to take on the auto-transformer This type can be used on motors from 30 h p to 80 h p
4 For starting against heavy loads and in general for drives above 80 h p it is usual to use slip-ring motors, having a control switch for the stator circuit and a rotor-resistance starter With this starter the rotor circuit is connected to a non-inductive resistance which can be varied and gradually cut out as the motor attains speed

Many industrial circuits with a motor load have a lagging power factor which is often below 80% unless special feature motors or equipment are used, and it may be desirable to improve the power factor

Where the energy used by such motors is charged for on a K W H basis only, the use of condensers is advantageous mainly from a reduction of current loading on switch gear, transformers, and cables More usually, however, where an electric supply is taken from an outside source, a two-part tariff built up of a 'fixed' charge on a recorded maximum demand and a K W H charge is in force. Where such a charge involves the kilo-volt-ampere demand, involving

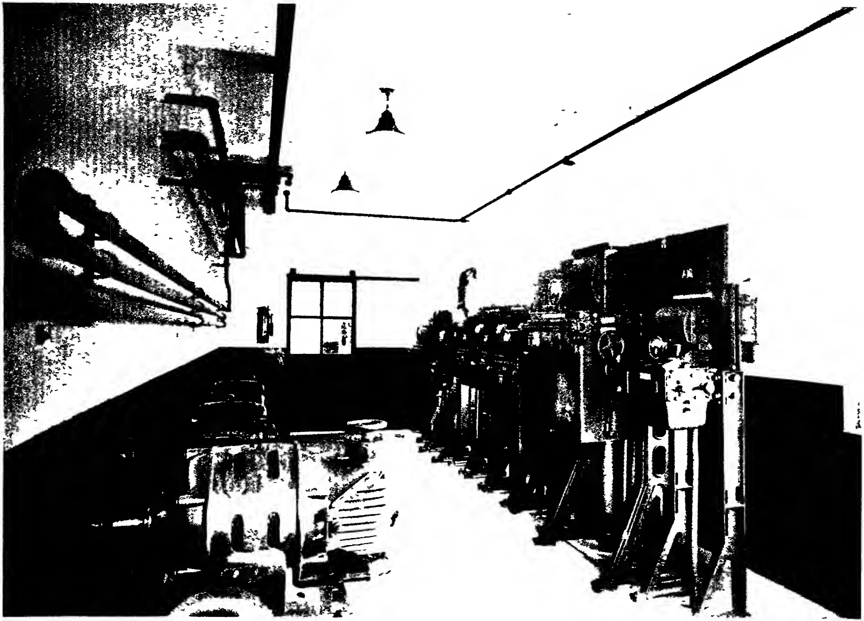

FIG 1 Electric motors and control gear driving pump through fire wall

rebates for high power factor and penalties for low, a saving can in many cases be effected by installing condensers or equivalent apparatus

The problems encountered in the application of electricity in oilfields cover an exceedingly wide ground, and their solution varies according to local conditions

Frequently one of the greatest difficulties encountered in development is that of obtaining a supply of water suitable in quality for boiler make-up, or in sufficient quantity for condenser circulation, and in this case electricity can be of the greatest value by permitting generation to take place at any site within a considerable radius of the field which offers facilities for water-supply The water question, of course, is not so serious where gas- or oil-generating plant is proposed, and in this case a suitable site central to the distribution network should be chosen

An oilfield load, apart from water pumping, gas compression, and similar plants, presents a load the centre of which is constantly shifting A comparative heavy load is taken while a well is being drilled, with peaks during hoisting operations, but once the oil is reached a small pumping unit is usually sufficient, and in some fields where the oil gushes out under natural pressure even this is unnecessary until the pressure falls away, when electric pumping may be required These conditions are generally met by providing high-tension feeders throughout the field area and tapping therefrom temporary or semi-permanent sub-stations where the power is stepped down and fed to the units concerned When drilling is completed, the drilling equipments are removed and connected into the power system at some other point

SECTION 38

POWER AND WATER SUPPLIES

POWER AND WATER SUPPLIES FOR REFINERIES

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THE initial consideration of these two services for a refinery is governed by the same factors and broad principles that pertain to other industrial works, and it is therefore necessary, first, to tabulate the nature and magnitude of the demands Analysis of these, together with the available local supplies of water and power, their cost, and the quality of the local labour, will then suggest the plants best suited for the conditions The consideration of these supplies, to be comprehensive, should cover sites where local electricity and water supplies are not available and where demands of staff and housing have to be considered

No attempt has been made in the following pages to tabulate costs, as these vary so widely in different countries, but rather an outline of the different alternatives has been given for individual assessment A broad tabulation of the uses of water and power is given below, as on these the ultimate choice of all plants must be based, and this table has been made to include the services outlined in the first paragraph

Water

1 Cooling
2 Washing
3 Condensing
4 Steam-raising
5 Fire-fighting
6 Drinking
7 Sanitation
8 Irrigation

Power

1 Lighting
2 Heating
3 Fans
4 Refrigeration
5 Air compressing
6 Distillation
7 Pumping water
8 Pumping oil
9 Transport

Water

With regard to drinking water (6), in most countries this is available from safe local supplies, but if this is not the case and the supply is drawn from a river, it may be necessary to have settling tanks, coagulating gear, and chlorination plant, when the capital and running costs will have to be carefully assessed

With reference to irrigation water (8), treatment plant or settling are rarely necessary, but the cost of separating the distribution from that of the drinking water must be considered

The quality of the boiler water-supply (4) is a matter of some concern also, for with the use of high-pressure water-tube boilers the treatment cost of some waters may be prohibitive, and the boring of artesian or other wells may be justified

The cooling, condensing, washing, and fire-fighting demands fall generally into the same class, whether drawn from sea, river, or well, as to quality, but to give an absolutely positive and uninterrupted service, water for fire-fighting often has its own supply and distributing system Depending on the total quantity called for and the pressure necessary for this service, a choice must be made where alternatives are available from municipal, river, sea, or well supplies, but it will be appreciated that the quality and the relative cost of treatment generally settle this automatically, and the major decisions become ones of plant and possible combinations of the same

With regard to the choice of plant, the prime movers being governed by practically the same conditions as to fuel and site as the power plant, these can be considered on the same lines and at the same time, but the speed of the type of pump chosen may affect the choice The type of pump is largely governed by the relation of quantity to head and the suction conditions, but, generally speaking, the centrifugal pump is preferable to the reciprocating or the various types of rotary rolling surface pumps, on account of first cost, cost of prime mover, maintenance, and reliability

Before leaving the water question and making a choice as to the source of supply, the cost of pumping, settling, storage, and treatment must be finally assessed

The relative merits of Zeolite and various chemical treatments—hot and cold—really do not call for consideration at this stage, but rather when the power plant has been chosen They should, however, be given cursory consideration, as if the water is to be used in boilers or in the cooling jackets of internal-combustion engines, some treatment may be justified The delivered cost of salt for regeneration and the cost of the chemicals will generally decide this, whether the plant be one of the above types or a combination of types

In regard to the 'hot' process when used for boiler feed, this is intimately connected with continuous blow-down and de-aeration, and their attendant economies, in fact, so great a problem does complete treatment become for high-pressure water boilers with heavy make-up that evaporators can often be justified to-day

Chlorination for drinking supplies and perhaps for condenser circulating water must also be considered in costing the treatments

Power

Having assessed the power demands from the magnitude of the users tabulated above, the alternatives of steam, steam-electric, gas-electric, Diesel-electric, and their several combinations and variations must have consideration

The refinery demands for lighting, fans, and pumps, together with the present-day reliability and ease of distribution of electricity, make it practically certain that one of the electric combinations will be chosen The choice of prime mover then lies between steam, Diesel, or gas, and generally the availability of the fuel settles this in spite of the higher thermal efficiency of the Diesel and gas-engine

In this connexion the efficiency comparison will be reversed in favour of the steam-turbine combination if a reasonable process-steam demand can be assured and bled off from the unit, and also considerable savings will be made by the reduction in condenser size and circulating water quantity for such combination

The Diesel requires a good fuel with a definite sales value, and whilst the same engine can be converted to use gas fuel, this takes time, and as gas supplies are generally insufficient and irregular, it has a limited application only

The case for the steam-engine or turbine-driven electric generator for a large refinery is strong, because steam may be generated with waste gas with heavy unsaleable residues, or even acid tar, and these, if so desired, may be used all at the same time and in varying quantities.

