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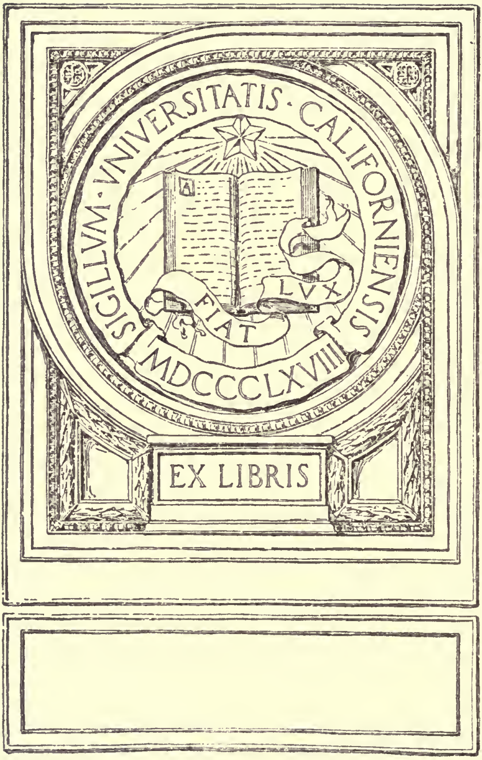
Edited by S. RIDEAL

THE PETROLEUM AND ALLIED INDUSTRIES

JAMES KEWLEY



Geo. W. M Chesney

INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A
COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

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THE PETROLEUM AND ALLIED INDUSTRIES

PETROLEUM, NATURAL GAS, NATURAL WAXES, ASPHALTS AND ALLIED SUBSTANCES, AND SHALE OILS

BY

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PREFACE

THE important part played by many petroleum products, notably motor spirits and liquid fuels, during the great war, the phenomenal growth of motor transport, and the development of aviation have directed the attention of a large section of the community to the petroleum industry. The development of the oilfields of the British Empire and the question of home supplies of liquid fuel have become matters of national importance. The possibilities of augmenting petroleum supplies or of partially replacing them by means of oils derived from the distillation of oil shales and even of coals, are receiving serious attention.

This great industry employs a multitude of men a large porportion of whom are necessarily engaged in non-technical work. Among these men there exists a very commendable desire to know something of the great industry with which they are associated, a desire which is shared by many others whose connection with the industry is indirect. This book has been written in the hope that it will appeal to such, and to many university graduates to whom a knowledge of the outlines of an industry may be of assistance in determining their choice of a career.

An effort has been made to make the book up to date as far as possible, and to include not only crude petroleum and its products but also some account of the closely related subjects, such as natural gas, the naturally occurring bituminous substances, the pyrobitumens and oil shales. The author wishes to express his thanks to Dr. H. G. Colman, Mr. J. E. Hackford and Dr. S. Rideal for valuable suggestions and advice; also to acknowledge his indebtedness to the many excellent bulletins published by the United States Bureau of Mines and other departments, to the standard works to which reference is made in the text, and finally to the Oil Well Supply Co., the Power Specialty Co., Messrs. Watts, Fincham & Co., the Sharples Centrifugal Co., and the Lucey Manufacturing Corporation for their kind assistance in the preparation of diagrams.

J. K.

LONDON,
June, 1922.

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ABBREVIATIONS USED FOR JOURNALS REFERRED TO IN THE TEXT

J.I.P.T.—Journal of the Institution of Petroleum Technologists.

J.S.C.I.—Journal of the Society of Chemical Industry.

J.C.S.—Journal of the Chemical Society of London.

J.R.S.A.—Journal of the Royal Society of Arts.

PETROLEUM AND ALLIED INDUSTRIES

PART I.—INTRODUCTORY

SECTION A.—TERMINOLOGY

THE terminology of petroleum is, unfortunately, somewhat confused, as there is a good deal of ambiguity and overlapping in the use of names. This is due, partly to the use of words, sometimes in a popular, sometimes in a scientific sense, partly to the meaning of many words having been expanded to include new ideas, and partly to the careless extension of the use of words to include meanings which they did not originally convey. Such misuse of words is only too common in other industries, *e.g.* granite is often used to designate such different rocks as marble and basalt. Although there is at present no standard system of terminology in use, the terms as used in this book will bear each a definite significance. A glossary of the more important terms is therefore appended :—

Asphalts.—Solid or semi-solid native bitumens, or solid or semi-solid artificial products made from crude petroleum. The asphalts are relatively easily fusible. This term includes also those native bitumens which contain a considerable proportion of mineral matter as well as those which are nearly pure, but does not include waxes.

Asphaltenes.—Those components of bitumens which are soluble in carbon bisulphide (benzol, or chloroform), but insoluble in alcohol, or ether-alcohol mixture.

Asphaltites.—Native bitumens, relatively difficultly fusible, largely soluble in carbon bisulphide (gilsonite, grahamite and the glance pitches). They are composed mostly of asphaltenes and diasphaltenes.

Asphaltic Pyrobitumens.—Pyrobitumens which are infusible, largely insoluble in carbon bisulphide, and relatively free from oxygenated compounds.

Astatki (Ostatki).—A Russian term designating a petroleum residual fuel oil.

Benzine.—The more volatile fractions resulting from the distillation of petroleums, shale oils, or low-temperature tars, up to the point at which the distillates merge into kerosene or illuminating oils. This term includes motor spirits, petrols, gasolines, naphthas, etc., which terms are all synonymous except when qualified. Benzine must not be confused with the hydrocarbon benzene C_6H_6.

Benzol.—The volatile or low boiling-point distillates from high-temperature coal tars, composed largely of aromatic hydrocarbons.

Bitumen.—A generic term covering native substances such as crude petroleums, natural asphalts, natural waxes, the non-mineral constituents of which are largely soluble in carbon bisulphide.

Carbenes.—Those constituents of bitumens which are soluble in carbon bisulphide, but insoluble in carbon tetrachloride.

Coal Oil.—A term sometimes used in America to include not only oil obtained by the distillation of coal and the illuminating oils obtained therefrom, but also illuminating oils obtained from petroleum.

Crude Oil.—Naturally occurring liquid bitumen.

Diasphaltenes.—Those portions of bitumens which are soluble in carbon bisulphide, and in ether, but insoluble in ether-alcohol mixture (equal parts).

Engine Distillate.—A product intermediate in character between benzine and kerosene.

Gasoline.—Synonymous with motor spirits, petrol, naphtha, or benzine. This term is in general use in America.

Goudron.—A Russian term, meaning a petroleum residue of high flash-point. French word for coal tar.

Kerites.—Natural solid asphaltic pyrobitumens, composed for the most part of kerotenes (*e.g.* wurtzilite and albertite).

Keroles.—Those portions of kerotenes which are soluble in pyridin but insoluble in chloroform.

Kerols.—Those portions of kerotenes which are soluble in pyridin as well as in chloroform.

Kerosene.—A mixture of hydrocarbons intermediate in character between the lighter benzine and the heavier gas- or solar-oil fractions. Kerosene is often miscalled "paraffin oil" in the British Isles and "coal oil" in the United States.

Kerotenes.—Those portions of bitumens, asphaltic pyrobitumens or pyrobitumens which are insoluble in carbon bisulphide.

Liquid Fuel.—A term usually confined to heavy (petroleum) oils of flash-point over 65° C. It is not usually taken to include motor spirits, although this certainly might reasonably be expected.

Malthenes.—Those constituents of bitumen (or pyrobitumen) which are soluble in volatile aromatic-free petroleum spirits (sp. gr. 0·645).

Mazout.—A Tartar word synonymous with liquid fuel.

Naphtha.—A word very loosely used to include volatile fractions derived both from petroleums and coal tars. Its use will be avoided in this work except in connection with coal-tar products.

Neutral Oils.—A term used in America to denote distillates from wax- or mixed-base crudes, containing paraffin wax and lubricating oils. It is also applied to the lubricating oils resulting after the removal of the wax from such distillates by chilling and filter pressing.

Ozokerite.—A naturally occurring solid, waxy bitumen, often known as earth wax.

Paraffin.—A hydrocarbon belonging to the methane series.

Paraffin Oil.—A term loosely used in the United Kingdom to designate kerosene or illuminating oils. The use of this word paraffin in this sense should be avoided. Also used in America to denote lubricating oils made by dry distillation of certain mixed-base crude petroleums. The use of the expression will be avoided in this work.

Paraffin Wax.—The solid waxes produced by the distillation of crude petroleums, shale or other oils.

Petrol.—Popular word for benzine or motor spirits.

Petroleum.—Liquid bitumen.

Pitch.—The solid or semi-solid residue obtained from the distillation of tars derived from the carbonization of coal, peat, lignite, resins, woods, etc. It should not be applied to the solid residues derived from the distillation of bitumens.

Pyrobitumens.—Solid, infusible, naturally occurring bodies, practically insoluble in carbon bisulphide, derived from the metamorphosis of vegetable matter (lignites, coals, anthracites), or of asphalts (*e.g.* elaterite and albertite).

Road Oil.—A trade name covering types of oils, varying from those used for spraying roads as a dust preventive to soft asphalts.

Stove Distillate.—A product made in California, intermediate in character between kerosene and gas oil.

Tar.—A liquid derived from the distillation of coal, lignite, peat, wood, or other vegetable substance. It is not, in this book, applied to any bitumen product.

Wax Tailings.—A heavy distillate obtained during the final stages of distilling certain mixed base oils down to coke. This product contains anthracene and chrysene produced by cracking.

Practically the first attempt to place the nomenclature of petroleum on a scientific basis has recently been made by J. E. Hackford, in a paper read before the Institution of Petroleum Technologists in February, 1922.

As a result of investigations with the so-called asphaltites, asphaltic and non-asphaltic pyrobitumens, their conditions of occurrence and their relation to the crude oils from which they have been derived, supported by laboratory data and the actual experimental transformation of one type into another, he has been able to put forward a theory, by means of which these bodies can be correlated and thus scientifically classified. So far, only the outlines of the scheme have been worked out and much work remains to be done before the conception can find general application. It is only when such work has been amplified and recognized that any scientific nomenclature for crude petroleums and allied products can be evolved.

SECTION B.—HISTORY

OF the industries dealt with in this book, that of petroleum is at the present day of outstanding importance, though really yet only in its infancy as far as technical development is concerned. That of shale oil, at one time more important, is now, owing to adverse conditions, in a state of arrested development. The growing demand for oils of all kinds, and the possibility of the petroleum industry alone being unable in the future to meet these requirements is, however, directing attention anew to the potentialities of oil shale, so that under favourable conditions, its great development in the future may be perhaps expected.

The allied industry of the low-temperature carbonization of coal is, at present, only in embryo. It is receiving much attention, and the day of its commercial development is probably not far distant.

The origin of the petroleum industry dates back to those early ages, of the history of which we know so little. The product of which we have the earliest records is, as would be expected from its non-volatile nature, asphalt.

This was used about 3000 B.C. by the Sumerians, a people skilled in sculpture, who inhabited the Euphrates valley. Works of art of these early peoples, now reposing in museums, show that asphalt was used as a basis or cement for inlaying mosaics. It seems strange that the resources of Mesopotamia, the country in which a bitumen was first used, have not yet been to any extent developed. The early Persians, 2500 B.C., used asphalt for similar purposes. The earliest known Egyptian mummies were encased in cloth treated with a liquid bitumen. Nebuchadnezzar constructed a high-road of burnt bricks laid in asphalt, the precursor of the modern pavement of stone blocks, grouted in with pitch or asphalt.

It is interesting to note in this connection that the name asphalt is derived from the Greek ἀσφαλής, signifying secure or firm.

The Bible contains many references to crude petroleum and asphalt. The " pitch " used in connection with the ark was undoubtedly a bitumen. The word " slime " used in connection with the Tower of Babel and elsewhere, undoubtedly refers to asphalt. Many of the references to oil, *e.g.* " oil out of the flinty rock," probably refer to crude petroleum.

For more than 2500 years issues of natural gas on the shores of the Caspian Sea have been objects of religious reverence.

Early Latin and Greek writers make many references, not only to asphalts, but also to crude oils and gas. Pliny, for example, mentions that Sicilian oil was burned in lamps in the Temple of Jupiter. Herodotus, in 450 B.C., described the so-called "pitch spring" of Zante, a seepage which exists to this day.

More than 1000 years ago Yenangyaung in Burmah was a developed oil-field. The Chinese sunk hand-dug wells before the Christian era, ventilating the shafts with large bellows with their usual ingenuity. They also used natural gas as a source of heat for evaporating brine. In Japan, too, the industry is of very long standing. The use of petroleum in that country was first recorded in 668 A.D., when the people of Echigo provinces brought forward as a present to the Emperor a marvellous burning water. In 1613, Magara found oil at Niitsu, and actually distilled it from a vessel, condensing the distillate, which he sold as an illuminant. This is probably the earliest instance of an attempt to split up crude oil into its components.

In the days of the early North American settlers numerous oil pits, lined with roughly hewn balks of timber, were often found in Pennsylvania. These were certainly of great antiquity, probably constructed by the "Mound-builders," the predecessors of the present race of Indians. In 1535 asphalt was discovered in Cuba and utilized for painting ships, and in 1595 Sir Walter Raleigh first described the famous Trinidad Asphalt Lake, which has since afforded such a prolific source of supply of asphalt for paving purposes. In the early part of the nineteenth century oil was often found in wells dug for brine, in the north-eastern States of North America, its presence being, however, regarded as a nuisance.

During the early part of the nineteenth century attempts were made to produce illuminating oils and lubricants by the distillation of coals and shales. As far back as 1694 Hancock and Portlock took out an English patent for shale tar and pitch. In 1746 Murdoch laid the foundations of the present coal-gas industry, and in 1846 Gessner manufactured an illuminant from the albertite of New Brunswick, calling it kerosene. (The older name of coal oil, however, still persists in America to the present day.)

In 1830 von Reichenbach isolated paraffin wax from wood tar, and gave it the name which it still bears. De la Haye and Laurent produced crude shale oil about the same time, and worked it up into illuminants, lubricating oils and wax, thus founding an industry in the south of France, which has persisted there up to the present day. Various attempts, which however met with little success, were made about the same period to utilize peat.

The work of James Young forms a landmark in the history of the distillation of shales. He first built a refinery for the treatment of the crude petroleum which was found in a coal-mine in Alfreton, in Derbyshire, and made lamp oils, lubricants, and a little paraffin wax therefrom. After a year or two, however, the flow of oil ceased, and Young was forced to look out for other sources of supply. After examining many samples he eventually hit upon the Boghead coal from Torbanehill, and at once set up a retorting and distilling plant, thus laying the foundation of the Scottish shale-oil industry. This industry enjoyed years of prosperity before the keen competition of the more cheaply manufactured petroleum products imported from America caused it to decline. In 1858 Riebeck erected the first important distillation plant in Saxony for the working up of lignite, thereby establishing a similar industry, which, like that of the Scotch shale oils, still exists.

The year 1859 marks an epoch in the history of the petroleum and allied industries. In that year, at Titusville, Colonel E. L. Drake, acting for the Pennsylvania Rock Oil Co., drilled the first well in the United States, really bored with the intention of finding oil. Oil was struck at a depth of only 70 feet. This find caused great excitement, and Oil Creek, Titusville, soon developed into an important oil centre. The methods of distillation and refining adopted by Young in Scotland were modified and adapted to the requirements of the new industry, and from that time onwards development was rapid. The new industry boomed. New oil-fields were discovered, and developed with feverish activity. Towns sprang up almost in a night, and rapidly disappeared when the field became exhausted or proved a failure.

It is lamentable to think that Colonel Drake died a poor man. Only recently indeed have his services to the industry been appreciated. A simple monument now stands on the site of his first well.

The development of the industry in the United States is well illustrated by the following figures, giving the approximate quantities of petroleum products marketed in the U.S.A. :—

	Tons.
1859	300
1860	70,000
1865	357,000
1875	1,255,000
1885	2,743,000
1895	8,233,000
1905	12,023,000
1913	33,874,000

The world's production in 1920 amounted to 97,512,000 tons (metric).

In Russia the Baku fields were worked from the early part of the nineteenth century. About 1872 the annual production, obtained from pit wells, had reached as high a figure as 25,000 tons. Five years later the output was nearly ten times as large, and in 1901 it had attained a figure of 10,850,000 tons. The Apscheron district has always been characterized by large gushers, which have, however, become smaller and less frequent owing to the increasing exhaustion of the fields. The industry in Galicia dates back to 1854, and in Roumania to 1866. The Burmah oil industry began to develop about 1891, and that of the Dutch East Indies about the same time. The industries in Persia, Egypt, Mexico, Venezuela, and also in many areas in the United States are of comparatively recent growth.

While the petroleum industry of North America was advancing with such rapid strides, the shale-oil industry in Scotland was fighting its way against adverse conditions, the relatively cheap imported illuminating oils proving serious competitors to the home-produced products. From 1850 to 1862 torbanite, a variety of cannel coal, which yielded as much as 100 to 120 gallons of oil per ton, was worked, but as supplies of this material became exhausted, oil shales were substituted. These shales yielded much less oil, 20 to 50 gallons per ton, but much more ammonia. In spite of the continually diminishing yields of crude oil given by the shales lying at greater depths, and subsequently worked, the industry has been able to hold its own owing to the increased value of the principal by-products, notably the ammonium sulphate. The progress of the industry in Scotland has been marked by great fluctuations. At various times, during its early days, nearly 120 concerns were operating. In 1871 this number had decreased to 51, in 1894 to 13, and in 1906 to only 6. These latter have now been amalgamated into one concern. In spite of the reduction in the number of the operating companies, the output, however, has shown a steady increase.

Year.	Tons output of Scotch Shale.
1873	524,000
1885	1,741,700
1895	2,236,200
1917	3,116,529
1920	2,763,875

Considerable development in the coal coking industry has taken place during the last sixty years. In the early 'fifties of the nineteenth century Knab, Hauport, and Carves developed recovery coke ovens. These have now largely replaced the old coke ovens of the beehive type, all by-products from which were invariably completely lost. Too many of these wasteful plants are, however, still in operation both in this country and in America. It is high time that the squandering of our country's resources in this disgraceful fashion was brought to an end. In 1887 Brunck introduced benzol recovery, a process which is now generally applied to coke-oven gases, though not to domestic coal gas.

Attention has of recent years also been paid to the recovery of tars from blast-furnace gases and producer plants.

The low-temperature carbonization of coal and the economic utilization of low-grade coals are questions which have not yet been economically solved. They are, however, receiving much attention, and the day is undoubtedly not far distant when the scandalous waste of these low-grade fuels, not to mention the inefficient methods of utilization of high-grade coals, will no longer be permitted.

Concurrently with the growth of the petroleum industry there developed a considerable expansion in the number of derivatives and by-products and their applications. The comparatively recent development of the various forms of internal combustion motor has gone hand-in-hand with the supply of suitable fuels.

Modern printing depends largely on petroleum natural gas for supplies of the best qualities of lamp-black; the electrical industries absorb large quantities of paraffin wax and asphalts; mineral lubricating oils are now generally used to the almost entire exclusion of vegetable oils, which are incidentally more valuable for edible purposes; and modern roads, in order to cope with the continual increase in the number of heavier and more rapid vehicles, depend more and more upon natural asphalts and the similar artificial petroleum residues.

The recent development of the mineral separation process which depends on the fact that certain minerals adhere to petroleum oils affords an interesting example of a modern application of petroleum products. The extraction of helium in large quantities from natural gas during the last few months of the great war, is surely one of the romances of industrial history.

Of recent years, changes in the relative values of products have brought about corresponding changes in the methods of working up crude oils. The volatile fractions, which are now of such value as fuels for internal combustion motors, were at one time regarded as waste products and were actually sometimes got rid of by burning. Kerosenes, in those days, were made so as to contain as much of the volatile fractions as the minimum legal flashpoint would allow. The position now is completely reversed, the problem being to include as much as possible of the kerosene light fractions in the motor spirit. Liquid fuel, at one time a drug in the market, is now in great demand. The high aromatic content of certain crudes, which at one time much depreciated their value, now renders them of great importance. Such changes are naturally only to be expected as the result of research and development.

The petroleum industry is, however, still only partially developed. The comparative ease with which large productions have been obtained, and the fact that the bulk of petroleum products have been, and still are, used for fuel purposes, are factors which do not make for efficiency. Appalling waste has until recently been a feature of oilfield development. Inefficient refining methods are still largely in use. The fuel consumptions of many refineries are still far too high, and many refining processes still in use involve large refining losses. The industry presents, therefore, many interesting problems ("The Problems of the Petroleum Industry," by W. A. Hamor, *Chem. and Met. Eng.*, 1920, p. 425).

The extraction of crude oil from its subterranean reservoirs leaves much to be desired, as it is estimated that not much more than 30 per cent. of the underground oil is ever brought to the surface.

The ever-increasing demand for volatile liquid fuels suitable for high-speed internal combustion motors, caused by the great developments in motor traction must before long bring about a shortage of the volatile petroleum fractions at present almost exclusively used for this purpose.

Methods of converting the relatively abundant heavier oils into more volatile products must be worked out. Many experimenters are indeed at work on this problem and are attacking it mainly from two directions, viz.: "cracking" and "hydrogenation."

So far, little work has been done in the direction of preparing from crude petroleum, products other than the various forms of fuels, lubricating oils, waxes, and asphalts. Such a complex mixture of hydrocarbons as a crude petroleum must surely some day form the starting-point for a large number of derivatives or by-products. The work now being done in the direction of producing fatty acids by the oxidation of petroleum oils probably foreshadows such a development. The opportunities for research in this direction are great indeed.

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SECTION C.—CHEMISTRY

IT is at first sight surprising to find that so little is really known of the chemistry of petroleum (and shale oil) in view of the enormous importance which the industry has now attained. When, however, the complexity of the subject and the difficulties of investigation are taken into consideration, the lack of knowledge, although deplorable, is readily understood. The same may be said of the chemistry of coal, and of its distillation products under various conditions. This subject is of even greater importance, as the supplies of petroleum are limited, the end of many great producing fields being already in sight. The world's supplies of shale and coal are undoubtedly far greater than of petroleum, and in years to come the shale oil and coal distillation industries must play a great part.

Crude petroleums, shale oils, and tars, are composed mainly of hydrocarbons, associated, particularly in the case of tars, with varying proportions of oxygen, sulphur, and nitrogen derivatives.

Owing to the enormous number of isomeric hydrocarbons which may exist when the molecule contains more than 5 or 6 carbon atoms, and to the similarity in the properties of members of any one series, the isolation and investigation of individual hydrocarbons from crude oils present very great difficulties, as a natural consequence of which the volatile hydrocarbons of relatively low molecular weight have received most attention. Many of these have been isolated in a state of purity. Several of the lower members, particularly those of the aromatic series, have actually been extracted commercially from petroleum. For example, many thousands of tons of trinitrotoluene were made from toluene derived from a Borneo petroleum during the recent war (Kewley, *J.I.P.T.*, 1921, p. 209).

A further difficulty in the isolation and examination of the constituents of higher boiling points, arises from the fact that chemical changes often take place during the distillation of crude petroleums, even at temperatures as low as 200° C., so that it by no means follows that components found in distillates are present as such in the crude. This is unfortunate, as distillation is naturally the obvious means of effecting some sort of separation.

Such decomposition or "cracking" as it is termed, finds, however, a technical use, being applied to the increasing of the output of light fractions (benzines) from certain crudes (*vide* Part VII., Section F).

Recently, however, Krieble and Seyer (*J. Am. Chem. Soc.*, 1921, p. 1337) have shown that by distilling under really high vacuum, as low as 0·1 mm., heavy hydrocarbon oils can be distilled up to temperatures as high as 300° C. without cracking.

If the various hydrocarbons or other bodies present could only be separated from each other by physical means, other than distillation, much more might be learned of their chemistry. The only physical means which at present appear to be available are :—

(1) Distillation under high vacuum.
(2) The differential action of solvents.
(3) Diffusion.

In connection with the first it may be mentioned that paraffin wax, which readily cracks on distillation, may be easily distilled in high vacuum without any appreciable change. High-vacuum distillation is technically employed in the manufacture of the best qualities of lubricating oil, in order to avoid decomposition as far as possible.

An example of the second method is afforded by Lessing's process for the treatment of coal tars (Eng. Pat. 130362 of 1919). When such a tar is treated with benzine containing no aromatic hydrocarbons, it is split up into a pitch which is precipitated out, and a tar oil which dissolves in the spirit, from which it is separated by distillation. The tar and oils so obtained are somewhat different from those obtained by distillation. The pitch contains much less insoluble free carbon than does that resulting from ordinary distillation treatment, as it lacks the free carbon formed by decomposition during distillation, and the tar oils also differ somewhat from those obtained by distillation. It is evident therefore that considerable changes take place during the distillation of coal tar. The application of a similar method (if a suitable solvent were found) to crude oils would doubtless lead to interesting results.

A further application of this method is afforded by the Edeleanu process, in which liquid sulphur dioxide at a low temperature is used for the removal of aromatic and unsaturated compounds from petroleum distillates (*vide* Pt. VII., Sec. C). The use of dimethyl sulphate (Valenta, *Chem. Ztg.*, 1906, p. 266) has been advocated for the separation of aromatic hydrocarbons, but its use has limitations, and it is, moreover, objectionable owing to its exceedingly poisonous nature. Various alcohol mixtures have been used as differentiating solvents by Charitschkoff and Wolochowitsch (*Chem. Ztg.*, 1902, p. 224), carbon tetrachloride by Graefe (*Chem. Rev.*, 1906, p. 30), acetic anhydride and alcohol ether mixtures, by Zaloziecki. A method of estimation of paraffin wax is based on its relative insolubility in a mixture of alcohol and ether at low temperatures (Holde, "Untersuchung der Mineralöle und Fette," 3rd edition, p. 28).

Little work has as yet been done on the lines suggested by method (3), Day (*Bulletin* 365, U.S. Geol. Survey), Gilpin and Bransky (*Amer. Chem. Journal*, vol. 44, p. 251), Engler and Albrecht (*Zeit. angew. Chem.*, 1901, p. 889) have examined the behaviour of crude oil when subjected to slow filtration through finely divided media, such as fuller's-earth. Day made the following observations: "(1) when petroleum is allowed to rise in a tube packed with fuller's-earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom. (2) When water is added to fuller's-earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards, when more water is added. (3) When petroleum is allowed to rise in a tube packed with fuller's-earth, the paraffin hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom.

This filtration process on a natural scale is undoubtedly responsible for the occurrence of many abnormal crude oils, the so-called white oils which have been found in Russia, Canada, and elsewhere, usually in small quantities. Indeed, many crude oils have undergone such a filtration to some extent, as the occurrence of oil in the formation in which it was formed (its mother rock) is unusual; migration has in most cases taken place.

Much work still remains to be done on these lines, especially in connection with the more complex compounds which constitute the natural asphalts, such as gilsonite, grahamite, elaterite, and others, the natural waxes or ozokerites, as well as on the heavy asphaltic crudes. It is undoubtedly by the examination of these bodies, rather than the volatile and simpler constituents, that light will be thrown on the relations of crude oil with each other and with coals, and incidentally on the much-discussed question as to the origin of petroleum.

Attempts have been made to utilize other physical characters for the determination of the class to which a hydrocarbon belongs. Darmois (*Comptes rendus*, 1920, p. 952) has examined the dispersion of several classes of hydrocarbons. He finds that the specific dispersion, *i.e.* the difference between the refractive indices for two definite wave lengths, divided by the density, is a constant for particular series of hydrocarbons. (In his work he used the two spectrum lines $\mathrm{H}\alpha$ and $\mathrm{H}\gamma$.)

In the case of hexane (n) he finds density $t/4$ 0·6634.

$$n_{\alpha}=1{\cdot}3750 \qquad n_{\gamma}=1{\cdot}3853$$

$$\Delta n=103 \text{ and } \frac{\Delta n}{d}=155$$

For six hydrocarbons of the paraffin series and for nine of the cycloparaffin series he finds $\frac{\Delta n}{d}$ = about 155.

For hydrocarbons with one double bond, *e.g.* amylene, he finds $\frac{\Delta n}{d}$ = about 193.

For hydrocarbons with two double bonds, *e.g.* methyl hexadiene, he finds $\frac{\Delta n}{d}$ = about 228.

And for the aromatic hydrocarbons he finds a value about 300.

Such work may prove of great value in future researches.

Apart from these physical methods, certain chemical methods may also be employed for the separation of the compounds of crude oil and for their estimation. There are, of course, objections to such chemical methods of analysis, as the behaviour of most of the compounds under investigation towards many reagents is by no means well known.

For example, unsaturated hydrocarbons are usually removed and estimated by absorption with sulphuric acid, aromatic hydrocarbons by absorption with oleum in the cold, after the removal of unsaturated hydrocarbons (Bowrey, *J.I.P.T.*, vol. 3, p. 287). These methods are by no means simple, however, as overlapping of the action of the acid takes place. Xylol, and higher aromatics, for example, are partly removed by 96 per cent. sulphuric acid, which also causes polymerization of some of the unsaturated bodies. Further, oleum certainly reacts with certain non-aromatic constituents too. The isolation, therefore, of even any one class of hydrocarbons, much more so of any individual of a class, is a matter of difficulty. This is, however, generally only a matter of minor importance in practice, though of greater importance from the point of view of research.

A further possible method of investigation is suggested by the recent work of Tausz and Peter (*Zentr. Bakt. und Parasit.*, 1919, vol. 49, p. 495; and *J.S.C.I.*, vol. 39, p. 357A) on the preferential action of certain bacteria. They found that paraffins can be separated from naphthenes by the action of *B. aliphaticum* and *B. aliphaticum liquefaciens*, bacteria which they isolated from garden mould. These species are inert towards cyclic hydrocarbons, but attack paraffins. In this manner Tausz and Peter have isolated 1.3 dimethylcyclohexane and 1.3.4 trimethylcyclohexane from a petroleum. This method is as yet in its infancy, but it certainly has possibilities.

Hydrocarbons of most of the known series have been detected in some one or other of the many varieties of crude petroleum. Those of the paraffin (aliphatic) and naphthene (alicylic) series, however, predominate, those of the aromatic series occur to a less extent and in fewer crudes, while members of the less known series are also undoubtedly of great importance.

There is no known crude composed exclusively of the members of any one series, but many crudes are characterized by the presence in predominating quantities of hydrocarbons of one of the series.

The **paraffin** series of hydrocarbons (C_nH_{2n+2}) are widely distributed, occurring to some extent in most crudes, particularly in the lighter fractions. They enter very largely into the composition of the crude oils of the eastern states of North America, to the almost complete exclusion of members of other series. They occur to a less extent in those of Galicia, Rumania, Persia, Burmah, Mexico, Sumatra, etc., and in smaller proportions still in those of Russia, Borneo, South America, and California. The more volatile members of the series, methane to pentane, occur in natural gases and the higher members constitute the paraffin waxes.

The liquid members have lower specific gravities than do those members of other series having similar boiling points.

		B.p.	Sp.gr. at 15° C.
Hexane	C_6H_{14}	 70	0·662
Cyclohexane	C_6H_{12}	 70	0·746
Hexylene	C_6H_{12}	 58	0·685
Benzene	C_6H_6	 80	0·884

Their specific gravities rise with the boiling points, *e.g.*—

n-pentane	sp.gr.	0·627/15° C.	b.p.	36·3° C.
n-hexane	,,	0·658/20° C.	,,	68·9° C.
n-heptane	,,	0·683/20° C.	,,	98·4° C.
n-decane	,,	0·730/20° C.	,,	173·0° C.

This is generally the case, but the aromatic hydrocarbons show the reverse effect.

Owing to the fact that motor spirits from Appalachian crudes were early in the market low specific gravity came to be regarded as a criterion of quality, a popular fallacy which died very hard.

In the case of a motor spirit composed entirely, or nearly so, of paraffin hydrocarbons, low specific gravity is an index to degree of volatility, but as a means of comparison for motor spirit of various origins it is entirely misleading, as may easily be seen from the fact that a heavy kerosene of paraffin hydrocarbons, utterly unsuitable as a motor spirit, has a specific gravity lower than that of benzol, an excellent motor fuel.

The paraffin hydrocarbons, though stable to most reagents, readily undergo cracking at high temperatures. Such cracking is easily effected in the case of paraffin wax (Mabery, *Proc. Am. Phil. Soc.*, 1897, p. 135). The unstability of the paraffins is also evident from the fact that they are the hydrocarbons which most readily show the phenomena of detonation (knocking or pinking) when used in automobile internal combustion engines. In this respect they show up badly in comparison with the naphthenes and worse still in comparison with the aromatics (Ricardo, "The Influence of various Fuels on the performance of Internal Combustion Engines," *Automobile Engineer*, February, 1921).

The higher paraffins occur as waxes also in wood tar, and in the various oils resulting from the distillation of cannel coals and shales, and in the oil produced by the low temperature distillation of coal. They occur also in ozokerit, a natural wax often found associated with petroleum, which contains the higher members of the series from $C_{24}H_{50}$ upwards.

It is not proposed to give here a detailed list of the various hydrocarbons and their properties. For these, reference should be made to Engler-Höfer, "Das Erdöl," vol. 1, where tabulated analyses of numerous crude oils are also given.

The hydrocarbons of the **olefine** series (C_nH_{2n}) are unsaturated open chain compounds. They are isomeric with the members of the naphthene series ($C_nH_{2n-6}H_6$) which, on the contrary, are saturated ring compounds.

The olefines occur in crude petroleums comparatively rarely and in small quantities. They are, however, present in shale oils and tars and in many petroleum distillates, as they are among the products resulting from the cracking of paraffins and other hydrocarbons. They are readily absorbed by sulphuric acid, are oxidized by permanganate, and form addition compounds with bromine. They are also soluble in liquid sulphur dioxide, and may thus be separated from aliphatic hydrocarbons. This reaction finds technical application in the Edeleanu process (*vide* Pt. VII., Sec. C). They react with ozone to form ozonides. The paraffins and naphthenes do not react in this way (Harries, *Lieb. Annal.*, 1906, p. 343; 1910, p. 374). They react with mercury salts, and these reactions have been proposed as the basis for methods of estimation of these hydrocarbons (Engler-Höfer, "Das Erdöl," vol. 1, p. 269). Small quantities of olefines have been found in Galician, Rumanian, Caucasian, Canadian, and South American oils.

The members of the diolefine, acetylene, and other unsaturated series (Tausz, *Zeit. angew. Chemie*, 1919, vol. 32, p. 233) are of minor importance in petroleums, but are normal constituents of many tars and shale oils. The diolefines, owing to their readiness to undergo oxidation and polymerization, are undesirable constituents in petroleum products (other than liquid fuels); in a motor spirit, for example, they give rise to the formation of gummy deposits. In removing them, unfortunately, quantities of olefines, which in themselves are not undesirable constituents, are removed too.

The members of the **naphthene** or *alicylic* series, on the contrary, play a very important part in the composition of well-known crude oils. These differ from the olefines, which have the same empirical composition, in that they are saturated ring compounds. As regards their behaviour towards reagents such as sulphuric and nitric acids, halogens, etc., they stand between the paraffin and the aromatic hydrocarbons. They are not attacked by sulphuric acid in the cold. They can be oxidized by vigorous oxidizing agents, the ring being then broken up. As the individual members of the series, however, do not all behave in the same manner towards any reagent, there is no general method by which members of this series can be separated from mixtures with paraffin hydrocarbons.

The hydrocarbons of this series are of higher specific gravity than the corresponding paraffins, *e.g.*—

Cyclohexane	0·799 at 0° C.
Hexane	0·676 at 0° C.
Methylcyclohexane	0·778 at 0° C.
Heptane	0·701 at 0° C.

Naphthenes occur in Caucasian petroleums, of which they constitute a large proportion; to a considerable extent also in the petroleums of Galicia, Rumania, Egypt, Borneo, Peru, California, and elsewhere.

From the practical standpoint naphthenic crudes yield good motor spirits, the naphthenes being superior to the paraffins in this respect, as they can be used in engines of higher compression and therefore of greater thermal efficiency. They yield also kerosenes of good illuminating quality, and good lubricating oils of low cold test.

Hydrocarbons of the **aromatic** series are of common occurrence in crude petroleum, though generally to the extent of below 10 per cent. In a few exceptional types, however, the percentage may be much higher. The crude oils of East Borneo are remarkable in this respect, containing as much as 40 per cent. of aromatics (Jones and Wooton, *J.C.S.*, 91, pp. 114, 1146).

These hydrocarbons occur also in coal tars, especially in those resulting from high-temperature distillations. Low-temperature distillation tars and shale oils are relatively poorer in aromatics and richer in paraffins. The hydrocarbons of this series are of relatively high specific gravity, which in this case decreases somewhat with the increase of molecular weight, *e.g.*—

Benzene	0·884 at 15° C.
Toluene	0·870 ,,
P. xylene	0·866 ,,
Cymene	0·863 ,,

They possess greater solvent properties than do the members of the paraffin and naphthene series, so that good extraction spirits can be made from crudes relatively rich in these compounds. They are readily sulphonated by sulphuric acid and on these properties methods of estimation have been based. They are soluble in cold liquid sulphur dioxide and are often extracted from kerosenes by a method based on this behaviour (*vide* "Edeleanu Process," Pt. VII., Sec. C). They are readily nitrated by a mixture of sulphuric and nitric acids.

Ross and Leather (*Analyst*, vol. 31, p. 285) in this way isolated decahydro- and tetrahydro-naphthalenes from a Borneo gas-oil distillate.

Several of the nitro-compounds, *e.g.* dinitrobenzene, trinitrotoluene, trinitroxylene, are used as explosives. The lower members of the series may be separated from admixture with other hydrocarbons by taking advantage of their ready nitration, as the mononitro compounds may easily be separated by distillation, and subsequently converted into the trinitro derivatives.

Aromatic hydrocarbons of the higher series C_nH_{2n-8}, C_nH_{2n-10}, and so on have been found in small quantities in various petroleums and have been isolated from the distillates boiling at temperatures over 200° C. But as chemical changes begin to take place at these temperatures, it is by no means proved that these hydrocarbons exist as such in crude oils. They are found also in coal-tar distillates. Indene, for example, was isolated from coal-tar light oils by Kraemer and Spilker (*Zeit. angew. Chem.*, 1890, p. 734). Naphthalene is an important constituent of coal-tar distillates, as are also methyl- and phenyl-naphthalenes, acenaphthene and its derivatives, diphenyl, fluorene, anthracene, phenanthrene and their derivatives, fluoranthene, pyrene, chrysene, retene, and others (Malatesta, "Coal Tars and their Derivatives," Chap. III.), but many of these have also been found in petroleums (Engler-Höfer, "Das Erdöl," vol. I).

In addition to the members of these main hydrocarbon series, members of many other less known and little investigated series have been found. The presence of many saturated hydrocarbons of unknown constitution, hydrocarbons of the terpene series and of other more complicated series from C_nH_{2n-10} to C_nH_{2n-20} have been indicated by many workers, such as Mabery, Coates, Markownikoff, Engler, Marcusson, and many others. Detailed references to these are given in Engler-Höfer, "Das Erdöl," vol. I. Hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4} have recently been isolated from the petroleum extracted from the bituminous sands of Alberta (Krieble and Seyer, *J. Am. Chem. Soc.*, 1921, p. 1337). Our knowledge of the properties of the hydrocarbons of these series is, however, very vague; indeed the field may be said to be practically unexplored.

Apart from the hydrocarbons and the higher, practically uninvestigated, asphaltic bodies, many other compounds occur as unimportant constituents (usually regarded as impurities) in petroleums and as normal constituents in tar. Sulphur compounds, and to a much less extent nitrogen and oxygen compounds, occur even in the lighter fractions of certain petroleums, more so in shale oils and tars; of the composition of the higher sulphur and oxygen compounds, which undoubtedly play an important part in the composition of many asphalts, very little is as yet known. Research in this difficult field should yield interesting results.