In addition to the above, the process demand for heating steam and small steam pumping units, &c, in dangerous locations can readily be met by the use of bled-off or back-pressure steam in cases as mentioned above, where a reasonable balance can be struck between electricity demands and process steam This possibility has led to gradually increasing boiler-pressures, and it is fairly common practice now to generate with steam up to 600 lb pressure and 750° F total temperature, and exhaust to process at about 200 lb With steam under these conditions, modern boilers and turbines give a reasonable efficiency, which, taken into consideration with the cheap fuels indicated above, offer a very attractive proposition

From a first cost point of view, the speed of the modern turbine keeps generator and gear costs down far below those of the Diesel, and balances to a small degree the cost of the boiler battery

The above remarks, it will be appreciated, apply to the refinery main generators only, and must be balanced carefully in connexion with the water demands For a refinery with a heavy demand for condensing water at the turbines, with low process steam requirements and a limited supply of raw water, the Diesel or gas-engine will have a very strong case on account of their reduced water consumption, if this is not outweighed by the multiplicity of units necessary to carry the load

For isolated units, compressing plants, &c, with no demands for heating or back-pressure steam, the high efficiency of the Diesel and gas units again attracts attention, and it must be borne in mind when considering these that in addition to the slow-speed, horizontal, high-compression type, it is now practicable to get these engines in vertical units running from 500 to 1,000 r p m according to size

In refineries adjacent to oil-wells or where dome gas at pressure is available, small turbines are to-day run expansively on gas and give trouble-free operation

If, then, we consider a reasonably large power station with high-pressure steam-driven generators, to get economic stand-by conditions, the visualized load should be divided by two, and three units of this magnitude installed, two working and one stand-by It may be noted here that steam sets will run 9 to 12 months for 24 hours a day without change-over against, say, 1/2 weeks for the Diesel and slightly longer for the gas-engine

The size of the condensing plants and the circulating water demands may then be decided upon, the former depending on the ratio of steam required for electricity generation to that required for process, and this may in some cases be helped by drawing current from an outside source or adjusting the process demand by the use of high-pressure steam and/or accumulators

With regard to the boilers, our choice is limited by their size and pressure, together with the quality and amount of the make-up For a station with an output of 12,000 kw and a 3/400,000 lb per hour demand for steam, the size of the boiler chosen will probably be above 80,000 lb per hour capacity, and therefore the straight-tube vertical type, with its advantages in cleaning, maintenance, and inspection, will be ruled out for manufacturing reasons Working at high pressure and with back-pressure 600 lb and 200 lb respectively, Lancashire boilers will also be ruled out for pressure reasons, apart from their small maximum outputs, whilst with regard to the smoke-tube type, pressure and scaling difficulties will render them undesirable.

The final choice, then, will probably lie with the bent-tube type in, say, 100,000 lb per hour units, due to its low initial cost, reliability, and low maintenance

For auxiliary or supplementary purposes, in the case of battery evaporations up to 100,000 lb per hour, and with bad water, the Lancashire boiler stands alone, in that it will evaporate untreated water with a reasonable efficiency and safety factor If the dish-ended type be used, scaling is readily dealt with, and the battery may in effect be the means of supplying the main boilers with distilled feed make-up to some extent

Efforts have been made from time to time to improve the accessibility for cleaning of the smoke-tube and locomotive types of boiler, but the use of these is confined generally to sites with good water, and even then they offer no advantages over the water-tube or Lancashire boiler, other than in the cost of foundations, or in the latter case foundations and settings In the former type the extra cost is very little, and in the latter it may be minimized by the use of steel casings

If the type of boiler chosen, then, is the water-tube of the bent-tube type, it will be found that higher efficiencies and less maintenance will be obtained if forced draught is used, and as the boilers will probably be working with at least two types of fuel and a poor class of labour, automatic control will be justified This may, for simplicity, be applied to the feed, the fuel, and the flue dampers only, the latter two are regulated from the pressure of the steam, and apart from labour economies, the staff will be enabled to operate far more efficiently and economically

Boiler-feed water regulators are a great asset, and both these and controllers are now available in types to which no objections as to lag and hunting can be taken

Very few other instruments, apart from level gauges, pressure gauges, thermometers, CO_2 recorders, and individual boiler-load indicators, can be justified, although with this type and size of boiler the former may have to be of the distant-reading type

The modern feed pump has very few limitations and is a distinctly reliable unit, and the old rule of dividing the load by two and installing three units also applies here

The type installed in a battery of this magnitude varies very little, except as to prime mover, the centrifugal—owing to its quantity-pressure ratio, ease in paralleling, flat pressure curve, and absence of vibration—holds the field apart from its low first cost

With regard to the prime mover, the speed of this type of pump suggests a steam turbine or electric motor, and the possible use of the turbine exhaust for feed heating, considered with the simplicity of the machine, the fewer links between fuel and work, and its ease of automatic control, render it the most popular

It is not proposed in this broad consideration to go into the question of de-aeration, evaporators, and closed-feed circuits, except to say that the return of condensate from process renders this a definite problem and that some de-aeration will be required

With the feed consideration is tied up the question of continuous blow-down on the boilers As it is now possible with continuous blow-down and careful feed treatment to keep boilers on steam for periods up to 4,000 hours without running into dangerous concentrations, it has now become general practice to adopt this and to link it in with a hot-feed treatment and flash recovery. This treatment, however, need not be regarded as final, for the advocates of water conditioning can with many waters justify additional treatment with Zeolite or alternatives It must be realized that with boiler pressures above 250 lb per sq in with certain waters there is a risk of caustic embrittlement, and that concentrations must therefore be kept down, and the combined carbonate hydrate to sulphate ratio of the feed must not exceed 1–3

Whilst comment on the superheaters has been left until now, the troubles experienced are so important that it is a moot point with gas and liquid fuel if the integral superheater must not give way to the independently fired unit.

With varying boiler demands and total steam temperatures in the region of 750° F it is difficult to attain and keep a steady degree of superheat apart from steam-quantity variations, and even with a radiant element in the combustion chamber, a rapid falling off with consequent loss of turbine efficiency is experienced at light loads This, it will be appreciated, is not so with independently fired superheaters, which also lend themselves admirably to automatic temperature control, and are not so readily affected by priming This latter point often becomes a major issue with modern rapid-circulation boilers, and time is well spent in considering the many baffling and drying devices now available for fitting in boiler drums

The question of burners must obviously be one for detailed consideration with the actual fuels being consumed, but no difficulty need be anticipated in getting combined burners for gas and oil fuel, or for acid tar, or, if desired, for pulverized fuel

Generally speaking, with boilers of the magnitude of those at present under consideration, in fact down to batteries of 100,000 lb per hour evaporation, there is no alternative to the pressure system for firing liquid fuel, and this is best combined with the continuous circulation of the fuel and, if necessary, a heater

The question of safety in cases of possible cessation and restart of the gas supply is generally met by the fitting of pilot oil-burners, so placed as to fire the incoming gas immediately, whilst on many installations, apart from the usual explosion or relief doors, it is usual to so arrange the flue dampers on a unit in commission that they cannot be shut, and to arrange all soot blowers inside the casing and for external operation

Whilst dealing with the flue conditions, the construction of these and the boiler casings can well be considered. Depending on the cost of refractories and brickwork, there is much to be said for 3-in firebrick-lined, steel circular flues, as these are cheap to manufacture, easy to support and maintain, and free from air leaks and cracks, such as must develop to the detriment of draught conditions in all-brick flues

With regard to boiler casings themselves, in these days of water-screened combustion chambers it has become possible to cut the boiler brickwork to a minimum and use light steel-cased boilers with an asbestos packing between the casing and the firebrick Asbestos is mentioned specifically, as the brittle nature of slag wool and glass silk renders them unsuitable from their tendency to powder and pack hard behind the lower plates, even to the extent of bulging them

Air preheaters and economizers will probably be justified, and these must therefore be considered with the relative flue exit and feed conditions

Leaving the boiler house and coming to the turbine or power house, it is necessary to consider the type of turbine The old controversy of impulse or reaction need not cause any anxious thought, for this matter has now settled itself, and the blade clearances being ample and safe, steam consumption then becomes the major issue Thus, it is clear, must include all auxiliaries, and in nearly all cases tenderers' figures will require adjusting

The case for the self-contained non-basement type of machine hardly arises with outputs such as are here under consideration, and is certainly ruled out if draw-off sets are to be installed with, say, two sizes of condensers, but it should be borne in mind that in other cases the fixed ratio of speed to the turbine of the circulating water and extraction pumps may be a great disadvantage, and that the drives of the auxiliaries are fruitful sources of trouble

In connexion with the circulating water, it will probably be found preferable to continue the normal practice of each machine having its own pump on account of the higher pressure on the process water-mains and the fact that the water may require treatment, but this choice will be dependent to a large degree on the suction conditions

The question of strainers and settlement can well be left at present for consideration with the equipment of the main refinery water pumping station, which in riverside sites may be adjacent to, or actually part of, the power station

Other points arising in the power station are type of building, lay-out, foundations, lighting, rail access, cranes, air conditioning, metering, and staff accommodation

The type of building should be spacious, whether in a temperate or tropical climate, as the effect on efficiency and personnel is great, and in the event of overhauls there should be ample room to dismantle and lay out any unit in the house without impeding rapid and easy access to the rest of the plant in emergencies If the house and plant are of the basement type, the wells should be extremely liberal in size, as apart from access the light value is such that some modern stations appear to have the turbines on platforms rather than the condensers in wells The switch gallery, since the introduction of remote instruments, need not be such a feature, but in the case under review, unless elaborate metering for refining cost subdivision is insisted on, the old type of raised gallery is recommended

With regard to the building proper, in industrial units lighting and efficiency should never be sacrificed for appearance, and therefore in temperate climates liberal window space should be the rule. The materials will, of course, be settled by local supplies, but a steel-framed brick building is all that can be desired

Lay-out. The question of basement or non-basement machines referred to above settles to some degree the layout, but consideration must be given to access between the boiler house and power station, if these are in separate buildings, and to the siting of hot-well de-aerators and other auxiliaries, both from the supervision and operating point of view A good arrangement is to have the boilers face to face with a central firing aisle leading directly into the end of the power-station building and remote from the end with the railway entrance

The feed and fuel pumps, de-aerators, and possibly the hot wells, could then be sited in the firing aisle or in an annexe to the power house to suit the method of supervision adopted The orientation of the sets, diagonally, longitudinally, or transversely, is then settled by the dimensions of the units and the available space

The crane in a three-set station need rarely be electrically driven with the lifting and traversing speeds now general with hand-operated units, but if the stand-by position is worse than this, then a power crane is often justified.

The disposition of the auxiliary units, such as ejectors, circulating pumps, extraction pumps, ventilating plant, &c, is subservient to the set designer's demands, and apart from accessibility for repair and observation does not call for much consideration

The effect of automatic and/or remote control on the lay-out is not drastic, if indeed it is used, for whilst in America it has made great headway on account of high labour costs, in England and on the Continent its use is more or less confined to very large stations

With regard to foundations, it cannot be emphasized too much that great care must be exercised as to the bearing value of the ground and the quality of aggregate used These remarks also apply to the chimney foundations, and whilst little has been said up to now as to the chimneys, unless architectural amenities have to be observed, the steel self-supporting type is the most economical, and it should always be fitted with a safety ladder and slings for painting

In this connexion it is well to consider the fuel being used, as with many fuels the sulphur content and flue-gas temperature are such as to justify lining the stack with refractory material to its full height

With regard to the lubricating oil used in the main turbines and auxiliaries, it is now almost standard practice to run a portion of the oil in circulation continuously through a centrifuge or pressure filter

Decisions having been taken on the above basis, the magnitude and nature of the auxiliary services, and particularly the water service, can be assessed

This being done, a decision as to the necessity, or otherwise, for cooling towers must be made This choice is affected by the local climate together with the source and magnitude of the water-supply, apart from the major comparison of pumping and transmission costs versus tower or tower and fan-power costs When this decision has been taken the water-pumping plant may be chosen

A decision, based principally on the distance of the supply from the main users, must now be made as to the prime mover, and if the magnitude of the demands is such as to justify an independent station, the fewer links between fuel and the live water-main will generally clinch the matter, and the pumping station will not be motor driven, but entirely distinct and independent of the power station, even to the extent of boilers if a steam station is adopted The available fuel will probably weigh against the more efficient Diesel once more, and as for distribution in quantity at pressures of 100 lb per sq in and over, the quantity-pressure ratio will again justify the centrifugal pump, and the choice of prime mover may well again be the turbine This decision permits a small compact and highly efficient automatically controlled plant to be installed entirely independent of the refinery power station, and unaffected by process demands, fires, or electrical storms

With regard to the boiler plant, the decisions made for pressure and superheat will apply again, as, for the probable size of boiler, 600 lb is quite a reasonable pressure and 750° F is as high as practicable with the metals at present available

In this case, unlike the last, bled-off or back-pressure steam, with or without accumulators, should not be considered if the plant is to be independent of process fluctuations, but consideration may be given to the waterworks type of condenser.

It is not proposed here to go into the suction conditions in detail, suffice it to say that turbines are applicable to vertical spindle or horizontal pumps, and that long suctions require careful design, straight runs, low water velocities, liberally sized strainers, and the avoidance of valves and possible air leaks.