Sulphur is found to some extent in practically all crude oils. In some cases it is an essential constituent of the crude, *e.g.* in the case of the thioasphaltic oils of Mexico, in other cases it is merely an impurity ; in some cases it is found in solution (Peckham, *Proc. Am. Phil. Soc.*, 1897, p. 108) in the oil. Many crude oils of Ohio, Canada, Mexico, Persia, Egypt, California, and Texas and elsewhere are relatively rich in sulphur compounds.

Thiophene has been found in German crudes, thiophene and its homologues in Canadian, Caucasian, and Persian oils; thioethers in Ohio oils and mercaptans in Persian oils. The sulphur compounds occurring in petroleum have, however, as yet received comparatively little attention (Mollwo Perkin, *J.I.P.T.*, vol. 3, p. 227).

The presence of sulphur in relatively large quantities is interesting to the student of the origin of petroleum, as such large amounts as are sometimes found could not have originated from animal or terrestrial vegetable matter. In certain cases sulphur in combination must have resulted from secondary changes owing to contact of the oil during migration with either sulphur or sulphates, and such sulphates, *e.g.* gypsum, are indeed often found in close association with oils relatively rich in sulphur (Hackford *J.I.P.T.*, 1922, vol. 8). Sulphur compounds are usually present in considerable quantities in shale oils. The difficulty of eliminating the sulphur compounds has always been one of the obstacles to the working up of the English shales for oil.

Nitrogen compounds occur in small quantities in many crude petroleums, *e.g.* in Californian, Japanese, and Algerian. They occur usually in the form of homologues of pyridin (some Californian crudes are unusually rich in quinolines). The presence of nitrogen compounds is, however, of no practical importance as they are usually eliminated in refining. They occur to a much larger extent in shale oils and various tars, mainly in the form of pyridin and anilin homologues.

Oxygen compounds are found to some extent in most crudes, and in the case of certain asphaltic oils are undoubtedly an essential constituent. In certain oils, *e.g.* some of California, the oxygen compounds are phenols and in others, *e.g.* Russian, naphthenic acids. Practically no work has as yet been done on the oxygenated compounds present in petroleums. Phenol and its homologues form important constituents of coal tar, while other oxygenated products, *e.g.* ketones and acids are found in wood tars.

Although the complete examination and identification of the constituents of a petroleum distillate is too difficult an undertaking ever to be of much practical value, still a ready means of determining even approximately the percentages of paraffins, naphthenes and aromatics in a light petroleum product, for use as a motor spirit, is of prime importance, owing to the very great difference in value, as motor fuels, of the hydrocarbons of these three groups. Chavanne and Simon (*Comptes rendus*, 1919, p. 285) have done much work in this direction by applying the aniline solubility critical temperature method. Tizard and Marshall (*J.S.C.I.*, 40, p. 20T) have developed and modified this method and find it particularly applicable to the estimation of aromatic hydrocarbons.

The temperature at which a mixture of equal volumes of pure freshly distilled aniline and the benzine separate out is called the aniline point. The aniline point for paraffins is high, about 70° C., for naphthenes it is lower, about 50° C., and for aromatics is much lower still.

It has been found that the difference in aniline point for a benzine, before and after the removal of the aromatics by sulphonation, is proportional to the original aromatic content, provided that unsaturated hydrocarbons are absent. Thus a lowering of aniline point of 4·2° C. corresponds to 5 per cent. by weight of aromatic hydrocarbons, of 18·1° C. to 20 per cent., of 39·8° C. to 40 per cent., and so on. The method has so far only been worked out for the first three members of the aromatic series. The method is capable of further development and its use may be considerably extended.

The chemistry of coal is a subject which has lately been receiving much attention, but is as yet little understood. The subject, however, lies outside the scope of this volume.

The question of the origin of petroleum and its possible, or probable, relation to coal has also been the subject of much discussion. Hackford (*Trans. Am. Inst. of Mining and Metallurgical Engineers*, September, 1920) has converted petroleum oils by slow oxidation or thionization aided by gentle heat into bodies termed by him "kerotenes," most of which are quite insoluble in any of the known solvents and are probably identical with certain constituents of coal. He has also shown that the portions of coal soluble in pyridine consisted partly of asphaltenes (*i.e.* those portions of bitumens which are insoluble in ether or ether-alcohol, but are soluble in carbon bisulphide). He concludes that most of the insoluble portion of coal consists of a true bitumen which has been transformed into an insoluble kerotene. The kerotenes (the portions of a bitumen which are insoluble in carbon disulphide) experimentally produced from petroleum, yield, on distillation, the same products as are obtained by the distillation under the same conditions of the kerotenes derived from coal.

Fischer and Gluud (*Ber.*, 1919, p. 1053) claim to have established that light paraffins exist as such in certain coals.

Tausz (*Zeit. angew. Chem.*, 1919, p. 361) has pointed out that all three xylenes and ethylbenzene are found, not only in the distillates from coal, but in some petroleums too.

A high melting-point paraffin wax was actually found in a Lancashire coal-seam many years ago (Sinnatt, *Colliery Guardian*, November 14, 1919).

Although the products up to the present commercially extracted from petroleum have been in the main those obtained by the physical methods of distillation and filtration, *i.e.* various motor and extraction spirits, illuminating oils, lubricants of various grades, fuel oils, waxes, and asphalts, there are indications that in the future products obtained by chemical means will play an important part.

Recently alcohol has been prepared from the ethylene present in coke-oven gases by Bury and Ollander (*Chem. Age*, 1920, p. 238, and Eng. Patent 147360 of July 22, 1920). The ethylene is absorbed by concentrated sulphuric acid and the ethylhydrogen sulphate so formed is subsequently hydrolysed by steam distillation, yielding ethyl alcohol and sulphuric acid again in the well-known manner.

$$C_2H_4+H_2SO_4=C_2H_5H.SO_4$$
$$C_2H_5H.SO_4+H_2O=C_2H_5OH+H_2SO_4.$$

In a similar way the propylene evolved from the cracking stills used to crack gas oils into motor spirits (*vide* P. VII., Sec. F) is converted into isopropyl alcohol (Carleton-Ellis, *Petroleum Mag.*, January, 1921, p. 40), and this alcohol is used in admixture with benzene as a motor fuel.

By chlorination, chlor derivatives of hydrocarbons suitable for use as non-inflammable solvents may be obtained. By chlorination and subsequent removal of the chlorine, drying oils may be obtained.

Much work has recently been done on the oxidation of the higher paraffins to fatty acids. Grün, Ulbrich, and Wirth (*Ber.*, 1920, p. 987) found they were able to oxidize paraffin wax and obtain a whole range of fatty acids therefrom. Löffl (*Chem. Ztg.*, 1920, p. 561) oxidized petroleum hydrocarbons with the assistance of lead or mercuric catalysts, to fatty acids which when mixed with tallow or coconut fatty acids yielded satisfactory acids for soap making. Schaarschmidt and Thiele (*Ber.*, 1920, p. 2128) chlorinated paraffin wax, and after removal of the chlorine by alcoholic potassium hydroxide oxidized the hydrocarbons to fatty acids. Fischer and Schneider (*Ber.*, 1920, p. 922) oxidized paraffin wax by means of air under pressure to fatty acids. These researches foreshadow a possible alternative supply of fatty acids for soap making and the consequent liberation of certain vegetable oils for more useful purposes.

Pentane can be converted by a rather complicated process into isoprene, the possibility of synthetic rubber from petroleum being thus opened up.

The investigation of possible petroleum by-products is one of the most promising fields for research. Our ignorance of the chemistry of petroleum as well as that of shale oils and tars of various kinds is really relatively profound.

With adequate research these industries will undoubtedly expand and considerably extend their yield of important products.

A distinctly new line in petroleum chemistry has been struck by Hackford, the preliminary outline of which has been published by him in a paper read before the Institution of Petroleum Technologists (*J.I.P.T.*, 1922, vol. 8). He has endeavoured to take a very broad view of the subject and has studied and correlated data, many of which are the result of his own investigations, with a view to arriving at some general conception as to the interrelation of various types of crude oil and the relation to crude oils of the natural gases, and natural asphaltic bodies such as asphaltites, elaterites, and the like, which are often found in close association with them. On the basis of this work he suggests a classification for bitumens, which has the merit of being based on their chemical compositions.

As all crudes contain some paraffins, he bases his classification on the content of other types of hydrocarbons, dividing them into four classes—

(1) aliphatic oils
(2) aromatic oils
(3) naphthenic oils
(4) naphthelynic oils.

Each of these may be subdivided into two classes, viz. thio- and oxy-oils, according to the presence of oxy- or thio-hydrols and/or ethers. He classes all solid bitumens as "Petrolites," subdividing them into those soluble in carbon bisulphide or *asphaltites*, and those insoluble in that solvent or *kerites*, as these solid bitumens have undoubtedly been derived from the corresponding classes of oils.

This work indicates the probability of being able to predict the type of oil to be found in an underground reservoir from a study of the composition of the natural gas and solid bitumens, which may be found in association therewith. Such a result would be of great technical importance, quite apart from the fact that a very profitable line of research is also opened up.

A rather interesting development during the last year of the recent war was that of the extraction of helium from natural gas. Certain natural gases were found to contain small quantities of this gas, previously known merely as a chemical curiosity. Though the helium content never exceeded 1·5 per cent. in the most favourable cases, and was usually much lower, if present at all, plant was actually set up for extracting this on the large scale, and at the date of signing the armistice, many thousands of cubic feet had been prepared.

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SECTION D.—GEOLOGY

THE geology of shales and coal is comparatively simple and well known; that of petroleum, on the contrary, is difficult and presents many unsolved problems, not only in specific cases, but in general. The origin of coals is invariably, and of shales usually, attributed to accumulations of vegetable matter or of vegetable matter and mud. Exactly what changes took place accompanying the transition to coal or shale is not yet understood. Coal and shale wherever found occupy the same relative positions to the under- and overlying strata as they have always done since their deposition They are, in fact, ordinary sedimentary rocks, they have undergone the same tectonic changes as the adjacent strata and the applications of geology to ordinary strata hold equally well in their case. It is assumed, therefore, that the reader is acquainted with the principles of geology and that nothing more need here be said about the method of occurrence of coals and shales.

As petroleum, however, is a liquid, the factors which determine its accumulation are much more complicated. Petroleum is comparatively seldom found in its mother rock, the strata in which it was formed; migration has usually taken place, so that the petroleum has either been arrested and retained when suitable conditions existed, or has escaped to the surface and been lost. This latter must have been the case in innumerable instances. The question of the ultimate origin of petroleum, therefore, may be neglected in studying the conditions of its accumulation. Petroleum in some form or another is found in all the geological systems down to the Cambrian. About 50 per cent., however, of the present production comes from

Tertiary rocks, 40 per cent. from Carboniferous and Devonian, and 8 per cent. from Ordovician.

The crudes of Ohio, Indiana, and Ontario are found in the Ordovician and Silurian; those of Pennsylvania in the Devonian. Those of the Illinois and Mid-continent fields occur in the Carboniferous, as does also the oil from the Hardstoft well, recently brought in, in England. The oil shales of Scotland also belong to this period. Certain of the Wyoming oils belong to the Triassic, others to the Jurassic period. The Kimmeridge and Norfolk shales of England belong also to this system. Much of the crude of California, Mexico, and Texas comes from the Cretaceous. The crudes of the East Indies are of Tertiary age, as are also those of Galicia, Russia, Burmah, and Egypt.

Bitumen in one form or another sometimes appears at the surface in the form of (1) springs of natural gas, (2) lakes or flows of asphalt, (3) seepages of crude oil, and (4) outcrops of impregnated rocks.

Examples of (1) are afforded by the natural gas springs of the Baku district, the gas from which has burned for centuries. (2) The largest and most valuable forms of semi-liquid asphalt occur in South America as the famous asphalt (wrongly called pitch) lakes of Trinidad and Bermudez. The native asphaltites, gilsonite and grahamite, are found in veins outcropping at the surface. (3) Crude oil seepages are common, and may be due to the oil-containing rock actually outcropping at the surface or to the existence of a fissure or fault through which oil can escape to the surface. Such seepages are common in Mesopotamia, Mexico, and elsewhere. The existence of seepages naturally depends on the depths at which the main supplies of oil occur, and on the degree of folding and fissuring to which the rocks have been subjected. In the case of the Appalachian fields of the eastern United States, for example, seepages have seldom been found owing to the fact that the oil-bearing beds have been only slightly tilted, and not at all broken up. In other regions, such as parts of Mexico, seepages are common, as the oil occurs in newer rocks which have been tilted and eroded. In some cases undoubtedly the oil may have almost completely escaped through fissures formed by faulting. Interesting cases of seepages are those in which the oil has been naturally filtered and decolorised. Certain such "white oils" have been found in Persia, Russia, and elsewhere. (4) Outcrops of rock impregnated with oil or asphalt are also well known, good examples being afforded by the so-called "tar sands" of Athabasca, which are now attracting much attention, and the asphalt-impregnated limestones of Val de Travers and Limmer, so much used for street asphalt paving.

By far the greater quantity of the world's output of bitumen is that of the liquid form, crude petroleum, and this is obtained from strata at various depths by means of borings or wells.

Liquid petroleum is invariably found in some more or less porous rock, such as a limestone, or sandstone, which acts as a reservoir. In some cases it is found in the mother rock, *i.e.* that in which it originated, more often in some rock into which it has migrated.

The question of the porosity and capacity for holding petroleum of various rocks has been studied by several authors. Beeby Thompson gives cases of sands capable of holding 20 to 30 per cent. of their volume of oil, and Hager reckons an average figure of about 13·5 per cent. A sand may thus contain as much as a gallon of oil to the cubic foot.

In all probability never more than 75 per cent. of the oil from a rock surrounding the bottom of a well can be recovered, and that only in the case of light oils.

The storage capacity of a rock for gas is, of course, enormously greater, as the gas is often present under a pressure of 500 lbs. to the square inch or more. A rock which could contain one gallon of oil to the cubic foot could contain nearly 5 cubic feet of gas at 30 atmospheres' pressure (Redwood, "Treatise on Petroleum," vol. 1, 1913, p. 113).

In addition to a suitable storage rock, another condition is necessary, viz. a suitable impervious covering bed. A fine-grained shale or clay, especially if wet, best fulfils the conditions, as it is impervious and not liable to fracture. Should such a covering exist, but be badly fractured, the oil will usually have escaped. The Utica shale overlying the petroliferous Trenton limestone affords a good example of such a cover or cap-rock.

It is comparatively rarely that petroliferous beds are found horizontal and undisturbed. In most cases the strata, as the result of earth movements, have been folded into anticlines or domes, the folds being sometimes complicated by faulting. The folding of the strata has a great influence on the accumulation of oil and gas in consequence of their fluid nature, and of their usual association with water. Owing to lateral pressure brought about by earth movements, the nature of which cannot be discussed here, the once horizontal strata have been thrown into wave-like folds or anticlines and synclines, the limbs of the folds being highly or very slightly inclined according to the conditions of the folding. The result of the superimposing of a series of folds with axes more or less crossing the axes of the original set, is a dome and basin structure similar to that of many of the English coalfields.

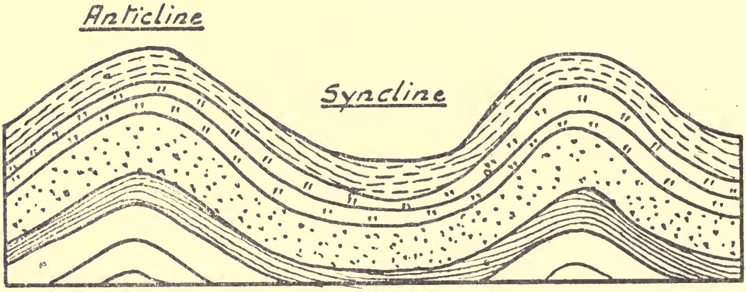

FIG. 1.—Diagrammatic section through anticlinal and synclinal folds.

These two types of structure are very common, but cannot be said to be characteristic of oil-bearing territory. In a field exhibiting such structure gas will be found accumulated along the crests of the anticlines, oil below this and water below the oil. If no water is, however, present, oil may be found in the synclines too. Such a distribution of the oil affords good evidence of movement or migration, the factors controlling which are differences in specific gravity and capillarity (M. R. Campbell, "Petroleum and Natural Gas Resources of Canada." Canada Department of Mines, 1914). The anticlines are, however, often asymmetrical, one limb of the fold being much steeper than the other. In such cases, the greater portion of the petroleum will usually be found in the gentler slopes.

Petroleum occurring under these conditions is often found to be under great pressure. This pressure may be due to: (*a*) artesian water pressure, (*b*) pressure of formation, the gradually accumulating gas having had no chance of escaping. Advocates for both theories are found and both theories may be correct. The latter view can, however, account for all cases of pressure, the former only for a few.

This anticline type of structure predominates in most of the oil-fields of the world, *e.g.* those of the United States, East and Mid-continent, those of Russia, Burmah, and the Dutch East Indies. Such folds being associated with mountain chains, it is noticeable that most of the large oil-fields of the world are found on the flanks of the main axes of mountain formation.

Other types of structure of less common occurrence are (*a*) the saline dome, (*b*) the igneous intrusion. The saline dome type of structure is found in the fields of Louisiana. Texas; and Rumania. These domes contain cores of crystalline salt, which have even, in some cases, been thrust up through the overlying clays and sands, the structure being then usually complicated by faulting. This is the case in certain of the Rumanian fields. The structure and method of formation of these saline domes is by no means as yet well understood.

The igneous intrusion type of dome is found in Mexico. The intrusion of a core of igneous rock evidently caused elevation of the strata into domes which produced suitable conditions for accumulation of petroleum. In some cases the intrusion of an igneous plug has caused tilting up of the strata near the edges of the plug, and petroleum has accumulated in these upturned edges, being sealed by the actual intrusive plug.

In many cases petroleum is found in strata nearly horizontal or only slightly inclined, provided that conditions of sealing, which prevent a possible escape of the oil, exist. Such conditions of sealing may occur in various ways. For example, a petroliferous sand may thin out on a slope, being sealed off by the coming together of the over- and underlying clays. Faulting may bring up a porous petroliferous rock against an impervious bed, and so make an efficient seal (Fig. 2). Conditions suitable for petroleum accumulation may be, and are, brought about in many different ways of which the above afford a few examples only.

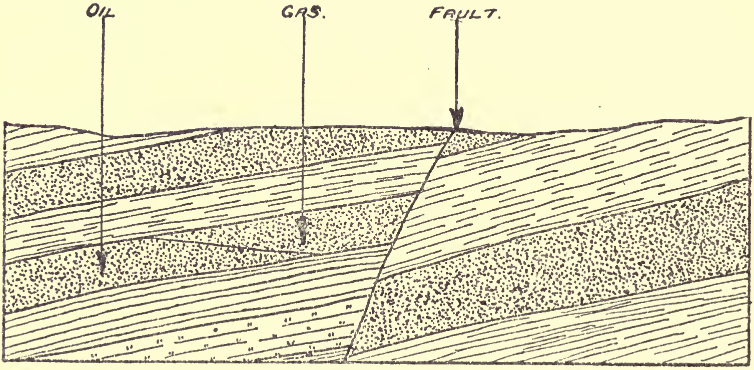

FIG. 2.—Oil-bearing layer sealed by a fault.

The detailed study of underground geological conditions is of the greatest importance, not only for the exploitation of new territory, but also for the selection of well sites in known fields.

The discovery of many oil-fields has been in the first instance due to so-called "wild catting," *i.e.* the sinking of wells as a speculation. In many cases, however, it is only by the making of test wells that an area can be proved petroliferous or not. The choice of sites for such wells should, naturally, always be guided by geological data as far as possible. Even in a proved field wells may turn out "dry" owing to some unexpected geological feature, such as a fault.

A careful correlation of the evidence afforded by the logs of all wells may enable the contours of the underlying beds to be plotted out, and the underground geology of the district to be eventually thoroughly well understood.

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SECTION E.—THEORIES OF ORIGIN

THE problem of the origin of petroleum is one, not only of academic interest, but also of great practical importance. It has received much attention during the last half-century, has given rise to much discussion and a voluminous literature, and is still regarded by many authorities as by no means solved.

At the outset it may be pointed out that the problem is complicated owing to the great differences in character of different crude oils, and to the fact that in many cases petroleums are found accumulated in rocks which were certainly not their birthplace, but into which they have migrated at some subsequent period.

Theories as to the volcanic or inorganic origin of petroleum were advanced by Virlet d'Aoust and Rozet as far back as 1834, by Daubree in 1850, by Chantourcois in 1863. This view was also held by Humboldt. Its chief advocate was Berthelot, who in 1866 suggested that petroleum might be produced by the action of steam on metallic carbides. This theory was also advocated by Mendelejeff in 1877, who considered that as carbides have been found in meteorites they might also be expected to occur in the earth's interior. There are no less than six meteoric stones which contain, though in very minute quantity, carbon compounds of such a character that their presence in a terrestrial body would be regarded as an indirect result of animal or vegetable life ("Introduction to the Study of Meteorites." British Museum). The modern production of carbides by the electric furnace has added interest to this theory, but present-day opinion is on the whole decidedly against it. The absence of petroleum from the archaic formations also militates against this view.

The presence of nitrogen bases and of complex organic compounds which exhibit optical activity may be taken as conclusive evidence that at least those petroleums which contain such compounds are not of inorganic origin. Unless, therefore, further work or evidence in support of this view be forthcoming, the inorganic theory must, in the vast majority of cases at any rate, be considered untenable.

Theories as to the organic origin of petroleum fall into two groups: (1) animal origin, (2) vegetable origin, both of which have their ardent supporters.

Any theory worthy of consideration must fit in with facts, must agree with the evidence both chemical, geological, and experimental, and of the evidence, the geological probably carries most weight.

The theory of the animal origin of petroleums rests largely upon experimental work, often carried out under conditions of temperature which certainly could never have existed. In many cases, however, *e.g.* certain fields in California, Egypt, Borneo, and elsewhere, geological evidence is also in favour of an animal origin.

Warren and Storer, by the distillation of Menhaden oil under pressure, certainly made kerosene oils and actually marketed them. Engler (*Ber.*, vol. 21, p. 1816; vol. 22, p. 592) at a later date repeated these experiments and obtained an oil distillate of specific gravity 0·815. After removal of the unsaturated hydrocarbons from this product, he obtained from it, by fractional distillation pentane, hexane, octane, and nonane, together with a kerosene and some paraffin wax.

Sterry Hunt, Briart, Orton, and others considered that certain of the American crude oils found in limestones originated therein from animal remains. Jaccard, from a study of the Jura asphalts, arrived at the same view.

Objections to the animal theory origin have been raised by Cunningham Craig, who points out that no accumulations containing organic animal matter in any quantity are being laid down at the present day. He points out further that the animal contents of marine organisms are either devoured or decay away before accumulation is possible. While admitting that such accumulations of animal matter are not now forming, it is, nevertheless, possible and even probable that conditions of rapid accumulation have obtained in the past. In fact, there are many cases where the geological evidence certainly points to animal sources.

Although the chemical distillations which have yielded petroleum-like oils postulate high temperatures which are obviously inadmissible, as often proved, for example, by the close proximity of unaltered coal beds, it must be allowed little is as yet known as to the nature of the chemical changes which may take place at such high pressures as may easily have obtained at considerable depth in the earth's crust. The development of the study of high-pressure reactions will, undoubtedly, throw further light on this question. The possible action of bacteria is also a point which must be considered. In many cases, undoubtedly, there are chemical facts which cannot be reconciled with the theory of an animal origin. Animal remains are relatively rich in phosphorus. The association of phosphorus containing compounds with petroleum is very unusual.

Although the geological processes going on at the present day do not lend much support to the animal origin view, and although the production of petroleum-like compounds by distillation of animal matter really lends no support (as the distillation of vegetable remains also yields similar bodies), it can certainly not be asserted that in no instance is petroleum of animal origin.

The theory of vegetable origin on the contrary rests on much surer evidence. Vast accumulations of vegetable matter have been formed and are now in process of forming. Of the vegetable origin of coal there is no doubt. Shales, coals, and lignites yield on distillation under suitable conditions petroleum-like bodies. The postulation of the necessary high-temperature conditions necessary for such distillation is, however, inadmissible, and is perhaps unnecessary.

Whether vegetable remains have passed under certain conditions into coal, and under other conditions into petroleum, or whether coal is a transition stage between vegetable matter and petroleum, are questions as yet far from settled. Cunningham Craig claims that the remains of terrestrial vegetation which under other conditions would develop into coal will, under certain conditions, result in petroleum.

The nature of coal and its relation to petroleum are a subject which has received much attention of late. Fischer and Gluud (*Ber.*, 1919, p. 1053) claim to have established that certain light petroleum hydrocarbons do exist preformed in certain coals. Mabery (*J. Am. Chem. Soc.*, 1917, p. 2015), from a consideration of the properties of vacuum distillates from Deerfoot coal, is of the opinion that this coal is an intermediate stage of decomposition between vegetable remains and petroleum.

Hackford (*Trans. Am. Inst. of Min. and Met. Engineers*, Sept., 1920), who has done much work on the constituents of petroleum of high molecular weights, holds that petroleum oils such as occur in nature are clearly not derived from coal, but that petroleum may have been produced under certain conditions from vegetable material containing no cellulose.

In the present stage of our knowledge, therefore, no definite general explanation of the origin of petroleum can be given. In certain cases, however, definite theories, well supported by facts, can be advanced. For example, Hackford (*J.I.P.T.*, 1922, vol. 8) makes out a good case for the derivation of Mexican petroleum from seaweed. The outstanding features of Mexican petroleum are :—

(1) High sulphur content.
(2) Asphaltic nature.
(3) Minute nitrogen content.
(4) Low content of aromatics.
(5) Multiplicity of elements present in the ash of the oil.

There is ample sulphur in the alga *Macrocystis pyrifera*, which is nowadays so abundant in the Gulf of Mexico, to supply all that is necessary. Algæ contain little or no nitrogen. The practical absence of aromatics in the oil may be accounted for by the absence of cellulose in the algæ. The presence of numerous elements in the ash also bears out this view. Different oils have undoubtedly originated in different ways, but the majority of crude oils are probably of vegetable origin, the mechanism of formation being not yet understood.

Further investigation and research are much needed for the complete elucidation of these interesting and important problems, especially in view of the fact that the available world's supply of crude oil is decreasing. Eventually the future of the petroleum industry can only be assured if the processes of nature can be imitated or improved upon so that vegetation, the pre-eminent agent for utilizing solar energy, can be converted into petroleum, so convenient a source of power, and so valuable as the source of innumerable indispensable products.

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PART II.—NATURAL GAS

SECTION A.—OCCURRENCE, DISTRIBUTION, AND COMPOSITION

THE term "natural gas" as generally used does not apply to those effusions of nitrogen, carbon dioxide, sulphur dioxide, etc., which are so common in almost every country, and which are often associated with volcanic action; nor does it include gases often given off during the working of coal seams. It is applied in this work only to those effusions which are connected indirectly or directly with underground supplies of petroleum.

It is often found escaping at the surface, as in the historic case of the Caspian Sea area, where the "sacred fire" was for long an object of religious reverence.[1] It is the cause of the curious "mud volcanoes" of Burmah and elsewhere, which usually afford good evidence of the existence of petroleum in the vicinity. The output obtained from such natural springs is, however, comparatively insignificant. From wells, on the contrary, bored either with the express purpose of yielding gas or for liquid petroleum, the output often attains stupendous figures.

It is much to be regretted that in the past countless millions of cubic feet of this valuable fuel have been allowed to run to waste, owing to the indifference of oil producers and the lack of government regulations to ensure its conservation. The history of the industry is in fact an appalling record of incredible waste.

It is estimated that in the few years prior to 1912 not

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[1] In this area it has long been used by the Tartars for burning lime. Piles of limestone were made over gas vents or fissures, and the gas ignited. When burning was complete the fire was extinguished by smothering with sand.

less than 425,000,000,000 cubic feet of gas were allowed to escape in the Mid-continent fields alone. This amount is equivalent in heating value to about 9½ million tons of fuel oil. In 1913 a single well in the Cushing field yielded 1,500,000,000 cubic feet of gas before being shut in.

Beeby Thompson (*J.I.P.T.*, vol. 8, p. 31) estimates that, leaving out of consideration the fields which yield only gas, 883,000,000,000 cubic feet of gas at least have been dissipated into the atmosphere up to the end of 1920. This is equivalent to a loss of 19,000,000 tons of oil, *i.e.* an amount exceeding the total production of Rumania for ten years.

In many cases, however, the loss has been unavoidable owing to the unexpected finding of the gas at very high pressures and the consequent running wild of the well.

In the majority of cases gas and liquid petroleum are closely associated, often occurring in the same beds. In many cases, however, gas is found in very large quantities in beds which yield little or no oil.

The North American continent yields by far the greater proportion of the world's total output of natural gas, and it is, therefore, in this area that the natural gas industry finds its greatest development. The chief producing fields are those of West Virginia, Pennsylvania, and Ohio, which alone produce about 600,000,000,000 cubic feet per annum. California, Louisiana, Kansas, and Texas, produce also in considerable quantities. Considerable quantities of gas have also been produced in Ontario; also in Alberta, where the output reaches 75,000,000 cubic feet a day. A certain output of gas is obtained from most oil-fields, so that apart from the gas-fields of the North American continent, the occurrence and distribution of natural gas may be taken as coincident with that of crude oil (*vide* Part III.).

As will have been gathered from the introductory section, the gas, when confined in an anticlinal or dome structure, lies in the crest of the fold, the oil lying on the flanks beneath. Care must therefore be selected in choosing sites for wells. These should be drilled on the flank of the anticline or dome into the oil zone, avoiding that portion occupied by the gas. A well drilled at A (Fig. 3) will penetrate the gas zone and will not yield oil until all the gas has been withdrawn. A well drilled at B will, on the contrary, yield oil, and this well will flow, the oil being ejected by the pressure of the gas, which latter will not appear in the well until much of the oil has been removed.

The gas is, in this case, not only conserved but is utilized for the ejection of the oil, pumping being thus unnecessary.

The site of a well can, however, not be so carefully selected until the confines of the underlying oil pool have been well delineated, and this unfortunately cannot be done in the early history of a field, when the gas is present in greatest quantity.

In the Appalachian fields of the United States vast gas-fields exist in the Palæozoic rocks, the strata of which are very slightly inclined, so that the fields cover a large area. This gas is particularly "dry," containing small quantities only of condensable constituents.

The gas is often found under great pressure, 500 lbs. to the square inch being quite usual. Pressures as high as 1500 lbs. have actually been recorded. When the gas zone is entered accidentally, or sooner than anticipated and before adequate precautions have been taken, the heavy boring tools and cable are often shot out of the well with great violence.

Gas wells of 40,000,000 or 50,000,000 cubic feet per day have often been drilled, and in a few cases an initial output of over 100,000,000 cubic feet has been estimated.

Natural gas was utilized for illuminating purposes in the United States as far back as 1826. In the early days of the industry huge gas flares were used for illuminating the fields, and usually burned day and night. It was also largely used as fuel for the drilling boilers, but practically only a small percentage was so utilized, the greater quantity being allowed to run to waste. It is only during the last decade or two that the value of this gas has been realized, and efforts made to conserve the supplies.

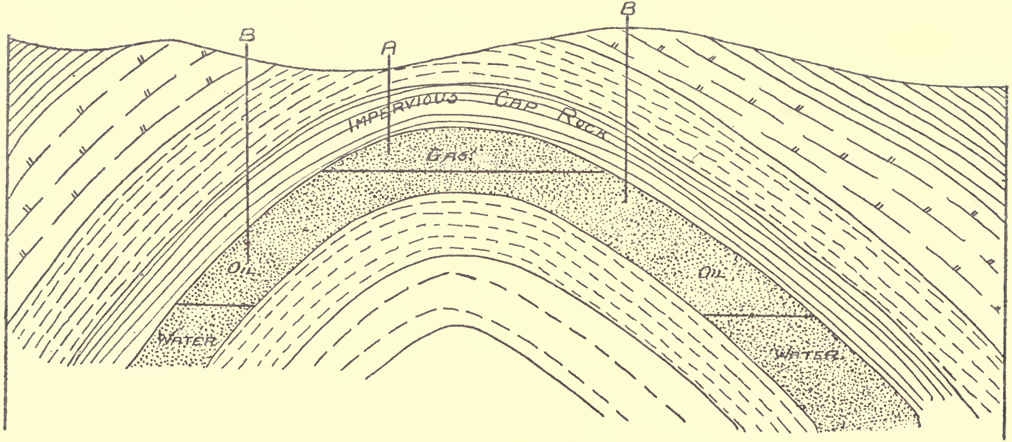

FIG. 3.—Ideal section across the axis of an anticlinal fold.

Quantities of gas are usually given off by flowing wells when yielding oil, the gas in such cases being often separated from the oil by means of special "separators" or "gas traps" and utilized. Natural gas obtained in this way is usually rich in condensable components and is known as "casing-head gas."

Natural gases consist for the most part of methane and other hydrocarbons of the paraffin series ethane, propane, butane, etc. Carbon dioxide and nitrogen are also usual constituents, but generally in small quantities. Oxygen, carbon monoxide, and hydrogen are rarely, if ever, present. There is, however, very great variation in composition.

The dry gas of the fields of Pennsylvania contain about 80 to 90 per cent. of methane, about 10 per cent. of ethane, and 2 or 3 per cent. of propane. Nitrogen is often present to the extent of a few per cents., but in certain cases, *e.g.* that of the Dexter well in Kansas, it constitutes the bulk of the gas. In certain Californian gases, the percentage of carbon dioxide rises to about 30. The wet or rich gases which escape from wells which are yielding oil naturally contain greater percentages of the heavier, more easily condensable hydrocarbons, such as butane, pentane, and hexane.

Several of the natural gases of Kansas, Texas, and Canada are remarkable in that they contain traces of helium and other gases of that family. As much as 1·8 per cent. of helium has been found in rare cases, and indeed this element has actually been prepared on a large scale from natural gas (McLennan, *J.C.S.*, vol. 118, p. 923).

The natural gas industry has been developed mainly in the United States and Canada, which, together, yield over 95 per cent. of the world's output. The extent of the gas-fields in the U.S. has been put at over 9000 square miles. Production figures for the early days of the industry are not available, but between 1906 and 1918 it is reckoned that the quantity produced and consumed amounted to 7⅓ trillion cubic feet. The total volume actually produced, much of which is unrecorded, must have been much larger. The actual production in 1918 was 720,981,141,000 cubic feet, that in 1917 (the highest recorded) was 795,110,376,000 cubic feet being produced by 39,370 wells. The production in 1919 showed a further slight decline. The bulk of the gas has come from Virginia, Pennsylvania, Oklahoma, Kansas, Ohio, California, and New York.

SECTION B.—APPLICATIONS

LESS than a score of years ago the natural gas industry may be said to have been non-existent. Its recent development is partly due to the introduction of legislative measures for minimizing waste, partly to the rapidly growing demand for motor spirits, and to the finding of new applications.

In many fields where gas is found under pressure, it is used instead of steam for driving the drilling and pumping engines, the exhaust gas being further utilized as a fuel for steam generation, and for the domestic needs of the camp. It is, moreover, often collected and pumped to adjoining towns and used for illuminating, heating, and power purposes. Many towns in America are well supplied with cheap power in this way, the gas being often retailed at prices as low as a few pence per 1000 cubic feet.

The heating values (gross) in B. Th. Units for one cubic foot of various gases at 0° C. and 760 mm. pressure are :—

Methane	Sp. gr. 0·553	1065
Ethane	,, 1·049	1861
Propane	,, 1·520	2654
Butane	,, 2·004	3447
Pentane	—	4250

1 cubic metre of average natural gas may be taken as equivalent to 1·5 Kgs. coal as regards heating value.

A very important product derived from natural gas is **carbon-black.** This is an amorphous form of carbon or soot produced by the incomplete combustion of natural gas. It is not to be confused with lamp-black, which is an inferior material made by the combustion of turpentine, resin, or such bodies. Carbon-black is much superior to lamp-black as a pigment—in fineness, miscibility with oil, and covering power. A cubic inch of carbon-black is estimated to have a surface of 1,905,000 square inches, the same volume of lamp-black having only 1,524,000.

It is manufactured by burning natural gas with a limited supply of air under such conditions that the carbon, which is produced in the inner part of the flame where the temperature is sufficiently high to decompose the gas, but where the oxygen supply is low, is quickly cooled by being deposited on a cooled surface.

Three types of plant, using the disc, plate, and cylinder processes are in common operation, the principle underlying each being the same (Roy. O. Neal, *Chem. and Met. Eng.*, 1920, p. 785).

In the disc or Blood process, the gas is burned and the flames allowed to impinge on a cast-iron rotating disc of 3 to 4 feet in diameter, the carbon-black being scraped off into a hopper as formed. In the plate or Cabot system, a large number of plates are arranged horizontally in a circle. The burners and scrapers revolve underneath the plates on a central axis. In the roller system devised also by Blood, the flames impinge on rotating rollers, from which the carbon-black is scraped off. This system produces a black of better quality, but the yield is smaller.

All these processes produce only about 0·8 to 1·4 lbs. of carbon-black per 1000 cubic feet of gas burnt. They appear very wasteful methods, but are apparently the only practical processes known which produce the carbon-black most sought after by the printing trade.

The quantity of carbon-black produced in the U.S.A. in 1920 amounted to 51,321,892 lbs. For the manufacture of this quantity 40,600,000,000 cubic feet of gas were consumed, the average yield per 1000 cubic feet of gas thus amounting to 1·26 lbs.

Thirty-nine plants in all were in operation. The producing States and their percentage output were West Virginia 52, Louisiana 36, Wyoming, Montana, and Kentucky together 11, and Pennsylvania 1.

Carbon-black is used primarily for the manufacture of printing ink. One pound of carbon-black will suffice to print 2250 copies of a sixteen-page newspaper. About 35 per cent. of the entire output is used for this purpose. It is also largely used in the rubber tyre industry. The addition of carbon-black renders the rubber more resilient. It increases the tensile strength of the rubber by about 25 per cent. and the elasticity by about 10 per cent.

About 10 per cent. of the total production is used for stove polishes, 1 per cent. for gramophone records, and large quantities for paper manufacture, Chinese and Indian inks, marking inks, boot polishes, tarpaulins, varnishes, etc. (Perrot and Thiessen, *J. Ind. and Eng. Chem.*, vol. 12, p. 325).

The great value of the condensable portions of natural gas for admixture into motor fuels has given rise to an important industry of recent years. In 1903 motor spirits were first collected from the condensates in natural gas pipes, and in 1905 the first plant designed for the specific purpose of recovery of these valuable volatile spirits from natural gas was erected. Since that date the development has been considerable. In 1914, in the United States alone 386 plants were in operation, treating about 17,000,000,000 cubic feet of gas and obtaining therefrom 42,650,000 gallons of light motor spirit. In 1920 the quantity had increased to 383,311,817 gallons, an amount which was extracted from 495,883,700,000 cubic feet of gas, an average of 0·77 gallon per 1000 cubic feet. Nearly 75 per cent. of this was extracted by the compression process. This amount represents nearly 8 per cent. of the total output of the United States of motor spirits for that year. The industry has been developed in other fields in other parts of the world, but as it is primarily an American industry, the American term "**Casing-head gasoline**" will, in future, be used to designate the product, this name having come into general use in the petroleum industry.

In addition to the natural gas obtained from gas wells, much casing-head gas also flows together with crude oil from oil wells, this gas being consequently richer in benzine (gasoline). Gases are usually designated "dry," "lean," or "wet" according to their gasoline content.

"Dry" gases are composed chiefly of methane and ethane and yield no condensable portions; "lean" gases contain also proportions of propane, butane, and pentane; and "wet" gases contain also proportions of the vapours of hexane, heptane, and perhaps some of the more volatile naphthene hydrocarbons, *e.g.* hexa-methylene.

Two methods of treatment for the extraction of casing-head gasoline are in general use, the compression and absorption methods, the former being usually applied to rich, the latter to lean gases.

The Compression Process.—The gas is pumped from the fields and after passing through a drip tank (1) to trap any condensed gasoline, enters the low-stage compressors (2).