In deciding pump speeds—particularly with large units—advantage should be taken of recent papers and American research on the effect of speed on cavitation or erosion, as otherwise heavy maintenance costs will be incurred, but with any size of unit it will be found necessary to introduce reducing gears to run the turbine at an efficient speed In this connexion no trouble need be anticipated with the gears, even with ratios as high as ten to one, for modern design and gear cutting is such that noiseless and efficient operation can be guaranteed

The circulating water and extraction pumps in this case can with advantage be driven by a separate turbine like the feed pumps, and these with automatic control will give little or no trouble

The boilers for this plant will obviously be smaller sized units than those at the power station, but for the pressure under review bent-tube boilers will offer many advantages and be the most economical

Further economies may be obtained if, say, for use at stand-by or cleaning periods, a steam line to the power-station boilers be installed to pool the reserve between the two batteries

Continuous blow-down with heat recovery and a hot-feed treatment may be installed, or the small make-up required may be taken from the power-station water softeners

The question of induced draught may be considered here, but it will probably again be found that forced draught gives the best economy for the least capital expenditure, and that the use of cheap and/or sulphurous fuels prevents this and many other finer economies from being economic propositions

Another point to consider is that there is probably a minimum height for safety beyond which it is unwise to reduce chimneys near or in a refinery area The lay-out of the building and the crane equipment will be governed by the same general principles as the power station, which need not be recapitulated

In considering the use of preheaters and/or economizers at this station or the power station, it is well to examine the probable sulphur content of the flue gases in relation to the exit temperatures, as corrosion may result in any fuel economies being negatived by maintenance costs

In completing the specifications for these two stations, it is worth while fixing a colour range for distinctive painting of the raw water, treated feed, high-pressure steam, low-pressure steam, and fuel lines, together with a standard opening rotation for valves

It is also now general practice to permit the extensive use of welding for piping and vessels to a firm specification and under good supervision

The fire service of an oil refinery, being perhaps the most vital plant, demands careful consideration, but it is not proposed here to go into detail as to the numbers and types of hydrants, foam systems, fire-station mobile equipment, or fireless locomotives in dangerous areas, but only to discuss the main supply and distribution of water at pressure. The pressure, adequate to serve the highest unit in the refinery, and the maximum estimated rate per minute having been decided, the lay-out and size of the distributing mains should be settled, using as far as possible a ring main principle to reduce pressure drop and to give a two-way supply. It is often wise to keep this system independent in all ways from other refinery services The pipe system, the pumps, and their prime movers should all be confined to this specific duty, and if steam is used, it should be made possible to isolate a boiler for the service in emergency

In choosing the prime mover for this duty, the usual considerations will not apply, but rather the siting of the pumps and the facility or speed at which they can be brought on load Here, again, steam has many advantages, and it is possible, with very little cost, to keep a turbine or engine constantly warm and drained ready for action at the mere turning of a hand wheel.

In some refineries the magnitude and reliability of the ordinary water service is such, thanks to the number of pumps on stream and its independence of the power station, that the fire pump or pumps may be boosters only

Efficiency would appear to have been neglected in many of the suggested plants, but where this has not been ruled out for simplicity, safety, and absolute reliability, it is on account of the reduced savings due to the use of otherwise unsaleable fuels In some refineries or districts, however, where the residues are saleable and the gas supply very inadequate, there is no doubt that a case can be made for a Diesel-electric station, or even for bulk electric supply

In the former case the station load should be carried in such a manner that in the event of a major overhaul of one of the sets it is still possible to release a set for routine overhaul about every 3 weeks and still carry the full refinery load In this way the engines will continue to develop their maximum efficiency for long periods without expensive replacements

The circulating water for these sets is well worth careful attention, as in spite of thermostatic control and liberal cooling a simple treatment is often justified

The Diesel type of unit can to-day be obtained in very large horse-powers, but its use is generally confined to small generating stations, as the use of Diesel generators above 1,500 kw is unusual and expensive It will be appreciated in this connexion that for a station approximating 10/20,000 kw capacity this would entail an undesirable multiplicity of sets running at relatively slow speed, with consequently heavier capital and running costs

The above remarks also apply to the gas engine if a constant fuel supply of adequate magnitude is available

The justification of instruments for increased efficiency and departmental costing is, of course, purely a matter of capital outlay and becomes more difficult as fuel values decrease, but their use for automatic control and ease of operation can often be justified on account of labour costs and reduction in maintenance

Little need be said about water settling, as it is rarely that this is necessary except for drinking, and perhaps in bad cases for boiler make-up water, as the equipment will be relatively small and can be made smaller still by the use of a coagulant

In conclusion, it may be said that the design and choice of power and water plant for refineries are governed by the same principles as those for public authorities and industrial factories, and that it is in the practical application of the differing demand and local conditions that care must be exercised, for it must be realized that only the price per kw per gallon of water or per lb of steam will justify the choice of plants, and that the capital and maintenance charges are the major items in the costing of these services

With regard to the modern trend towards the super-boiler, these can rarely be justified for refinery operation, as the increased efficiencies become merely a fuel saving, and this saving with cheap and often unsaleable fuel does not provide a sufficient credit to balance the enhanced capital cost Apart from this, the site is not usually congested, and the value of the space is generally low in comparison with ships or town sites

Another of the advantages of some of these new boilers is the rapidity with which they can be brought on to steam, but this is discounted in refinery operation, as the load curve is extremely flat and some notice is always possible of a heavy increase in demand

Passing mention has also been made of pulverized fuel, but this, of course, could only come into commercial consideration if a good market for the refinery residues were obtainable and slack or cheap coal refuse were available locally

With reference to safety precautions generally where continuity of operation is so vital, electrical development has been such that it is now possible to get reliable visible and/or audible alarms for practically all services, and remote or push-button control for essential valves or auxiliaries

With general reference to modern turbine design, the principal features of interest to the refinery engineer are the more general use of stainless steel, the displacement of the old type air pumps, and the better lubricating oil and governing equipment In fact, engineering progress to date is such that reasonable efficiencies and 365 days per annum operation can be guaranteed for any refinery if reasonable care is expended on the choice of plant and stand-by equipment

SECTION 39

FIRES

ELECTRICAL PROTECTION OF OIL STORAGE CONTAINERS

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THE petroleum industry annually suffers an important economic loss through the destruction of oil in storage by fire Probably no other single factor has been responsible for so many fires, or for the physical destruction of so much crude petroleum, as lightning, and protection against this natural hazard constitutes one of the most important considerations in the construction and lay-out of oil storage farms In the present article explanations are given of the several ways in which lightning and static electricity may ignite oil in storage, and descriptions of various devices that have been adopted and precautions that may be taken in minimizing the risk of fires from these sources

In considering the means available for electrical protection, we must differentiate between the various types of containers in which crude petroleum may be stored and the character of the oils Most crude oil is now stored in large all-steel tanks with vapour-tight accessories which present a comparatively small fire hazard However, there are still many older tanks in use which were constructed with wooden or composition roofing on a steel shell These are not vapour-tight and are easily ignited under proper conditions Some of the most disastrous oil fires have occurred in large concrete-lined oil storage reservoirs Such containers cannot be made vapour-tight, and because of the very large quantity of oil stored under one roof present a serious fire risk unless proper precautions are taken, particularly in storage of oils of high volatility The less volatile oils, which do not yield inflammable vapours at normal storage temperatures, are not likely to become ignited in any type of storage container

Conditions attending Oil Storage

To better understand the precautions taken and protective devices employed in safeguarding stored oil from destruction by fire, it is desirable to briefly review the conditions attending storage Storage 'farms' usually comprise a number of storage containers, either tanks or reservoirs, or both, spaced as closely as security against spread of fire from one container to another will permit Earthen fire walls are generally constructed about each container to restrict flow of burning oil from one container to another in case of collapse of a tank or 'boil over' of the tank contents in time of fire Storage units are of large size, tanks of 55,000 to 80,000 bbl capacity being common, while reservoirs range in capacity from about a quarter of a million to more than 4,000,000 bbl In some instances many millions of barrels are in storage on an area of but a few hundred acres

The most common type of storage container is the steel tank, which consists of a vertical cylindrical shell and flat bottom made up of riveted steel sheets The roof is usually conical in form and of low pitch or slope from a central peak to the eaves where it is attached to the top of the cylindrical shell Diameters and heights vary with the capacity, a 55,000 bbl tank being 117 ft in diameter and 29 ft high at the top of the cylindrical shell, while the 80,000 bbl tank is 42 ft high and has a diameter of 117 ft Some storage tanks are equipped with special forms of flat roofs, designed to prevent evaporation losses 'Water-top' and 'floating-roof' tanks are of this type, but these special forms are more widely used in the storage of refined and semi-refined products of high volatility than for crude storage Conventional conical roof tanks vary chiefly in the type of material used in constructing the roof and the precautions taken to avoid vapour loss through the hatches and about the eaves Modern tanks have riveted sheet-steel roofs resting on steel supports with vapour-tight fittings and securely riveted around the edge to the top of the vertical cylindrical shell A cheaper roof construction makes use of timber supports and a roof of wooden sheathing covered with roofing paper, composition sheet roofing, or thin sheet metal Such roofs are seldom vapour-tight about the eaves, and it is difficult to make the sheathing and its covering secure against gas leakage along the many joints

Oil storage reservoirs are usually constructed within earthen embankments, and lined with several inches of reinforced concrete The greater part of the reservoir is generally a depression below the prevailing earth surface, so that the sloping walls require no support and the roof is at an elevation of but a few feet above the surrounding terrain Reservoirs are usually round or oval in horizontal projection, the actual dimensions varying with the storage capacity The smaller circular reservoirs are 250 ft or more in diameter, and the larger elliptical tanks range up to as much as 1,425 ft along their major axes Depths of oil in storage in these reservoirs range from 20 to 41 ft The reservoir bottoms are usually nearly level, sloping only slightly towards a drainage outlet at one point near the side wall The sides range in slope from 1 to 1 to as much as 2½ to 1 The roof is customarily of wooden sheathing resting on timber supports and covered with roofing paper or composition sheet roofing To facilitate drainage, the roof has a low pitch from a slightly elevated central peak Such roofs are seldom if ever vapour-tight, it being particularly difficult to secure a gas-tight joint about the eaves

Temperatures of oil in storage will depend upon climatic conditions and upon precautions taken to insulate the contents of tanks from exterior heat White or aluminium painted tanks have lower interior temperatures than tanks painted with black or other dark-coloured paints Temperatures within oil stored in reservoirs partly below ground surface are likely to be lower than in above-ground steel tankage Irrespective of all precautions that may be taken, storage temperatures are usually high enough to permit of vaporization of the more volatile constituents of the oil, which accumulate in vapour form in the space between the tank roof and the surface of the stored oil With changes in temperature such as occur between day and night, vapour is alternately expelled and air drawn in through any openings that permit of movement of gas through the tank roof or about the eaves Though the differences in pressure between the vapour space within the tank and that of the atmosphere without are slight, it is very difficult to prevent loss of vapour through minute crevices and openings as a result of this 'breathing' action of the tank with changes in temperature Where the more volatile crudes are stored, the space above the oil surface in a tank or reservoir is nearly always filled with hydrocarbon vapour under a pressure slightly above atmospheric, and the surrounding atmosphere above the roof surface and about the roof hatches and vapour vents may contain sufficient vapour to present a distinct fire or explosion hazard Within the vapour space below the roof of the tank there may be insufficient air to form explosive mixtures, or even to support combustion, but the presence of a large volume of vapour capable of explosion or combustion on admixture with proper proportions of air is a potential hazard in the event of damage of the tank by lightning

Ignition of Oil in Storage Containers by Lightning and Static Electricity

As is well known, lightning discharges are the result of accumulation of high differences in electrical potential between cloud masses or between the earth and electrically charged cloud masses When the differential potential is sufficiently great, a discharge of electricity will arc across the intervening air, giving rise to the phenomenon known as 'lightning' Since a lightning discharge results in a very rapid release of energy, usually concentrated along a very narrow path and on a small area, its effect may be violently destructive The discharge naturally follows the path of least resistance and is often circuitous For many years it has been known that grounded metallic objects provide a path of low resistance for lightning discharges, hence the use of 'lightning rods' in seeking protection of buildings and other structures from the destructive effects of lightning

While steel oil-storage tanks and the steel reinforcing mesh of concrete-lined reservoirs are usually well grounded, and would no doubt in most instances form a likely point for grounding of electrically charged clouds in the vicinity, there are very few known instances in which tanks or stored oil have been destroyed by lightning striking the tank or reservoir directly Usually when oil tank and reservoir fires have accompanied electrical storms, other near-by objects have been 'struck', or the discharge has been between overhead cloud masses

The probable explanation of the many tank and reservoir fires that have occurred at such times lies in the known development of induced static charges that build up on the exposed tank and reservoir surfaces These induced charges possess voltages sufficiently high to arc across intervening spaces between insulated or imperfectly bonded portions of the tank or reservoir roof Since these same spaces afford paths of escape for hydrocarbon vapours communicating with the vapour space within the tank, the conditions favour ignition of the gas or perhaps explosions of air-gas mixtures of sufficient violence to damage the roof plates and release large quantities of stored vapour from the space below Only by ignition of hydrocarbon vapour above an oil surface may the oil itself be ignited, and the vapour will only ignite in the presence of sufficient air to support combustion and only by a flame or sufficiently hot spark

It has been experimentally determined that it is impossible to produce, by exterior forces, a difference in potential between two objects within a completely enclosed metal tank. Hence, such fires as occur within steel storage tanks have their origin outside or between the roof plates or different layers of roofing material, and are transmitted to the vapour space within, along a vapour-filled channel of communication Tests have also indicated that the oil and associated vapour have no direct function in the development of conditions which bring about or promote electrical discharges Their ignition is accomplished only by electrical discharge between surrounding objects

Static charges may be developed on an oil surface within a tank or reservoir by rapidly flowing or spraying oil into the vapour space of a tank, as may sometimes happen when oil enters, perhaps with some occluded gas, through an 'over-shot' lead line entering the tank through a roof hatch Static electricity, of this kind, of course, is of frictional origin and is in no way related to lightning discharges or secondary charges induced by electrical atmospheric conditions Static charges on the surface of a large area of oil may not be promptly drained away, and if by any means a conducting medium should suddenly ground this charge through the roof or shell of the tank, static sparks are possible Such a conducting path may be provided by lowering a steel gauging tape through a gauge hatch in the tank roof Injecting steam into oil tanks for cleaning or other purposes may also be responsible for building up static charges on the oil surface within the tank It is considered improbable, however, that many tank or reservoir fires have originated through frictional static electricity, particularly in large storage tanks and reservoirs, where conditions are seldom such as to promote rapid accumulation of static charges from frictional sources

Protection of Oil Tanks and Reservoirs against Lightning and Static Electricity Hazards

Knowledge of the character and behaviour of lightning and related phenomena suggests that protection of storage farms against direct lightning strokes may be secured by erecting conducting rods or towers in the vicinity to a suitable height Protection against secondary or induced charges may be secured by completely enclosing the oil in a steel tank equipped with a thoroughly bonded and well-grounded steel roof, or by a suitable network of wires above the reservoir or tank roof A modern well-constructed and properly grounded steel tank with a riveted steel roof presents little or no electrical hazard, hence the various protecting devices are applied to large storage reservoirs and to tanks having wooden or composition or poorly bonded sheet-metal roofing