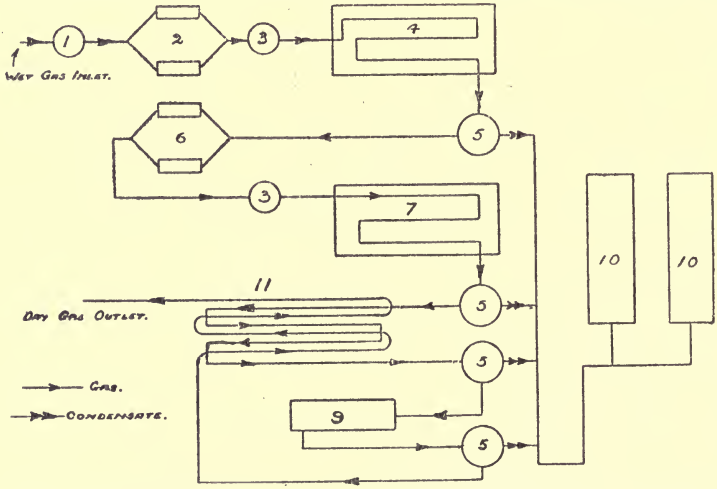

Fig. 4.—Diagram illustrating operation of compression gasoline plant.

After compression it passes through the cooling coils (4), and then goes on to the high-stage compressors (6). After further compression it passes through the cooling coils (7). The gasoline which separates out is drawn off from the separating tanks (3 and 5). The cooled compressed gas then goes on into the regenerative expansion coils (11) and expansion motor (9), the exhaust from which passes back through the regenerator expansion coils (11). Compressors of any well-known type are used, the gas being compressed up to 20 to 50 lbs. per square inch in the low-pressure stage. The gas, heated by compression, is then cooled, a certain amount of condensate being formed which is separated off, depending of course on the nature of the gas under treatment. The gas is then further compressed in the second set of compressors up to as much as 300 lbs. per square inch or more. The gas, now at a temperature of perhaps 250° C., owing to the compression, is again cooled. In the second set of coils, a further quantity of condensate separates out. The residual gas is then further cooled by expanding and doing work in an expansion motor, the cold exhaust from which further cools the gas on its way to the motor, so that a further condensate is obtained.

General practice shows that a gas of sp. gr. 0·9 (air=1) is about the leanest which can be successfully handled by a compression plant.

The gasoline obtained is too volatile (and too valuable) for general use, and is consequently used for blending with heavier grades of gasoline to make motor spirits. Mixtures containing a large quantity of such compressor gasoline, suffer much evaporation loss on standing, *e.g.* a mixture of 50 per cent. compressor gasoline of sp. gr. 0·630, and 50 per cent. gasoline of sp. gr. 0·739 on standing in an ordinary graduated litre cylinder for one hour lost 4 per cent. by evaporation.

The Absorption Process.—The first absorption plants were installed on the gas transmission lines for absorbing as much as possible of the condensable vapours in order to avoid the deterioration of the rubber jointings and the formation of condensed liquid in the line pipes. The installation of such drying absorption plants is commercially justifiable on these grounds alone.

Much natural gas contains too little gasoline for extraction by the compression system (¾ gallon gasoline per 1000 cubic feet is the practical minimum), but may be economically treated by an absorption plant, even if the gasoline content is as low as one pint per 1000 cubic feet.

The operation of an absorption plant is similar to that of the benzol washing plants, so largely used during the war, for the recovery of benzol from coal gas.

The natural gas is passed through a series of absorption towers where it meets a descending stream of non-volatile distilled oil, which dissolves out the condensable portions of the gas. The gasoline is then recovered from solution in the heavy oil by distillation, the gasoline-free heavy oil being used over again. The factors which control the design of the plant are pressure, temperature, gasoline content of the gas, time of contact with the absorbing medium together with the nature of the tower packings, and other such details which affect the efficiency. The higher the pressure, the greater the absorption, but too great an absorption means too great a loss by evaporation when the

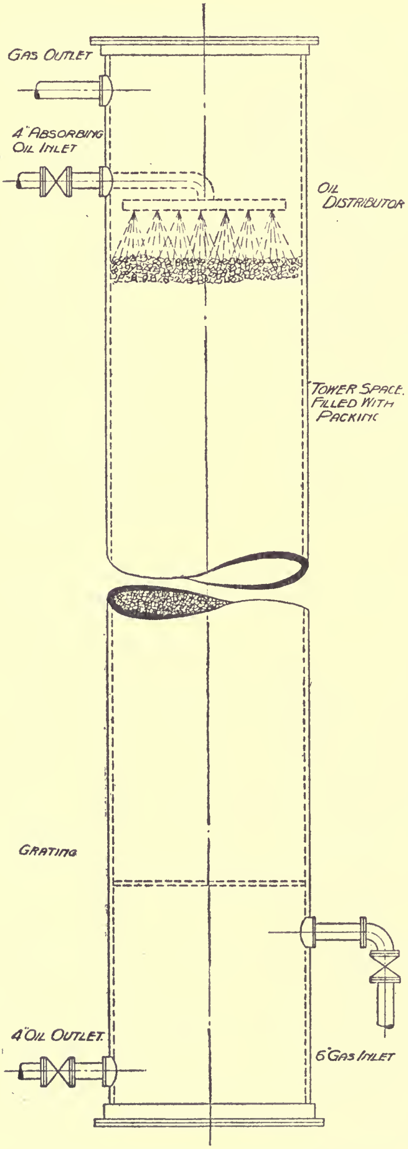

FIG. 5.—Absorption tower for treatment of natural gas.

gasoline is subsequently distilled and blended. The lower the temperature, the better the absorption. The intimacy of contact is affected by the nature of the tower packing, and the time of contact must be sufficiently long.

The absorbers in most general use are of the vertical tower type. Lean gases are treated at higher pressures than are rich gases, so the construction of the tower must be arranged for accordingly. They are usually constructed of diameters up to 12 feet and of height 20 to 60 feet or more (Fig. 5).

A grating, on which the filling rests, is placed a few feet above the bottom, the gas being introduced by a pipe entering below the grating. The absorbing oil is introduced a few feet below the top of the tower, being distributed over the surface of the packing by a perforated pipe. The extracted gas outlet and solution outlet are placed at the top and bottom of the tower respectively. Several towers are usually arranged in series and connected by piping so that any one can be by-passed for repairs without shutting down the plant. The towers are designed so that the velocity of the gas is from 30 to 75 feet per minute in the unpacked portion of the tower.

The towers are filled with wood gratings, cobbles or other form of packing. The modern forms of packing such as Raschig rings or those of the types used in acid absorption towers would certainly be more efficient, as the surface presented per cubic foot of volume is so much greater.

The oil used for absorbing is generally a heavy distillate, such as gas oil, heavy kerosene or light lubricating oil fractions. The initial boiling point of the absorbing oil should be much higher than the final boiling point of the absorbed gasoline, in order to render the subsequent separation by distillation as easy and effective as possible.

The absorbing oil should also be of low viscosity and of a type which does not readily emulsify. It should be cooled as far as possible before entering the tower. For this purpose cooling coils immersed in water are usually used. About 3 or 4 square feet of cooling surface per gallon of oil per minute is usually allowed, but this of course depends on the temperature of the incoming oil.

When the gasoline content in the oil rises to about 4 per cent. the absorbing power begins to fall off. The amount of oil circulated varies enormously in practice according to conditions and the character of the gas, from 3 or 4 gallons to as much as 70 per 1000 feet of gas, 7 to 10 being the usual figure.

After leaving the towers (1) the oil flows into the "weathering tanks," (2) where it is allowed to stand at a reduced pressure in order to give up some of the gas which it dissolved in the tower. This gas could not be recovered as gasoline by distillation and is usually not sufficiently rich for retreating. It is passed on into the extracted gas mains with the rest of the treated gas.

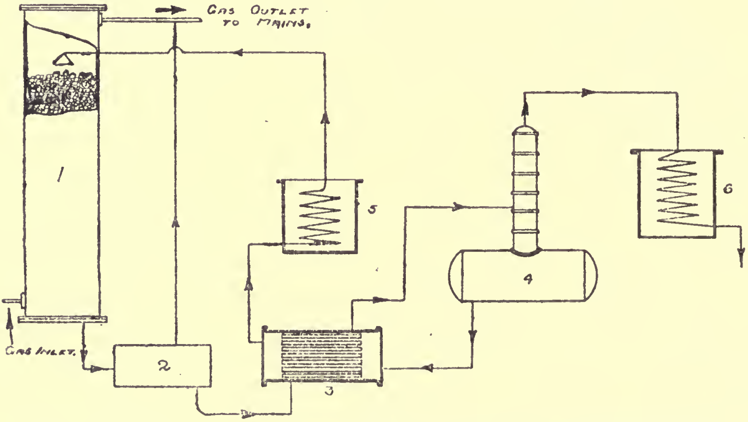

Fig. 6.—Diagram illustrating operation of absorption gasoline plant.

From the weathering tank the oil is passed through the heat exchangers (3), to the still (4), where the dissolved gasoline is distilled off and condensed, the gasoline-free oil returning via the heat exchangers and the cooling coil (5), to the top of the absorption tower (1). The same absorbing oil is thus used over and over again, a small amount of make-up oil being added from time to time to balance unavoidable losses.

The heat exchangers used are of the ordinary types, for a description of which reference may be made to Part VII., Section A.

Any of the ordinary types of still may be used, as the operation of separating the volatile gasoline from the heavy absorbing oil is very simple. The ordinary form of steam redistillation still is often used, the oil from the absorber being admitted into the column. A simple vertical still fitted with steam-heated baffle plates and supplied with a live steam coil at the bottom would also serve quite well. For details as to still construction reference may be made to the section on "Distillation of Crude Oil" (see Pt. VII., Sec. A). Fire-heated stills are however rarely used.

The gasoline produced from absorption plants has a higher specific gravity and a lower vapour pressure than has compression gasoline owing to its lower dissolved gas content. It naturally also possesses none of the heavy fractions found in gasoline distilled from crude. About 80 per cent. of the product may be expected to boil over below 100° C. in an Engler flask, and the final boiling point will be under 150° C.

Absorption plants are, on the whole, more efficient and much cheaper in operation than those of the compression type. An absorption plant can indeed be operated successfully on the exhaust gases from a compression plant, and several such plants have been installed. The gasoline from absorption plants, moreover, loses relatively less by evaporation on standing than does compressor gasoline. A modification of the absorption plant which is sometimes used, consists in replacing the absorbing oil by heavy benzine, so that this benzine becomes lighter and more volatile and is used for blending, the distillation process being thus avoided. This type of absorbing plant is often used in connection with the recovery of vapours given off during the distillation of crude oil or distillates, the distilling loss being in this way considerably reduced.

In addition to the two processes above described there is a third which has so far not found extensive application, but which gives good promise of future development. It is based on the absorptive power of charcoal (Anderson and Hinckley, *J. Ind. and Eng. Chem.*, vol. 12, 1920, p. 735; Oberfell, Sprinkle, and Meserve, *ibid.* vol. 11, 1919, p. 197; Burrell and Oberfell, *Oil and Gas Journal*, July, 1920, p. 84). Three vertical absorbers 20 to 35 feet high and 2 to 3 feet diameter are used. They are packed with a special porous, granulated charcoal. The gas is passed through the first absorber until the charcoal is saturated, and is then passed into the second, the gasoline being distilled out of the first by means of steam. Each unit acts, therefore, both as absorber and still. The charcoal lasts indefinitely and indeed its action improves with use. A portable apparatus for the examination of natural gases in the field, based on this action of charcoal, has been designed.

In 1907 Cady and McFarland (*J. Am. Chem. Soc.*, vol. 29, p. 1523) had already discovered the presence of **helium** in Kansas natural gas. In 1916, a survey of most of the available natural gases in the British Empire was made, and it was found that certain gases from Ontario and Alberta, Canada, contained this gas in quantities up to 0·36 per cent. Certain gases in Texas, however, contain nearly 2 per cent. The superiority of helium over hydrogen as a gas for filling airship envelopes, and the urgent need for supplies at any cost, gave rise to a wonderful helium industry, which at the date of signing of the armistice in 1918 was a technical and almost a commercial success. The method used for the extraction of the helium was that of producing refrigeration sufficient to liquefy all the gases except the helium, this method being applied in the Norton plant, similar in general to the Claude oxygen-making plant (McLennan, *J.C.S.*, vol. 107, p. 20, p. 923).

Helium of 97 per cent. purity was obtained at a cost of as low as 2½*d.* per cubic foot, a notable achievement indeed, considering that but a few years ago helium was merely a chemical curiosity.

It has been estimated that the United States alone could produce nearly a million cubic feet of helium daily.

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PART III.—CRUDE PETROLEUM

SECTION A.—OCCURRENCE, DISTRIBUTION, AND CHARACTER

BITUMEN in its liquid form has been found in almost every country of the globe, in many cases, however, only in small quantities incapable of commercial exploitation. As about 65 per cent. of the earth's land surface is made up of sedimentary rocks, and as enormous areas have not yet been examined, the possibilities of future development are great, even when taking into consideration the limitations arising from the need of the existence of tectonic structures suitable for petroleum reservoirs.

The recent discovery of oil in Northern Canada (*Oil News*, 1920, p. 1051) undoubtedly foreshadows many such developments in the near future.

Although so widely distributed, the bulk of the world's supplies up to the present have been drawn from a relatively small number of important areas, many of which have already reached their peak production. Certain fields of Russia and the United States have produced steadily for half a century; fields discovered at later dates, *e.g.* those of Mexico and Persia, are now important producers; others, *e.g.* those of South America, are as yet in their infancy. Crude oils from different fields show great variation in character, as is only to be expected from the fact that they are drawn from strata of very varying geological ages, and have been formed in varying ways, from varying materials.

In many cases, therefore, as might be expected, a field yields different types of oils from strata at different depths, *e.g.* those of Alsace and East Borneo, though, broadly speaking, the crudes of any one field usually belong to one type, in many cases quite characteristic of the particular field.

The main producing fields with the chief characters of their crudes are detailed below.

Although crude oils vary enormously in character from the remarkable white oils (which are naturally filtered oils of comparatively rare occurrence and of no economic importance), and the very light oils rich in volatile fractions, such as those of Sumatra, to the heavy viscous oils found in parts of Mexico, they may be divided roughly into three main groups, (*a*) the paraffin-base oils, (*b*) intermediate- or mixed-base oils, and (*c*) naphthene- or asphalt-base oils. These last two groups are usually included in the term " asphalt-base oils."

Paraffin-base crudes are those containing relatively high percentages of aliphatic hydrocarbons, naphthene-base oils those containing relatively high percentages of cyclic hydrocarbons.

Distillates of a given boiling range from paraffin-base oils have a lower specific gravity than do those of similar boiling range from naphthene-base oils. Also paraffin-base distillates are of lower viscosity than naphthene-base distillates of the same boiling-point range, or, expressed in another way, naphthene-base oils have lower flash-points than paraffin-base oils of the same viscosity (Dean, *Nat. Pet. News*, 1921, p. 24A).

The term "paraffin-base crude" is often used to mean, containing relatively large percentages of paraffin wax. Numerous inconsistencies will be found to occur, *e.g.* the distillates of certain types of Borneo crude, which are certainly rich in paraffin wax, are of very high specific gravity owing to the presence of relatively large quantities of aromatic hydrocarbons.

The **Appalachian** field, once the most important, is the oldest field in the United States. It includes all the fields east of Central Ohio, *i.e.* those of Pennsylvania, New York, Kentucky, South-east Ohio, North Alabama, Tennessee, and West Virginia. The crudes from this area are of the paraffin-base type, and are of Devonian and Carboniferous age. They contain as a rule 2 to 3 per cent. of paraffin wax. They are of light specific gravity, usually varying from 0·790 to 0·825. They consist, for the most part, of saturated hydrocarbons of the paraffin series. They are relatively free from sulphur, rich in benzine, and yield good lubricating and cylinder oils.

The ratio carbon/hydrogen is the lowest, viz. 6·2.

The crudes of the **Lima-Indiana** field, comprising Indiana and North-west Ohio, are of similar nature, but are contaminated with sulphur compounds, which make the refining of these oils more difficult. They are of somewhat higher specific gravity as they contain hydrocarbons other than paraffins. They are of Ordovician, Silurian, and Carboniferous age.

Those of the **Illinois** field are of naphthene-base, but also contain some paraffin wax. They contain small percentages of sulphur compounds. They are mostly of Carboniferous age.

The fields of Oklahoma, Kansas, Louisiana, and North Texas are usually grouped as the **Mid-Continent** field. Several types of crude are here found, both of asphalt- and paraffin-base, with varying per cents. of sulphur, and varying benzine content. They resemble on the whole the crudes of Texas and California rather than those of the Appalachian type. They occur in Tertiary, Cretaceous, and Carboniferous strata.

The **Gulf** field includes those of South Texas and South Louisiana. These fields yield oils of several types, both light oils of sp. gr. 0·820 to 0·850, somewhat similar to those of Ohio, of a mixed-base type, and heavy oils of sp. gr. 0·920 to 0·970 containing no paraffin wax. They are mostly of Cretaceous and Tertiary age. These oils contain hydrocarbons of the series C_nH_{2n-2} and C_nH_{2n-4}, terpenes and naphthenes.

The carbon/hydrogen ratio is about 6·9, and sulphur is present in amounts up to 2 per cent.

The **Rocky Mountain** area includes the fields of Colorado, Wyoming, Utah, New Mexico, and Montana. These crudes are of naphthene-base type and of Carboniferous and Cretaceous age.

California is now the chief producing state. The oils from its many fields differ very considerably. Those from the earlier known fields were of high specific gravity and of high asphaltic content, though latterly lighter oils have been found. The sulphur content varies, but is usually below 1·5 per cent. California crudes are mostly of Miocene age.

The production of the **United States** amounts to about 65 per cent. of the world's output.

The fields of **Mexico** may be divided into two main areas:—The Gulf zone comprising the Ebano, Panuco, Topila, Los Naranjos, Potrero, and Alamo fields; the southern zone comprising the Tehuantepec and Tabasco districts. Production, however, practically all comes from the Gulf zone.

Two types of crude are found: (*a*) a light crude of a mixed-base type, containing paraffin wax and asphalt, and a heavy asphaltic type. These crudes resemble each other in that their volatile constituents are composed mostly of hydrocarbons of the paraffin series. They are very rich in sulphur, containing up to about 5 per cent.

Light Mexican crude (sp. gr. 0·925) yields about 15 per cent. of benzine, 7 per cent. of kerosene, gas oil and lubricating oils of good quality, and asphalt or coke.

(*b*) A heavy crude of high specific gravity (about 0·980), which yields only a small percentage of benzine. This yields excellent asphalts of various grades and heavy liquid fuels.

The oils of **Venezuela** are also of high specific gravity and of the asphalt-base type; they yield only small quantities of benzine and kerosene, and are used mainly for liquid fuel. They contain about 2 per cent. of sulphur.

Trinidad produces a considerable quantity of crude petroleum apart from that of asphalt from the famous lake. The crude oils are of the naphthene-base type, those from the deeper sands being of lower specific gravity than those from the shallower strata. Mixed-base oils have also been found.

The production of crude petroleum has never reached a high figure in **Canada**, though great efforts have been made to encourage the industry. Several small fields in Ontario, *e.g.* those of Oil Springs and Petrolia, have already passed their zenith. The oils are similar to those of Ohio, containing about 1 per cent. of sulphur. They consist for the most part of saturated paraffins, but contain hydrocarbons relatively poorer in hydrogen in the higher fractions.

Very large deposits of asphaltic sands (usually wrongly termed tar-sands) are found in Northern Alberta, outcropping on the banks of the Athabasca and other rivers (S. C. Ells, "Bituminous Sands of Northern Alberta," Dept. of Mines, Canada). These sands contain from 7 to 20 per cent. of soft asphalt (Krieble and Seyer, *J. Am. Chem. Soc.*, 1921, p. 1337).

Peru produces an oil of naphthene-base type, in considerable quantities.

The **Argentine Republic** is developing a crude oil production from four distinct fields. The oils are similar in character to those of Peru.

Brazil has potential areas which have not yet been developed, and **Bolivia** and **Colombia** have so far received little attention.

The country which has played the second most important part in the development of the petroleum industry is **Russia.**

The two chief oil-producing areas are the Caucasus and the Ural Caspian. The oils are mostly of Miocene age.

The production of the Russian fields from 1910 to 1916 was at the rate of 10,000,000 tons per annum. The present disturbed political condition of the country (1921) has caused a reduction in output to about one-third of this figure.

The oils from the **Balachany, Saboontje, Romany, Surachany,** and **Bibi-Eibat** fields contain little or no paraffin wax, and are composed largely of hydrocarbons of the naphthene type. They yield good lubricating oils of low cold test, and good non-viscous liquid fuels.

The **Grosny** fields produce crudes of two types, the one almost free from paraffin, the other relatively rich (about 5 per cent.). These crudes are also rich in naphthenes and contain aromatic hydrocarbons in small quantities.

The **Maikop** fields yield crudes rather richer in volatile constituents than those of the other Russian fields. The content of paraffin wax is low (about 0·5 per cent.), and aromatic hydrocarbons are present.

Rumania possesses several important fields which yield several types of oil. These crudes generally consist of hydrocarbons of the paraffin, naphthene, and aromatic series, with small proportions of terpenes. The presence of aromatic hydrocarbons lowers the burning quality of the kerosenes.

The crudes of Bustenari, Campina, Baicoi, and Tzintea contain paraffin wax in quantities up to 7 per cent.

The crude oils of **Galicia** are intermediate in character between those of East North America and of the Russian Caucasus. Those of East Galicia contain paraffin wax up to 12 per cent., those of the West are nearly paraffin-free. They are usually practically free from sulphur. They are of Cretaceous, Eocene and Oligocene age.

There are fields of relatively minor importance in **Alsace** (Pechelbronn). Oil has been found also in Italy, France, Spain, and Greece. It is of particular interest to note that the test well recently put down in **England** (Derbyshire) has produced several hundred tons of a remarkable oil.

The Derbyshire (Hardstoft) crude is of low sp. gr. 0·823, greenish brown in colour with marked fluorescence. It yields 17 per cent. of motor spirits and 30 to 40 per cent. of excellent kerosene (0·785 sp. gr.). The residual oil after removal of benzine, kerosene, and gas oil is a cylinder oil of remarkable quality, containing no asphaltic matter, similar in properties to a Pennsylvanian filtered cylinder oil. The crude contains also about 3½ per cent. of paraffin wax.

In Asia important oil-fields have been exploited in **Persia, Burmah,** and the **Dutch East Indies**. Less important fields exist in **Japan** and **Assam**. Large fields probably exist in Mesopotamia, and various parts of Siberia, but these have not yet been exploited.

The crude oils of **Persia** consist of hydrocarbons of the paraffin series, with smaller quantities of naphthenes. Aromatic hydrocarbons are also present. They contain also sulphur compounds. They are rich in volatile fractions, yielding 20 per cent. or more of motor spirits.

The **Burmah** crude oils are rich in paraffin wax. They consist of hydrocarbons of the paraffin series, with members of the naphthene series and aromatics also present in considerable proportions.

The potentialities of **Mesopotamia** as an oil-producing country are undoubtedly great, but have not yet been adequately examined. Oil is produced in trifling quantities near Mosul and at Mandali on the Persian frontiers. The oil is similar to the crudes of Mexico in character, and is rich in sulphur compounds.

In the Dutch East Indies many important fields are found. North and South **Sumatra** produce light oils, very rich in benzine and kerosene fractions. Those of North Sumatra are of paraffin-base, those of the South of asphaltic-base. Both types contain appreciable percentages of aromatics and considerable percentages of naphthene hydrocarbons. Oils of very varying character are found in **Java.** The fields of **East Borneo** (Koetei) produce three types of crude, heavy asphalt, light asphalt, and paraffin wax base oils. The crudes of the Koetei field are remarkably rich in aromatic hydrocarbons, as much as 40 per cent. being found in the volatile fractions of the crude. Those of the Tarakan field are paraffin-free, as are also those of the **Sarawak** fields. These latter are very rich in hydrocarbons of the naphthene series.

Japan possesses several small fields which yield oils of varying character.

Africa has up to the present only one producing field, that of Egypt on the coast of the Red Sea. Preliminary work is, however, being carried on in Algeria.

The **Egyptian** fields yield heavy oils of mixed-base type. They contain only a small percentage of benzine, and after topping this off the residue is an oil of high viscosity.

The presence of paraffin wax gives the residue a high setting point. Sulphur is contained in the crude oil to the extent of 2 or 3 per cent.

In **Australasia** no oil-fields are as yet developed. Oil has, however, been found in Taranaki, New Zealand.

In the island of **Papua** exploitation work is going on.

The foregoing is merely a very condensed summary of the most important fields in active exploitation. Space does not permit of reference to the numerous localities where crude oil in small quantities has been obtained.

It will be seen from the foregoing that crude oils from different sources exhibit a great diversity of character, both as regards their physical constants and chemical constitution. No scientific system of classification has as yet been evolved, and this will not be possible until a great deal more is known about the chemical constitution of their components.

The colour of crude oil ranges from practically colourless in the case of the so-called white oils, which are naturally filtered oils of rare occurrence, through shades of brown and greenish brown or black of varying transparency, to the deep black of asphaltic heavy oils such as those of Mexico.

The specific gravity varies from as low as 0·760 in the case of some of the very volatile oils of Rumania and Pennsylvania, to nearly 1·000 in the case of some heavy Mexican oils.

The viscosity varies from that of oils as limpid as ordinary kerosene to that of semi-solid asphalts.

The chemical properties show similar variation.

The carbon percentage ranges from 80 to 87, the hydrogen from 9·6 to 14·5. The ratio carbon/hydrogen from 5·6 in the case of the volatile oils of high paraffin content to 8·0 or more in the case of heavy asphaltic oils.

The yield of commercial products also varies enormously. Light oils containing 50 per cent. or more of benzine are known, and heavy oils containing no benzine or kerosene fractions whatever. Great variation is often shown by the crude oils from a particular field, so that without going into very great detail no general summary, other than one very rough, as given above, is possible.

The world's output of crude oil for 1920, as contributed by various countries, was as follows :—

United States	443,402,000	brls.,	*i.e.*	64·4	per cent.
Mexico	159,800,000	,,	,,	23·2	,,
Russia	30,000,000	,,	,,	4·36	,,
Dutch East Indies	16,000,000	,,			
Burmah	8,500,000	,,			
Rumania	7,406,318	,,			
Persia	6,604,734	,,			
Galicia	6,000,000	,,			
Peru	2,790,000	,,			
Japan (incl. Formosa)	2,213,083	,,			
Trinidad	1,628,637	,,			
Argentine	1,366,926	,,			
Egypt	1,089,213	,,			
France	700,000	,,			
Venezuela	500,000	,,			
Canada	220,000	,,			
Germany	215,340	,,			
Italy	38,000	,,			
	688,474,251	,,			

The United States, Mexico, and Russia thus at present produce over 90 per cent. of the world's output.

The estimated production for 1922 is 760,000,000 barrels.

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SECTION B.—DRILLING AND MINING OPERATIONS

SEVERAL methods of drilling are employed in the petroleum industry, the choice of the particular method in any one case depending on various factors, such as the depth of the well (500 feet in Ontario, 4000 or more in Galicia or California), the nature of the strata to be penetrated, and the amount of water present or available.

The methods employed may be classified into three groups—

- (*a*) Abrasion or core drill methods.
- (*b*) Percussion methods.
- (*c*) Hydraulic rotary methods.

(*a*) **Core drill methods,** being slow and expensive, are seldom used except for prospecting or test holes. In hard formations a complete core of the material drilled through can be obtained, and this may afford valuable geological data, such as the dip of the strata, and fossils intact and unbroken.

The tool used is a circular shoe or bit attached to the end of a hollow tube which is rotated. The lower end of this shoe may be either (1) set with diamonds, (2) cut into teeth somewhat like a saw (calyx), or (3) plain, revolving on a number of chilled shot, placed in the hole.

The diamond drill was first used in 1863. The calyx method was developed in 1873, and the chilled shot method later. By these methods cores up to 15 inches diameter may be obtained. When using such drills a stream of water is pumped down the hole to remove the abraded material.

(*b*) **Percussion methods** are, however, most generally used.

Percussion methods may be classified into—

(1) Cable tool systems.
(2) Pole tool systems.

Various sub-divisions of these systems exist, differing from each other in details only. For example, in the Canadian system ash poles are used, in the Galician light rods of steel.

For any system of drilling a derrick is required, but those used in the various systems differ considerably in detail, being, however, similar in fundamental points. Space will not permit of a detailed description of the various types. For this, the reader must be referred to any of the standard works on petroleum mining, such as that of Beeby Thompson.

The type of derrick used depends on the locality, on the nature of the strata and the depth to which the well is to be bored. Those used in the Ontario fields, where the wells are only a few hundred feet in depth, often consist merely of three poles fastened together at the top so as to make a tripod.

For such shallow wells a portable drilling machine is often employed. Derricks are often constructed of timber cut locally, but where timber is scarce steel is often used.

The standard derrick which is largely employed is built up of four legs braced together (Fig. 7). At the top is placed the "crown block" (1), which carries the crown pulley, over which the drilling cable passes. At the side of the derrick far from the engine stand the "bull wheels" (2). These consist of a drum on which the drilling cable is wound, attached to a wheel at either side. The wheel on one side acts as a driving wheel, being grooved to receive the driving belt, that on the other side is fitted with a steel band brake.

At the opposite side of the derrick is set the "samson post" (3), which carries the "walking beam" (4). One end of the walking beam is connected by a rod called the "pitman" (5) to the crank of the "jack" or "band wheel" (6). This band wheel is driven by the engine and transmits power to the bull wheels by means of a belt or "bull rope." The other end of the walking beam supports the drilling cable.

Just behind the band wheel the "sand reel" (7) is placed. This is carried on a movable axis so that it can be driven from the band wheel by a friction pulley. A light cable passes from the sand reel over a light pulley at the top of the derrick, and is used for raising and lowering a sand pump for cleaning out the hole during drilling operations.

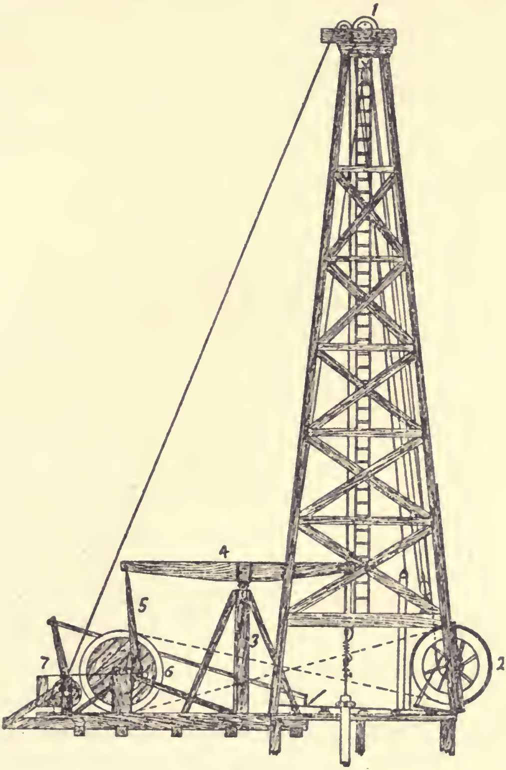

Fig. 7.—A drilling rig.

Derricks used for deep-well drilling are often 140 feet high, the great height allowing several lengths of casing to be hauled up without disconnecting.

The drilling engine is controlled by a " telegraph cord " and reversing lever extending into the derrick. Steam is supplied from a vertical boiler usually of about 20 to 40 h.p. placed some little distance away.

The complete set of drilling tools is usually termed a " string." It consists of the following : " rope socket," " sinker bar," " jars," " auger stem," and " bit."

The rope socket is a device for attaching the drilling cable to the tools ; the sinker bar is a long heavy steel bar, which merely functions as a weight. It is often omitted, but is sometimes placed below the jars. The jars are practically a pair of interlocking links. They have a play or lost motion of about 2 feet.

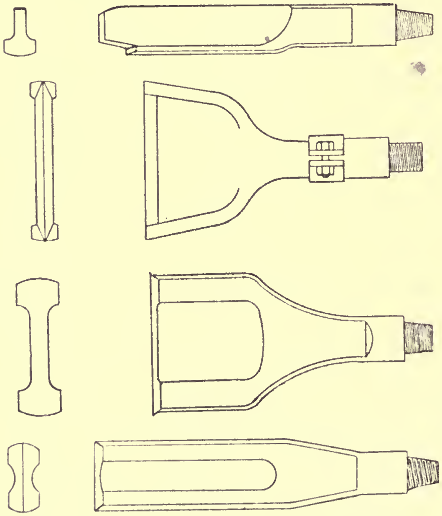

Fig. 8.—Types of drilling bits.

When the links of the jars engage on the upstroke a sudden jerk is given to the bit which loosens it, should it tend to stick. When drilling, the cable should be adjusted so that the upper link of the jars does not descend far enough to strike the lower link. This can easily be adjusted by an experienced driller by feeling the vibration transmitted through the drilling cable.

The auger stem is a long cylindrical piece of steel. It adds weight to the bit and helps to keep the hole straight.

Many types of bit are used according to the nature of the rock through which the hole must be drilled. The usual type is chisel shaped, the diameter of the cutting edge being larger than that of the stem (Fig. 8).

Drilling tools are usually fitted with a conical screw which fits into a corresponding socket on the lower end of the auger stem. The jars, sinker bar, and drilling poles (if used) are all so fitted. They are screwed together by means of a very powerful wrench or jack operated on the derrick floor.

The first stage in the actual drilling of a well is the insertion of the "conductor." This is usually an ordinary steel drive-pipe, 10 to 30 feet long. This must be very carefully fixed in a vertical position as it serves to guide the first lengths of casing fixed into the well.

Owing to the length of a complete string of tools, drilling cannot be started in the normal manner used when the hole is deeper. The method termed "spudding" is therefore adopted. A bit and auger stem are connected to the cable and lowered into the hole till they touch bottom, and the cable is fixed. A "spudding shoe" is then fixed on to the cable near the bull wheel and connected by a "jerking" rope to the crank of the band wheel.

As the crank revolves, the bull wheels being fixed, the cable is drawn forward and then released, an up-and-down motion thus being transmitted to the tools (Fig. 9).

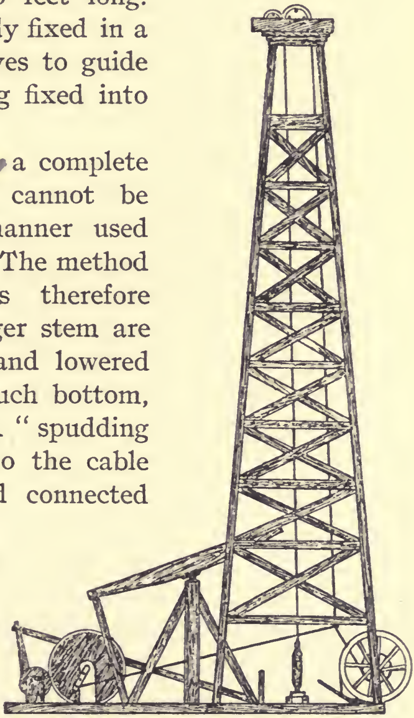

FIG. 9.—Arrangement for spudding.

As the hole is bored detritus rapidly accumulates and must be removed from time to time. This is effected by raising the tools from the well and lowering the "sand pump" or "baler." This consists merely of a length of tubing with a valve at the bottom opening inwards, which is operated by a projecting stem. As this stem strikes the bottom of the hole the valve opens allowing the muddy debris to enter. As soon as the sand pump is raised from off the bottom of the well the valve naturally closes again, retaining the contents, which are discharged into a drain at the top of the well by means of lowering the sand pump on to the ground, the valve being thereby opened. The hole is usually drilled by spudding in this way to a depth of about 150 feet or so. The string of tools is then attached to the "walking beam" by means of the "temper screw," an arrangement whereby the cable can be let out a few inches at a time as drilling proceeds.

Drilling is then carried on by means of the walking beam, a manilla cable being often used. For great depths, however, this is usually replaced by a steel cable.

In the case of hard strata the walls of the well require no protection, but when the strata are soft or yielding the well must be lined with "casing" in order to prevent the caving in of the well. Lengths of casing or drive-pipe are lowered or forced down into the well following the drill, the lengths of pipe being screwed together. As an indefinite length cannot be sunk owing to friction it is usual to start the well with a tool of large diameter, and to insert large diameter drive-pipe or casing, driving this to as great a depth as the friction will allow.

The initial diameter of the well depends on the depth to which it is to be drilled and on the nature of the strata.

Casing up to diameters of 14 inches or even more is in general use, but in Russia pipes of larger diameter, constructed of plates riveted together, are often used. Casings of several different types are used dependent on local conditions.

The lower end of the string of casing is usually armed with a "casing shoe," a ring with a sharp edge. The casing can be "set" by driving this into any suitable stratum when the casing cannot well be driven to a greater depth.

To enable the casing to sink in the well "under-reaming" is often necessary. This is carried out by a special under-reamer, which is a tool with an expansible bit, so that the cutting edges of the bit can be squeezed together to allow of its passage through the casing. When it reaches a point below the casing the cutting edges are forced apart by means of powerful springs, so that a hole of larger diameter than the casing can be bored.

Casing performs a further and very important function in the shutting off of water.

Water-bearing levels are often encountered in boring a well. If these are not adequately sealed up or shut off, water will descend, perhaps even behind the casing, to lower levels and may enter the oil-producing layer, thus spoiling not only that particular well but probably others in the same stratum. The adequate shutting off of water is thus of the greatest importance. In many countries this is recognized, and regulations are in force to ensure that this is properly carried out.

The process most generally used is that of "cementing." The lower edge of the outside string of casing is set in position, usually in an impervious layer. Cement is then forced down to this point, between the outer and inner casing; or the inner casing may be cut off just above this point and the space between the two filled by cement, the well being plugged at this point temporarily to allow of this being done. A description of the methods of shutting off of water from oil wells is outside the scope of this work. Detailed descriptions may be found in such works as Beeby Thompson's "Oil Fields of Russia" and in the various bulletins published by the U.S.A. Bureau of Mines on this subject.

When a string of casing has been set, drilling is continued with a bit of smaller diameter, this being followed up by a string of casing of smaller diameter, which of course must extend to the top of the well. This second string of casing is forced down as far as possible and eventually set, the drilling being then continued with another bit of still smaller diameter.

A finished well may thus have a diameter of 16 inches or more at the top and 4 inches at the bottom, and may have several strings of casing extending to successively greater depths, arranged one inside the other in telescope fashion (Fig. 10).

It is not, however, necessary that each string of casing should extend to the surface after the well has been completed and found to be successful. The upper or free portions of the inner strings may be cut off by a special tool lowered into the well, and removed, the points at which one string of casing is set and the next smaller size starts being well sealed up by cementing.

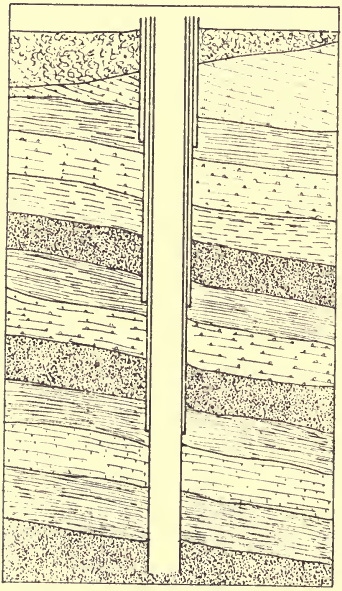
Fig. 10.—Strings of casing in a well.

In drilling wells many difficulties are usually encountered, and many ingenious devices are adopted for overcoming these difficulties.

Boulders are sometimes encountered in a clay, and if large may easily be mistaken for a bed of hard rock. These are usually broken to pieces and removed sometimes by the aid of explosives. When drilling through highly inclined strata there is often a tendency for the drill to deflect to one side especially when a hard stratum is encountered, tending to follow the dip of the strata and so causing the hole to diverge from the vertical. This can be avoided by slow and careful drilling with a long auger stem.

Dry sands also cause trouble, as they absorb water, so that very large quantities would need to be pumped into the hole. If drilling were attempted without water the bits would overheat and the sand would impede the action of the drill. In such a case mud is pumped into the hole. This fills up the pores of the sand by a puddling action and allows drilling to proceed.

"Spalls" of rock or loose stones may fall from the sides on top of the bit and jam it so that it cannot be moved. These may then require drilling out by a smaller bit, to render the large bit free again.

Soft muds and clays are difficult to deal with as they fill up the hole as soon as it is formed. In such cases drilling must be quickly carried out and the casing must closely follow the bit. Cavities are sometimes found, particularly in limestone strata.

Quicksand is sometimes encountered, and if the hydrostatic pressure is great this may quickly flow into the hole so as to engulf the tools, making their withdrawal very difficult. A quicksand can, however, usually be driven through by keeping a good head of water in the well, so as to overcome the hydrostatic head of the sand. In some cases cement may be introduced into the well so as to percolate into the sand and form a solid block which may be subsequently drilled through. An ingenious method of drilling through quicksand was devised by Poelsch in 1883. He drove pipes into the quicksand and circulated cold brine through them, thus freezing the sand into a solid mass through which boring could be conducted in the usual way. The need for such methods, however, very rarely arises.

A variation of the percussion system of drilling as described above is the **Water flush method.** The cable is replaced by a string of pipes screwed together, through which water can be pumped, emerging through two holes in the upper part of the bit. The stream of water carries up the debris to the surface, thus obviating the need for sand pumping.

(*c*) The **Hydraulic rotary method,** which was first used in the famous Spindle Top field of Texas, has now come into general use, especially in cases where soft materials are to be penetrated.

The plant consists of a heavy revolving table driven by cog gear and a chain and sprocket wheel. The drill pipe passes through the centre of the table, being gripped by clamps which, however, are arranged so as to allow the piping to be gradually lowered. The drill pipe is usually made of heavy 4-inch piping and carries a fish-tail drill

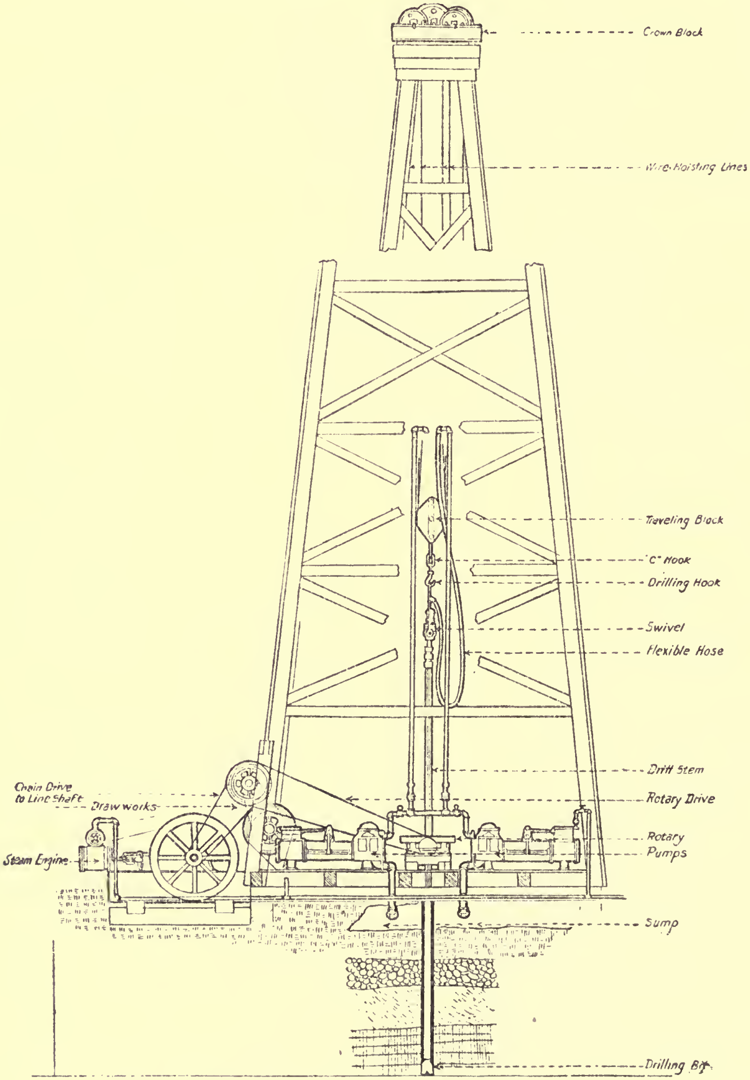

FIG. 11.—Arrangement for drilling by rotary method.

at its lower end. Water is supplied to the upper projecting end of the pipe by a flexible hose and swivel joint. As the drill is rotated water is continuously pumped down the pipes, and emerges through holes in the bit, carrying the detritus upwards through the hole. The detritus is allowed to settle out of the water, and this can then be used again. In fact, muddy water is often used in order to clog up the pores of any sand which is being penetrated so as to avoid loss of water. In drilling through clay, however, clear water is used. The well often requires no casing, as the mud puddles its sides so that the material is able to stand up alone.

In this system of drilling it is essential that the operation be continuous. If it be stopped then the accumulation of mud will jam up the bit and drill pipes. A recent improvement is the Sharp-Hughes patent cone bit. This consists of two hard steel-toothed cones which can revolve on bearings supplied with lubricating oil by a special pipe fitted inside the drill tube. The use of this bit enables the rotary outfit to be used for drilling through hard rock also.

The hydraulic rotary can penetrate soft strata at a great speed. In Texas wells have been drilled at the rate of 30 feet an hour.

The fact that the mud puddles up the sand is a disadvantage in drilling in an area the underground geology of which is not known, as it is possible to pass through an oil sand without noticing it, if the hydraulic pressure of the water column in the well is greater than that of the oil in the sand.

Fishing.—In spite of all precautions tools occasionally become detached; a cable may break, tools may become unscrewed, or the screw pins may break. The difficulties of extracting such lost tools, "fishing" as this is called, are great.

In the first case some information must be obtained as to the position of the tools in the hole. This is often obtained by lowering down a special tool with a bell-shaped opening filled with wax. An impression of the top of the lost tools may be so obtained and a special fishing tool may then be designed to catch hold of them. Many ingenious tools and methods have been designed and even special photographic apparatus has sometimes been lowered into a well.

Several standard types of fishing tools such as the "slip socket" and "cable spear" are often used. The slip socket consists of a tube containing two movable slips, one on either side, with teeth pointing upward. The apparatus is lowered over the lost tools, and on raising it the toothed slips, falling as low as they can in the bevelled grooves in which they slide, bite into the tool and hold it firmly while it is pulled up (Fig. 12). The cable spear is simply a "spike" with barbs pointing upwards so as to engage in the cable which may have broken and slipped down into the well.

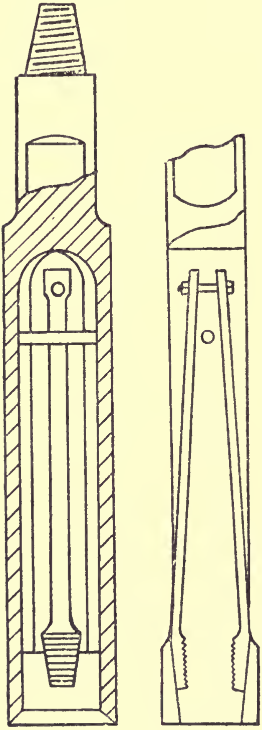

FIG. 12.—Slip socket.

Further trouble may be encountered by casing slipping into the well, or becoming distorted. For details of methods of dealing with these various difficulties reference must be made to one of the standard works on drilling. They fall outside the scope of this book.

Flowing Wells.—When the drilling has been completed and the oil sand reached, the well may gush, or quietly flow, or need pumping, according to the gas pressure.

In Russia, California, and Mexico "gushers" of enormous size, yielding 10,000 tons or more per day, have often been struck. Such large wells frequently get out of control, a large part of the oil may be lost and much damage to surrounding property may ensue.

The greatest oil well so far brought in was the Potrero del Llano No. 4 of Mexico, which produced at one period at the rate of 25,000 tons per day.

Many wells, under control, flow for years at a continually decreasing rate owing to the gradual fall in gas pressure. In the case of flowing wells the oil is led by pipes connected to the casing-head, through a gas separator, if necessary, to storage tanks.

Methods of Raising Oil.—Many wells, however, do not flow but require pumping.

This is usually effected :

(*a*) by means of mechanically operated pumps,
(*b*) by means of an airlift system, or
(*c*) by baling.

(*a*) The **pump** consists of a working barrel to the lower edge of which is attached the suction pipe, on the upper end of which is the suction valve. The piston or plunger of the pump is fitted with several cup-leathers, which expand against the walls of the barrel forming a tight piston. This is necessary, as such a long column of oil requires lifting. The plunger is operated by means of a cable or steel rods attached to the walking beam.

In many fields where the wells are close together a number of wells are pumped from a central station. An oscillating wheel or "jerker" has attached to it a number of steel rods or cables which operate the pumping jacks at the various wells. In this way pumping is economically carried out, as the wells can be so connected up that half the pump rods are descending while half are ascending. In the Petrolia field of Canada many such wells may be operated by a 12-h.p. engine.

(*b*) In some fields the **airlift** system is used. The operation of this system depends on the aeration of the column of oil in the well by means of a jet of compressed air emitted from the bottom of a central tube lowered to the bottom of the well. The pressure due to the aerated column of liquid must of course be less than the pressure due to the previously existing column of liquid in order to obtain a flow (Stirling, "The Airlift System of Raising Oil," *J.I.P.T.*, 1920, p. 379).

The chief advantages of this system are—

1. Automatic action and reliability.
2. No moving parts to get out of order.
3. Applicability to oils containing sand in suspension.
4. Applicability to wells of small diameter and to crooked boreholes.
5. Low operating costs.
6. Concentration of machinery in one building and transmission of compressed air with little or no loss.

In cases where the airlift system cannot be used, and where owing to the sand content of the oil ordinary pumping methods are inapplicable, resort must be had to **baling.** This method is largely used in Russia and Rumania. The baler consists merely of a long tube with a valve at the bottom, a sand pump, in fact, which is alternately lowered into and raised from the well. Such a method of operation is, of course, the most expensive.

Another method, somewhat similar in principle, is that known as **swabbing.** A string of tubes fitted with an expanding packer is lowered into the well, the packer being fixed some 20 feet or more from the lower end of the tubes. The arrangement is then hauled up, a valve in the tubing automatically closing. The tubes and packer thus act as a piston and exert a great suction on the oil. This process is of great use also for cleaning out a well which may have become clogged with waxy deposit or sand.

Shooting.—In order to increase the yield of an oil well the method of "shooting" is often employed. A charge of many quarts of nitro-glycerine is lowered in a canister into the well, and exploded by means of a time fuse. The powerful explosion at the bottom of the well shatters the rock in the vicinity, with the result that a series of cracks radiating from the well enable the oil to flow thereto more easily, the daily yield being thereby often considerably increased.

A method of **mining for oil by means of shafts and galleries** has been applied in the fields of Pechelbronn, Alsace, by which it is maintained that a greater yield of oil can be obtained than by boring methods (Paul de Chambrier, *J.I.P.T.*, 1921, p. 178). The method in this particular area has proved of value, but its application would appear to be limited, especially in the case of fields where the oil is found at great depths and which yield oil of high volatility. Moreover, in many fields where the anticline or dome structure predominates and where water underlies the oil, the upward percolation of the water consequent on the gradual removal of the oil must remove from the oil sands most of the oil which they would otherwise retain.

Oil Well Fires.—Oil and gas wells occasionally catch fire, owing to lightning, frictional electric sparks, or carelessness. Various ingenious methods for extinguishing such fires have been devised. In some cases they have been choked out by steam, in others by the use of a foam caused by the interaction of two aqueous solutions liberating carbon dioxide. An ingenious method of extinguishing a gas-well fire was recently described in the *Oil Trade Journal*, April, 1920. A package of dynamite was drawn on a suspended cable until it was in the close vicinity of the flame, and was then exploded, the explosion wave literally blowing out the flame.

Oil-field Waste.—Oil-field operations are unfortunately often associated with great waste, both of material and labour. This subject has recently been dealt with in a paper read by A. Beeby Thompson before the Institution of Petroleum Technologists on November 8, 1921. Oil-field waste may be divided into: (*a*) Development waste. Owing to the mobility of petroleum a well put down on one lease may draw supplies partly from an adjacent lease. As a result of this an unnecessary number of wells are put down (often too hurriedly) along the boundary line between adjacent leases, especially when the leases are of small area.

(*b*) Extraction losses. The occasionally bringing in of uncontrollable wells results in much loss of both valuable oil and gas. Moreover, even with the most improved methods of extraction, a large proportion of the oil contained in a porous bed necessarily remains underground.

(*c*) Fuel Waste. Owing partly to the flexibility and fool-proofness of the steam engine, this is still the favourite source of power, often in spite of the fact that enormous supplies of gas are running to waste. Owing to fire risks the boilers (which are usually of low efficiency) are placed some considerable distance from the derrick, so that the losses in transmission of steam (often through unlagged lines) is very considerable.

(*d*) Evaporation losses. The importance of this is too seldom recognized. It has been calculated that (Wiggins, *Pet. Age*, 1920) the losses by evaporation in the Mid-Continent fields of America amounted to nearly 3 per cent. of the total gasoline output of the United States. Even in well-designed storage tanks the loss by evaporation of a benzine may amount to several percents. per annum. This subject is now receiving serious attention, insulated tanks have been tried and systems of vapour absorption are being introduced.

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Arnold and Garfias, " The Cementing Process of excluding Water from Wells." *Technical Paper* 32, U.S. Bureau of Mines.

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Ockenden and Carter, " Rotary System of Drilling Oil Wells." *J.I.P.T.*, vol. 6, p. 249.

Ockenden and Carter, " Plant used in the Percussion System of Drilling Oil Wells." *J.I.P.T.*, vol. 5, p. 161.

SECTION C.—STORAGE AND TRANSPORT OF CRUDE OIL AND ITS LIQUID PRODUCTS

THE conditions of storage of crude oil on the fields often leave much to be desired. Particularly in the case of opening up of new fields, when the probable output is a matter of conjecture only, adequate storage facilities have often not been provided, and much oil has in consequence been wasted. Occasionally exceptionally large gushers are brought in and may get out of control, so that hastily constructed earthen reservoirs are perforce used for temporary storage, the loss by leakage and evaporation in such cases being very great, especially in the case of light and volatile crudes.

The practice of storing oil in open reservoirs, at one time common, when the volatile fractions were a drug in the market, is happily now rare and need not, therefore, be described.

In Canada and Galicia underground storage tanks are extensively used. They are constructed by excavating circular holes, lining the sides with wooden planks and puddling behind these with clay. Wooden roofs covered with asphalt roofing-felt are used.

Wooden cylindrical tanks made of staves, hooped together with steel bands, are still largely used in America. Such tanks are, however, always of small capacity, and are used merely as receiving tanks at the well mouth.

The use of steel storage tanks is, however, now almost universal. Such tanks are constructed of various capacities up to 55,000 barrels, *i.e.* 8000 tons, sometimes larger. Such tanks may have diameters up to 100 feet or more and usually range in height up to about 36 feet.

They are constructed of steel plates riveted together, the thickness of the plates diminishing towards the top of the tank. The lowest course of plates is riveted to the bottom by means of a heavy angle iron. The roofs are usually of the self-supporting type, consisting of thin sheet plates supported on the rafters and purlins. Wooden roofs are sometimes used, but this is inadvisable, particularly in areas where thunder-storms are frequent. Good metallic contact of the roof plates with the side is of great importance, otherwise electric disturbances may cause sparking and the loss of the contents of the tank by fire.

Tanks designed for the storage of volatile crudes or distillates should always be made gas-tight, and fitted with some form of pressure and vacuum valve (7, Fig. 13).

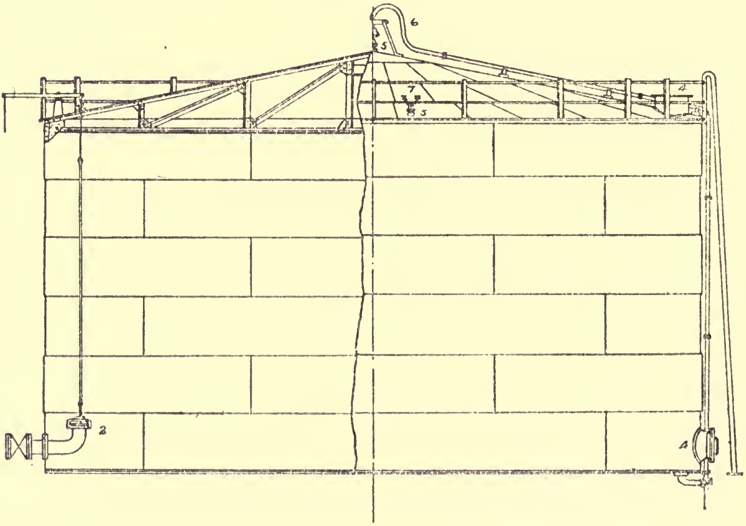

FIG. 13.—Diagrammatic view of steel tank for storage of oil.

The tank must be fitted with: a water draw-off valve (1) at the bottom, which can be closed by an internal valve; one or more inlet and outlet pipes situated near the bottom of the tank, and provided either with internal valves (2) or with a swing pipe arrangement (3).

These internal valves or swing pipes are a necessary

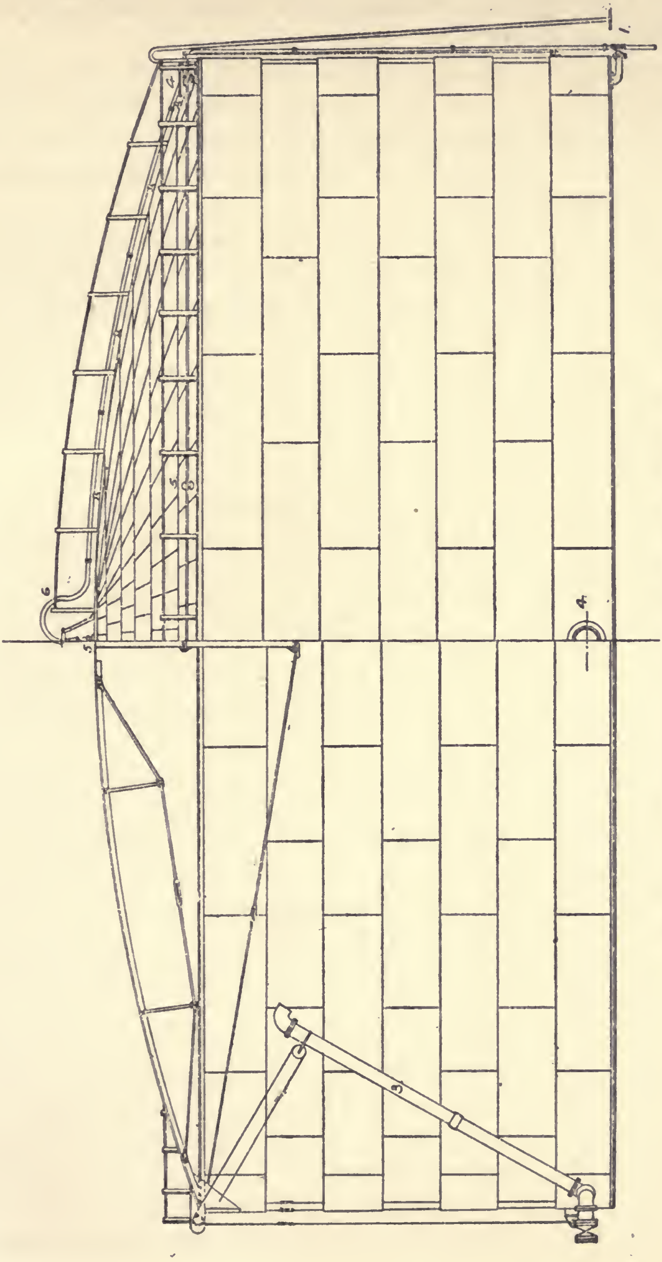

FIG. 13A.—Diagrammatic view of steel tank for storage of oil.

precaution against the breaking of the external valves and consequent loss of oil.

Tanks are further provided with one or more manholes (4, Fig. 13A), on the bottom course of the plates and on the roof, to allow of entry for cleaning purposes, with one or two " dipping holes " (5) in the roof fitted with plugs for gauging purposes.

Some form of water sprinkling arrangement (6) is also usual, for cooling the roof and sides of the tank in hot weather, or in the event of an adjacent tank being on fire.

The loss by evaporation of volatile fractions is a very serious question, which has in the past received far too little attention.

Recent tests carried out in the United States (J. H. Wiggins, *Petroleum Age*, July, 1920) have shown that the losses, owing to filling tanks in the summer by overshot connections, may amount to 1 to 2½ per cent. a day.

Light crude oil containing 30 per cent. of benzine was found to lose 3 per cent. of its volume in being stored in a well-made steel tank for a year. As the most volatile fractions are lost, the monetary loss amounts to much more than 3 per cent.

With well-made tanks, fitted with gas-tight roofs, in the tropics, the losses can be reduced to about 3 per cent. per annum, but nevertheless usually exceed this figure even in temperate climates.

The chief causes of **loss in storage** are :—

(1) Leakage through faulty seams ;

(2) Expulsion of air and benzine vapour when pumping into a tank ;

(3) The alternate expulsion of a mixture of air and benzine vapour during the day and the sucking in of air during the night, the so-called " breathing " of a tank.

Leakage can be minimized by careful construction. The use of welded tanks will doubtless become common in the future, a few having already been constructed.

Evaporation losses due to pumping and breathing cannot be entirely avoided, but may be minimized in several ways.

The storage tanks should always be painted white. Some experiments conducted in Mexico showed that a loss of 0·59 per cent. per annum for a tank painted black, could be reduced to 0·28 per cent. by merely painting it white.

Storage losses may also be considerably reduced by connecting tanks by means of vapour lines to a scrubbing-tower, down which heavy distillate or gas oil is trickling. Vapours will thus be largely absorbed and may be recovered by distillation of the gas oil. Such installations are, however, as yet very rare.

Crude oil after collection at a central tank farm is transported to the refineries by pipe-line, tank car, or tank steamer.

The **pipe-line** system of the United States is now very extensive, about 45,000 miles of transport pipe-lines now being in use.

Many other pipe-lines of considerable length, *e.g.* those from the fields of Rumania to Constanza, and that from Baku to Batoum, have also been laid down.

These pipe-lines, which are usually of diameters of from 4 to 12 inches, are laid underground. Pumping stations are set up at intervals along the line, the distances between the pumping stations being determined by the viscosity of the oil to be pumped. Pressures up to 800 or 900 lbs. per square inch are often employed. In the case of very viscous oils, heating arrangements are usually installed at the pumping stations.

A list of the principal pipe-lines in the United States is given in Bulletin No. 14 of the Kansas City Testing Laboratory.

The rate of flow of liquid moving through a pipe-line depends on various factors: the pressure at which the liquid is fed in by the pumps, the viscosity of the oil, and the diameter, length, nature of internal surface, and number and nature of bends of the pipe-line.

A discussion of this subject is to be found in the *J.I.P.T.*, vol. 2, p. 45, Glazebrook, Higgins, and Pannel, and tables for calculating the flow of oil in pipes are given by Preston in *Chemical and Metallurgical Engineering*, 1920, pp. 607, 685.

Railway **tank cars** are also largely used for the transport of crude oil and liquid petroleum products. Tank cars supplied with steam coils, which can be connected up to a steam line, at the discharging stations, are used for the transport of heavy lubricating oils and even asphalts which are solid at ordinary temperatures.

The design of such cars depends to a large extent on the conditions laid down by the railway companies over whose lines the cars must run. Cars designed to carry benzines or other inflammable products are usually not permitted to have any connections to the bottoms of the tanks, but must be pumped out by means of the manhole or connections on the expansion dome on the top of the car.

Transport by sea is effected by means of specially designed **tank steamers,** which are sometimes fitted with steam-heating coils to facilitate the discharge of heavy viscous fuel oils. In the majority of tank steamers the engines are usually fitted aft, in order to avoid the necessity for constructing an oil-tight shaft tunnel which must pass through the oil tanks, if the engines were placed midships. The engine space aft, and the stores, and crew's accommodation forward, are separated off from the oil tanks by means of "coffer-dams." These are made of two water-tight steel transverse bulkheads, a few feet apart, the space between these forming tanks which are filled with water. The oil tanks are thus isolated fore and aft from the rest of the ship by means of two solid walls of water. The ship is usually divided into a number of tanks by transverse bulkheads, and each tank is divided into a port and starboard portion by means of a longitudinal bulkhead. In order to avoid "slack tanks," *i.e.* tanks partly filled, and to allow for the expansion and contraction of the oil owing to changes of temperature, there are fitted on to the top of the tanks "expansion trunks" of relatively small cross section. These expansion trunks further allow of more accurate gauging of the quantity of oil in the tanks. Further, in order that the full carrying capacity of the ship may be utilized when carrying oils of low specific gravity, several smaller tanks on top of the main tanks, termed "summer tanks" are usually fitted. The arrangement of the tanks will be readily understood from an inspection of the diagram (Fig. 14).

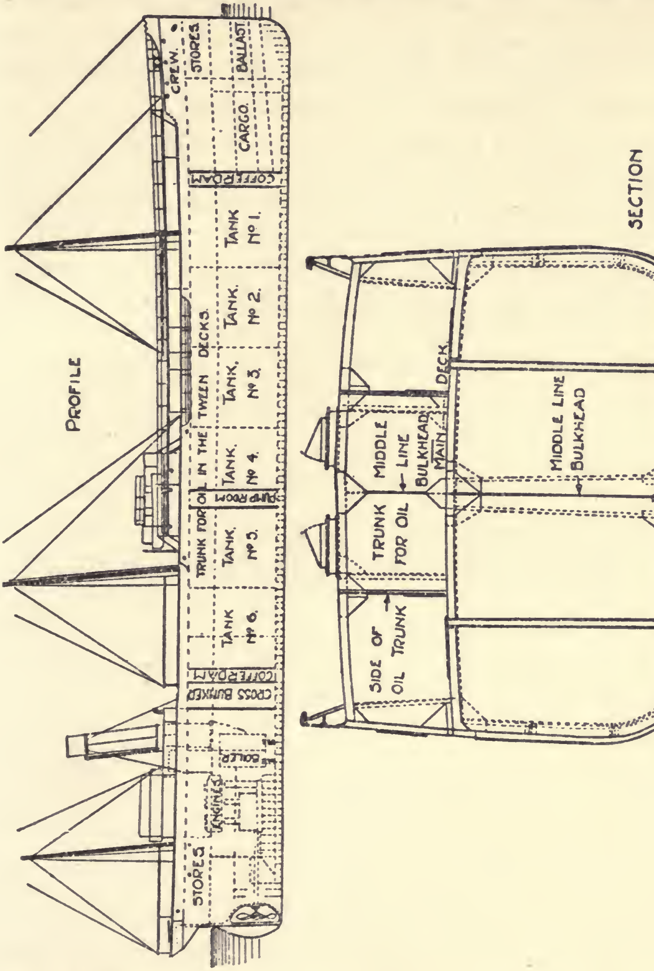

Fig. 14.—Sections of tank steamer.

The ship is fitted with one or more pump-rooms in which the discharge pumps are situated as low down as possible. One or more suction lines extend through the tanks, and are fitted with valves operated by spindles extending to the upper deck. The discharge line is connected to the line on the wharf by means of flexible hoses or a jointed steel swing pipe. Modern tank steamers are built up to capacities of 15,000 tons and can discharge this oil at the rate of as much as 400 tons per hour.

The total tanker tonnage of the world now amounts to over 3,500,000 tons. This large fleet consists of 709 steam or motor driven vessels and 124 sailing ships, and a further 250 or thereabouts are under construction.

The evolution of the modern tank steamer has been well described by H. Barringer in the *J.I.P.T.*, vol. 1, 1915, p. 280.

REFERENCES TO PART III., SECTION C.

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Engler-Höfer, "Das Erdöl," vol. 5. Hirzel, Leipzig.
Pogue, "Economics of Petroleum." J. Wiley & Sons, New York.

SECTION D.—THE DEHYDRATION OF CRUDE OILS ON THE FIELDS

CRUDE oil as it issues from the well is often mixed with water, which is often saline, the water being emulsified in the oil. As the transport of such water-containing oil by pipe-line or tank steamer really involves freight charges on the contained water, steps are taken to dehydrate such oils on the fields as far as possible before transport to the refineries. This dehydration may often be more or less completely effected, especially in the case of crudes of low specific gravity, by merely standing in storage tanks. In such cases most of the water settles out, sometimes clear, but often in the form of a thick emulsion (known as B.S. or "bottom settlings") which can be drawn off. This emulsion still contains considerable proportions of oil, and may be separately treated by one of the methods described below. Many heavy crudes do not, however, readily separate out the water, some in fact retain it obstinately. Such must be subjected to special treatment, as apart from the question of unnecessary transport of water, the distillation of emulsified oil presents difficulties.

Several methods for treating such heavy emulsions or watery crude oils have been devised.

(*a*) Methods depending on the **action of electrolytes,** *e.g.* dilute acids, or solutions of metallic salts, have been suggested and occasionally employed. Such methods have, however, met with little success.

(*b*) **Centrifugal Methods.**—The separation of emulsified oil is usually effected in the laboratory by an ordinary hand-driven centrifugal apparatus, the action being accelerated by the dilution of the oil with benzine. Such a method would, however, be generally too costly in practice, as the benzine would need to be separated off again by distillation. The centrifugal principle has recently been employed with success in the Sharples super-centrifugal apparatus, which is now in operation in many fields for the treatment of crudes containing water in suspension.

The centrifugal machine employed operates at a speed of 17,000 revolutions per minute, exerting a separating force nearly 17,000 times that of gravity. The machine consists of a rotor, a cylindrical vessel 36 inches long and $4\frac{1}{2}$ inches diameter, suspended in a vertical position from a spindle rotating in a ball bearing.

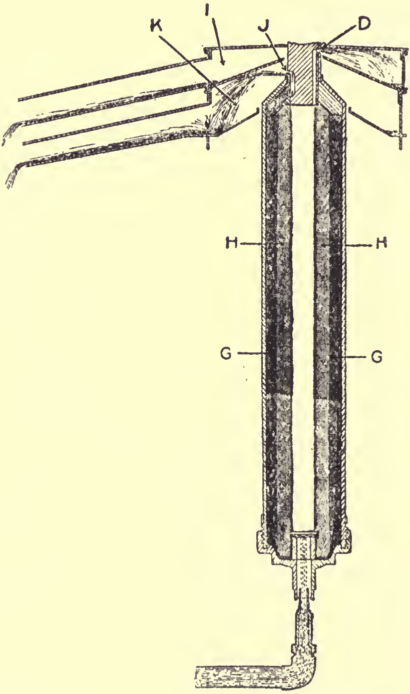

FIG. 15.—Sharples super-centrifugal machine.

The rotor or bowl (Fig. 15) is a plain cylindrical tube provided with an inlet port at the lower end and outlet ports at the upper end, through the outer of which water runs off, and through the inner, oil. The machine thus functions as a separating tank acting under an enormously increased gravitational force.

The oil to be dehydrated is fed in at the bottom and under the influence of the centrifugal force separates into two layers, the outer (G) being water with little or no oil, the inner (H) being oil with little or no water. The water flows off through the lower port (J), the oil through the inner port (D), these being collected separately in the receivers K and I

The rate of flow through the apparatus is controlled by the rate of feed, this being adjusted so as to permit the oil to remain in the apparatus sufficiently long to allow of separation of the water taking place.

The capacity of a machine of the dimensions given above will naturally depend on the nature of the emulsion under treatment, but it may be taken that an emulsion containing 8 per cent. of water could be handled at the rate of about 1½ tons per hour. The apparatus can also be used to effect a separation of oil from the sludge which settles out on the bottoms of storage tanks, a product which is otherwise difficult to handle (U.S. Pat. No. 1232104).

(*c*) **Electric Methods.**—It has been found that crude oil emulsions readily separate out into their constituents when placed in a strong static electric field. This principle has been employed in various processes which are now in common use for treating watery crudes.

A usual type of plant consists of a tank, eight or nine feet diameter and about double that in height, fitted with water draw-off and heating coils. The body of the tank is filled with a series of flat parallel plates, alternate members of which are earthed to the tank, the others being connected up to a transformer which supplies single phase alternating current at 11,000 volts.

The emulsified crude oil is pumped in near the bottom of the tank, the water separates out and is drawn off, and the emulsion-free oil passes off from the top. In another well-known type of plant (the Cottrell) one electrode consists of a central revolving cage built up of a central axis carrying metallic discs, the other electrode being the outer wall of the cylindrical tank. The actual way in which the separation of the emulsion in such plants takes place is not fully understood.

Oil containing 85 per cent. of water has been in this way successfully treated. The cost of operation is very low and the plant requires very little attention. (*Electrical Review*, New York, October 25, 1919.)

(*d*) **Heating under Pressure.**—Most crude oil emulsions may be separated effectively by heating under pressure. Pressure is necessary as the splitting point is usually above the boiling point of water at ordinary pressure. This method, which works well in the laboratory, has not, however, so far been applied in practice.

(*e*) **Distillation Methods.**—The distillation of wet crude oil in ordinary stills presents technical difficulties owing to the liability to boil over or "puke." This difficulty is got over by distillation in tubular retorts, the foaming mass of hot oil, steam, and vapours being allowed to pass into a large vessel, a separating box, whence the steam and vapours pass off to condensers, the dehydrated crude running out from the bottom through heat exchangers to storage. Such dehydrating plants are now common, and are often used to distil off some of the volatile fractions from a crude oil as well as the water. They are consequently often termed "topping" or "skimming" plants. They are described in detail under distillation plant (*vide* Part VII., Sect. A), to which the reader is referred.

GENERAL REFERENCES TO PART III., SECTION D.

Sherrick, "Oil Field Emulsions." *J. Ind. and Eng. Chem.*, Feb. 1920.

Thomas, "Review of the Literature of Emulsions," *J. Ind. and Eng. Chem.*, Feb. 1920.

PART IV.—CRUDE OILS PRODUCED BY THE DISTILLATION OF SHALES, COALS, LIGNITES, AND THE LIKE

SECTION A.—CHARACTERS AND DISTRIBUTION OF OIL SHALE

THE shale oil and petroleum industries, though of about the same age, have developed to very different extents, the former being at the present time of relatively little importance. Shale oils have so far always been in the unfortunate position of having to face the competition of the more cheaply manufactured products of petroleum, in consequence of which the shale-oil industry has had a somewhat checkered career. It owes its continued existence indeed largely to the fact that ammonium sulphate is produced as a by-product.

There can be no doubt, however, that a great future is in store for this industry, the development of which will become of increasingly greater importance as the demand for petroleum products increases. Immense though the potentialities of petroleum production are, the end of many important oil-fields is in sight. In the United States, for example, where enormous deposits of oil shale exist, the importance of the development of this industry is fully realized and active efforts are being made to establish it on a firm basis.

Oil shales as distinct from oil sands do not normally contain oil as such, as they yield up little or no portion of their organic content to solvents. The oil obtained from oil shales is produced as a result of the chemical changes brought about by the action of heat. Oil sands, on the contrary, readily yield up their bituminous material to such solvents as carbon disulphide. There are, however, certain types of shale which do yield an appreciable content of soluble material. J. Gavin, in a report recently issued by the U.S. Bureau of Mines, entitled "The Solubility of Oil Shales in Solvents for Petroleum," has investigated this subject. He finds that in the case of a Colorado shale 2·04 per cent. in carbon tetrachloride, 1·85 per cent. in carbon bisulphide, 1·33 per cent. in acetone, 2·23 per cent. in benzol, and 2·41 per cent. in chloroform, these figures representing from 10 to 18 per cent. of the yield of oil obtainable by distillation. He points out, however, that the extracted material is not oil, in the common sense of the word, but resembles certain of the natural products which are supposed to have resulted from oxidation of petroleum. He also points out that the solubility of an oil shale is not an index of its relative oil yield.

Oil shales are often termed bituminous shales, just as types of coal are described as bituminous. The author does not like the use of the term "bituminous" in this connection as the shales really contain no bitumen as such. Pyrobituminous shales is a more accurate term; however, to avoid any misunderstanding the term "oil shale" may be used. A shale saturated with petroleum would be termed a "petroliferous" shale.

Oil shales are thus composed of two classes of constituents, the inorganic material which remains as ash after distillation, and the organic material, the thermal decomposition of which gives rise to the crude oil. The organic material of shales is usually designated by the term "kerogen."

Oil shales show great variation in properties, not only of the inorganic, but also of the organic components. In general they are stratified rocks composed largely of argillaceous, though sometimes of calcareous material. They are usually dark in colour, but sometimes brownish or even yellowish, sometimes hard and brittle, but often tough and capable of being cut with a knife. They occur in beds ranging from a few inches in thickness to many feet. In many cases the total thickness of the shale beds in one shale-bearing formation amounts to many hundreds of feet.

The inorganic portion of a shale may be considered merely as a carrier for the organic material. The organic portion, the so-called "kerogen," shows great differences of character in different shales.

This great variation in character is illustrated by the following ultimate analyses of the organic part of various shales from different sources :—

Shale.	% C.	% H.	% O.	% N.	% S.
1	76·9	8·8	4·4	2·7	7·1
2	70·8	9·6	14·5	2·3	2·8
3	69·6	8·1	20·3	0·2	1·8
4	68·4	8·6	4·9	0·9	17·2
5	66·8	9·3	17·7	1·8	4·4
6	64·1	6·8	23·6	2·1	3·4
7	58·6	8·0	22·4	1·1	9·9

The ratio carbon/hydrogen varies from 7·2 to 9·4. The extreme variations in oxygen and sulphur content are very noticeable. The above analyses were made on individual shales from various countries. Individual samples from various seams in the same area even display considerable variation in character.

Considerable attention has been given by Cunningham-Craig to the microscopic study of oil shales, torbanites, and cannel coals (*J.I.P.T.*, vol. 2, p. 238). He points out that a distinct substance varying in colour from a pale yellow to a deep reddish-brown as viewed in a microscopic section, is characteristic of all oil shales and cannel coals. This peculiar yellow body shows no definite structure, and under the microscope shows irregular shapes often completely imbedding portions of the mineral matter. As a result of a considerable amount of microscopic research, Craig has come to the conclusion that in the case of boghead coals, or torbanites, this "kerogen" has developed *in situ*, but that in oil shales it may have been largely introduced from some outside source.

Of the chemical nature of this "kerogen" little definite is at present known, but there is evidence which points to its being derived, at least in the case of certain oil shales, from crude petroleum. It has not yet been isolated, as it is practically insoluble in any of the known solvents. In this respect it bears some resemblance to the naturally occurring kerites (usually termed "asphaltites"), wurzilite, and albertite. This resemblance is further borne out by the fact that the carbon/hydrogen ratio is of the same order, 7 to 1, being markedly different from that characteristic of bituminous coal, 15 to 1, but not so different from that of cannel coal, 10·5 to 1.