Experimental tests conducted with miniature tanks and artificially developed electrical discharges comparable in intensity with natural lightning confirm the above reasoning and show that a high degree of protection is secured by the means suggested Tests of this character in two different laboratories and by different investigators indicate that if properly grounded conducting rods or towers are erected in the vicinity of the oil storage containers, so that no portion of the container is more than from 2½ to 4 times the height of the rod or tower from its base, any electrical discharges originating in the atmosphere above will be conducted to the rods or towers and grounded without danger to the stored oil The actual ratio of rod height to area protected is a function of the cloud height, or height of the source of the electrical discharge above the highest part of the container, but ranges between 2½ and 4 for cloud heights prevalent during most thunderstorms Experiments also indicate that while absolute protection is not assured, the hazard created through the development of induced charges on tank and reservoir roofs is minimized by use of a well-grounded wire network above the roof and by thorough bonding and grounding of all elements of the roof structure

Another method of insuring against fire hazards in stored oil, that is effective in preventing ignition from electrical as well as other sources, is that of filling the vapour space of the tank or reservoir, above the oil surface, with inert, non-combustible gas Boiler-plant flue gases, which contain chiefly nitrogen and carbon dioxide and very little oxygen, are effectively used for this purpose Hydrocarbon vapours and gases may only burn or explode when oxygen is available in suitable proportions to support combustion By diluting the hydrocarbon vapours in the storage containers with inert gases of the character mentioned, and with insufficient oxygen present to support combustion, the possibility of fire or explosion becomes very remote, even though electrical discharges may occur in the vicinity Frequent tests of tank vapours where this character of protection is applied indicate that it is a most effective means of preventing tank fires

Types of Towers used in Lightning Protection

Following several disastrous fires in which many millions of barrels of oil were destroyed during electrical storms, California oil companies adopted a system of protection against the lightning hazard which involves the use of high towers and grounded wire networks

The towers used are generally of light latticed construction, ranging from 75 to 200 ft high and from 4 to 24 ft square at the base Latticed steel 'poles' of rectangular cross-section are sometimes used, or, in some instances, simple poles made up of pipe forms (see Figs 1 and 2) The upper portion of the tower usually terminates in a joint of pipe supported in a vertical position and equipped at its upper end with a pointed tip of copper or other conducting material The towers or poles rest on concrete foundations to which they are attached by foundation bolts embedded in the concrete It is important that the tower be well earthed This may be accomplished by connecting the tower at its base with pipes driven in the earth to permanently moist subsoil In some cases wells are sunk beneath the towers to permanent water-level and the towers are carefully bonded to the well casings which are set in metal lathe turnings or charcoal Often the towers are bonded to pipelines in the vicinity

Frequently the towers are connected by wires or cables high above the ground, and these connecting cables are earthed midway between towers by other connecting cables that are bonded on pipelines buried in the earth One-eighth-inch flexible copper sash cord is conveniently used for this purpose One company has employed a system in which each tower supports at its summit a cross bar, which in turn supports three lines of a special barbed wire, strung from tower to tower (see Fig 3)

The towers are arranged at suitable intervals about the edge of the reservoir or tankage area to be protected In accordance with the results of experimental studies previously mentioned, the tower spacing is such that no part of the reservoir or tankage to be protected is more than 2½ to 4 times the height of the towers from the base of one of them Three towers or rods of suitable height may be conveniently used to protect a tank or reservoir of normal proportions Elliptical reservoirs require a greater number Where tanks are closely spaced, the ratio of the number of towers or rods to tanks may be less than 3 to 1 In order to reduce the hazard from side flashes at the base of a tower in the grounding of a lightning discharge, the towers should be situated at least half the tower height away from the side of the tank or reservoir If guy wires are used, it is desirable that they be short and attached as near the base of the tower or rod as possible

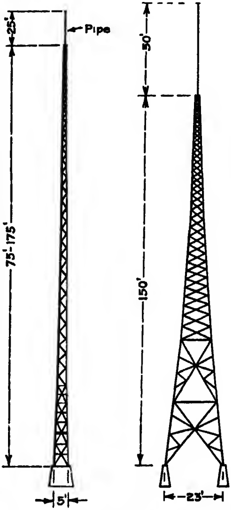

Fig 1 Types of towers used for lightning protection about California oil storage reservoirs *(By the courtesy of Mr R J Reed)*

Overhead Network Protection for Tanks and Reservoirs

For protection against induced charges on the roofs and other exposed parts of tanks and reservoirs, a well-grounded network of wires or wire mesh gives partial protection Complete protection against secondary sparks from induced charges is secured by a complete metal roof the parts of which are well bonded with each other and with the metal sides For new construction, tanks are preferably of the all-steel variety, and no special attention need be given to electrical protection, other than to make certain that the shell of the tank is suitably grounded and that all parts are properly bonded Only in cases where tanks or reservoirs are constructed with wooden or composition roofing will it be necessary to consider the necessity for electrical protection and the type of protection to be provided A complete sheathing of sheet metal will be preferable, but much more expensive than a wire network protection

FIG. 2 Tower and wire network lightning protection over a California oil storage reservoir

FIG. 3 Tower and elevated 3 wire system for lightning protection over a California oil storage reservoir

By the courtesy of Johns Manville Corporation

FIG. 5 Wire network lightning protection over a California oil storage reservoir

By the courtesy of Johns Manville Corporation

FIG. 6 Wire network lightning protection over a California oil storage reservoir

By the courtesy of Johns-Manville Corporation

FIG 7 Tower and wire network lightning protection over a California oil-storage reservoir

which most authorities believe to be sufficient to reduce the hazard to negligible proportions The efficiency of a wire network in rapidly and effectively grounding induced charges depends upon the diameter and spacing of the wires, their height above the roof, and the cloud height

Wire networks above tanks and reservoirs may take a variety of different forms Poultry netting or welded wire mesh may be used, or a system of wires may be employed, the wire being supported either in parallel lines at short distances apart or in radiating lines from a post at the roof peak to the eaves The latter is the so-called 'umbrella construction' and is probably used more than any other In any case, the wire network should be supported at an elevation of several feet above the roof of the tank or reservoir In some instances where umbrella construction is used on cylindrical tanks, the wires are attached to a single post 9 ft high at the peak of the roof, and radiate to galvanized iron brackets attached 15 ft apart around the eaves of the tank Supplementary wires connect across the wider spaces between the radiating wires near the rim of the tank, so that at no point are the wires more than 4 or 5 ft apart No 12 galvanized wire is used A copper-wire cable around the periphery of the tank or reservoir above the eaves is electrically bonded to each of the radiating wires, and this peripheral cable is in turn grounded at a number of points around the circumference, through the supporting guy cables, to a buried pipeline or copper wire or cable

On the roofs of large reservoirs, auxiliary post supports for the radiating wires are provided at suitable intervals

Around the edge of the reservoir embankment, posts are erected about 12 ft high and 40 ft apart. A ⅜-in stranded steel cable supported near the top of each pole extends completely around the reservoir To this the radiating or parallel wires above the reservoir roof are attached (see Figs 4, 5, 6, and 7) One or more guy wires attached to each post serves to strengthen the network system and also to ground the peripheral cable to a buried copper cable which surrounds the reservoir This, in turn, is bonded to all pipelines in the vicinity The network system should extend well beyond the edge of the reservoir at all points, being carried out as much as 16 ft in some instances Some authorities consider it also advisable to ground the reinforcing mesh in the concrete lining of the reservoir to the encircling buried cable, but the necessity for doing this is somewhat questionable