Some light on the probable origin of this kerogen has been thrown by the recent researches of Hackford (*Trans. Am. Inst. of Mining and Metallurgical Engineers*, 1920). He found that by treating a Pennsylvania lubricating oil with oxygen or sulphur at a temperature of only 100° C. practically the whole, after a long period, gradually changed into bodies practically insoluble in any of the known solvents. These substances he termed kerotenes, and he found them to bear a great resemblance to the kerogen of shales. Naturally occurring bodies, intermediate in character between petroleum and these kerotenes, are indeed known, the asphaltites and glance pitches. The following table illustrates this point :—

Substance.	Per cent. soluble in carbon bisulphide.	Per cent. soluble in petroleum spirit. Sp.gr. 0·645.	Per cent. fixed carbon.
Asphalt made from Mexican petroleum	99·9	60	12
Gilsonite	about 98	40 to 60	10 to 20
Barbados Manjak	about 98	25 to 30	25 to 30
Grahamite	about 99	about 1	45 to 55
Albertite	slightly	trace	about 55

The work of Hackford indicates that these bodies represent steps in a process of gradual change which petroleum may undergo, the final result of which is the kerotenes, which are certainly very similar to, if not identical with, the kerogen of some pyrobituminous shales.

On this view, then, an oil shale would appear to be the result of such a change having taken place in a rock which had been saturated with crude petroleum. This gradual transformation has been termed "inspissation." Evidences that this is actually going on in nature are not wanting. Oil sands more or less weathered and oil from seepages, and intruded asphalts have been shown to contain proportions of insoluble kerotenes up to as much as 30 per cent.

The well-known albertite vein of New Brunswick is connected with a bituminous sandstone which still contains oil. There can be little doubt that this albertite, which so nearly resembles coal in some respects, is a highly inspissated petroleum product. The rocks which this vein traverses have actually been converted into true kerogen-containing oil shales.

This process of inspissation seems further to bring about a concentration of the sulphur and nitrogen found in the original crude oil. For example, many crude petroleums contain less than 1 per cent. of sulphur, the heavy asphaltic oils of Mexico 5 per cent., the thiokerite wurzilite 5·8 per cent., and a similar thiokerite from Nova Zembla as much as 15 per cent. (Hackford, *loc. cit.*). Ohio crude oil contains 0·2 per cent. of nitrogen, some Californian oils 1·75, and albertite 1·75 per cent. The relatively high nitrogen and sulphur content of shales perhaps also lends support to the view that oil shales are merely shales (or other types of rock) which were once impregnated with crude oil, which has slowly undergone inspissation in the manner suggested above. As Craig says, "an oil-shale field may be considered as the relics of a former oil-field."

Conacher, on the other hand (*Geol. Soc.*, Glasgow, 1916, p. 164), considers that the organic matter in the shale is of vegetable origin, partly resinous in character. As the solubility of resins decreases with age, the failure of solvents to extract the organic matter from shales does not disprove this theory.

Engler (*Petroleum*, vol. 7, p. 399) considers that the pyrobitumens of shales are of vegetable origin, formed perhaps with such bodies as montan wax, as intermediate products.

It is interesting to note in this connection that Jones and Wheeler (*J.C.S.*, 1916, p. 767) state that coal can be resolved into cellulosic and resinic parts, the former of which on distillation yields phenolic bodies, the latter hydrocarbons.

Oil shales differ greatly in character. It is highly improbable that shales so diverse in character should have similar origins. Some would appear to be derived from petroleum, others directly from organic matter. As in the case of crude petroleums, the question of their origin is at present far from being decided.

For comparative purposes a few shale analyses are appended :—

Locality.	Sp.gr. of shale.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.
Scotland—		%	%	%	%
1. Torbanite ..	1·27	61·42	8·81	29·17	0·277
2. Cobbinshaw ..	1·62	37·16	8·24	53·64	1·435
3. Tarbrax ..	1·81	30·86	8·82	58·71	3·053
4. Newliston ..	1·81	27·38	8·78	62·27	1·110
5. Hayscraigs ..	2·05	22·43	5·15	70·70	0·622
6. Deans	2·23	15·28	4·83	77·7	0·528
Kimmeridge	—	39·1	11·8	46·6	—
,, ...	—	22·7	11·7	65·6	—
Norfolk	1·3	35·1	15·3	39·8	—
,, ...	—	32·9	9·0	55·0	4·0
Colorado	1·95	37·5	5·0	56·8	1·2

Locality.	Imperial gallons per ton.	Lbs. ammonium sulphate per ton.
Albert, N.B.	35	47
Argentina, Rio Grande	80	—
California, Kern Co.	52	—
,, Santa Maria	32	—
Esthonia	160	—
France, Autun	18	27
Kentucky	23	98
New South Wales, Newnes	80	—
New Zealand, Waikaia	38	19
Picton, Nova Scotia	14	41
Queensland, Narrows	28	47
Scotland, Broxburn	37	12
,, Fells	26–40	20–35
,, Raeburn	54	7
Tasmania, Mersey	40	—
Transvaal	28	—
Utah	40	17

As the variation in character, even of different seams in the same group, is so great, generalizations about the characters of various shales in various localities cannot be drawn with any degree of accuracy.

A scientific classification of shales is hardly yet possible. They may, however, be roughly grouped into asphaltic pyrobituminous shales, *i.e.* those of which the organic matter contains little or no oxygen, such as those of New Brunswick and Nova Scotia, and non-asphaltic pyrobituminous shales, *i.e.* those of which the organic matter does contain oxygen. This class includes cannel coals, torbanites, and many oil shales (McKee and Lyder, *J. Ind. and Eng. Chem.*, 1921, p. 613).

Oil shales are widely distributed and found in many parts of the world where oil has not yet been proved to exist.

In the British Isles shales are found in **Scotland**, in the Lothians on the south side of the Firth of Forth, where a thriving industry has now been established for more than half a century. The shales here occur in the calciferous sandstone series, the lowest division of the Carboniferous system (Cadell and Wilson, " The Oil Shales of the Lothians," *Memoirs Geological Survey*, Scotland).

The Torbane Hill shale, which was extensively worked there, at one time yielded from 80 to 130 gallons of crude oil per ton. This material has now, however, been completely exhausted. The shales now worked yield on the average not more than 20 to 30 gallons of crude oil per ton, but yield also about 60 lbs. of ammonium sulphate to the ton. The shales from individual seams show great variation, some of those worked yielding only 16 gallons of oil to the ton, others as much as 50.

Extensive oil-shale deposits are now being developed in Norfolk, **England** (Forbes-Leslie, *J.I.P.T.*, 1916, p. 3). The dip of the strata here is very gentle and the covering surface deposits are thin, so that the shale can be quarried from the surface. These shales are richer than those of Scotland, and it is claimed that the crude oils resulting from the distillation are of good quality and can be easily refined in spite of their high sulphur content. The industry in Norfolk, however, is in its infancy, so developments will be awaited with great interest. These shales are of the same age as those which are found in Dorsetshire in the Kimmeridge Clay. These latter shales were actually worked as far back as 1848, and for the following twenty years or so various companies attempted to carry on the industry but in every case without success. The crude oil from Kimmeridge shale is very rich in sulphur compounds (the crude oil containing about 8 per cent. of sulphur), and as these compounds are as stable as the hydrocarbons themselves, no methods of successfully refining this oil have yet been evolved (Mansfield, *J.I.P.T.*, vol. 2, p. 162).

The shale-oil industry in **France** dates back to 1830. The deposits at Autun and at Broxière Les Mines have an annual output of about 750,000 tons of shale. These shales yield about 50 gallons of oil to the ton. Richer shales, yielding 80 to 120 gallons per ton, are also worked in the Riviera (*Petroleum Times,* September 20, 1919). Oil shales occur also in **Wurtemburg, Spain, Sweden, Italy, Bulgaria, Turkey,** and **Austria** (*Journal Royal Society of Arts,* December 24, 1920), but none of these deposits have yet been commercially exploited. In **Canada** vast deposits are found.

The rich shales of **Esthonia** have recently given rise to an industry. They are used for (1) distilling to obtain oils, (2) for gas making, (3) mixed with pulverized coal for cement burning, (4) as fuel in place of coal. These shales are very rich, yielding 29 per cent. of oil, *i.e.* about 75 gallons to the ton (*Shale Rev.*, 1921, Nos. 4, 5).

In **Canada** vast deposits are found in Northern Saskatchewan. In **New Brunswick** oil shales are found in three areas. These yield from 27 to 57 gallons per ton of crude oil, varying in specific gravity from 0·890 to 0·925, and ammonium sulphate in quantities varying from 30 to 110 lbs. per ton. These shales are now being exploited (R. Ells, "The Bituminous Shales of New Brunswick and Nova Scotia," Canada Dept. of Mines, 1910). The oil shales of

Nova Scotia are relatively poor in respect to both oil and ammonium sulphate. Those of **Newfoundland** cover a large area and yield about 50 gallons crude oil and 80 lbs. ammonium sulphate per ton. Deposits of similar character are found in the province of **Quebec.**

In the **United States,** vast deposits of oil shale occur, those of **Colorado** alone covering an area of 2500 square miles, being estimated to be capable of supplying 8,000,000,000 tons of crude oil. In **Utah** more than 40,000,000,000 tons of shale capable of yielding 35 gallons to the ton are available. Those of **Kentucky** yield 22 gallons of oil and 97 lbs. of ammonium sulphate per ton. **Wyoming, Texas, Montana,** and **West Virginia** possess extensive deposits, as do also **California, Kansas, Oklahoma, Nevada,** and **New Mexico.**

Vigorous efforts are now being made in the United States to set the oil-shale industry on a sound economic footing.

Shales in the **Transvaal** have yielded from 30 to 90 gallons of crude oil to the ton, but the beds are usually thin and therefore expensive to work (T. G. Trevor, "An Oil-Shale Industry for South Africa," *South African Journal of Industries*, August, 1920).

There are indications too of extensive deposits in **Brazil** and in **China.**

Extensive deposits of rich oil shales are found in the Wolgan Valley area in **New South Wales.** These have been worked for some years, but so far with disappointing results. In **New Zealand** and **Tasmania** oil shales are also known. These latter deposits have been estimated at 5,000,000 tons and are now in process of development.

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Cronshaw, "Oil Shales." *Imperial Institute Monograph.* J. Murray, 1921.

Greene, "A Treatise on British Mineral Oil." Griffin and Co.

Quarterly Journal of the Colorado School of Mines.

Scheithauer, "Shale Oils and Tars." Scott, Greenwood and Co.

SECTION B.—THE MINING OF SHALES

THE shale-oil industry, in contrast to the petroleum industry proper, must always be severely handicapped by the fact that the crude shale oil, the real starting point for the manufacture of the oil products, must in every case be manufactured. The factor of the cost of mining the shale becomes, therefore, one of supreme importance, the more particularly so as the percentage of oil derived from the shale is often less than twenty. The cost of mining the shale, therefore, will often be the factor which determines the chance of success of any shale proposition.

The method of mining to be adopted in any locality will depend upon various factors, such as the depth at which the shale strata are found; their dip or inclination to the horizontal; the thickness of the shale seams, and the nature of the overlying beds.

The methods employed may be divided into two groups:

(*a*) The open cut or quarrying method.
(*b*) The mining methods.

In many localities, such as Grand Valley, Colorado, the shale forms prominent hills, so that the shale can be quarried by ordinary methods and transported by gravity conveyors to the shale retorting plant at lower levels, this being the cheapest method of working. In other areas, such as Norfolk, the shale beds lie close to the surface with a gentle dip. Under these conditions steam shovels may be used. In any case, however, a considerable quantity of surface material must be removed. The cost of such operations is low, being only three or four shillings per ton.

In some cases, the shales may be worked by horizontal adits driven into the side of a hill, as is the case in Wolgan Valley, New South Wales.

In many cases, however, the shales may be at greater depths, the strata being either inclined or more or less horizontal. In such cases ordinary mining methods must be adopted. A vertical shaft may be sunk from which the level crosscuts may be driven ; or an inclined shaft may be sunk along one of the beds of shale, from which the crosscuts branch off.

The oil shales of Scotland are worked in this manner. After the mine has been driven, the shale is worked either by (1) the Stoop and Room method, or (2) the Long Wall method. A detailed description of the methods used is, however, beyond the scope of this work. For such details reference may be made to "The Oil Shales of the Lothians," Part II., by W. Caldwell, *Memoir of Geological Survey of Scotland*, 1906.

The work of mining shale is generally simpler than that of coal, as gas is absent. Moreover, grading is unnecessary as all the shale from the seam being worked goes to the retorts after being broken up to suitable size in the crushers.

SECTION C.—LABORATORY EXAMINATION OF OIL SHALES

As the actual yield of products obtained on retorting will naturally depend to a considerable extent on the method of retorting employed, it is difficult or impossible to devise a laboratory method of testing shales which will always give results comparable with those obtained in practice. Nevertheless, some method of testing on the laboratory scale is necessary, and highly useful, both for exploratory work and for the control of operations on the large scale.

Moreover, if the relation between the laboratory results and those obtained from large-scale operations has been worked out in one case, other laboratory results may be interpreted in the same way with the reservation, of course, that such interpretation is not rigid.

Elementary analyses giving the nitrogen, carbon, and hydrogen content can be easily carried out by the well-established methods. Determinations of ash and volatile matter are also easily made. Great care must, however, be exercised in deducing conclusions from such elementary analyses. The nitrogen content alone cannot indicate the quantity of ammonium sulphate obtainable, because the whole of the nitrogen cannot be converted into ammonia.

Many shales contain in their mineral matter appreciable and often considerable amounts of carbonates, and also combined moisture, the latter and the carbon dioxide in the carbonates being evolved on ignition. The apparent " volatile matter " derived from the organic matter is thereby often materially increased, and in the elementary analysis, the percentages of carbon, hydrogen, and oxygen in the organic substance are also exaggerated. Hence, in the majority of cases few deductions of value can be made from either the elementary analysis or from the determination of volatile matter, so without additional information the results of such analyses may be very misleading.

The United States Bureau of Mines has for the present adopted the method of laboratory testing of shales, as worked out by Bailey, and applied to the control of shale retorting in Scotland. Full details of the method are published in "Notes on the Oil-Shale Industry" by Gavin, Hill, and Perdew, Bureau of Mines, Washington, 1919, from which the following description is abstracted :—

A malleable iron tube 6 feet long and 2 inches in diameter, welded up at one end, is used as the retort. About 15 inches of the tube is partly filled with shale crushed to pieces of the size of peas. The tube is placed with about 18 inches of its length (which contains the shale) in a furnace, the other 4½ feet projecting outside the furnace inclined downwards towards the open end, and acting as a condenser.

The tube is gradually heated by flue gases during six hours, being finally heated to a bright red. The portion of the tube projecting outside the furnace is then gradually warmed so as to melt any oil which might have solidified therein, and to enable it to run down into the collecting vessel placed below the end of the tube. The oil must be separated from the water which comes over with it, or the water in the mixture must be estimated by one of the standard methods, *e.g.* by distillation with xylene.

The yield of ammonium sulphate is estimated in a similar fashion. A 1-inch tube of malleable iron about 28 inches long is used. One end is connected to a steam supply, the other to a wash bottle or tower containing dilute sulphuric acid (2N), an empty flask to act as receiver being placed between the end of the iron tube and the sulphuric acid container. About 30 grams of the shale are placed in the centre of this tube, which is heated to bright redness in an ordinary combustion tube. After 5 or 6 minutes' gentle heating, when vapours begin to appear in the flask, steam is allowed to pass through the retort at such a rate that after about 1½ hours' heating to bright redness about 600 c.c. of liquid has collected in the flask. The contents of the flask and sulphuric acid absorber are then filtered and washed into a litre flask and made up to a litre, so that three successive portions can be removed for estimation. This may be done by concentrating by evaporation, the nitrogen in the concentrate being estimated by the nitrometer.

The United States Geological Survey (*Bulletin* No. 641, p. 148) have standardized a simple apparatus for field work. It consists merely of a small iron retort of about a half-pint capacity fitted with closely fitting iron lid with clamps, which can be heated by a kerosene burner, and which is connected to a small metal Liebig condenser. The condenser is connected to a flask with a two-holed cork, one of which takes the end of the condenser, the other a glass tube to lead the permanent gases to an ammonia scrubber. A well-mixed sample weighing 8½ oz. is taken, ground so as to pass through a ½-in. sieve. The number of cubic centimetres of oil obtained is equal to the yield of oil in U.S. gallons per ton of shale, provided that 8½ oz. of shale be taken for the experiment.

The percentage of nitrogen given by the elementary analysis multiplied by 94 gives the approximate yield of ammonium sulphate in lbs. per ton which may be expected. It must be remembered, however, that the yield of nitrogen as ammonia depends on the amount of steaming given.

A modified method of laboratory analysis, which allows both oil and ammonia yield to be determined simultaneously, is described by Lomax and Remfry (*J.I.P.T.* vol. 7, 1921, p. 36). These two investigators have noticed the surprising fact that the changes which take place during the weathering of shale affect to a considerable extent the obtainable yield of oil. After a short period of exposure to the weather, the oil yield is found to improve by as much as 20 per cent. in some cases, but after longer exposure falls again, reaching its original value in the course of a month or two and then falling still lower. It is evidently important to seize the right moment for retorting the shale.

SECTION D.—THE RETORTING OF OIL SHALES

As the oil obtained from oil or pyrobituminous shales does not exist as such in the shale, but is formed during the process of retorting, the questions, what takes place in the retorting process, and how far the conditions of retorting affect the yield and quality of the product, are of the very greatest importance.

It has long been recognized that the changes taking place in the retort are of a twofold nature, viz. (1) the production of certain volatile compounds by the thermal decomposition of the pyrobituminous constituents of the shale, and (2) the subsequent cracking or further decomposition of these primary volatile products. It has also been regarded as probable that considerable chemical changes take place by the action of heat even before the above-named primary volatile products make their appearance, and recently this view has been experimentally verified. Messrs. McKee and Lyder (*J. Ind. and Eng. Chem.*, 1921, 613, 678) have studied this point and have shown that whereas the pyrobituminous constituents of the original shale are scarcely soluble in neutral organic solvents such as carbon bisulphide, if the shale is heated for some time at a temperature just below that at which volatile products are evolved in appreciable amount, the pyrobituminous portion undergoes change into a heavy bitumen which is then for the most soluble in carbon bisulphide. In the case of a certain Colorado shale which they investigated, this first resolution of the original pyrobituminous matter into simpler but still very complex substances took place at temperatures of 400° to 410° C., and a slight further increase of the temperature above

410° brought about cracking and the production of light hydrocarbons.

These results verify the above-mentioned view that two quite distinct sets of chemical reactions take place in the process of retorting. The retort functions not only as a producer of a bituminous substance, but also as a cracking still.

Two distinct reactions thus take place, the second following closely on the heels of the first. It is, however, of importance that the second stage, viz. the cracking, should be under control to some extent at any rate. The question of the control of this cracking is, therefore, one of the most important factors which should influence retort design.

As all pyrobituminous shales leave a more or less carbonaceous residue on retorting, the question of the utilization of this carbon, and also of the nitrogen contained in the residue is also of great importance.

This may be effected by the introduction of steam alone where the carbon content of the residue is low, or of steam with a limited amount of air where the carbon content is higher, into the bottom of the retort whereby the residue is converted into water gas or producer gas and ammonia, the latter being recovered in the well-known manner, and the former mixing with the gas formed from the bituminous matter. This gas after separation of the oils is used for heating the retorts or other purpose if there is any surplus. In addition, however, such water gas or producer gas production has a marked effect on the oil production of the shale, as the sensible heat of this gas assists largely in the thermal decomposition of the shale through which it passes, thus considerably reducing the time required for completion of the elimination of the oil from it. When the percentage of carbon in the residue is fairly high, the sensible heat in the producer gas thus made is in itself sufficient to effect the removal of all the volatile matter from the shale, and no external heating of the retort is required.

Such production of water gas or producer gas within the retort has the further result that the primary oil vapours are removed from the zone of heat more rapidly, and the crude oil produced contains a larger proportion of saturated hydrocarbons. The decomposition of the shale and the subsequent cracking of the primary vapours also then take place in an atmosphere containing a much larger proportion of hydrogen and steam, and this further favours the production of saturated hydrocarbons, and consequently improved quality of the crude oil obtained.

Certain disadvantages follow from such production of water gas or producer gas in the retorts, although these are far outweighed by the above-mentioned advantages. Thus the higher production of gas involves a greater cost for condensing and scrubbing apparatus, and the large volume of gas carries away from the condenser most of the lighter hydrocarbons in the form of vapour, making their recovery by oil-washing more expensive.

The principal points to be borne in mind when considering the design and functions of a retorting plant are—

(*a*) The carrying out of the initial stages of the distillation at as low a temperature as possible. This is necessary in order to obtain relatively large oil and small gas yields, and to obtain oil of paraffinous rather than of aromatic nature.

(*b*) Efficient arrangements for removing the vapours from the retort as soon as possible, and for ensuring that they come into contact with highly heated shale and retort walls as little as possible, in order to avoid secondary reactions and cracking or decomposition of the oils first formed.

(*c*) The necessity of ensuring efficient transfer of heat through the mass of shale to be retorted. As the shale is such a poor conductor of heat, either the layer of shale in the retort must not be more than a few inches in thickness, or mechanical means of keeping the shale in motion must be adopted.

(*d*) Arrangements for enabling the shale to be further distilled in contact with steam, either in the same or in a separate retort, in order to obtain the maximum ammonia yield.

(*e*) The problem common to all plants, that of efficient utilization of heat as far as possible, *i.e.* minimum fuel consumption.

(*f*) Simplicity of operation and control.

(*g*) Capacity for working continuously over long periods, with high rate of throughput and low maintenance costs.

(*h*) Low initial capital expenditure.

In the case of plants for the low-temperature distillation of coal, or at any rate of caking coals, the difficulties caused by the caking into a sticky mass of the intumescing coal and its consequent inability to pass down the retort, are so great that, up to the present, no really good type of retort has been handled for dealing with such coals.

McKee and Lyder have also determined some data, which will be useful for designers of shale retorts.

The heat required to convert the kerogen into oil was found to vary from 421 to 484 calories per gram of oil and gas produced, in the cases of the three shales investigated by them. The heat conductivity of the shale was found to be 0·00086 in c.g.s. units and the specific heat about 0·265.

Outside of Scotland, few shale-oil works of any large capacity exist. It will be as well, therefore, to describe the retorting process as used in Scotland, before considering the very numerous types of retorts designed and patented, but so far not found working in practice on a large scale.

The shale is first broken up into small pieces before being fed into the retort hoppers. The type of crusher used depends to a large extent on the nature of the shale. The tough Scottish shales are broken up in a heavy toothed roller machine. For more brittle shales a head motion jaw-crusher will prove more satisfactory. In crushing shales any rubbing or grinding movement should be avoided in order to minimize the production of dust or fines, as the presence of dust gives trouble owing to the clogging up of the condensing plant.

The shale retorts employed in the Scottish shale-oil industry are all modified forms of the original Young and Beilby continuous vertical retort brought out in 1882. One of the most successful of these is the Pumpherston or Bryson type. This retort is made up of two parts The upper is of cast iron, 15 feet long, 2 feet in diameter at the top, tapering to 2 feet 4 inches at the lower end. The lower portion is of firebrick, 20 feet in length, 2 feet 4 inches diameter at the top where it joins the cast-iron upper part tapering to 3 feet at its lower end. This retort is circular in cross section. A few inches below the lower end of the

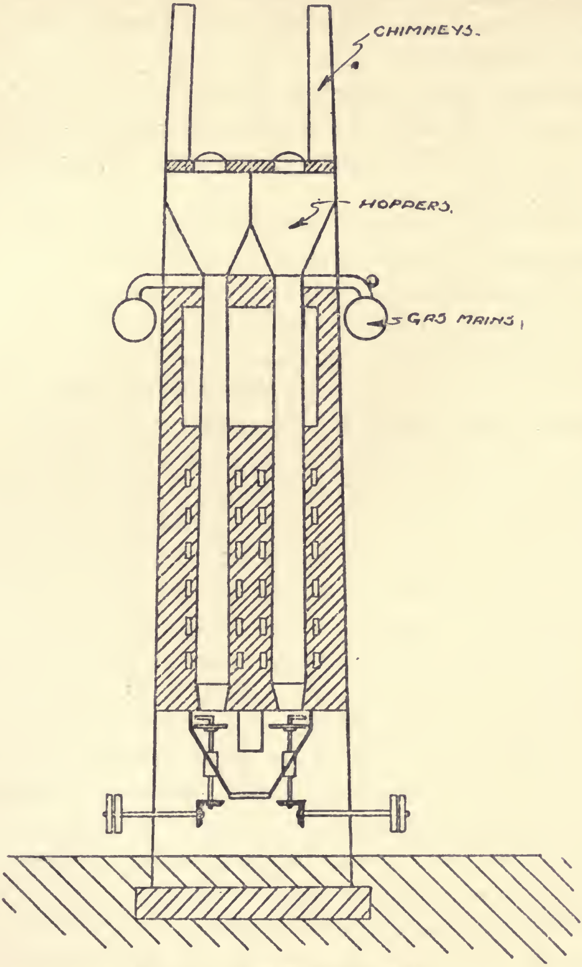

FIG. 16.—Bryson shale retort.

retort is a circular table on which the spent shale rests. On this table works a revolving arm which slowly scrapes the spent shale over the edge of the table, thus providing continuous removal of the spent shale from the retort, enabling supplies of fresh shale to be fed in continuously through the hopper at the top.

The upper iron portion of this retort is kept at a dull red heat, and it is in this section that the oil distillation takes place. The oil vapours pass out just below the hoppers, into a large main.

In the lower firebrick portion of the retort the shale is subjected to a higher temperature in presence of steam, the carbon of the residue being converted into carbon monoxide, and the nitrogen partly into ammonia, this part of the retort thus functioning as an ammonia and gas producer.

With a retort of the above dimensions about 4 to 5 tons per day of shale yielding say 25 gallons per ton of oil can be handled. For each gallon of oil produced about 4 gallons of water in the form of exhaust steam is introduced into the bottom of the retort. This steam serves several purposes; it absorbs a certain amount of heat from the spent shale, produces water gas from the fixed carbon left in the shale after distillation, produces ammonia (about 60 per cent. of the total nitrogen of the shale being so recovered), helps to equalize temperatures throughout the cross section of the retort and to carry off the vapours. A discussion of the action of steam on yield of ammonia in this connection is given by A. J. Franks in *Chemical and Metallurgical Engineering* for December 15, 1920, p. 1149. Franks points out that the steam has a synthetic action at high temperatures and that it removes the ammonia so formed before decomposition can take place to any great extent, the rate of dissociation of ammonia at the temperatures in question being low.

The quality of the oil obtained depends on the temperature employed in retorting. The higher the temperature the greater the proportion of unsaturated hydrocarbons in the oil, the greater the subsequent loss in refining the crude oil, and the lower the proportion of paraffin wax (Stewart, *J.S.C.I.*, 1889, p. 100).

The gases evolved after passing through the scrubbers and condensers are used for heating the retorts, no extra fuel being necessary.

There are three other types of retort in use in Scotland, viz. the Henderson, Young and Fyfe, and the Crichton. These are all similar in principle, being based on the original Young and Beilby retort.

Although such retorts have given very satisfactory results with Scottish shales, it by no means follows that they can be applied with equal success to all shales, as shales from different localities exhibit very great differences in character. Nor may it be taken for granted that these types are the best possible even for Scottish shales. The throughput per retort is very low and the capital expenditure on plant therefore high. The chief difficulty in designing a vertical gravity feed retort of this type arises out of the low thermal conductivity of the shale. If the centre of the mass undergoing distillation be more than a few inches from the retort wall, the heat transference is so poor that either the internal mass does not attain a temperature sufficiently high, or the portions of the shale near the retort wall are subjected to a temperature too high, resulting in excessive cracking of the oil and diminished yield.

Numerous other types of retorts have been devised, few of which have passed and many of which have never reached the large-scale experimental stage. These types may be divided into classes—

(*a*) Continuous vertical with gravity feed (the Scottish type).

(*b*) Continuous vertical type with some form of mechanical feed.

Examples of this type are the Colorado continuous, fitted with a helical conveyor, and the Simpson, fitted with a means of keeping the charge in continuous movement by means of two revolving rollers at the base of the retort. An interesting retort of this class is that recently designed by Freeman (*Pet. Times*, January 14, 1922, p. 43). This retort is made up of a number of distinct chambers set vertically one above the other. Each chamber is separately heated by gas burners and the temperature is accurately controlled by a special automatic apparatus. The finely divided shale rests on a revolving table in each chamber and is transferred gradually from one chamber to the next below it by means of revolving arms, the action being similar to that of a pyrites burning oven. Each chamber is provided with separate vapour off-take pipes. One advantage which this retort possesses is that of the driving off of the water mostly in the first chamber so that emulsified oil distillates are largely avoided.

(*c*) Horizontal continuous types fitted with mechanical feed.

Examples of this are the Del Monte, a tubular externally heated retort fitted with an internal worm, and the Thyssen, the retort being slightly inclined and revolving like a cement kiln, but with external heating.

(*d*) Horizontal continuous type fitted with mechanical feed and internal heating, *e.g.* the Burney retort. This is of several feet diameter, and is fitted with a large internal screw, through the vanes of which the heating gases pass, the difficulty of heat transmission thus being to some extent avoided.

(*e*) Types in which the heating is effected internally and directly by means of the sensible heat of gases.

Examples of this are the Maclaurin type which has had some success even when applied to the low-temperature distillation of coal, and the Nielsen, which consists of an inclined rotating cylinder, in which the shale is heated by direct contact with the heated gases from a producer in which a part of the carbonaceous residue is treated.

A summary of the forms of plant used or under trial in America for shale retorting is given in the *Chemical Age*, New York, January, 1921, vol. 29, p. 30.

As practically all oil-shale retorts, with the exception of those used in Scotland, are as yet in the experimental stage, the writer feels that no opinion of value as to their relative merits can as yet be formed.

It would appear, however, that retorts constructed on the principle of heating by direct contact with heated gases, products of combustion, or better, heated combustible gases from a producer, could be constructed of large dimensions with great potentialities as to throughput, the difficulties dependent on the low thermal conductivity of the shale being in such cases overcome. One objection to this type is the dilution of the oil vapours with large volumes of gases, which renders condensers of greater capacity necessary (Simpson, "Plant Design for Hot Gas Pyrolytic Distillation of Shale," *Chem. and Met. Eng.*, 1921, p. 341).

The issuing gases and vapours from the retorts are often passed through some form of centrifugal separator, their temperature being kept above 100° C. The heavier portions of the distillate are thus collected free from water. The remainder of the vapours are then condensed in water-cooled condensers, then passed through scrubbers in contact with sulphuric acid for the purpose of removing ammonia, then through scrubbers in contact with heavy oil, to which the vapours give up the last traces of volatile fractions. The residual gas leaving the scrubbers is used for heating the retorts or for other purposes in the works.

GENERAL REFERENCES TO PART IV., SECTION D.

Ells, "Bituminous Oil Shales of New Brunswick and Nova Scotia." Canada Department of Mines.
Greene, "Treatise on British Mineral Oils." Griffin and Co.
Scheithauer, "Shale Oil and Tars." Scott, Greenwood and Co.
Stewart, "Oil Shales of the Lothians." *Memoir of Geological Survey.*

SECTION E.—THE CHARACTERS OF SHALE OILS

THE crude oils derived from the retorting of shales exhibit great differences in character, dependent on (*a*) the nature of the pyrobituminous organic matter of the shale, and on (*b*) the conditions under which retorting is effected. Although resembling to some extent crude petroleums, shale oils usually exhibit special characters in consequence of their relatively high content of unsaturated hydrocarbons.

The method of determining the unsaturated hydrocarbons present is somewhat rough and ready, but serves the purpose sufficiently well. The crude oil is treated with two volumes of sulphuric acid (sp. gr. 1·84) and allowed to settle out. The volume of the oil remaining, expressed in percentage of the volume of oil taken, gives the percentage of saturated hydrocarbons. The difference is not strictly due to the absorption of unsaturated hydrocarbons only, as basic nitrogen compounds may be present, certain aromatic hydrocarbons may be absorbed, and certain compounds may be polymerized and subsequently dissolved by the sulphuric acid.

A number of shale oils examined in the laboratory of the Colorado School of Mines (C. W. Botkin, *Chem. and Met. Eng.*, 1921, p. 876) gave the following results :—

Shale retorted.	Per cent. of saturated hydrocarbons in the oil.
Colorado	13·6 to 28·0
Utah	15·8 to 26·5
Nevada	41·2
England	16·0
Scotland	38·0

The high content of unsaturated hydrocarbons as compared with petroleums is due to the low content of hydrogen of the kerogen, there being insufficient to combine with the carbon. Even although so large a proportion of unsaturated hydrocarbons are produced, there is always free carbon left in the shale residue.

The ratio of carbon to hydrogen for the kerogens of shales varies approximately from 7 to 8 or more, whereas the ratio for paraffins, such as are usual in petroleum, varies from 5 to 6. Moreover, it is probable that some of the saturated hydrocarbons formed during the distillation undergo secondary cracking, with the further production of unsaturated hydrocarbons.

The probability of this cracking indicates the necessity for designing the plant and carrying out the retorting so as to remove the products of distillation as soon as formed.

A series of experiments to investigate the influence of temperature in retorting and the influence of steam or hydrogen gas were carried out on Colorado shale oil in the laboratory of the Colorado School of Mines (*Quarterly of the Colorado School of Mines*, vol. 16, No. 2, April, 1921).

Retorting was carried out under four different conditions: (*a*) at low temperature without use of steam, (*b*) at low temperature with use of steam, (*c*) at low temperature with hydrogen in place of steam, (*d*) at higher temperatures, the oil being partly returned to the retort by means of a reflux condenser so as to obtain good cracking conditions.

It was found that under none of these conditions was (1) oil obtained from that particular shale containing less than 70 per cent. of unsaturated hydrocarbons. This is, of course, primarily due to the low hydrogen content of this shale. (2) That the presence of free hydrogen had no effect other than that of diluting and assisting in the removal of the vapours, a function performed equally well by steam. (3) That when the cracking is minimized by the use of steam, the unsaturated hydrocarbons are actually about 15 per cent. higher than when the cracking is at its maximum. This latter result is, at first, rather surprising, but it is explained by the fact that the yield of oil is 10 per cent.

less, owing to the cracking of unstable, unsaturated hydrocarbons with the formation of coke and some lighter saturated oils. This is an extremely interesting result as it indicates that it may be more economical to retort at higher temperatures, the loss in yield of crude oil being, perhaps, counterbalanced by the lower loss in the subsequent refining operations.

These conclusions were further borne out by the behaviour of the resulting oils on distillation. The oil obtained by the low-temperature steam distillation containing 85·4 per cent. of unsaturated, cracked to the greatest extent, yielding 10 per cent. of coke, 2·95 per cent. of gas, and 86·6 per cent. of oil containing only 65 per cent. of unsaturated hydrocarbons.

This work was followed up by an examination of the effect of distillation on various shale oils, from which the following conclusions were drawn: (1) There is a large amount of decomposition during the subsequent distillation of the crude oil, this being least for paraffinous, and most for asphaltic oils. (2) The cracking is most rapid when the still temperature exceeds 320° C. (3) That the once run oils are more stable and suffer relatively little cracking on further distillation. (4) That the decomposition is apparently one of heavy unsaturated compounds, which are unstable at the still temperatures necessary for distillation at atmospheric pressure, without the introduction of steam.

Stewart, "Oil Shales of the Lothians," *Memoir of Geological Survey, Scotland*, pp. 155–157, gives data *re* the character of several crude oils from Scottish shales—

Specific gravity	from 0·864 to 0·909
Setting point	,, 67° F. to 93° F.
Benzine fraction 0·730/0·740 ..	up to 4·65%
Burning oil 0·807/0·812	15·92% to 40·59%
Medium oil 0·840	up to 9·18%
Lubricating oil 0·865/0·885 ..	,, 34·02%
Solid paraffin 114/116° F. ..	about 10% to 15%
Loss in refining	24·55% to 35·94%

It will be noted that the loss in refining is many times greater than that incurred in working up a crude petroleum.

A sample of Kimmeridge shale oil was found to have the following properties :—

Specific gravity	1·009
Sulphur	5·8 per cent.
Viscosity Redwood I. at 70° F.	62 seconds
„ Engler at 20° C. ..	2·2
Paraffin wax	1·2 per cent.
Fraction to 150° C.	Sp. gr. 0·867. Sulphur 7·2 per cent. Saturated hydrocarbons 10 per cent.
Fraction 150° C. to 270° C. ..	Sp. gr. 0·936. Sulphur 4·1 per cent.
Residue 54 per cent.	Sp. gr. 1·060. Sulphur 4·1 per cent. Viscosity Eng. at 20° C. over 200°.

A sample of fuel oil from Scottish shale oil was found to possess the following characters :—

Specific gravity at 15° C. ..	1·009
Sulphur	0·46 per cent.
Calorific value	8347, *i.e.* 15,025 B.Th.Us.
Flash-point	140° F.
Viscosity Redwood I. at 70° F.	37 seconds
Tar acids	30 per cent. by volume.

The low calorific value is to be attributed to the high percentage of tar acids.

It will thus be seen that shale oils differ materially in character from crude petroleums. The presence of large proportions of unsaturated hydrocarbons, renders their refining into commercial products a difficult proposition, as chemical reagents, which might be employed to remove undesirable sulphur compounds, will also attack the unsaturated compounds. Moreover, unsaturated hydrocarbons are unstable, and water-white sweet products made from them are very liable to change on standing. The quality of a shale oil is thus in the present state of our knowledge determined chiefly by its content of unsaturated hydrocarbons. If some process of commercially converting unsaturated into saturated hydrocarbons were only known, the problem of the satisfactory utilization of many shale oils would be much nearer solution. The methods of working up Scottish shale oil are in the main those usually employed in petroleum refining, for which reference may be made to Part VII.

SECTION F.—VARIOUS TARS

UNDER the term "tars" may be grouped a number of products resulting from the distillation of coal, lignite, peat, wood, or other organic material. Such products are described as tars because, in addition to hydrocarbons, they contain large proportions of other bodies such as phenols and nitrogen bases. Moreover, their hydrocarbon constituents are often very different from those normally occurring in petroleum. The chief examples of this class are the tars derived from the carbonization of coal under various conditions, *e.g.* horizontal coal tar, vertical coal tar, low-temperature coal tar, and coke-oven tar, together with tars such as Mond-gas tar and blast-furnace tar. Tars resulting from the distillation of peat, lignite, wood, etc., are of less common occurrence.

As the subjects of the production of tars or liquid fuels from coal, lignite, peat, and wood, have been dealt with in the book of this series of H. S. Taylor on "Fuel Production and Utilization," little need be said here. A description of the methods adopted for the distillation of coal in coke ovens or low-temperature carbonization retorts is quite beyond the scope of this work. The reader may be referred to such works as V. B. Lewes, "The Carbonization of Coal," Benn Brothers. The subject of low-temperature carbonization of coal has received much attention during the last few years, but its successful commercial development has not yet been assured. Apart from the questions of marketing of the solid carbonaceous residues, and the low-temperature tars, the engineering difficulties of designing suitable retorting plant, especially in the case of caking coals, are much greater than those met with in the designing of plant for the distillation of pyrobituminous shales. In character the various tars resulting from the distillation of coals of different types under various conditions are intermediate between ordinary horizontal coal tar on the one hand, and crude petroleum on the other. The character of these tars can best be explained by comparison with these two extreme types.

In general, the character of a coal tar depends on the temperature at which carbonization takes place. The tars derived from horizontal gas-works retorts, which are operated at high temperatures, are rich in aromatic hydrocarbons and practically paraffin free; those from low-temperature carbonization are rich in paraffin, and poor in aromatics. Coke-oven tars, and tars from vertical gas-works retorts are intermediate in character between these two extreme types.

This difference in character is largely due to the secondary reactions which take place in the highly heated horizontal retorts, the paraffin hydrocarbons first formed being cracked into aromatic hydrocarbons, hydrogen, and coke. In consequence of this, high-temperature tars are relatively rich in so-called "free carbon," insoluble in carbon bisulphide, low-temperature tars containing sometimes as little as one per cent.

Low-temperature tars are richer in tar acids, the cresols and higher homologues predominating over phenol.

High-temperature tars contain much naphthalene, low-temperature tars little or none.

The nitrogen of high-temperature tars is largely in the form of pyridin homologues, of low-temperature tars largely in the form of aniline.

The following table indicates the chief points of difference between these tars :—

	Sp.gr.	Per cent. tar acids.	Per cent. free carbon.	Per cent. naphthalin.	Aromatic content.	Per cent. pitch.
Horizontal	1·22	3	20	10–15	rich	65
Coke oven	1·18	5	12	10	│	60–65
Vertical	1·12	7	4	5–10	│	40–50
Low-temp. carbonization	1·10	12	2	0	↓	30–50
Peat	0·99	10	1	0	poor	30

The above figures are approximations only, and may serve merely to indicate the general relations of the various tars. The characters of individual tars of any one class show great variation.

The fundamental difference between such tars as a whole and crude petroleum is indicated also by their elementary analysis. The ratio of the content of carbon to that of hydrogen ranges from 8 to 11 for the tars, whereas, even for heavy petroleum it is not more than 8, and for the lighter as low as 5·5. This relative shortage of hydrogen, together with the presence of oxygen, is the chief cause of the great difference between tars and petroleum oils. Tars of the low-temperature type may yield small percentages of light hydrocarbons suitable for motor use. After these have been removed the residue is only fit for use as liquid fuel, at the present day at any rate.

Such tars serve as reasonable fuels for furnace use. Their calorific powers are, however, relatively low compared to those of petroleum fuels, say 16,000 as compared with 18,000 B.Th.U. Owing to their content of pitch they cannot be blended with a fuel of petroleum origin, owing to the precipitation of the pitch. Such low-temperature tars may also be successfully used as diesel engine fuel. In addition to low-temperature tars made by the direct distillation of coal, other types such as producer-gas tar, which is condensed out of producer gas, blast-furnace tar, condensed out of blast-furnace gases, and Mond-gas tar from Mond-gas producers, are also produced in relatively small quantities. These tars are similar in their general character to low-temperature tars and need not be further described.

In Saxony there exists quite a considerable industry, dependent on rather peculiar types of lignite. These lignites contain a bituminous material which is soluble in solvents, such as benzene, carbon tetrachloride, ether, or acetone. The material so extracted is utilized for the preparation of montan wax, which is described in Part VI. These lignites on distillation yield tars rich in paraffin wax. When raised from the mine these bituminous lignites present a greasy brownish appearance, and dry to a lighter colour, the richest of them, viz. the peculiar material termed "pyropissite" being yellow in colour. This has a specific gravity of about 1·0, whereas ordinary or pyro-bituminous lignites have specific gravities ranging from 1·2 to 1·4.

Various types of retort have been used, the most successful being that devised by Rolle, which works continuously. This retort consists of a cylindrical firebrick structure about 20 feet high and 5 to 6 feet internal diameter. Inside this cylindrical retort is built up a series of bevelled iron rings superimposed one on the other, forming an internal core or cylindrical chamber, the surface of which presents the appearance of louvre boards. The lignite is fed by means of a hopper into the annular space between the central cast-iron chamber and the outer firebrick cylinder. Distillation is effected in this annular space by the heat transmitted through the walls of the outer cylinder, which is heated by flues as in the case of the Scottish type of retort described previously. The vapours liberated pass between the cast-iron rings into the centre of the chamber, whence they pass off by the vapour delivery pipe.

The tars obtained from the distillation of such lignites and from pyropissite in particular (which may yield up to 20 per cent. of tar) are light (the specific gravity varying from 0·8406 to 0·910), and are rich in paraffin wax.

The vast quantities of peat found in various parts of the globe will doubtless one day also serve as a basic material for the manufacture of fuel and other oils.

Up to the present, however, little has been done in this direction except in Germany, the removal of the large percentage of water found in all peats presenting an economic difficulty. The nature of the oil obtained depends on the nature of the peat and on the method of distillation. Peat oils mainly composed of saturated hydrocarbons have been described, also others composed largely of unsaturated.

Peat tars contain tar acids in large quantities, usually also paraffin wax, and yield a useful soft pitch as distillation residue (*Technical Paper*, No. 4, Fuel Research Board).

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PART V.—NATURAL SOLID AND SEMI-SOLID BITUMENS AND ALLIED SUBSTANCES

SECTION A.—OCCURRENCE, CHARACTERS, AND PRODUCTION

NATIVE solid or semi-solid bitumens, pure or associated with varying quantities of mineral matter, are very widely distributed, being found in some form or other in most countries.

The materials included under this head show great variation in character, not only in respect to their admixture with mineral matter, but also in the chemical composition of the bituminous matter.

Asphaltic substances, practically free from mineral matter are found, and also asphaltic rock, which may be a limestone impregnated with quite small quantities of bituminous material. They are found also in strata of all geological ages from the Silurian to the Pleistocene.

Little is yet known of the chemistry of these bodies; they have really only been studied from the point of view of solubility in various solvents, and of physical properties and behaviour when subjected to distillation.

There is little doubt that they are derivatives of petroleum, formed by the removal of the more volatile constituents and by gradual transformation of the non-volatile fractions. There is in many cases definite geological evidence that such transformation has taken place. Their frequent occurrence in veins bears out this view.

In consequence of their mode of formation, types illustrating various stages in the transformation exist; in fact, a definite series ranging from ordinary petroleum residual asphalts such as are made by the concentration of certain crude oils, to bodies like albertite which are so similar in appearance to coal as to have been mistaken for such, may be distinctly traced.

The differentiation of these bodies into definite classes is therefore difficult. However, a rough subdivision into asphalts proper, asphaltites, and asphaltic pyrobitumens may be adopted.

(*a*) **Asphalts Proper.**—These melt below or not far above 100° C. They are more or less equally soluble, and almost entirely so in carbon tetrachloride and carbon bisulphide, and to a large extent also in petroleum spirit of sp. gr. 0·645. Under this heading are included also the artificial residual asphalts resulting from the distillation of asphaltic base crude oils.

(*b*) **Asphaltites.**—These have high melting points, a higher fixed carbon content, are less soluble in carbon tetrachloride, and still less so in petroleum spirit of sp. gr. 0·645.

(*c*) **Asphaltic Pyrobitumens.**—These are infusible and are only slightly soluble in carbon tetrachloride, carbon bisulphide, or petroleum spirit of sp. gr. 0·645.

The **asphalts proper** are by far the most common. They are found often in a relatively pure condition, often in association with mineral matter, and often merely as an impregnating material.

Relatively pure native asphalts have been found in Cuba, France, Greece, Mexico, the Philippine Islands, Siberia, Syria, Venezuela, and in California, Kentucky, and Utah.

Of these deposits one of the largest in the world is that found in Venezuela, known as the Bermudez asphalt lake. This covers an area of over 900 acres, and has an average depth of about 4 feet. It is supplied from various springs from which the asphalt exudes in a semi-liquid condition, gradually hardening as it is exposed to the air. Similar deposits are found on several of the islands in the delta of the Orinoco, and at Maracaibo. The asphalt is practically free from mineral matter, but contains much water. The water, which may amount to as much as 30 per cent., is not emulsified, and is easily separated off by heating. Refined Bermudez asphalt has the following characteristics :—

Fracture	conchoidal
Lustre	very bright
Streak	black
Specific gravity at 25° C.	1·06 to 1·08
Penetration at 25° C.	20 to 30
Ductility	about 11
Melting point (K. and S.)	,, 58° C.
Fixed carbon	13 to 14 per cent.
Solubility in carbon bisulphide	about 95 ,,
Solubility in 0·645 petroleum ether	,, 65 ,,
Volatile matter 7 hours at 163° C.	,, 5 ,,
,, ,, 7 hours at 204° C.	,, 9 ,,

Elementary Analysis—

C	82·9 per cent.
H	10·8 ,,
S	5·9 ,,
N	0·7 ,,

This asphalt contains a considerable percentage of hydrocarbons volatile below 200° C., differing in this respect markedly from the other noted natural asphalt supply, viz. that of Trinidad.

Its soft character is due to the high percentage of malthenes (soluble in 0·645 petroleum spirit).

The Maracaibo asphalt is similar on the whole to the Bermudez product possessing the following characteristics :—

Specific gravity at 25·5° C.	1·062 to 1·078
Penetration at 25° C.	about 25
Soluble in carbon bisulphide	92 to 97 per cent.
Soluble in 0·645 petroleum spirit	46 to 54 ,,
Fixed carbon	15 to 19 ,
Volatile at 163° C., 7 hours	1·5 to 5·3 ,,
Melting point	about 100° C.

Some samples, however, contain considerable quantities of vegetable matter. It differs from Bermudez (and Trinidad) asphalt in having a higher softening point and a lower percentage of malthenes (soluble in 0·645 petroleum spirit).

A similar asphalt lake is known on the east coast of the island of Sakhalin, in Siberia, but this has not yet been exploited.

The pure asphalt deposits of France, Greece, Syria, and the Philippine Islands have not yet received much attention.

Native asphalts associated with varying amounts of mineral matter are also common, many of the deposits being worked commercially. Occurrences have been noted in Algeria, Arabia, Argentine, Austria, Canada, Cuba, France, Germany, Greece, Italy, Japan, Mesopotamia, Mexico, Portugal, Russia, Sicily, Spain, Switzerland, Syria, Trinidad, and in the United States, in California, Indiana, Kentucky, Louisiana, Missouri, Oklahoma, Texas, and Utah.

Of these the Trinidad deposit is the most important. The main deposit occurs in the form of a lake of about 115 acres in extent, estimated to contain over 9,000,000 tons of asphalt. The asphalt is softer in the centre, where it seems to be replenished from underground sources. The consistency is such that it will easily bear the weight of a man, and it may be easily excavated by means of pickaxes in the cool of the day. It consists of an emulsion of asphalt, water, and finely-divided mineral matter. This latter is in such a fine state of subdivision that it does not separate out even after the melted asphalt has been kept standing for many months. The crude asphalt is refined by heating to 160° C. for some time to drive off the water. The dry (so-called refined) product analyses :—

Fracture	conchoidal
Lustre	dull
Streak	black
Specific gravity	1·40 to 1·45
Penetration at 25° C.	about 7
Ductility at 25° C.	about 2

Melting point (K. and S.)	about 87° C.
Mineral matter	„ 40 per cent.
Solubility in carbon bisulphide	„ 55 „
Solubility in 0·645 petroleum ether	„ 34 „

The pure bituminous matter freed from mineral matter analyses :—

Melting point (K. and S.)	about 55° C.
Fixed carbon	„ 12
Soluble in carbon bisulphide	100 per cent.
Soluble in 0·645 petroleum ether	about 60 per cent.

Elementary Analysis—

C	82·3 per cent.
H	10·7 „
S	6·2 „
N	0·8 „

As far back as 1883, 35,000 tons of Trinidad asphalt were imported into the United States, and in 1892 the Bermudez product appeared on the scene.

The production of asphalt in Trinidad amounted to over 74,000 tons in 1918, but in 1913 the amount was over 230,000 tons. Of recent years, however, the production of asphalt from Mexican and other petroleums has advanced with great strides, so that at the present day the actual amount of asphalt from the Trinidad lake, imported into the United States, constitutes less than 5 per cent. of the total consumption of that country (Hubbard, *Chemical Age*, New York, 1921, p. 331).

Many native asphalts are found in Cuba; the deposits are small, but considerable quantities have been exported.

With the exception of the above-mentioned cases, practically all the important natural asphalt deposits take the form of a rock impregnated with varying quantities of asphalt, often not more than 5 to 10 per cent.

The chief deposits worked are found in Ragusa, in Sicily, Seyssel in France, Limmer in Hanover, and Val de Travers in Switzerland.

The Ragusa deposits, which yielded about 100,000 tons per annum, vary in quality, some specimens containing as much as 30 per cent. of asphalt, the usual percentage being, however, about 9. The Seyssel deposits contain about 8 per cent., Val de Travers about 10, and the Limmer about 14 per cent.

These asphalt rocks find application particularly for compressed asphalt pavements. For such work, the mineral constituents should consist, as far as possible, of carbonates of calcium and magnesium. Asphalt rocks containing appreciable quantities of silica do not prove so suitable.

Enormous deposits of an asphalt-impregnated sand, the (wrongly) so-called tar-sands of Athabasca exist in Alberta. The bituminous material from these sands has recently been examined by Krieble and Seyer (*J.A.C.S.*, 1921, p. 1337). They find the asphalt to make up from 7 to 20 per cent. of the sand.

It is soluble in carbon bisulphide ..	100 per cent.
,, ,, petroleum ether ..	86·9 ,,

These deposits have, however, not yet been exploited.

The natural asphalt rocks of the United States, though often used locally, have not found favour in comparison with artificial mastics made from petroleum residual asphalts.

The **asphaltites** fall into three groups: The gilsonites, the glance pitches, and the grahamites, which differ from each other somewhat in fusibility and fixed carbon content, but the line of demarcation is not distinct, intermediate products being found.

Gilsonite or uintaite is found only in the United States, in a belt in the Uinta basin, mostly in Utah, occurring in vertical veins. The largest of these veins is about 18 feet in diameter and several miles in length.

About 30,000 tons of gilsonite per year are produced from this one region. It has the following properties:—

Fracture	conchoidal
Lustre	very bright
Streak	brown
Specific gravity at 25° C.	1·0 to 1·1

Penetration 25° C.	nil
Ductility 25° C.	nil
Melting point (K. and S.)	120 to 180° C.
Fixed carbon	10 to 20 per cent.
Soluble in carbon bisulphide	over 98 ,,
Soluble in 0·645 petroleum ether	40 to 60 ,,
Sulphur	2 ,,

A sample from Syria had the following properties :—

Specific gravity at 15° C.	1·101
Fixed carbon	15 per cent.
Soluble in carbon bisulphide	completely
,, tetrachloride	,,
,, 0·645 petroleum ether	28·7 per cent.
Melting point (K. and S.)	132° C.

The **Glance pitches** have been found in various localities, *e.g.* Mexico, Barbados, Columbia, Egypt, and Palestine. They resemble gilsonite in many respects, but have a higher specific gravity 1·10 to 1·15, a black streak instead of brown, and a higher fixed carbon content ranging from 20 to 30 per cent.

The deposits in Barbados are worked and the product sold under the name of Barbados manjak. This has the following properties :—

Colour	black
Fracture	conchoidal
Lustre	bright
Streak	black
Specific gravity	1·10
Melting point	110° C.
Penetration at 25° C.	0
Soluble in carbon bisulphide	over 99 per cent.
,, 0·645 petroleum spirit	about 27 ,,
Fixed carbon	25 to 30 ,,

The occurrence of glance pitch has recently been noted in Australia (North-east Kimberley) *Times*, October 13, 1921.

The **grahamites** occur in many localities, usually in small quantities, often associated with mineral matter. The chief deposits occur in Jackfork Valley, Oklahoma, in a vein 20 feet thick and 1 mile in length.

Deposits in Colorado, Cuba, and Trinidad are also worked.

They are lustrous or semi-lustrous, black, with a fracture sometimes conchoidal, sometimes hackly, and black streak.

Specific gravity at 25° C., ...	1·15 to 1·50.
Fusing point ranges from 180° to 130° C., but melting does not take place as intumescing occurs on further heating	
Fixed carbon high	up to 55 per cent.
Solubility in carbon bisulphide	over 99 „
„ 0·645 petroleum spirit ..	less than 1 per cent.
Sulphur	variable up to 8 per cent.

A soft variety, known as Trinidad manjak, is also mined extensively. Its properties are somewhat similar to those of Barbados manjak, but its specific gravity is about 1·170, melting point 180° to 230° C., and fixed carbon 31 to 35 per cent.

The **asphaltic pyrobitumens** comprise the elaterites, albertites, wurtzilites, impsonites, and the asphaltic pyrobituminous shales.

These first four classes are sometimes found practically free from mineral impurity. There is little doubt that these substances are derived from crude petroleum and represent the last stages in its transformation. They differ markedly from the previously described asphaltites in their relative insolubility in carbon bisulphide.

Elaterite has been found only at Castleton (Derbyshire), in South Australia, and Siberia (Lake Balkash). It is of scientific interest only.

It has a brown streak, is of indiarubber-like nature, of specific gravity 0·90 to 1·05. It is insoluble in carbon disulphide.

The word elaterite is loosely used in America in place of wurtzilite.

Wurtzilite is found only in Uinta County, Utah, where it occurs in veins, as does gilsonite. These veins are generally less than 3 feet in thickness, but may be a mile or two in length. About 820 tons were produced in 1917.

It is a hard, lustrous substance, with light-brown streak, and conchoidal fracture. It can be cut into thin flakes which are somewhat elastic, rather like mica in this respect.

Specific gravity	1·05 to 1·07
Decomposes before fusing	
Fixed carbon	about 10 per cent.
Soluble in carbon bisulphide	,, ,, ,,
Practically insoluble in carbon tetrachloride and 0·645 petroleum spirits.	
Sulphur	about 5 per cent.

It is an example of a thio-kerite, composed chiefly of kerotenes.

Albertite.—This occurs typically in Albert County, New Brunswick, where it was mined for many years, being falsely regarded as a coal. Its mode of occurrence, however, clearly proves that it is not a coal, as it is found in a fissure or vein cutting across a series of asphaltic pyrobituminous shales. In this particular case there is no doubt that the asphaltic pyrobituminous shales were formed by the impregnation of the shales by the same petroleum which formed the albertite. Both substances, as a matter of fact, yield the same distillation products.

Albertite has the following properties (Abraham) :—

Specific gravity at 25° C.	1·07 to 1·10
Penetration at 25° C.	nil
Ductility	nil
Melting point	intumesces and decomposes
Fixed carbon	25 to 50 per cent.

Solubility in carbon disulphide	slight, 2 to 10 per cent.
,, 0·645 petroleum ether	,, up to 2 per cent.
,, hot pyridin	about 30 per cent.

Elementary Analysis—

C	83·4 to 87·2
H	9·2 to 13·2
S	up to 1·2
N	,, 3·0
O	about 2 per cent.

A variety called **Tasmanite** is found in Tasmania. Other deposits have been noted in Cuba, Oklahoma, Utah, and Mexico.

Impsonite, which is found in Arkansas and Oklahoma, is black and has a semi-dull lustre. Specific gravity at 25° C., 1·125. It is infusible and insoluble in carbon bisulphide, has a high fixed carbon content (up to 80 per cent.).

A variety from Mesopotamia analysed as follows :—

Specific gravity	1·231
Melting point	infusible
Fixed carbon	44·8 per cent.
Solubility in carbon disulphide	10·6 ,,
,, carbon tetrachloride	nil
,, 0·645 petroleum ether	nil
,, pyridin	9·7 ,,

This, apparently the most advanced stage in the transformation of petroleum, differs from the non-asphaltic pyrobitumins (the coals, etc.) chiefly in its low oxygen content.

The **asphaltic pyrobituminous shales** are distinct from the pyrobituminous shales, in that they are really shales impregnated with asphaltic pyrobitumens. It is naturally difficult to differentiate the two types, as the asphaltic pyrobitumens are so slightly soluble in solvents. The percentage of oxygen in the asphaltic pyrobituminous shales is low, being below 2 for wurtzilite shales and less than 3 for albertite shales. For non-asphaltic shales it varies from

3 to 28 (Abrahams, "Asphalts and Allied Substances," p. 159). Moreover, on treating in a closed retort to 300° to 400° C. the asphaltic pyrobituminous shales will depolymerize and become more soluble in carbon bisulphide; the non-asphaltic shales do not do so.

The non-asphaltic pyrobituminous shales have apparently been derived from the decomposition of vegetable matter in a manner similar to that by which coal was formed. These two types of substances, moreover, differ in respect to the products yielded by destructive distillation. The asphalts, asphaltites, and asphaltic pyrobitumens yield usually open chain hydrocarbons, the non-asphaltic pyrobitumens, chiefly cyclic hydrocarbons. The properties of the asphalts, asphaltites, and asphaltic pyrobitumens may be most readily compared by means of the following table :—

	Sp. gr.	M. pt.	Fixed carbon %.	Sol. in 0·645 pet. ether %.	Soluble in CS_2 %.	Sulphur.
Asphalt manufactured from Mexican petroleums ..	1·06	57° C.	14	60	100	5
Trinidad lake asphalt, free from mineral matter ..	1·065	55	12	63	100	7
Gilsonite	1·11	120/180	10/20	40/60	100	2
Glance pitch	1·15	120	25/30	25	100	8
Grahamite	1·3	Intumesce with decomposition.	55	traces	100	8
Wurtzilite	1·06		10	nil	10	5
Albertite	1·1		40	nil	5	1
Impsonite	1·2		80	nil	nil	—

The above figures are approximate only, being given merely for purposes of comparison.

It will be realized from a consideration of the above that the chemical nature of the asphaltites and asphaltic pyrobitumens is very far from being understood. The means of discrimination between the various classes of the series are inadequate and empirical, many intermediate varieties being known. There are however, undoubtedly, grounds for the presumption that these substances are petroleum derivatives and that they form a series representing stages in its transformation.

Richardson (*J. Ind. and Eng. Chem.*, vol. 8, p. 493) gives data from the analyses of a number of gilsonites and grahamites which bear out this view, and demonstrate that the changes which particular types of petroleum undergo in nature depend on the environment.

	Flow-point °F.	Sp. gr.	Per cent. soluble in 0·645 petroleum spirit.	Per cent. fixed carbon.
Gilsonites—				
Utah softest	285	1·011	55·5	10·0
,, ,, ...	—	1·037	46·9	12·3
,, ,, ...	260	—	47·2	12·8
,, ,, ...	345	1·037	46·1	13·9
,, hardest	intumesces	1·057	24·5	16·7
Grahamites—				
Cuba Bahia	intumesces	1·157	38·8	40·0
Trinidad	,,	1·156	14·8	40·0
W. Virginia	,,	1·130	9·4	36·8
Colorado	,,	1·160	0·8	47·4
Oklahoma	,,	1·184	0·4	51·4

The occurrence of a material intermediate in character between asphalt and gilsonite in the central valley of California at Asphalto further confirms this idea.

The development of this extremely interesting question will entail much patient research.

A considerable industry connected with the native asphalts has developed in the United States. In 1919 the production reached 88,281 short tons (Cottrel, "Asphalt and Related Bitumens," "Mineral Resources of the United States," 1919, p. 279). Of this amount 53,589 was rock asphalt, the balance being made up of gilsonite, grahamite, wurtzilite, and impsonite (Hubbard, *Chemical Age*, New York, 1921, p. 331).

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SECTION B.—APPLICATIONS

THE applications of the natural solid and semi-solid bitumens are many and varied. Enormous quantities of the rock asphalts and asphalts proper are used for road-making or paving purposes, smaller quantities of the asphaltites are used for many special purposes, while some of the natural pyrobitumens are little used. Of the mining of these materials little need be said.

The rock asphalts are quarried according to usual methods. They are largely used for surfacing roads which are required to stand very heavy traffic. The broken pieces of rock asphalt as received from the mine, are passed through disintegrators and reduced to a fine powder, which forms the basis of the made-up products. The rock from the quarries may contain various percentages of asphalt and so usually requires blending with either mineral matter or asphalt to obtain a mixture containing the requisite proportion of asphalt. In many cases a powdered rock asphalt rich in asphalt, is blended with one poor in asphalt to obtain the desired result. In other cases the powder is incorporated with petroleum asphalt, heated, cooled, and again disintegrated. The asphalt is first melted in a special mixer and the powdered rock is added and thoroughly incorporated at a temperature of 200° C. It is then run off into moulds arranged on a concrete floor and allowed to cool. The floor and sides of the moulds are previously coated with whiting or other material to prevent the adhering of the asphalt. In some cases coal-tar products, or shale-oil products are used in place of asphalt, but the resulting product is unsatisfactory. This rock asphalt is applied to road surfaces by the compressed powder method. A good concrete foundation is essential. The powder must be laid down on a dry surface in dry weather. The powder is heated to a temperature varying from 100° to 150° C., spread out on the surface of the concrete, raked to the necessary thickness, and then compressed by tamping with heated rammers, the surface being finally smoothed off by heated irons. As a decrease of volume of the heated powder, to the extent of 40 per cent. takes place on compression, allowance for this must be made when laying down the powder.

This method of road-making is to some extent being superseded by rock asphalt tiling. Tiles of about a square foot in area are made in the factory, being subjected to compression in hydraulic presses. A more uniform and denser material is thus assured. The tiles are easily laid, the edges being sealed by dipping in melted asphalt.

A rock asphalt surface stands up very well to heavy vehicular traffic, the constant heavy pressure keeping the material in good condition. The natural asphalts of Trinidad and Bermudez are also largely used for road work. In the case of the Trinidad lake the crude asphalt is obtained by a quarrying process, as the asphalt is sufficiently hard to allow of its being broken up by pickaxes, except in the hottest part of the day. A movable decauville track is laid down on sleepers on the surface of the lake, the surface being sufficiently hard to allow of this temporarily.

The asphalt as mined from the Trinidad lake contains about 50 per cent. of its bulk of water, decayed wood, and vegetable matter. The impure product is heated for some hours in large cauldrons, the temperature being finally raised to 160° C. The vegetable refuse which floats to the top is skimmed off, and the molten asphalt is then drawn off leaving the excess of solid mineral matter at the bottom of the cauldron. The so made "Trinidad epuré" is then, however, far from pure. Such a crude method of refining undoubtedly harms the product, as the portions of the asphalt near the sides of the cauldron must often be overheated. The material is more satisfactorily treated by superheated steam, avoiding the use of direct fires. Trinidad asphalt cannot, however, be purified completely in this way. About 35 per cent. of exceedingly finely divided mineral matter is obstinately retained emulsified in the asphalt. The marketed product always contains this mineral matter. The pure bituminous material could only be obtained by means of extraction by solvents. This is, however, unnecessary as the bulk of the Trinidad asphalt is used for road-making, for which purpose it must in any case be mixed with mineral "fillers." The water and mineral matter associated with Bermudez asphalt separates out much more easily.

By far the most important application of the Trinidad and Bermudez asphalts is that of road-making. For the same purpose, too, the asphalts made from certain crude petroleums, notably those of Mexico, are used to a very great extent, and the application for road-making purposes of both types may well be considered together.

The asphalts made from crude oil possess one great advantage in that they can be made of any desired consistency simply by varying the extent to which the crude oil is concentrated down in the process of manufacture.

The naturally occurring asphalts are more or less of constant composition, too hard for certain classes of work. They therefore require to be "cut-back" or "fluxed" with less viscous oils in order to give products of the required consistency.

The consistency of an asphalt for road-making purposes may be judged by the "penetrometer." This is an instrument which records in tenths of a millimetre the distance to which a standard No. 2 sewing needle, loaded with a weight of 100 grams, will sink into the asphalt at a temperature of 77° F. (25° C.) in five seconds. This is known as the "penetration."

The types of asphalts used for road work have penetrations varying from 40 to 200, according to the class of work. The penetration of Trinidad lake asphalt is only about 7 owing to the high content of mineral matter, that of the Bermudez product being about 25.

Apart from "compressed asphalt paving" as described above, there are, broadly speaking, three systems of road construction involving the use of asphalt.

They are: (1) Asphalt carpet; (2) Asphalt macadam; (3) Grouting or penetration work.

For asphalt carpeting work the asphalt is mixed with definite proportions of sand, stone (or clinkers, etc.) and filler, all carefully graded to specification. The mixture is spread hot on the road and carefully rolled. Such carpets may be laid down on cement or on a previously existing macadam surface.

In many cases two-coat work may be carried out, a sub-coat of 3 inches or more of a coarse asphaltic concrete being laid down and consolidated, a 1½-inch carpet, made of more finely graded material being laid down on top. The material used should be graded so that a voidless matrix may be obtained.

For asphalt macadam work the macadam is heated in a mixer with sufficient asphalt to coat the aggregate completely. The mixture is then carted into position while still warm, laid down and rolled.

For grouting or penetration work an asphalt of softer quality may be used. The aggregate suitably graded is laid down and rolled and the hot asphalt is poured over, or sprayed on by a special machine, at the rate of about 1½ gallons to the square yard. The surface is then lightly covered with dry chippings and the road is then well rolled. A sealing coat of asphalt is then applied and a final dressing of chippings. Dryness is essential to the making of a good asphalt road.

As a road binder petroleum asphalt is superior to coal tar in many respects. For example, coal tar contains water soluble constituents, also volatile constituents such as naphthalene. Moreover, it is difficult to obtain coal tar of uniform composition, and the gradual introduction of vertical retorts and of carbonization at lower temperatures is bringing about the production of tars less suitable for road work than those produced by carbonization in horizontal retorts.

The subject of road-making is, however, beyond the scope of this work, so for further details the reader must be referred to any of the many books now published dealing with this subject.

The other uses of natural asphalts will be described in the section dealing with petroleum asphalts.

The natural asphaltites which occur in veins are generally mined by crude methods. The largest known vein of grahamite, namely that at Jackford Creek, in Oklahoma, where the asphaltite fills a fault in sandstone, is mined by means of inclined shafts, in a manner similar to that used in Scotland for shales.

The natural asphaltites are often employed just as mined. Should, however, they be mixed with adhering mineral matter, they may be refined by merely melting off.

Gilsonite is used principally in the manufacture of paints, japans, and varnishes. Its value in this respect is enhanced by the fact that it is easily miscible with fatty acid pitches (grahamite is not).

Such bituminous paints are made from a variety of substances such as natural asphaltites, petroleum asphalts, blown asphalts, various tars and pitches, montan wax, fatty oils and acids, and various resins, together with various mineral fillers, incorporated with various solvents such as benzine, kerosene, turpentine, resin oils, coal-tar products, carbon tetrachloride, alcohols, acetones, etc. Gilsonite is also largely used in the rubber industry for incorporation into motor-car tyres, as a vulcanized mixture of rubber and gilsonite is much more resistant to oxidation and changes of temperature than is rubber alone.

Grahamite is also used in the manufacture of varnishes, rubber substitutes, insulating material, as is also manjak.

Wurtzilite is used for the manufacture of the so-called wurtzilite asphalt or pitch, commercially known as "kapak." This is made by heating wurtzilite to about 300° C. under pressure. Decomposition sets in and oils are evolved which are condensed and returned to the vessel. The mass is thus converted into a fusible substance differing from the original wurtzilite in being soluble in carbon bisulphide and 0·645 petroleum spirit. This kapak is used for manufacture of varnishes, insulating material, and for weatherproof coatings, etc.

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Tillson, "Street Pavements and Paving Materials." J. Wiley and Son.

PART VI.—THE NATURAL MINERAL WAXES

UNDER this heading may be described the two substances ozokerite and montan wax, the former of which is found native, the latter extracted from certain lignites by a solvent. These two substances differ fundamentally in character, both from each other and from the asphaltic substances dealt with in the last part.

Ozokerite is a naturally occurring hydrocarbon substance. It is known also as mineral wax, rock tallow, mineral adipocere, citricite (in Moldavia), nestegil (Caspian area), and baikerite (Siberia).

It is composed of hydrocarbons of higher melting point than those constituting the paraffin waxes. It is usually found associated with petroleum and often contains an admixture of paraffin wax, in which cases the melting point is lower. Such mixtures, intermediate in character between pure ozokerite and paraffin wax, are known as "kindebal."

It is usually found in fissures or veins, irregular in character. It has in all probability entered these veins from below, and is a derivative of paraffinaceous petroleum. A product known as rod-wax, often found clogging up the pumps in paraffin wax-base oil wells, is similar to ozokerite in nature.

It is found chiefly in Galicia, the largest deposits being in the Boryslaw area; also in Moldavia (Rumania), and in Cheleken in the Caspian Sea (*Petroleum World*, 1917, p. 136).

In the United States it has been found in Utah (Higgins, *Salt Lake Min. Rev.*, 1916, p. 17). It is a waxy substance varying in colour from yellow through brown to black, according to the impurities present. It varies in consistency, sometimes having a conchoidal fracture, sometimes being quite soft. Its specific gravity varies from 0·85 to 1·00, melting point from 60 to 90° C. Its fixed carbon value ranges up to 10 per cent. If pure it is completely soluble in carbon bisulphide and in 0·645 petroleum ether. The elementary analysis of the purified hydrocarbon product is C. 85 per cent., H. 15 per cent. It can be distilled in high vacuum without decomposition, but at ordinary pressures it decomposes yielding oils, paraffin wax, and an asphaltic residue. The total output does not amount to more than a few hundred tons per year.

Ozokerit is mined by the normal methods applicable to any such substance, a mixture of ozokerit and gangue or associated mineral contamination being raised to the surface. The mixture is then separated by hand picking. Those portions which consist of lumps of rock with small quantities of ozokerit adhering or enclosed are boiled up with water, and the wax which rises to the surface is separated off.

The wax so obtained, together with the picked wax, is then melted, care being taken to keep the temperature as low as possible, the molten wax free from mineral impurities being drawn off from the surface and cast into moulds.

Ozokerit is usually refined, the resulting product being termed **Ceresin.**

The dried and melted ozokerit is heated with a few per cent. of fuming sulphuric acid, with adequate mixing, at a temperature of about 120° C., the process being repeated as often as necessary in order to obtain a colourless product, a considerable quantity of acid tar being formed. Alternately, instead of allowing the acid tar to settle, the whole mass is heated up to from 160° to 200° C. An energetic oxidation sets in, with copious evolution of sulphur dioxide. The temperature is maintained at 200° C. until all the free acid has been expelled. If a little free acid still remain this may be neutralized by an alkaline fuller's-earth added in the air-dry condition to the ceresin at a temperature of about 150° C. After settling the wax is drawn off and treated with a decolorizing powder, the carbonaceous residue from the manufacture of ferrocyanides being usually used. Separation of the wax from the decolorizing powder is effected by filter pressing.

The refined ozokerit or ceresin is amorphous in character, resembling beeswax in character. Its specific gravity is about 0·920. Melting point 60 to 90° C. Owing to its high melting point and its miscibility with vegetable and animal fats and oils it is a valuable product, commanding a much higher price than does paraffin wax, with which it is consequently often adulterated. The question of the identification of paraffin wax in ceresin is therefore of importance.

As mixtures of ceresin and paraffin have no well-defined melting point, a series of fractions may be obtained by carefully cooling the mixture. The examination of the melting points of these fractions will disclose the presence of paraffin (Berlinerblau, "Das Erdwachs," 1897, p. 195). The other adulterants, *e.g.* saponifiable fats, resins, etc., are more easily detected, as the determination of the saponification value will at once indicate their presence. For details of these methods reference should be made to one of the standard works such as Holde, "Examination of Hydrocarbon Oils, etc."

Ceresin is largely used for making candles, its hardness and high melting point rendering it superior to paraffin in this respect. It is largely used in the manufacture of polishes, waterproofing, and insulating materials, of sealing waxes, leather-treating greases, and so forth; also as a basis for pomades and ointments, and for modelling waxes, gramophone records, and many such kindred uses.

Montan Wax.—A product of an entirely different nature which may be described here is that known as "Montan wax." This interesting substance is obtained from certain Thuringian and Bohemian lignites, and the peculiar lignite known as pyropissite. These lignites by extraction with solvents such as benzol yield montan wax; on distillation in the usual manner they yield oils rich in paraffin wax (p. 127). Pyropissite as brought to the surface is a lightish yellow, earthy-looking substance, containing much water, which, however, readily dries off on exposure to the air. Supplies of this mineral are now however rapidly nearing exhaustion.

If pyropissite be extracted with various solvents a bituminous product similar to ozokerite in appearance is obtained, the nature dependent to some extent on the solvent used. This bituminous product, however, is very difficult to refine to a white product, except by using more than an equal weight of oleum, followed by decolorizing powder and subsequent extraction of the mass by benzine. Boyen found that this bituminous product could be distilled with steam, yielding a pale yellowish, crystalline body with a high melting point (over 70° C.). This method forms the basis of the manufacturing process now adopted. The raw bituminous material which is the starting point for the manufacture of montan wax, is obtained from the lignite either by extraction or by distillation in presence of much superheated steam in cylindrical retorts. The distillate so obtained differs from the distillate obtained by distilling at higher temperatures with less steam, the latter containing much paraffin wax.

This bituminous product, or the product obtained by extraction of the liquid with benzol, is then subjected to several distillations in vacuo with the aid of superheated steam. The mineral wax so obtained is subsequently refined in a normal way, by treating it in benzol solution with decolorizing powders, the benzol being subsequently distilled off. The montan wax so obtained is a faintly yellow-tinted, hard crystalline substance, somewhat like stearin in appearance, possessing a faint, pleasant, aromatic odour. The specific gravity varies from 0·9 to 1·0; the melting point from 80° to 90° C. It contains 82 to 83·5 per cent. carbon, 14 to 14·5 per cent. hydrogen, 3 to 6 per cent. oxygen, and traces of sulphur and nitrogen (Marcusson, *Chem. Rev. Fett-Harz. Ind.*, 1908, p. 143).

Montan wax differs fundamentally from paraffin wax in that it is composed of a mixture of an acid (montanic) of high molecular weight, with esters of an alcohol of high molecular weight. This montanic acid has a melting point of 83° to 84° C. Tetracosanol, ceryl alcohol, and myricyl alcohol have been identified in montan wax by Pschorr and Pfaff (*Ber.*, 1920, p. 2147). Montan wax is used in admixture with paraffin wax for candle-making, in making substitutes for the valuable carnauba wax, for insulating materials, polishes, and many other such purposes. Owing to its high melting point as compared with paraffin wax, it commands a higher price.

GENERAL REFERENCES TO PART VI.

Berlinerblau, " Das Erdwachs." Vieweg und Sohn.
Graefe, " Braunkohlenteer Industrie." Halle.
Gregorius, " Mineral Waxes." Scott, Greenwood and Co.

PART VII.—THE WORKING UP OF CRUDE OILS

SECTION A.—DISTILLATION OF CRUDE OIL

IN few cases only does crude petroleum issue from the wells in a condition ready for marketing, the content of volatile fractions, which may be low, being usually sufficient to cause the flash-point of the crude to be below 150° F., the value usually accepted as the low limit for commercial fuel. Certain heavy crudes have, however, flash-points higher than this figure, and such crudes may be marketed directly as liquid fuels, provided that they are free from admixed water and have not too high setting points or viscosities.

In the majority of cases, however, crude oils require treatment in order to remove volatile constituents, valuable lubricating oil or wax fractions, or asphalt, as the case may be.

The actual detailed treatment necessary for any particular crude will depend on (*a*) the nature of the crude, (*b*) the market value and cost of extraction of the various products it contains.

The method of general application for the working up of crude oils is that of distillation under various conditions, refrigeration, filtration, and chemical treatment being also applied for certain purposes. As crude oils are composed of a complex mixture of substances of varying boiling points, a rough separation only into fractions of narrower boiling point ranges may be effected by simple distillation.

Distillation may be carried out in various ways, in many different types of plant and with very varying results.

The methods usually adopted may be divided into—

(1) Distillation at atmospheric pressure.
(2) ,, under vacuum.
(3) ,, under pressure.

It is superfluous to explain here that the boiling point of a liquid depends on the pressure. As the constituents of petroleum of relatively high boiling points are unstable at high temperatures, *i.e.* begin to "crack" or split up into hydrocarbons of lower molecular weight, usually with separation of carbon and sometimes hydrogen, the method of distillation employed will be that which enables the boiling points to be lowered or raised according as cracking is to be avoided or effected. For example, the distillation of lubricating oils, in which case the presence of cracked products is undesirable, may be conducted under vacuum, whereas when the production of cracked products, as motor spirits, is desired, distillation under pressure may be employed. On account of its relative simplicity, distillation under atmospheric pressure is, as far as possible, the usual practice. This is usually, however, modified by the introduction of live steam into the oil during distillation, a method which to some extent gives the advantages of distillation under reduced pressure, owing to the lowering of the partial pressure of the oil by the admixture with steam.

Distillation with steam consequently yields distillates of higher flash-point, of better colour, and of higher viscosity than does the so-called dry distillation of the same oil.

Further, in the case of distilling a paraffin wax crude oil, fractions of higher melting point, but less easily crystallizable, are obtained than when distilling without steam. The subject of fractional distillation is fully treated in Young's book, "Fractional Distillation," Macmillan and Co.