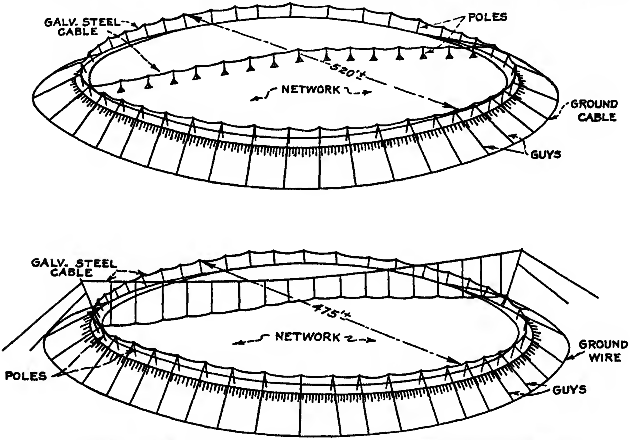

FIG 4 Sketches illustrating two methods of supporting wire network lightning protection above oil storage reservoirs
(By the courtesy of Mr R J Reed)

Economic Aspects of Electrical Protection of Oil Storage Farms

Though electrical protection of oil storage tanks and reservoirs is costly, it is considered worth the cost This is evidenced by the many different oil companies that have adopted it in one form or another, and the large number of tanks and reservoirs that have received protection during recent years This development has been in no small part due to the activities of a special committee of the American Petroleum Institute, which has made an exhaustive study of the problem and given wide distribution to its findings and recommendations

Nearly all of the large storage reservoirs in California

aggregating upwards of 100 million barrels in storage capacity, have been equipped with tower protection and many with roof network protection Modern all-steel tanks do not need electrical protection, but many hundreds of the older wooden-roof tanks in the Mid-Continent, California, and Appalachian regions have been provided with roof network protection The necessity for this has been emphasized repeatedly by tank and reservoir fires attending electrical storms, in which large quantities of oil and other property have been destroyed and lives lost In two storms, only a few weeks apart during the year 1926, upwards of 8 million barrels of oil were lost together with the containers in the firing of California storage reservoirs by atmospheric electricity. California operators have further reduced the hazard during recent years by storing the more volatile crudes in steel tankage, using concrete-lined reservoirs only for the storage of heavy crudes and 'topped' fuel oils of low volatility

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PETROL FIRES IN RELATION TO AIRCRAFT

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PETROL is the most dangerous substance present in quantity on aircraft and the problem of lessening the fire risks attendant on its use has received considerable attention

One method of attacking the problem is to develop the use of a safer fuel

Aviation petrol has a flash-point of about −50° C If this could be replaced by a fuel having a flash-point above normal atmospheric temperature an appreciable measure of safety would be achieved Any increase in flash-point above this would still further lessen the fire risks

It is true that under certain conditions high flash-point fuels are more readily ignited in contact with hot engine surfaces than petrol, but the intensity of the initial fire and the rapidity of its spread to the main bulk of the fuel decreases with increase in flash-point The use in petrol engines of so-called 'safety' fuels having a flash-point of 30° C to 40° C has been proposed and tried to a limited extent, but a greater degree of safety is obtained with Diesel oil, and it is probable that any fire which arose from its use could be extinguished without difficulty

This fact has been a powerful incentive in the development of compression ignition engines None of these alternative fuels has, however, been found to provide the efficiency demanded of a modern aircraft engine, and safety measures have, therefore, to be based on the acceptance of aviation petrol as the fuel in general use

In view of this, the problem has therefore resolved itself into

(*a*) finding the causes of aircraft fires,
(*b*) devising methods of prevention,
(*c*) extinguishing fires before they have reached dangerous dimensions

Causes of Aircraft Fires

As regards the possible causes of aircraft fires much information has been obtained from investigations of numerous accidents and from experimental work related thereto

Fires in the Air.

Fires in the air are now comparatively rare They generally arise from ignition of petrol released from a broken pipe or other failure in the supply system The source of ignition may be a spark or short circuit in the electrical system, or ignition may be due to a fault in the intake or exhaust system of the engine

Fires on Crashing.

Fires on crashing are more frequent and are generally of a more serious nature than fires in the air, due to the large amount of petrol which may be involved In the United States [5, 1936], 171 aircraft crash fires were reported in the period 1930–5, involving 357 fatalities It is stated that in a number of these fires the victims were injured in the crash and were trapped by the fire resulting from the crash Had it not been for the fire the injured persons might have been saved

A number of lists of possible causes of fires on crashing have been published These include the direct ignition of the petrol by the electrical system, the exhaust system, and by materials other than petrol which have been ignited by coming into contact with hot metal

Crash experiments at Wright Fields [4, 1928] with old aircraft appeared to indicate that electrical systems are a minor cause compared with exhaust systems

The possibilities of ignition of petrol by hot exhaust pipes have been investigated by various observers [3, 1930] It has been shown that petrol spilt on to the outer surface of a hot exhaust pipe does not catch fire The petrol assumes the spheroidal state on contact with the hot metal and rapid evaporation occurs which causes local cooling, so that the vapour never reaches the ignition temperature before the whole of the liquid has disappeared

Mineral oil under the same conditions was found to ignite at 420° C

Conditions more favourable to the ignition of petrol exist in the interior of an exhaust pipe and tests have been carried out to determine the minimum temperature at which petrol will ignite under these conditions The exhaust pipe of a Lion engine was allowed to attain a temperature of 500 to 600° C , and the engine then stopped. The burnt gases were cleared out and the pipe allowed to cool to a predetermined temperature A definite amount of petrol was then introduced and observations made This procedure was continued at different temperatures with various quantities of petrol The lowest temperature for ignition was found to be within the range 300 to 320° C with a time lag of from 5 to 7 sec In further tests in the laboratory under more controlled conditions, a minimum ignition temperature of 280° C was obtained with a lag period of about 12 sec

Using jacketed vessels it was found that petrol and air mixtures exploded after a lag period of about 10 minutes at 235° C At higher temperatures the lag period was shorter, and at 350° C explosion occurred immediately the petrol was introduced It was concluded that risk of fire exists if petrol finds its way into an exhaust pipe the temperature of which is above 280° C The risk is apparently less for lubricating oil as its minimum ignition temperature was found to be 50° C higher than that of petrol, but Diesel oil had a slightly lower ignition temperature than petrol Ignition of petrol and air mixtures by contact with the exterior surfaces of exhaust pipes may also conceivably occur at 280° C if the mixtures are trapped in enclosures surrounding the pipe under conditions similar to those existing in the interior of the pipe. Such enclosures may possibly be formed by collapse of aircraft structures in a crash

If before a crash the ignition is switched off and the engine then makes several revolutions before it is stopped by the crash, a slowly burning mixture may remain in the exhaust pipe or possibly an unburnt mixture which may explode if the temperature is above 280° C In actual crashes it is sometimes found that there is a delay which may amount to several minutes before fire breaks out This may possibly be explained by the lag period observed above when ignition occurs at temperatures below 350° C

If the engine is still running when the aircraft strikes the ground the exhaust gases or a backfire through the carburettor may ignite the petrol liberated from a burst tank or broken pipe

Besides the direct ignition of petrol by the exhaust, ignition through the intervention of other inflammable substances may take place It has been shown that lubricating oil, fabric, timber, and dried grass will ignite in contact with hot exhaust pipes Some of the recorded ignition temperatures are given below

	°C
Dried grass	400
Lubricating oil	420
Fabric	460
Timber	560

Apart from the exhaust, fires may be caused by the electrical system which may be damaged in a crash and give rise to sparks and short circuits It is probable that this is a less likely cause of fires on crashing than the exhaust system