Methods of distillation may be further classified under two main headings: (*a*) periodic, and (*b*) continuous.

Periodic methods were naturally those first employed. They are still largely employed for certain purposes, particularly where the residue requires to be brought carefully to a certain specification, and, of course, in those cases where the residue is a solid coke. Continuous methods offer many advantages which will be discussed later and are now in general use.

Periodic Distillation of Crude Oil at Atmospheric Pressure.—Periodic distillation at ordinary pressures is usually carried out in steel stills of cylindrical shape.

These stills may be of large capacity, usually of from 30 to 50 tons, but often much larger. They are constructed of steel plates riveted together, the bottoms, when possible, being made of one piece.

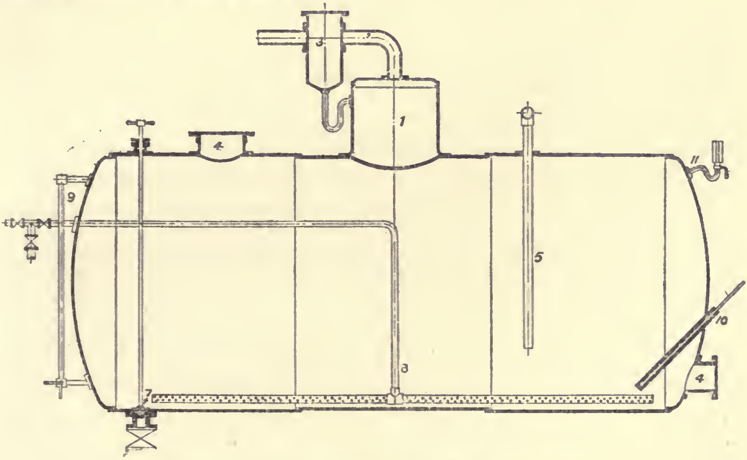

FIG. 17.—Diagrammatic view of crude oil still.

Each still is provided with the following fittings :—

1. One or more domes, to which are connected
2. The vapour line.
3. A trap in the vapour line to return to the still any spray of oil mechanically carried over.
4. One or more manholes,
5. A filling pipe.
6. A draw-off pipe, with
7. Internal valve.
8. A perforated steam pipe.
9. Gauge glasses.
10. Thermometer.
11. Vacuum and pressure gauge.

Large stills, particularly those used for lubricating oil and asphalt manufacture, are fitted with two or three domes. The vapour line is usually 6 or 8 inches diameter for small stills, but of 12 or 15 inches, or larger for the larger sizes. The trap in the vapour line, an important item too often omitted, may be fitted with perforated baffle plates. The effect of this in retaining and returning to the still particles of black oil mechanically carried over is very marked. Without it distillates of poorer colour are obtained.

The draw-off pipe should always be made of cast steel. One or more perforated pipes for the introduction of live steam are distributed over the bottom of the still, placed an inch or so above the bottom, with the perforations pointing downwards and outwards. One or more gauge glasses should be fitted, which should preferably be placed a little distance from the still. Sample cocks may also be fitted and are sometimes used instead of gauge glasses. Floats of various designs are also often employed to indicate the level of the oil in the still. Some form of thermometer is a very necessary adjunct.

Stills are often fitted with internal fire tubes, just as are Cornish boilers, the heating surface being thus considerably increased. Such fire tubes are usually placed a little to one side of the vertical diameter of the still, in order to assist in the circulation of the oil, but such fire-tube stills cannot be used for periodic work, as the reduction in volume of the crude would cause the level to fall below the top of the fire tube. Stills of elliptical cross section are also sometimes employed. The type and dimensions of the still to be employed depends to a large extent on the nature of the work which it is called upon to do. Obviously a still constructed to stand the conditions necessary for the distilling off of volatile fractions, will not stand up to the heavy work of distilling down to a solid residual coke. Stills for work of this type must be specially constructed with heavy riveting, with bottoms made of as few plates as possible, preferably a single plate if the size of the still allows it.

The still is mounted in a brickwork setting with a slight fall (an inch or two) towards the draw-off end. The setting is usually arranged so that the furnace gases after passing along the bottom of the still return along the sides. Dampers are arranged so that, as the volume of the oil in the still diminishes, the side flues can be cut out and the furnace gases passed directly to the chimney. One square metre of heating surface is usually allowed for one ton of distillate per 24 hours.

The vapour pipe leads, in the simplest types of plant, direct to the coolers, but as a general rule some form of fractional condensing plant is interposed. The coolers or condensers consist essentially of a system of pipes cooled by water in which the vapours are condensed and cooled. The question of design of condensers depend upon various factors, such as the availability of water supply, and whether this is fresh or salt, the presence or otherwise of corrosive vapours in the oil distillates, and the question of economy and conservation of heat. The obvious method of effecting this is the use of crude oil as a condensing agent instead of water. This modification is often employed in continuous plant, but as its application to periodic plant is not so simple, water condensing is usually adopted.

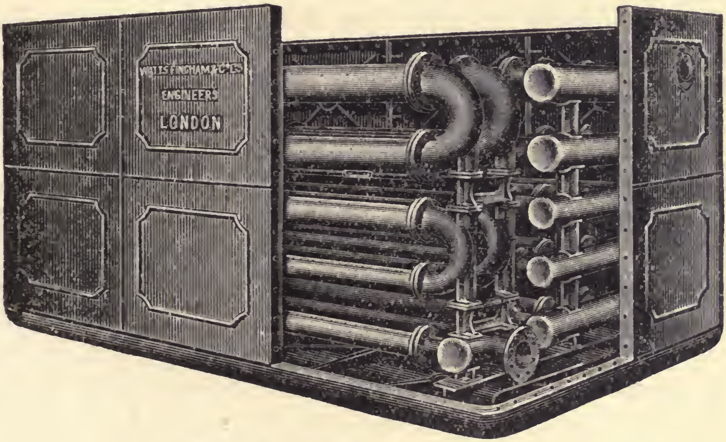

FIG. 18.—Cast-iron box condenser.

The simplest form of condenser consists of a series of cast-iron pipes of diminishing diameter, placed in a cast-iron box (Fig. 18). The vapours enter at the top and descend, issuing at the bottom as condensed distillate.

It is usual to attach a gas vent to the outflow pipe in order to allow any uncondensed gases to escape.

The condensing surface necessary depends on many conditions, the thickness of the tubes, temperature of the distillate to be condensed, condensing water, and so forth. As the efficiency of the condenser depends largely on the degree of cleanliness of the surfaces of the pipes, it is well to allow ample margin. For light distillates a cooling surface of 70 square metres per ton of distillate per hour is usually considered ample.

It must, however, be borne in mind that relatively large quantities of steam are employed, and must be condensed during the distilling over of the higher boiling-point fractions, so allowance must be made for the condenser to deal with this, although in the case of fractions which are not volatile, cooling of the distillates to atmospheric temperature is not necessary.

Many other forms of condenser are employed in the petroleum industry, the steel tubular type, similar to the boiler of a locomotive engine being very common. A recent innovation of very high efficiency is the multiwhorl cooler. In this form the vapours are condensed in a nest of parallel tubes placed vertically, round which the ascending stream of water (or crude oil) is made to ascend spirally by suitable baffle plates. The heat exchange is consequently very good and the efficiency high. The description of the many forms of condenser in use is, however, beyond the scope of this book.

When crude oil is distilled on the periodic system, the following method of working is adopted. The crude oil is filled into the still (to about two-thirds full), which is then gradually heated. A volatile crude will even begin to distil before its temperature rises to 100° C. In the case of crude oils which are thick and heavy and contain water, much care must be exercised to avoid the contents of the still foaming over when 100° C. is passed. Such crudes are, however, best distilled by one of the continuous methods described later.

The temperature of the crude oil is gradually raised up to about 125° C., and then small quantities of steam (preferably superheated) are admitted by means of the perforated steam coil. The rate of distillation will be at once increased, and will continue at temperatures as much as 50 degrees lower than if no steam were admitted. When the specific gravity of the distillate reaches a certain figure, which depends on the nature of the crude, and which has been determined by laboratory tests, a cut is made, *i.e.* the distillate is run into another receiving tank.

The first fraction taken may in some cases yield a product of boiling-point range (when examined in an Engler flask) suitable for benzine or motor spirit, a product boiling up to say 220° C. The next distillates will be a mixture of benzine and kerosene, the point at which the cut is made depending again on laboratory tests. A point will then be reached when the boiling-point range and flash-point of the fraction allows this to go into the kerosene fraction, and the distillation will be continued until the colour or boiling points of the fractions indicate the necessity of a change.

The next fraction will, in most cases, be a gas oil, but the higher fractions will depend on the nature of the crude. At this point the distillation is often stopped, as the residue in the still is considerably reduced in bulk. This residue is run off through a cooler into a separate tank or, better, filled direct hot into another still for further distillation.

In the case of a paraffin-wax-containing crude, the further distillation carried out with ample supply of steam will yield wax distillates. When the wax distillates (which contain lubricating oil) have been distilled off, the residue may be, in the case of certain crudes, *e.g.* those of Pennsylvania, a steam-refined cylinder oil. In other cases a wax-free residue is not obtained, so that the distillation may be carried on further, yielding wax tailings and eventually petroleum coke.

In the case of asphaltic oils the distillation may be carried on so as to give lubricating oil distillates and a residual asphalt of varying properties according to requirements. Such a periodic distillation of crude oil may also be carried out without the introduction of steam. In this case the distilling temperatures are higher and a certain amount of decomposition or cracking takes place, resulting in a higher yield of benzine and kerosene fractions. When crude oils are distilled down to asphalt of a particular specification, ample steam is used to avoid cracking as far as possible, but when they are distilled down to coke, steam is not employed, so that the distillates obtained may be thin and relatively volatile oils.

A distillation carried out in a simple plant, as above described, is naturally far from complete. Well-defined fractions cannot be obtained; for example, no clear cut between benzine and kerosene can be made, a large intermediate fraction being obtained. The larger these intermediate fractions, the more redistillation is necessary.

In order to diminish the yield of such intermediate fractions, fractional condensers, towers, or dephlegmators as they are often incorrectly termed, are introduced into the vapour line before the condensers. These fractional condensers behave to some extent as fractionating columns.

It would be difficult to fit an efficient form of fractionating column to a periodic crude oil still, owing to the large range of distillates to be handled in one run. These towers or dephlegmators are of more simple construction, but do considerably improve the separation of the fractions and obviate the necessity for much redistillation.

In some cases a series of vertical pipes, the bottom bends of which are connected to run off pipes passing through a cooler are used. As the vapours pass through these pipes, the higher boiling portions condense first, so a series of condensates of increasing volatility are drawn off from the successive vertical pipes. A similar series of large diameter pipes laid horizontally is also used in lubricating-oil distilling plants.

Other types, consisting of vertical cylindrical vessels fitted with various forms of baffle plates and sometimes with water-cooling coils, are often employed.

An example from actual practice will illustrate the effectiveness of such an arrangement. A still fitted with two cylindrical dephlegmators, each containing a series of baffle plates arranged alternately and fitted with a small water coil, yielded three separate condensates, one running from the bottom of each dephlegmator, the third running from the end of the main condenser. Samples of these three condensates taken simultaneously gave the following results on distillation in a standard Engler flask :—

Fraction from	Sp. gr. @ 15°C.	Percentage boiling up to				
		200° C.	225° C.	250° C.	275° C.	300° C.
Dephlegmator I	0·836	—	—	5	21	52
,, II	0·830	—	5	18	47	80
Main condenser	0·816	7	24	57	80	94

These three condensates show considerable difference in properties ; that from the main condenser could just go into kerosene distillate direct, the other two could not ; that from dephlegmator II would be worth redistilling for kerosene ; that from dephlegmator I might not. If all three had been collected together, the whole fraction would have required redistillation.

A type of tower largely used in the United States (Fig. 19) is made up of three or more sections, each consisting of a series of tubes A expanded into tube plates, exposed to atmospheric cooling ; between each nest of tubes is a closed chamber which contains a trough B which collects the condensates from the tubes and delivers them to coolers outside the tower. The vapours rise through the tower and partially condense, yielding several condensates of necessarily increasing volatility as the vapours pass through the system, which often consists of several such towers in series. The uncondensed vapours from the top of the last tower pass on to a water-cooled condenser.

The condensates from the towers may, if necessary, be led back to the still. This is usual when distilling certain types of oil, when cracking is necessary.

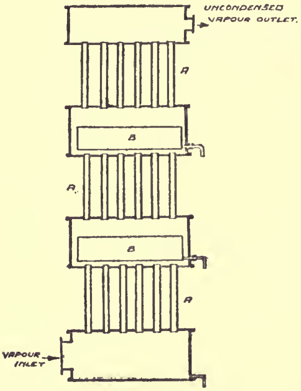

FIG. 19.—Fractionating tower.

The actual method of distilling a crude oil depends to such an extent on the nature of the crude and of the products desired, that any detailed description for a particular crude would be of little value. The method of distillation settled upon must be decided by careful laboratory analyses of the fractions obtained. Consideration of the boiling-point ranges, specific gravities, flash-points, cold tests, viscosities and colours of the distillates will determine their distribution into various fractions. The distillates after cooling are led by separate pipes to the "tail- or separating-house," where they are collected in separate compartments of a special tail-box, or run by means of adjusting valves in a manifold to separate tanks.

The actual control in the tail-house is usually effected by the determination of the specific gravity of the distillate, laboratory determinations having previously indicated the properties of the fractions of particular specific gravities.

It will be readily understood that the process of periodic distillation as above described cannot be the most economic possible. The plant is not fully occupied, as time is lost in filling and emptying the still. Much heat is also lost in alternately heating and cooling the brickwork setting, a process which does not tend to increase its life. The waste heat of the hot residue cannot be easily utilized owing to its intermittent production; moreover, one single plant cannot be well designed to handle such different distillates as light benzine and heavy gas oil or wax distillate. These and other considerations have brought about the development of—

Continuous Systems for Distillation.—Continuous plants can, in the majority of cases, do the work of periodic plants in a more efficient manner.

In addition to the considerations mentioned above, the following advantages are derived. The general wear and tear on the plant is much less as each section works at a uniform, instead of a varying, temperature. The capital expenditure for a given throughput is much less as fewer stills are required; the fuel consumption is less and operating wages are lower. Moreover, a continuous system lends itself much more easily to economical utilization of the latent heat of condensation of the vapours and the specific heat of the residues.

A simple continuous distillation plant consists of a number of stills, usually from five to twelve, arranged cascade fashion in a bench or battery, with a difference of level of from six inches to a foot between successive stills, each still being fitted with condensing arrangements. The crude oil is admitted to the first still, whence it flows into the second, thence to the third and so on through the whole series, losing a certain percentage of distillate at each still, and eventually issuing as residue from the last.

The arrangement of piping is simple, as will be seen from the diagram (Fig. 20).

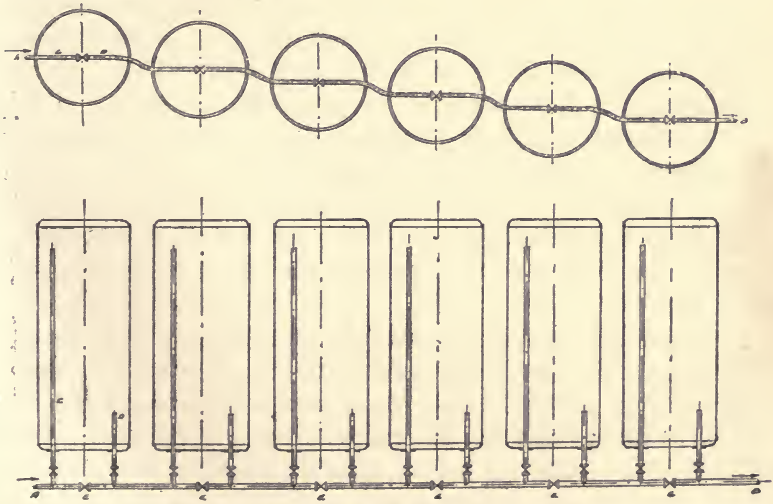

FIG. 20.—Arrangement of continuous stills.

The crude oil enters the bench at A, flows into the first still by the inlet pipe C, extending to the far end of the still, flows out by the outlet pipe D into the next still, and so on. The residue finally flows out at B. Each still is provided with a by-pass valve E, so that any one still can be cut out of the bench for cleaning or repairs. Each still is fitted with its separate condenser, and in the better plants, one or more "dephlegmators" or fractional condensers are fitted in the vapour lines, so that from each still several separate distillates may be obtained.

The system is regulated so that each still is kept at a constant temperature and yields a vapour of constant composition, giving a distillate (or series of distillates) of constant composition.

The working temperature for each still depends upon the number of stills in the bench, and on the nature of the crude, as it must be arranged that each still does approximately the same amount of work.

The table on next page shows the Engler distillation tests of a series of distillates from a continuous bench and illustrates how these distillates vary in composition, and how they may be grouped together. In this case each still was fitted with two dephlegmators or air condensers, each of which yielded a distillate, while a third distillate, which passed through the dephlegmators without condensation, was condensed in a separate condenser. These three distillates are designated D1, D2, D3 respectively.

Distillate 1D2, 1D3, 2D2, 2D3 could be collected together as "straight-run benzine distillate"; 2D1, 3D1, 3D2, 3D3, 4D2, 4D3, 5D3 together as "benzine-kerosene distillate for redistillation"; 6D1, 7D2, and perhaps 8D3, might be collected for redistillation into kerosene and gas oil.

In continuous systems of distillation use may be made of the heat of the outflowing residue, the temperature of which may be over 300° C. This residue must in any case be cooled, so its available heat can be economically used for preheating the ingoing crude oil before entering the first still of the bench. This is effected by means of "heat exchangers," many types of which are in use. The most efficient type is the tubular. This is constructed like a tubular condenser, but is usually placed in a horizontal position (Fig. 21, p. 166).

Still no.	Distillate.	Sp. gr. @ 15° C.	Percentage of distillate boiling up to					
			100° C.	150° C.	200° C.	250° C.	300° C.	Flash pt.
1	D1	—	—	no condensation				—
	D2	0·732	30	90	all	—	—	ord. temp.
	D3	0·726	48	93	all	—	—	,, ,,
2	D1	0·770	1	54	93	all	—	,, ,,
	D2	0·765	12	65	97	all	—	,, ,,
	D3	0·750	20	75	all	—	—	,, ,,
3	D1	0·785	—	35	80	all	—	,, ,,
	D2	0·777	—	48	88	all	—	,, ,,
	D3	0·765	5	58	95	all	—	,, ,,
4	D1	0·815	—	3	50	79	all	40° C.
	D2	0·807	—	10	65	92	all	30° C.
	D3	0·785	1	30	75	all	—	ord. temp.
5	D1	0·825	—	—	32	70	97	42° C.
	D2	0·816	—	3	50	80	all	35° C.
	D3	0·800	—	15	70	90	all	30° C.
6	D1	0·840	—	—	8	38	85	46° C.
	D2	0·831	—	—	20	50	93	43° C.
	D3	0·818	—	1	42	75	98	37° C.
7	D1	0·854	—	—	—	10	60	—
	D2	0·844	—	—	1	30	82	—
	D3	0·829	—	—	20	48	90	—
8	D1	0·866	—	contains wax			—	—
	D2	0·855	—	,,	,,	,,	—	—
	D3	0·847	—	—	—	12	65	—

The cold crude oil enters at C, and after being heated by the hot residue flowing counter-current from A to B, emerges hot at D. In the case of crude oils which contain a large percentage of residue, the quantity of heat disengaged may be so great as to allow even of a little distillation taking place in the heat exchanger, which may then be fitted with a dome vapour pipe and condenser, and thus function as a still.

Although such a continuous bench is an undoubted improvement on a battery of periodic stills, it is, however, far from efficient, the efficiency indeed rarely exceeding 35 or 40 per cent. This efficiency can, however, be improved in various ways, *e.g.* by utilizing the latent heat of the vapours for heating and even partly distilling the incoming crude, and by inserting heat exchangers or economizers in the flue gases. Many modern continuous benches are fitted with a series of distillate preheaters (Fig. 22). These preheaters are practically stills heated by internally placed coils through

Fig. 21.—Tubular heat exchanger.

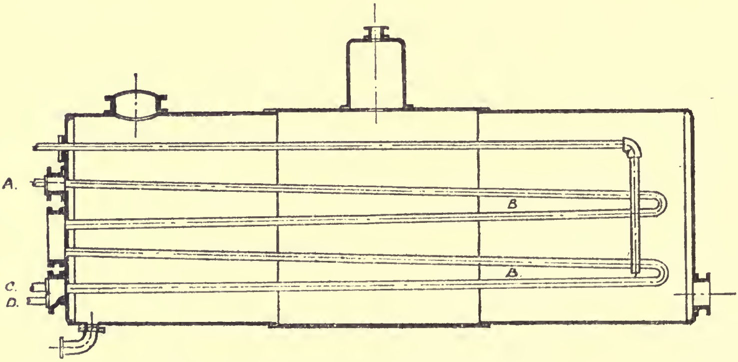

Fig. 22.—Distillate-crude oil preheater.

which the vapours from the main stills are passed, these vapours being therein completely or partially condensed.

The vapours from the main stills enter the distillate preheater at A and are partially condensed in passing through the nests of tubes B, thereby heating the contents of the preheater. The condensed vapours pass off by the lower pipe D to their coolers, the vapours which have escaped condensation passing on by the pipe C to further water-cooled condensers. Each preheater is connected up with inlet and outlet pipes just as is a continuous still.

Figure 23 illustrates the principle of such an arrangement.

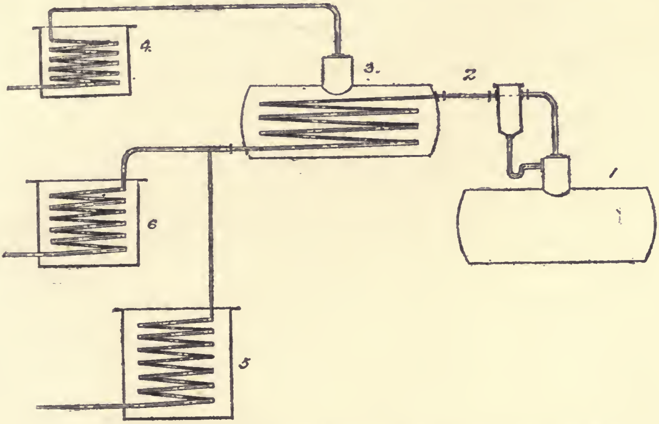

FIG. 23.—Arrangement of still fitted with distillate preheater.

1 is the main still; 2, the main vapour pipe; 3, the distillate preheater in which the crude is heated and to some extent distilled by the latent heat of the condensing vapours; 4, the condenser for the distillates given off from this distillate preheater; 5, the cooler for the condensed vapours which issue from the heating coil of the distillate preheater; and 6, the condenser for the vapours which escape condensation in that heating coil.

From every set of main stills and distillate preheaters, therefore, three distinct distillates may be obtained.

The following table will give some idea of the manner in which the distillate preheaters function:—

	Sp. gr. @ 15° C.	Per cent. distilling in Engler flask up to			
		100° C.	150° C.	200° C.	250° C.
Portion of the distillate from a main still condensing the distillate preheater	0·804	—	—	57	92
Portion of same distillate escaping condensation in the distillate preheater, but condensed in water-cooled condenser	0·783	—	51	95	all
Vapour distilled off from the distillate preheater	0·698	76	97	all	—

In a complete plant arranged on this system (Fig. 24) the crude oil enters the residue heat exchanger D, where it is heated up by the outgoing residue to such a temperature that it may even begin to distil the vapours condensing in condenser C 11. The temperature to which the crude oil will be heated depends naturally on the percentage of residue from the crude, and this may vary between very wide

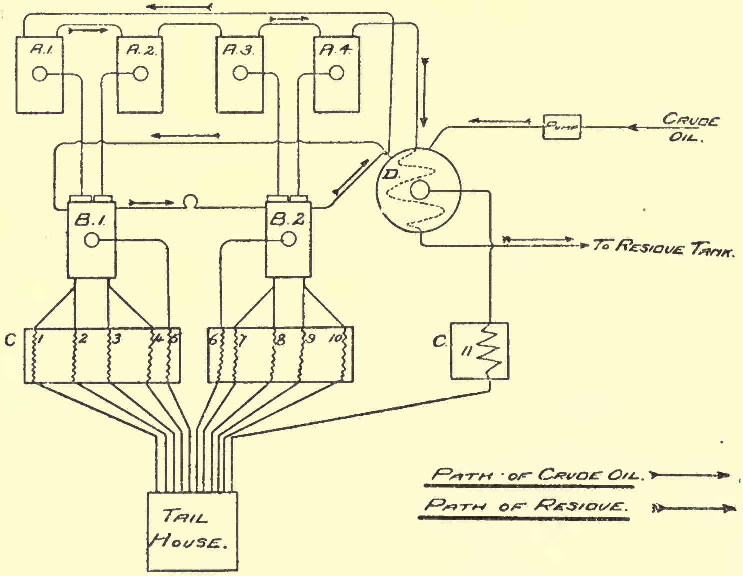

FIG. 24.—Arrangement of continuous bench with preheaters.

limits for various crudes. The crude oil then passes through the distillate preheaters B 1, B 2 in succession, and then through the main stills, A 1—4, finally issuing as residue from the last still. The preheaters and also the stills are arranged in cascade fashion, the former naturally at a higher level so as to allow the crude oil to flow by gravity through the series.

In the above diagram,

A 1—4 represent the main stills.

B 1—2 two double distillate preheaters, each containing two separate sets of coils.

C 1, C 4, C 7, C 10 coolers for the portions of main still vapours condensed in the preheaters.

C 2, C 3, C 8, C 9 condensers for the portions of main still vapours which escape condensation in the preheaters.

C 5, C 6 condensers for the vapours from the preheaters.

C 11 condenser for vapour from residue heat exchanger.

D residue crude oil heat exchanger.

With such an arrangement very great fuel economy is effected.

As a general rule the complete distillation of a crude oil is effected in two stages. In the first stage the lighter fractions, benzine and kerosene distillates, and perhaps a little gas oil are distilled off. In certain cases no further distillation of the crude is necessary, the residue, after the removal of the benzine and kerosene being marketed as a liquid fuel.

In many cases, however, it is desirable to work up this residue further as (1) it may be too asphaltic and thick for use as fuel oil directly as is the case with many Mexican and Venezuelan fuels; or, (2) it may contain so much paraffin wax as to make the extraction of this worth while, as is the case with Pennsylvanian, Mid-continent, and Burmah crudes, for example; or, it may contain valuable lubricating oil fractions, which can be removed, *e.g.* Russian crudes.

As much higher temperatures are required for completing this distillation, somewhat different arrangements are necessary, consequently the second stage of the distillation is usually carried out in a separate bench of stills.

The dephlegmators for lubricating oil stills are often replaced by a series of horizontal pipes of large diameter, through which the vapours pass on their way to the main condenser. From each of these large pipes a condensate fraction may be drawn off. These condensates will usually be dry, as the steam should condense only in the condenser. During distillation for lubricating oil fractions and for paraffin wax relatively large volumes of steam are blown into the still to avoid cracking of the oil as far as possible. In distilling off the higher boiling-point fractions, the amount of steam blown into the still may exceed the amount of oil distillate obtained.

Certain crude oils, *e.g.* some from the Pennsylvanian fields, may yield a cylinder oil residue after a large percentage of the crude has been distilled off. Lubricating oil distillates also are often concentrated down to heavier oils or cylinder oils. In this case care has to be taken not to overheat the oils, copious supplies of steam being used for this purpose, and the fires being extinguished some time before the end of the operation. As the quality of the distillates is much improved by **distilling under high vacuum,** this process is nowadays often applied.

A modern successful type of high vacuum plant is that designed by Steinschneider (U.S. Pat. 981953) (Fig. 25).

The stills used (A) are of the usual cylindrical type often fitted with an internal fire tube. They are strengthened internally in order to stand the external pressure. They are arranged in a bench of six or more for continuous working. Each still is fitted with one or more domes connected to a vapour pipe (B) of large dimensions, 14 inches or more, in order to allow the vapours to pass away as quickly as possible so as to maintain a vacuum in the still. This vapour pipe usually bends back on itself once or twice forming an air-cooled condenser. Any distillates condensing here are pumped away through a cooler.

This large vapour pipe leads into an air-cooled dephlegmator C, in which a further fraction condenses, then into a further water-cooled dephlegmator D, in which the bulk of the distillate condenses. The vapours then, consisting mostly of steam, pass on into the barometric condenser E, where they are condensed by a jet of water. This barometric condenser is placed at an elevation of over 30 feet and the effluent pipe leads downwards to a water seal so that the condenser forms practically a water barometer.

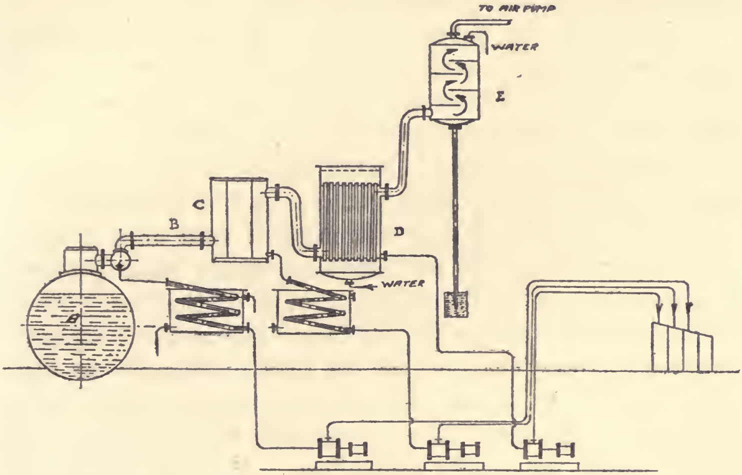

FIG. 25.—Arrangement for distilling under high vacuum.

The vent of this condenser is connected to a suitable air pump.

The distillates running from the dephlegmators, after passing through coolers run into sealed receiving tanks of small capacity (not shown in the diagram), whence they are pumped out by low-level pumps to the tail-house. This arrangement of pumps enables the distillation plant to be constructed without the necessity of making each distillate discharge a barometer tube. All that is necessary is to make the height of the discharge pipes equal to the head which the pumps can easily maintain when evacuating.

Such a continuous bench of high vacuum stills can easily be operated at a pressure of only 10 or 15 centimetres pressure absolute, and under these conditions the temperature of the oil in the still need not exceed 300° C., a temperature about 50° lower than would be reached without vacuum. In order to avoid pumping out the hot residue from the last still, it is usual to operate the last two stills periodically and alternately, so that the one when its contents are distilled as far down as desired, may be cut out from the vacuum and pumped out while the other is being filled and functioning as last still.

Distillation for paraffin wax is carried out in similar continuous plant, usually at atmospheric pressure. The determination of the setting points of the distillates in this case indicates how the distillation is proceeding.

In the case of certain crudes, *e.g.* some of the Pennsylvanian, practically all the paraffin wax may be distilled off, so that the residue in the still may be used as a so-called steam refined cylinder oil. In the case of other crudes it is impossible so to distil off the bulk of the wax; much remains in the residue, which forms a very thick asphaltic substance, too thick for use as fuel. Attempts to distil this further with the use of steam would result in the production of very viscous distillates, containing wax which would not easily crystallize. Both distillates and residue would thus be very difficult substances to handle. This thick residue is, therefore, usually further distilled in so-called "tar or coking" stills. These are special stills of strong construction, the bottoms of which are usually made in one piece. They are usually set so that the whole of the bottom is exposed to the furnace gases, no return flues being used. They are often fired from the side instead of from the ends, a more uniform distribution of heat being thus obtained. The distillation is conducted rapidly without the use of steam. A further yield of paraffin wax distillate is thus obtained, which is thin and easily crystallizable owing to the presence of these cracked oils. Towards the end of the distillation the stream of distillate changes in character owing to the presence of high melting point hydrocarbons of the aromatic type. This distillate is known as "wax tailings." When the bottom of the still shows dull red, the fires are turned out, and the distillation is allowed to complete itself. The residue is then a petroleum coke. After cooling somewhat the still is opened and the coke is dug out. The life of a still subjected to such strenuous use is naturally short.

In the case of crude oils rich in asphalt, *e.g.* the heavy crudes of Mexico, California, and Texas, the distillation may be conducted so as to produce an asphalt to definite specification. Distillation to asphalt is usually carried out periodically in stills of large capacity, 100 tons or more. The distillation may also be conducted in continuous plants, the control being effected by examination of the outgoing residue rather than by the character of the distillates.

In order to obtain asphalt of good quality it is necessary to avoid overheating, particularly as the periodic distillation takes a considerable time (24 hours or more). Copious supplies of steam are therefore blown into the still, so that towards the end of the distillation, three or four times as much water as oil is condensed in the condensers. The distillates produced will usually be gas oils or perhaps light lubricating oil distillate according to the grade of asphalt produced. It is usual not to allow the temperature of the oil in the still to exceed 350° C. during this operation.

During the last few years stills of the conventional type have been to some extent replaced by the much simpler **tubular stills**. The development of this type of plant arose from the difficulty of handling crude oils containing emulsified water in ordinary stills, as there is very great danger of the whole contents of the still frothing or "puking" over when the temperature passes 100° C. The distilling operation must, therefore, be carried out with very great caution. The idea of the tubular still for dehydrating such crude oils was developed in the United States by Bell, Brown, Trumble, and others. Its use was then extended to the distilling off of light fractions from heavy crudes in order to raise the flash-point to liquid fuel standard. From this the name "topping plant" was derived, a term now in general use. The plant has now been considerably further developed, so that its use extends to the distillation of rich crude oils yielding 60 per cent. or more of distillate, and to the distillation of heavy crudes down to asphalt. The principle of such plants is very simple, the variations in construction found are very numerous.

In general, the crude oil first flows through a series of heat exchangers where it is heated by the condensing vapours and by the hot residue. It then flows on to the tubular retorts which consist of 4-inch tubes set in a furnace. In passing through these tubes the oil is partially evaporated, and any water it may contain completely so. The mixture of oil vapour and steam then passes through an uptake pipe to some form of separating box into which it issues as a foam. Separation of the vapours takes place here; the vapours pass off by suitable vapour pipes to the condensers, and the residue passes off via the heat exchangers to the residue tanks.

One fundamental difference between such a plant and a continuous bench of stills is immediately noticeable. In the case of the continuous bench each still yields a certain fraction; in the case of the tubular retorts the whole of the distillate is taken off at once. In the case of the continuous bench the residue in the last still is in equilibrium with the vapours from the last still only, whereas in the separating box of the topping plant the residue is in equilibrium with the whole of the vapours. For any given percentage of distillate, therefore, the flash-point of the residue from a topping plant will be somewhat lower than that from a continuous bench.

The taking off of the distillate *en bloc* necessarily involves considerable redistillation in order to effect the separation into commercial fractions. This can be and usually is, however, effected by means of fractional condensation and partial redistillation by means of the heat of the residue.

A description of a modern complete plant working on this system will, therefore, be given, a Trumble plant being selected as representative.

The heaters or retorts are made up of 4-inch steel pipes arranged in six rows, each of twelve pipes, placed one above the other. The ends of these pipes are connected by flanged return bends, which may be removed for cleaning purposes. These bends are placed outside the brickwork setting of the retort, and may be insulated either individually by asbestos jackets, or by being enclosed in a space closed by folding doors. The whole number of pipes are thus connected in series as a single tube. Two such sections are set side by side to make one battery. The heating is effected by liquid fuel firing, the arrangement of the furnace being such that direct flames do not play on the tubes. The most effective method of heating is naturally the counter current method, the heated flue gases descending round the nest of tubes through which the crude oil passes upwards (Fig. 26).

The internal heating surface of two such heaters would be 2430 square feet. These two heaters may be connected in series or in parallel as required. Several thermometers are fitted, so that the temperature of the crude oil as it flows through the system may be accurately controlled.

Automatic controlling apparatus may now be obtained actuated by the thermometer placed in the pipe leading from the last retort to the vapour separating vessel. In this way an increase of temperature can be made to bring about an acceleration of the crude oil-feed pump and vice versa, so that the personal element can be eliminated in this particular case.

The working temperatures will naturally depend on the nature of the crude oil being distilled and on the fractions to be distilled off. The heated crude oil leaves the heaters in the form of a foamy mixture of vapour and oil and passes by an uptake pipe which discharges into the top of the vapour separating vessel, where the vapours have an opportunity of separating themselves from the residual oil.

In the case of the Trumble plant, this consists of a vertical steel cylinder, 6 feet diameter and 25 feet high,

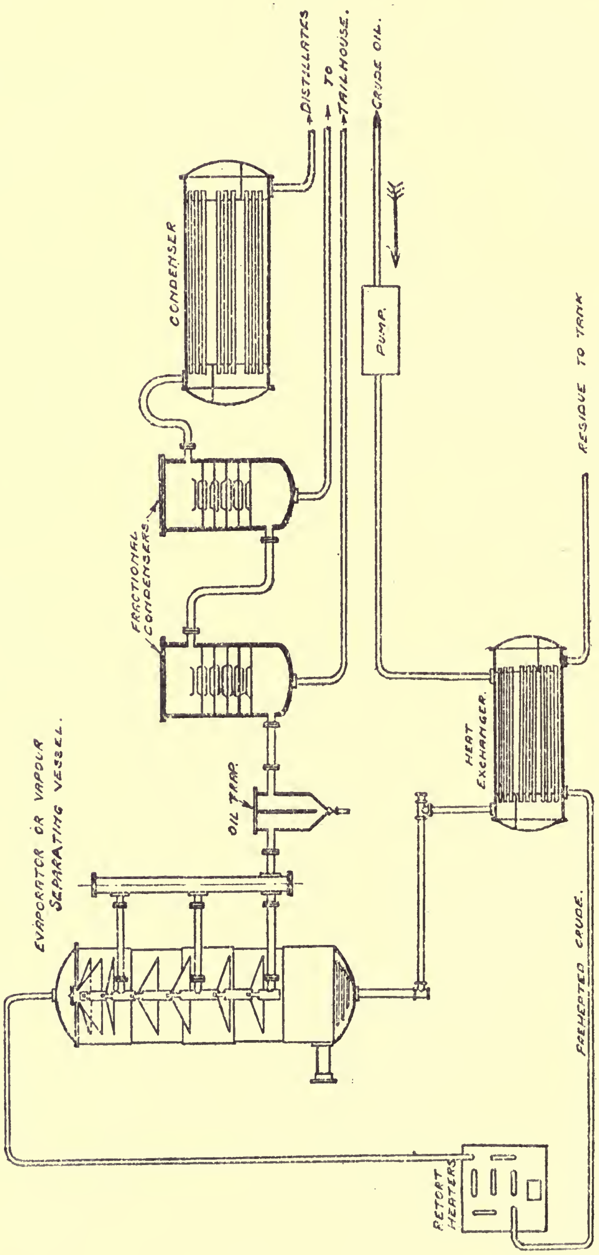

FIG. 26.—Diagrammatic view of arrangement of Trumble plant.

which is enclosed in a brickwork stack, so that the flue gases from the heaters can pass through the annular space

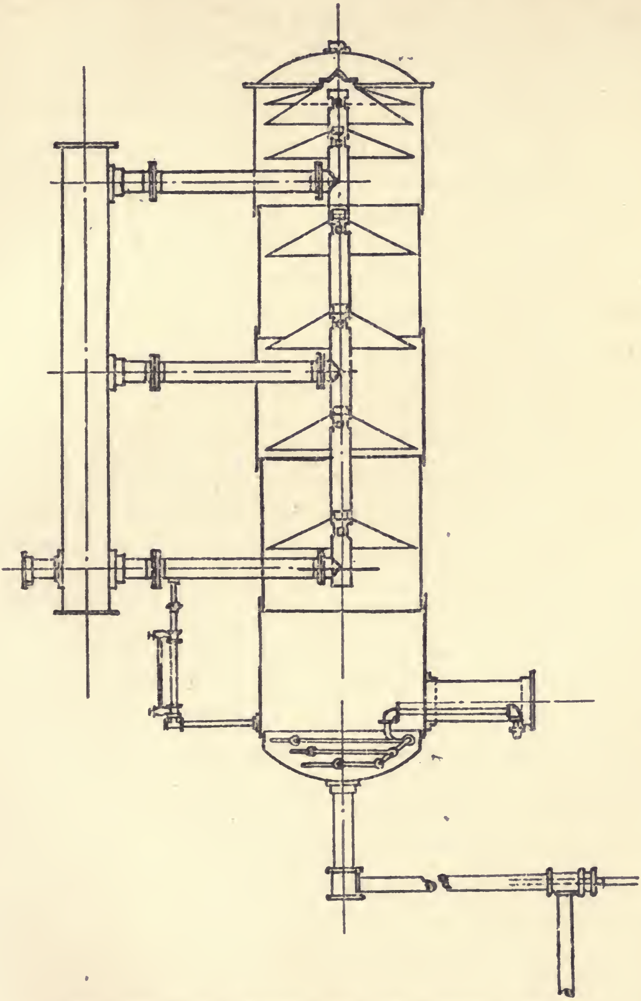

FIG. 27.—Trumble evaporator or separating vessel.

separating the brickwork from the steel cylinder, thus effecting further distillation. Fitted inside this vessel is a vertical vapour pipe closed at the top, which carries a number of umbrellas the outside edges of which extend almost to the cylinder walls. The object of this arrangement is to ensure the liquid flowing down the sides of the vessel. Directly under the apex of each umbrella the central vapour pipe is perforated so that the vapours may enter. One or more side pipes connected to this central vapour pipe allow of the vapours being led off. A perforated steam coil is usually placed at the bottom of this "evaporator" so that steam may be admitted in order to assist in the distillation (Fig. 27).