Methods of Prevention of Aircraft Fires

There is no doubt that a considerable measure of safety from petrol fires can be obtained by adopting precautionary measures in the design of the aircraft [1, 1922] Fire-proof bulkheads of steel or asbestos faced with aluminium, inserted between the engine and the rest of the aircraft, serve to localize any fire which may break out in the engine compartment It is desirable that carburettor intakes should be placed outside the engine cowling away from exhaust pipes or when placed inside should be fitted with flame traps and that the use of combustible material in the engine compartment should be avoided Other elementary precautions advocated are the draining and ventilation of the cowling to prevent the collection of pools of petrol and to clear places where an explosive mixture might be formed, the avoiding of an accumulation of petrol from flooded jets, the use of a fireproof electrical system, the placing of petrol tanks as far away as possible from the engine, the fitting of electric leads away from petrol supply pipes and places where petrol vapour may be present, the arrangement of exhaust pipes to prevent exhaust gases from a defective manifold coming into contact with petrol vapour, and the bonding of aircraft for wireless installations

Careful attention to design has in recent years reduced considerably the number of fires in the air It is stated that the fire prevention rules introduced by the French Air Ministry [6, 1929] reduced the number of fires in the air from 8% of all accidents in 1926 to 3% in 1927

The problem of preventing fires on crashing is much more difficult [2, 1922] Some of the precautions advocated above will undoubtedly assist in this direction

As the exhaust system may be responsible for the majority of fires on crashing it is desirable that the temperature of the exhaust pipe should be kept as low as possible and that the pipe should have the maximum possible rate of cooling Additional safety would be obtained if a fire-extinguishing liquid was injected into the engine intake and exhaust pipe and the latter as well as dangerous parts of the electrical system sprayed with the fire-extinguishing liquid at the moment of crashing

Impact devices have been designed which operate along the longitudinal axis of an aircraft and function under a deceleration greater than 4g along this axis As no air manœuvre is known which will produce an acceleration along this axis greater than 3 5g, these devices will only operate automatically on crashing

They can be arranged to shut off the petrol, cut off the engine ignition, and release a supply of fire-extinguishing liquid to any desired part of the aircraft They can also be actuated at any time by the pilot as a precautionary measure before a forced landing

To remove the danger due to the bursting of tanks, much inquiry has been directed to the subject of crash-proof tanks and many tests have been carried out In 1921 the British Air Ministry arranged a safety-tank competition, and a number of designs were submitted The tanks were tested by fitting them behind concrete blocks the shape and size of an engine and dropping them from a height of 90 ft at an angle of 45° None of the designs was, however, adopted

The problem of safety-tank design is to obtain crash proofness with little sacrifice of fuel capacity and also to make tanks of the shape required by the aircraft designer So far, the development has not reached a stage when it can be brought into general use

Extinction of Aircraft Fires

Fire-extinguishing Media.

In dealing with petrol fires on aircraft the following extinguishing media are in general use

Carbon tetrachloride
Methyl bromide
Carbon dioxide
Foam

Carbon tetrachloride, b p 76–77° C, was the first of these extinguishing media to find an extended use on aircraft It acts by forming a blanket of non-combustible gas The vapour having a high density, 5½ times that of air, is able to maintain a very effective air shield over the petrol for a sufficient period to arrest combustion Carbon tetrachloride readily vaporizes in contact with hot surfaces, and the accompanying cooling assists to a small extent fire extinction It is most effective when applied from a jet in a highly atomized condition

Methyl bromide, b p 4 5° C, acts in a similar way to carbon tetrachloride Its vapour has a density two-thirds that of carbon tetrachloride and is formed more rapidly Owing to its high vapour-pressure methyl bromide is mixed with 20% of pentachlorethane for use on aircraft fires Methyl bromide is best applied in the form of a solid jet

As regards the relative effectiveness of carbon tetrachloride and methyl bromide, tests carried out on burning petrol in trays fitted with baffles showed that if the extinguishing fluids were applied soon after the fire had started, approximately 3 to 4 times as much carbon tetrachloride as methyl bromide was required to obtain complete extinction, but if the burning was allowed to continue until the metal became very hot, the difference in the quantities of the two fluids required for extinction was negligible

The vapours of both these fluids are toxic and they give rise to toxic decomposition products

Carbon dioxide is supplied in liquid form in steel cylinders at a pressure of 50 atm. On ejection of the liquid, reduction in temperature takes place and a spray of gaseous and solid carbon dioxide snow is obtained. Its fire-extinguishing action depends upon reducing the oxygen content of the air and on its cooling action. It has advantages over carbon tetrachloride and methyl bromide in being odourless, non-toxic, and cheap, but on a weight basis it is less effective for aircraft fires

Foam is produced by mixing aqueous solutions of aluminium sulphate and sodium bicarbonate in presence of saponine or it may be obtained by the mechanical agitation of air and water in presence of soap or saponine Its action is to form a blanket over the burning material, thus shutting out the air To get complete extinction of petrol it is essential that the whole of the burning surface should be covered with the foam For fires in the air it is less effective than the other three

Extinction of Fire in the Air.

Normally every aircraft carries one or more fire extinguishers These are now generally of the methyl bromide or carbon dioxide type As the effectiveness of fire extinguishers depends on the rapidity with which they can be brought into action, attention has been directed in recent years to the development of the automatic type of extinguisher This consists essentially of a sealed vessel containing the fire extinguishing liquid under pressure, connected to a number of distributing pipes situated in the engine compartment The liquid is released on the outbreak of fire by the action of detectors placed at the most effective positions

Tests have shown that by careful arrangement of the distributing pipes and the detectors, a fire from petrol flowing at the rate of 3 gallons per minute over an engine can be extinguished by 3 pints of methyl bromide The weight of the complete installation need not exceed 15 lb

Success with this type of extinguisher can only be achieved by making the delivery of extinguishing fluid so rapid that the fire is extinguished in its early stages

In the absence of an effective fire extinguisher many fires in the air have been extinguished by shutting off the petrol and side slipping the aircraft

Extinction of Crash Fires.

If the crash is a severe one the petrol tank may be smashed and large volumes of petrol instantly liberated The inertia forces on the petrol may give rise to a large cloud of fine spray If ignition takes place, the whole of the aircraft is at once enveloped in flame and the possibility of rescuing the occupants is almost hopeless

In a less severe crash, however, the damage to the petrol system may only amount to the breaking of pipes or the development of small leaks in the tank, in which case if a fire breaks out its development may be slow in its early stages If a fire-extinguishing appliance can be rapidly brought into action, the fire, even if it cannot be completely extinguished, may be partly subdued or prevented from reaching overwhelming dimensions, and rescue work may then proceed with safety, especially if the rescuers are provided with asbestos suits The extinguishing media used in crash fires are foam and carbon dioxide A foam producing equipment may consist of cylinders of 30 gallons or more capacity containing one of the components An inner chamber is fitted into each cylinder containing the other component In action the solutions are mixed and the foam is forced through a hose and projected from a suitable nozzle Carbon dioxide is usually supplied in cylinders each containing 50 lb of liquid A tender equipment may contain nine such cylinders in sets of three each being connected to a hose and discharge horn

Comparative tests on foam and carbon dioxide have shown that the latter is much more rapid in action Under favourable conditions relatively large fires have been extinguished by 80 lb of carbon dioxide in about 1 minute The action of foam is slow, since it is necessary to form a complete blanket over the burning petrol It is, therefore, difficult to completely extinguish a crash fire, particularly if petrol is still flowing from pipes and tanks

An important difference between carbon dioxide and foam is that with the former, unless the fire is quickly put out, flames may flash back—due to the rapid dispersion of the carbon dioxide—to areas of petrol previously extinguished This constitutes a danger to operators The fire may also quickly regain its original intensity if the application of the carbon dioxide is stopped and a small hidden flame has been left In the case of foam, however, a relatively permanent blanket is formed which prevents serious flash-backs It has been found that using carbon dioxide in conjunction with foam a greater success in dealing with crash fires can be obtained than is possible with either alone

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