An oil catcher, consisting of a small vertical cylinder 2 feet diameter and 3 or 4 feet high, containing a number of perforated steel baffle plates, is placed in the vapour line, to arrest any spray of heavy oil which might be carried over mechanically with the vapours. Such an arrangement has already been mentioned in connection with an ordinary distilling plant (p. 156).

The residue, after leaving this evaporator or separating vessel, may pass off through crude oil heat exchangers or may be utilized for supplying the heat necessary for redistilling some of the fractions, as described later. The residue-crude oil heat exchangers are usually of the tubular type. The number to be used depends on the nature of the crude and the percentage of residue obtained from the plant.

The vapours, after leaving the separating vessel, pass on, not directly to the main condensers, but through a series of "dephlegmators" or fractional condensers. These consist of vertical steel cylindrical vessels about 30 inches in diameter and 7 feet high. These vessels contain a number of horizontal saucer-shaped baffle plates. Half of these fit closely to the walls and have a central hole, the other half placed alternately are of smaller diameter with no central hole. The vapours thus zigzag through the annular spaces and central holes. The heavier fractions condense on these plates and fall back to the bottom of the dephlegmator, whence they are led off by a special pipe. At the top of the dephlegmator is placed a water coil, by means of which a certain amount of distillate may be condensed in order to furnish a quantity to flow back down over the baffle plates.

In this way the dephlegmator functions to some extent as a fractionating column (*vide* p. 190). Further below the point at which the vapours enter the dephlegmator a further number of baffle plates are situated and means is provided for blowing in steam at the bottom, so that the down-flowing condensate may be subjected to steam distillation (Fig. 28).

The main vapours pass through several (as many as eight in modern plates) of these dephlegmators, being thus condensed into as many condensates which flow from the bottom of each dephlegmator. The vapours from the last dephlegmator pass on into condensers cooled by the entering crude and finally into water-cooled coolers.

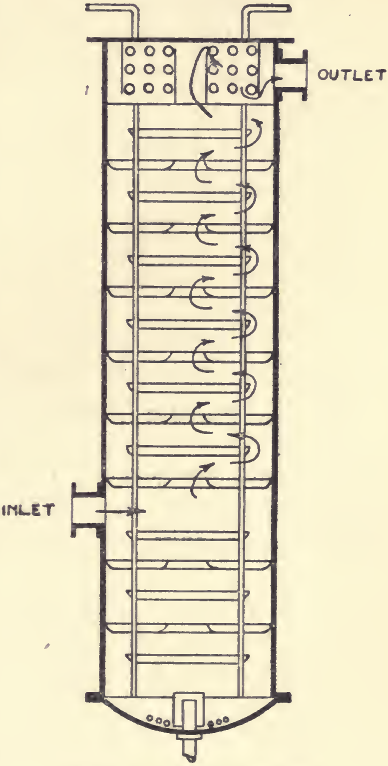

FIG. 28.—Dephlegmator.

These various distillates may then be collected separately in the tail-house, or may be partly redistilled in the "separators." The separators, several of which may be fitted, consist of rectangular boxes 18 by 6 feet by 40 inches high, along the bottoms of which run several 3-inch pipes connected to manifolds, through which hot residue can be run. These pipes are supplemented by perforated steam pipes through which steam can be blown. To the top of these boxes vapour lines are attached. These separators are thus practically stills. The condensates from the dephlegmators which require further distillation, run into these separator boxes where they are redistilled, the vapours passing through condensers to the tail-house and the residues running off through coolers.

The accompanying flow-sheet diagrams, Figs. 29 and 30,

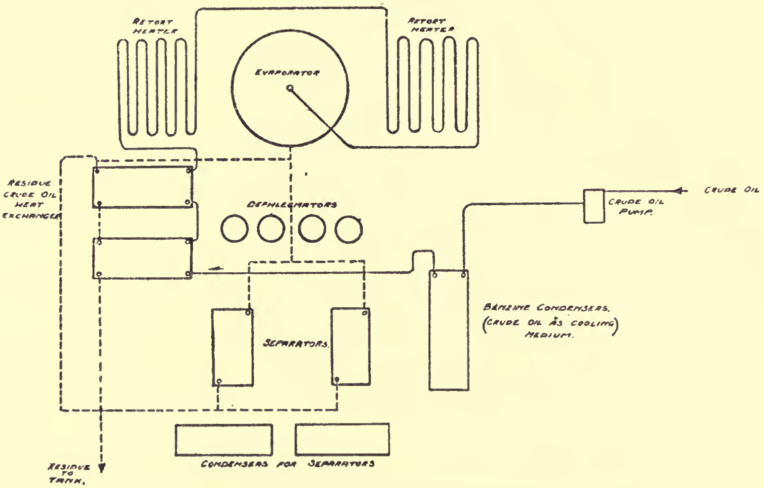

Fig. 29.—Course of crude oil and residues through Trumble plant.

will explain the several courses of crude oil, residues and vapours through the plant. These diagrams represent simple cases only, and must not be taken to represent

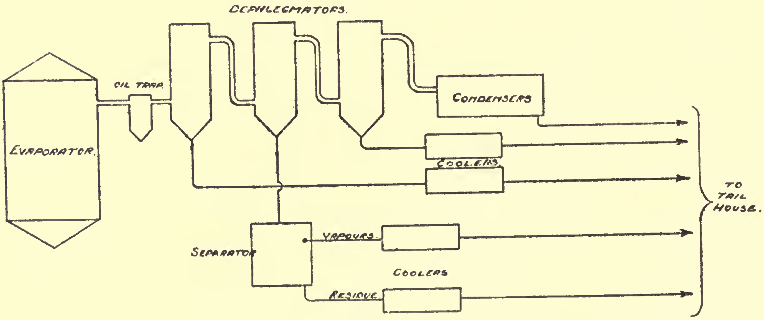

Fig. 30.—Course of vapours through Trumble plant.

actual practice. The subject of topping plants or tubular retort distillation plants is very well set forth in *Bulletin* 162, Petroleum Technology 45, U.S. Bureau of Mines, by

J. M. Wadsworth, where very full details as to plant and operation are given.

The following table, giving the analyses of the products obtained from the dephlegmators during an actual run, will illustrate to what an extent the total distillates taken off *en bloc* may be separated by fractional condensation :—

Sample from	Distillation in Engler flask, percentages boiling over up to					F. b. pt.	Fl.-pt.
	100° C.	150 C.	200° C.	250° C.	300° C.		
Dephlegmator 1 ..	—	—	—	5	40	>350	90° C.
,, 2 ..	—	—	—	11	78	350	75° C.
,, 3 ..	—	—	13	65	—	299	46° C.
,, 4 ..	—	1	33	90	—	265	33° C.
,, 5 ..	—	7	70	—	—	235	25° C.
,, 6 ..	—	22	95	—	—	225	16° C.
Vapour from 6 ..	7	87	—	—	—	175	—

Of the above products D1 would run to gas oil, D2 might be worth redistilling to extract therefrom some kerosene, D3 and D4 might run to kerosene distillate, D5 should be redistilled and perhaps D6. The vapour from 6 would naturally run to heavy benzine. The work of the separators is exemplified by the following analyses :—

——	100°.	125°.	150°.	175°.	200°.	F. b. pt.	Flash-point.
Oil running to separator ..	—	—	15	53	80	235	20° C.
Distillate from separator ..	—	22	70	93	—	192	—
Residue from separator ..	—	—	2	38	75	245	33° C.

It will be seen, therefore, that such a distillation plant is complete in itself, as it yields a series of finished products which do not require to be subjected to a further process of redistillation. Such a plant, therefore, presents many advantages over the system of stills and redistillation stills usually employed. It is more compact, much less steel is required in its construction, the need for tanks for intermediate products disappears, there is minimum loss of heat as the products for redistillation are not cooled before passing into the separator, *i.e.* redistillation stills. The fuel consumption is low and the efficiency relatively high compared to those of an ordinary distilling plant.

Though in the first place designed for dehydrating or topping crude oils, the system has been extended to dealing with crude oils yielding as much as 60 per cent. of distillates. In such cases, however, limitations are imposed by the lack of heat necessary for redistillation, owing to the low percentage of residue available.

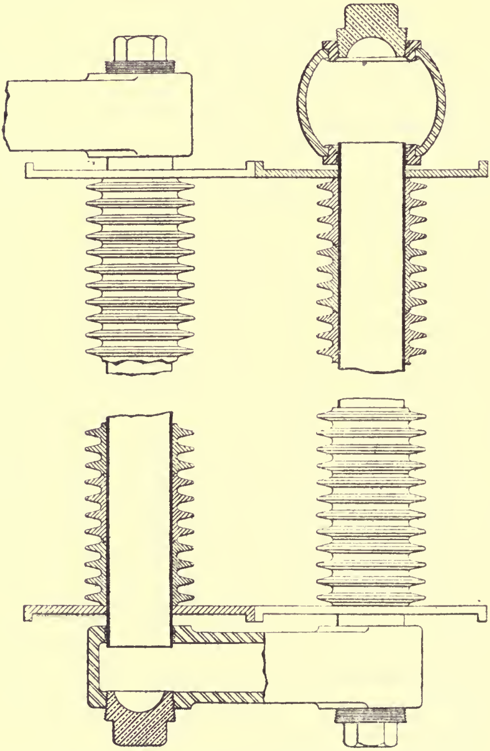

FIG. 31.—Details of header for tubular still.

Tubular or pipe stills are now coming into general use for various purposes, such as preheating crude oil preparatory to pumping it through long pipe-lines, and for cracking furnaces.

It is obvious that the circulation of the oil in a pipe still must be much better than can be possibly attained in a cylindrical still, consequently the chances of overheating the oil are much less. Even if coke is formed, it can be easily removed, and moreover, if coke deposition goes so far that tubes are damaged, then these can be quickly and cheaply replaced. Patching the bottom of a cylindrical still is a difficult and expensive job and unsatisfactory when finished. Much better heat exchange is possible as oil and furnace gases can run counter current, fuel consumption being thus reduced. Moreover, the still can be designed so

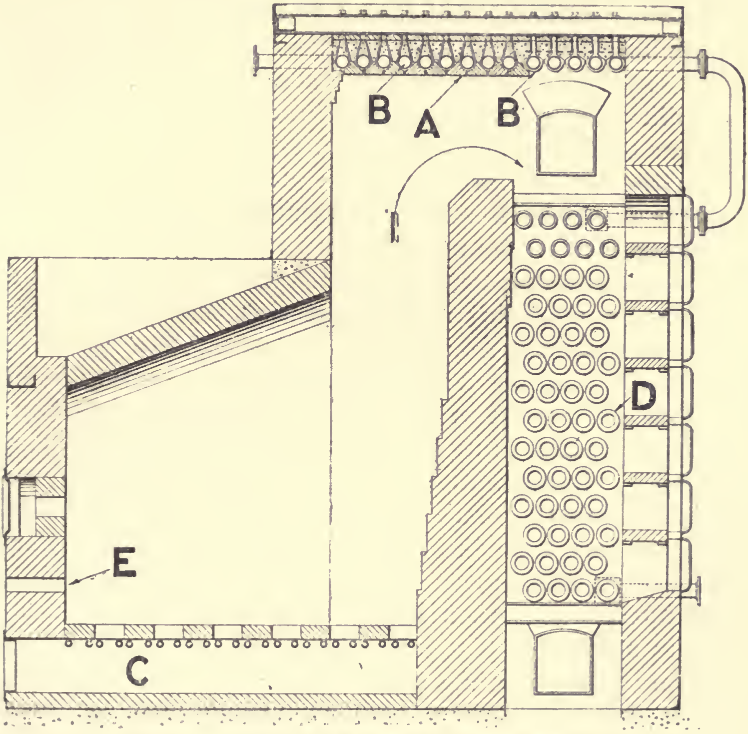

FIG. 32.—Special type of tubular still or heater.

that the fuel can be properly burnt in a suitably designed furnace. In modern types, the pipes of the tubular stills are constructed with a covering of cast-iron corrugated sleeves, similar to those used in Foster superheaters (Fig. 31).

One of the difficulties in distilling oils at high temperatures, such as are necessary for cracking, whether it be in cylindrical or tubular stills, is the deposition of coke on the still walls. Although this cannot be entirely avoided it can be minimized in the case of tubular stills by designing the plant so that the tubes are not exposed to direct radiation. In a still recently designed by the Power Speciality Company this has been effected in an ingenious manner (Fig. 32).

In the roof of the furnace are placed a series of tubes B, through which the crude oil to be distilled is first circulated before passing to the main heating tubes D. The portion of the roof covering the combustion chamber is lined with a covering of insulating material, so that the pipes in this area are protected from direct radiation. The pipes in the area of the roof directly over the main heating tubes are thus not exposed to any extent to any direct radiation, and their presence prevents this portion of the roof becoming red hot. Consequently, the main heating tubes D are protected from the direct radiation which they would receive from the roof were the tubes B not placed there. This arrangement has proved very efficient in practice and is undoubtedly a marked advance in the construction of tubular stills.

The efficiency of the older types of periodic still, with simple furnace settings and no arrangement of heat exchangers, must have been low indeed. The efficiency of many, if not most, plants operating at the present day leaves much to be desired. A simple calculation, taking the specific heat of oil at 0·45 and the latent heat at 70 calories, would show that a fuel consumption of 1·2 per cent. reckoned on the crude oil treated would be theoretically sufficient to distil off say 50 per cent. of distillates, allowing for no heat exchange arrangements whatever.

In actual practice, with no heat exchange, distilling periodically with old-fashioned plant, a fuel consumption at least six or seven times as high would be required. Wadsworth (U.S. Bureau of Mines, *Bulletin* 162) cites a case where the overall efficiency of a battery of crude oil stills working continuously, fitted with residue-crude oil heat exchangers, amounted to 34·8 per cent. He also cites the case of a modern Trumble plant adequately supplied with heat exchangers and separators as 57 per cent. Even such a figure leaves room for considerable improvement when it is considered that the efficiency of modern Spencer-Bonecourt steam boilers is actually over 90 per cent. There is no reason, however, why a battery of continuous crude oil stills, equipped with distillate preheaters, residue-crude oil heat exchangers, and heat exchangers placed in the flues (after the fashion of a Green's economizer) should not have an efficiency as high as that of a tubular retort distillation plant. It is naturally, however, much more easy to ensure an efficient furnace in the case of a tubular still. With highly efficient continuous batteries, however, the fuel consumption, when distilling an oil yielding 70 per cent. or so of distillate, may be reduced to below 2 per cent. of the crude oil distilled.

The methods described above are those in general use in the petroleum industry. There are undoubtedly still great possibilities in the direction of more efficient distilling plant. One of the great objections to distilling oil at high temperatures in any usual form of plant, especially in cracking plants, is the formation of coke on the inside of the still or retorts. Such coke, being a poor conductor of heat, gives rise to overheating of the iron plate through which the heat must be transmitted, so that damage soon results. An obvious way of getting over the difficulty would seem to be the method of distillation by direct contact with heated gases, a method which is successfully applied to the concentration of sulphuric acid. This idea is, in fact, very old. In 1860, W. Gossage (Eng. Pat. 1086) patented a method of distilling bituminous substances by injecting highly heated gases obtained by the combustion of suitable fuel. Dalley

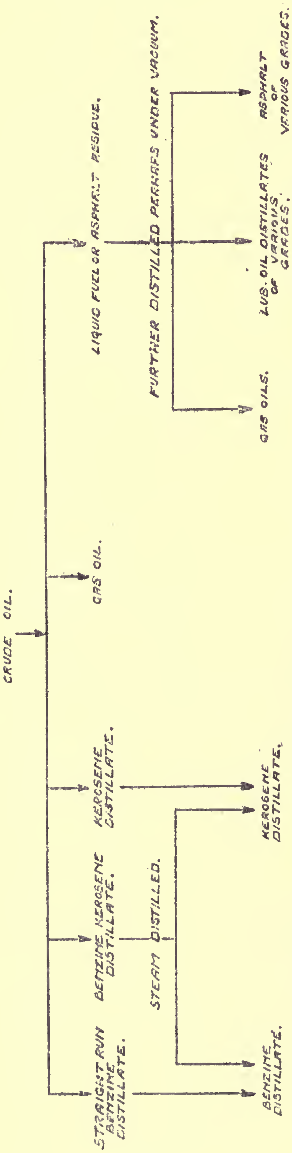

FIG. 33.—Diagram illustrating distillation of certain types of naphthene base (asphaltic) crude oils.

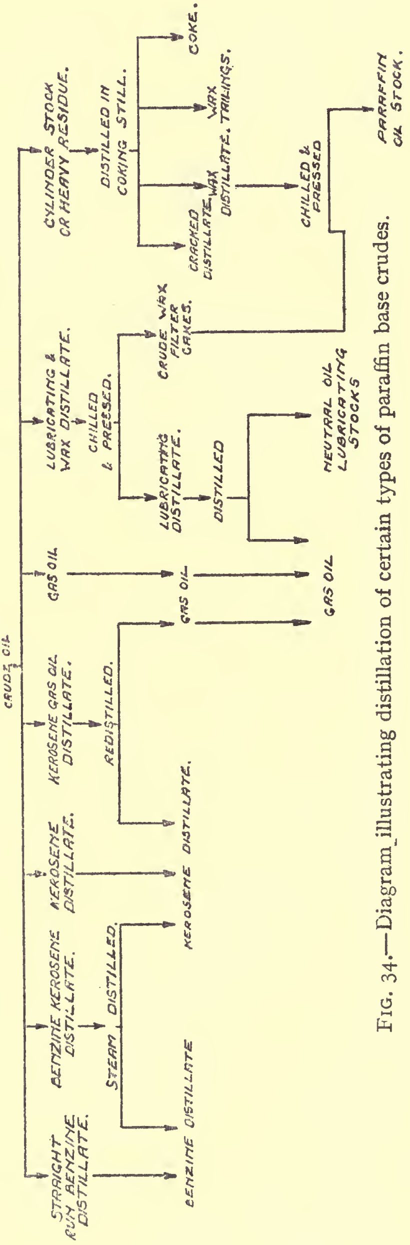

FIG. 34.—Diagram illustrating distillation of certain types of paraffin base crudes.

(Eng. Pat. 163347, July 21, 1919) proposes to inject a spray of the oil to be distilled on to the surface of solid fuel in a retort or producer, air for combustion being blown in at the bottom. Knibbs (Eng. Pat. 165863 of July 11, 1921) suggests an apparatus based on the same principle.

As far as the writer is aware, this method of distilling by direct contact with furnace gases, which seems to present such obvious advantages, has not as yet found successful application.

As crude oils show such great variation in character, a definite working scheme must be drawn up for each individual oil. Two diagrams are given above illustrating typical methods of working up crude oils.

Fig. 33 illustrates the simple case of working up a crude oil into benzine (motor spirits), kerosene, gas oil and liquid fuel only, the fuel residue being further, perhaps, worked up into lubricating oils and asphalt.

Fig. 34 represents a scheme for working up a paraffin wax base crude oil. Reference will be made to this diagram in further sections of this work.

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SECTION B.—REDISTILLATION AND FRACTIONATION OF LIGHT OILS

IT has been pointed out that in the ordinary process of distillation of crude oil, a fraction intermediate between, or rather consisting of, benzine and kerosene is obtained. The more efficient the system of primary distillation, the smaller this fraction. In general, however, quantities of such distillate must be redistilled in the average refinery. Moreover, fractions of definite boiling ranges, special boiling-point spirits, white spirits, and so forth are often required. For the manufacture of such benzines a more or less intensive fractionation is demanded.

In the simplest cases a separation of the light oils into benzine and kerosene only is required. As the difference in price of these commodities is considerable endeavours should be made to obtain a separation as sharply as possible. Generally, however, sufficient attention is not paid to this point and the separation is by no means well effected. The benzine from the average refinery may boil up to 200° C., and the kerosene may have as much as 30 per cent. boiling below that temperature.

This redistillation is usually carried out in so-called steam stills, which may be, and often are, operated continuously. They differ little from ordinary crude oil stills chiefly in the mode of heating. This is usually effected, as the name indicates, by means of steam. Nests of high pressure steam coils are arranged in the lower part of the still, the exits being fitted with steam traps. Steam at pressures up to 160 lbs. pressure is usually employed. This enables temperatures up to about 170° C. to be obtained in the still. As in the case of crude oil distillation, live steam is also blown in through perforated pipes lying on the bottom of the still to assist the distillation.

Direct firing may also be employed, but in some cases this tends to discolour the kerosene residue left in the still, thus rendering necessary a more intensive treatment. The control by means of steam coils is easier, but the fuel consumption is naturally much higher.

The steam stills are usually fitted with some form of simple dephlegmator, sometimes water-cooled, sometimes air-cooled. In many cases, however, no dephlegmator is employed, the fractionation being so much the less efficient. In cases where efficient fractionation is required, efficient columns are used.

The benzine-kerosene distillate is distilled in such stills until the residue shows the requisite flash-point, care being taken that the final boiling point of the distillate does not exceed a predetermined value.

The following table shows the result of distilling such a benzine-kerosene fraction in a simple steam still with a simple type of dephlegmator :—

Engler distillation.	Benzine-kerosene distillation before distillation.	Benzine distillate.	Kerosene residue.
Up to 125° C. ..	—	2 per cent.	—
,, 150° C. ..	4 per cent.	31 ,,	—
,, 175° C. ..	31 ,,	75 ,,	—
,, 200° C. ..	65 ,,	98 ,,	20 per cent.
,, 225° C. ..	88 ,,	all	66 ,,
,, 250° C. ..	95 ,,	—	86 ,,
,, 275° C. ..	all	—	95 ,,
Final boiling point	265	200	285

40 per cent. of benzine distillate and 60 per cent. kerosene residue being obtained in this case.

The benzine distillate would be mixed with the straight-run benzine from the primary distillation, and the residue with the kerosene distillate. The percentage of benzine-kerosene distillate obtained from any crude oil will depend on (*a*) the nature of the crude oil, (*b*) the efficiency of the primary distillation. In practice, for example, an actual crude oil yielded :—

Straight-run benzine distillate ..	11·3	per cent.
Benzine-kerosene distillate ..	15·7	,,
Direct kerosene distillate ..	10·3	,,
Residue	61·5	,,
Loss	1·2	,,

The straight-run benzine distillate would be cut so as to give a final boiling point of not more than 200° C. The direct kerosene distillate would be cut so as to give a flash-point of about 100° F. and final boiling point not over say 280° C., the intermediate fraction being redistilled as described above.

In many refineries, however, quantities of benzines of narrow boiling point ranges are made. Such benzines, for example, are "lighting spirits," used for producing air gas, or "petrol gas," for lighting purposes. Such benzines must be very volatile, boiling completely below 100° C. For dry-cleaning purposes, vegetable seed extraction, and so forth, benzines boiling between say 80° C. and 100° C., or 100° C. and 120° C. are required; for solvent purposes benzines boiling between 100° C. and 150° C. may be demanded; and for "white spirits," or "mineral turpentine," benzines boiling between 140° C. and 200° C. may be required. The manufacture of such spirits necessitates the use of efficient "fractionating columns."

The equipment necessary for such distillation consists of a still of the usual type, a fractionating column and a dephlegmator for returning a supply of condensate to run back through the column.

Fractionating columns may be of several types, *e.g.* simple columns fitted with baffle plates, bubbling columns of the Heckman type, or columns of the absorption type filled with rings or other form of packing.

Columns fitted with perforated plates are largely used in the coal-tar industry for the extraction of toluene and xylene from light coal-tar benzols. The vapours pass upwards through the perforated plates, being subjected to a scrubbing action by the enforced bubbling through the layer of liquid on the plates. Such simple columns cannot, however, be well controlled as the plates would drain dry when running slowly. In columns of the Heckmann type a layer of liquid is maintained on the plates, the up-going vapours being forced to take one path, the down-coming liquid another. The action of such a column is best explained by reference to the diagram (Fig. 35). The column, which may be 20 feet high and 5 feet diameter, is fitted with a number of plates or trays 9 inches or so apart. Each tray is fitted with one or more down-take pipes, the top of which projects a short distance above the tray, and the bottom of which extends almost to the underlying tray, projecting below the level of the liquid on that tray, so that the lower end is sealed. The distance to which the upper end of the liquid down-take pipes A project above the tray determines the depth of liquid which remains on that tray. Each tray is fitted with a large number of vapour up-take pipes, the upper ends of which project above the level of the liquid on the tray. These up-take pipes are covered with hoods, the edges of which are usually serrated and which dip into the liquid lying on the tray. The vapours are thus forced to take a path, bubbling through the layers of liquid, while the returning liquid flows back down the column by the down-take pipes.

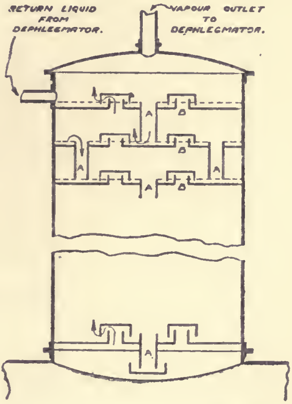

FIG. 35.—Heckmann column.

The vapours issuing from the top of the column pass through a dephlegmator on their way to the condenser. In this dephlegmator they are partially condensed, the condensate being returned by a sealed pipe to the column. The amount of condensate so returned to the column which determines the efficiency of the fractionation may be controlled by the water supply admitted to the dephlegmator (Fig. 36).

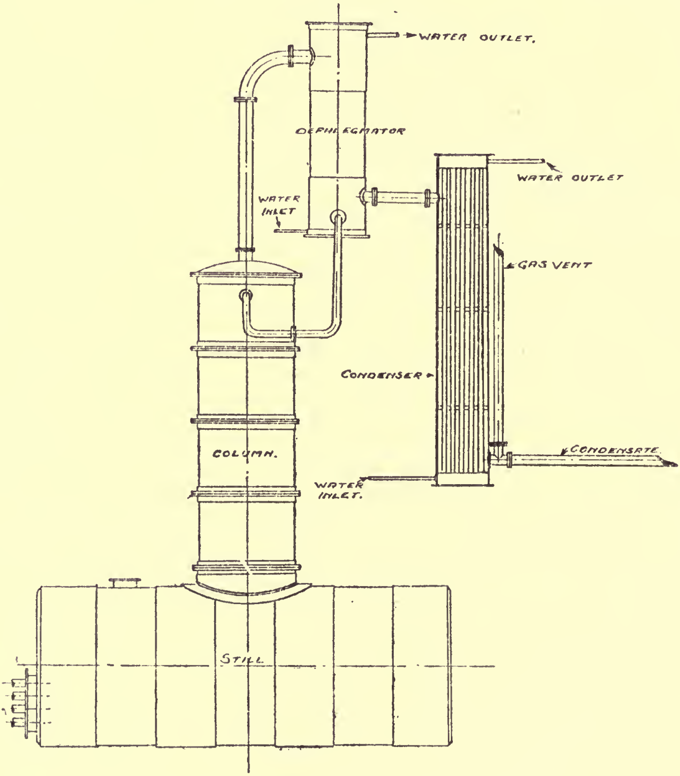

FIG. 36.—Complete fractionating plant.

By means of such a column, fractions boiling over a range of only a few degrees C. may be obtained.

The process of fractionation as it goes on in the column is well exemplified by the following analyses of five fractions taken simultaneously from various points in a Heckmann column :—

Samples from column.	Initial boiling point. °C.	Distillation in Engler flask. Per cent. boiling up to temperatures °C.					Final boiling point. °C.
		105	105/110	110/115	115/120	120/125	
Top 1	98	48	46	5	—	—	112
2	100	37	54	8	—	—	114
3	101	14	68	13	4	—	117
4	102	4	66	21	4	4	124
Bottom 5 ..	103	—	32	38	16	7	134

The following table gives analyses of samples taken at various points simultaneously :—

Sample.	Sp. gr. 15° C.	Initial boiling point. °C.	Distillation in Engler flask. Per cent. boiling up to °C.						Final boiling point. °C.
			100°	110°	125°	135°	150°	170°	
Liquid in still ..	0·766	124	—	—	—	22	68	91	197
Vapours in still	0·755	110	—	—	39	—	94	all	165
Vapour from top of column ..	0·739	96	49	98	—	—	—	—	110
Liquid returning from dephlegmator ..	0·743	98	16	—	—	—	—	—	112
Liquid from condenser ..	0·734	94	88	—	—	—	—	—	104

Should a fraction of very narrow boiling range be required redistillation of a fraction may of course be necessary.

The type of fractionating column filled with rings or some other type of packing is as yet little used in the petroleum industry. High efficiency is, however, claimed for this type of column. It presents the advantage of a very great wetted surface for contact between vapour and scrubbing liquid.

Raschig (Eng. Pat. 6288/14) patented simple rings; modifications of such rings with even greater surface have been patented by Lessing, Prym, Goodwin, and others. These rings may be made of various materials and dimensions. If made of sheet iron 25 mm. high and 25 mm. diameter, 55,000 may be packed into a cubic metre, and so present a total surface of 220 square metres.

The following data supplied by Dr. Lessing illustrate the superiority of such a column over a column of the Coffey type for removing benzol from a solution of this in a heavy green oil. In this particular case the column was employed to remove the benzol from the scrubbing liquid used for absorbing the benzol from coal gas. The columns compared were of the same height, but of different diameters, that of the Coffey column being 2 feet, that of the ring column 18 inches. The volume of the ring column was therefore only 56 per cent. of that of the other.

	Coffey column.	Ring column.
Benzene and toluene in benzolized oil	3·85 per cent. vol.	3·8 per cent.
Benzene and toluene in debenzolized oil	1·35 ,,	0·4 ,,
Benzene and toluene in crude benzol distilled off	73·5 ,,	79·5 ,,
Efficiency of recovery of benzene and toluene	66·1 ,,	89·6 ,,
Throughput of column gallons per day	1065	890

These figures indicate the superiority of the ring column, especially when taking into consideration its much smaller volume.

The objections to this type of column would apparently be the difficulty of running with small quantities of return liquid and the possibility of channelling, *i.e.* of the vapours taking the path of least resistance, and thus diminishing largely the contact area.

Numerous other types of columns have been patented. Those designed by Kubierschky (*Chemical Age*, June 21, 1919, p. 11) are designed so that the hot vapours enter at the top of each compartment of the column and leave at the lowest point, passing from one compartment to another by vapour up-take pipes leading from the bottom of any one compartment to the top of that immediately above it, while the liquid flows back through the finely perforated plates which form the bottoms of the compartments.

The fuel consumption for carrying out such distillation is necessarily high owing to the large quantity of distillate which is condensed and returned to the still to be again distilled. The amount of distillate obtained per ton of steam used in a simple distillation without fractionation may amount to 10/12 times the amount obtained when distilling to obtain a fraction of 20° range of boiling point.

Several such stills with columns may be arranged to work in series continuously. Such plants do operate and successfully separate benzene, toluene, and xylene continuously from crude coal-tar naphtha.

Really intensive fractional distillation, however, is not adopted in the petroleum industry. The isolation of pure products from petroleum by distillation on the large scale would be very difficult if not impossible, and would be so costly as to be quite out of court as a commercial process. The subject of commercial fractional distillation can be much better studied in connection with the coal tar, alcohol, and other industries.

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Mariller, " La Distillation Fractionée." Dunod et Pinat.
Thorpe, " Dictionary of Applied Chemistry," p. 263. Longmans.
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SECTION C.—THE CHEMICAL TREATMENT OF PETROLEUM AND SHALE OILS

THE products obtained by distillation are comparatively seldom marketable without chemical treatment. Benzines from certain crudes, *e.g.* those of Sumatra, are, however, so free from bad smelling and objectionable constituents as to be directly marketable, but kerosenes and lubricating oil distillates practically always need refining.

The particular method of treatment employed depends largely on the nature of the product to be treated, and on the extent to which it is desired to improve the quality. In the case of benzines which are to be used for such purposes as the extraction of edible oils from seeds, the removal of all objectionable constituents is of prime importance. The impurities usually present are sulphuretted hydrogen and organic sulphur compounds of the mercaptan, thioether, or thiophene type. In some cases, particularly when "cracked" products are present, reactive unsaturated hydrocarbons must be removed. In rare cases pyridins may be found as impurities, and in benzines derived from the distillation of shale oils or coal tars phenols may also be present. The removal of phenols and pyridins presents no difficulties, the usual methods of washing with dilute alkali and dilute acid being adopted as in the coal-tar industry.

The removal of certain sulphur compounds or the desulphurizing of oils is a problem which has excited the interest of many chemists, but has not so far met with any solution of general application. Sulphuretted hydrogen may easily be removed by means of strong caustic soda alone. The other sulphur compounds present difficulties.

This problem is of particular importance in the case of shale oils. Such oils usually contain sulphur compounds, sometimes to a considerable extent, so that the actual sulphur content may sometimes be as high as 7 or 8 per cent. Any method devised for the desulphurizing of oils must, of course, not only be a technical but a commercial success. The cost of the refining process must be reasonable.

Strange to say, the method of refining first introduced is still that in most general use to-day. Sulphuric acid is the agent mostly used. This method of treatment is in general use for benzine, kerosene, and lubricating oil distillates. In general principle the method adopted for these three distillates is the same. The benzine is violently agitated in a suitable vessel with the necessary percentage of concentrated sulphuric acid, the tarry residue separates out and is drawn off, the benzine is washed with water, treated with caustic alkali, and again washed. The acid treatment is usually given in two or three portions, the sludge being drawn off before the addition of the next charge. Generally, amounts of acid up to 2 per cent. or even more may be used in the case of benzines; in the case of certain lubricating oil distillates as much as 25 per cent. of acid may even be necessary. Economy may often be effected by using the sludge from the second or third treatment, as acid for the first.

The function of the sulphuric acid is not fully understood. It appears to act, certainly in the first application, as a drying agent; it undoubtedly absorbs unsaturated hydrocarbons and even aromatics, and it removes also oxygenated bodies. It undoubtedly also acts to some extent as an oxidizing agent, as sulphur dioxide is usually evolved during the refining process. The strength of the acid is an important factor. If this falls below 97 per cent. the efficiency rapidly diminishes.

Oleum of various strengths may be used, but it must be remembered that the stronger the acid, the more readily aromatic hydrocarbons are sulphonated. As these hydrocarbons are the most valuable from a motor fuel point of view (*vide* Pt. VIII., Sect. A), it is advisable to avoid their removal during the treating process as far as possible. The presence of nitric acid in the sulphuric acid is undesirable, as this will form nitro-compounds with aromatic hydrocarbons which will give a yellow tinge to the finished products. The presence of selenium dioxide is stated to have the same effect. It is commonly observed that distillates which have been standing for a long time are more difficult to refine.

After the successive acid treatments the benzine is allowed to stand until all the acid sludge has settled down. This is then drawn off, the benzine is washed with water and then neutralized with caustic soda. Of this, usually only a very small percentage is required. A further wash with water after draining off the soda sludge, usually completes the process.

Mixing is effected by either mechanical means or by blowing in of air. In either case the operation is usually conducted in an "agitator." This consists of a steel cylindrical vessel fitted with a conical bottom. The capacity is usually not over 20 tons for mechanically operated plant, but when air-mixing is used, vessels of 200 tons or more capacity may be employed (Fig. 37). In either case the agitator is fitted with an inlet pipe for the benzine, and inlet pipes for acid and soda. The chemicals may be blown up into the agitators by means of montejus, or may be run in from measuring tanks placed above. The latter is the preferable method.

Mechanical agitators are fitted with a central shaft carrying some sort of propeller. The whirling round of the contents of the agitator as a whole is avoided by baffle plates dipping just below the surface of the liquid. Such an arrangement produces a very lively agitation and thorough mixing of the liquids. In the case of air-operated agitators, the air is led down into the tip of the cone by means of a 4-inch pipe. The agitator (or at any rate the conical portion) is often lined with lead.

The top of the agitator is completely closed in, and usually fitted with a number of explosion doors. These are arranged so as to open outwards, and automatically fall back into position. Steam pipes are also usually led into the top of the agitator. This is advisable, as the vapours above the liquid have often been known to flash. Should this occur the explosion doors fly open and relieve the pressure, thus preventing the roof of the agitator from being blown off. It is in some refineries common practice to blow steam into the top of the agitator during the period of introduction and mixing with soda, as this, strangely appears to be the danger point.

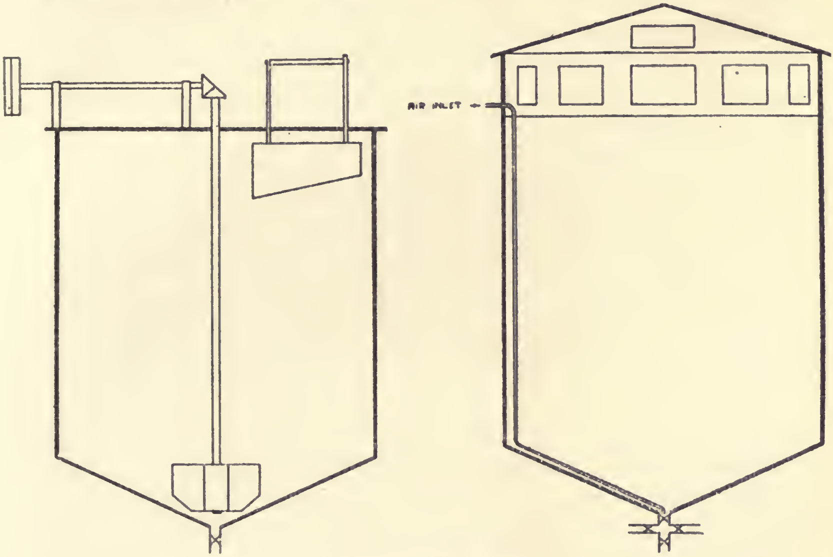

FIG. 37.—Agitators.

At the bottom of the cone is placed a main valve connected to a cross piece, by means of which the acid sludge, waste soda, washings, and the finished product may be drawn off to their various receptacles (Fig. 37).

In the case of benzines, agitation by means of air is inadvisable owing to the large evaporation losses caused. Where the refining loss may be less than 1 per cent. when mechanical agitation is used, it may be more than double that amount when air agitation is used, particularly, of course, in a warm climate.

The method of treatment as outlined above is that in most general use for benzines and kerosenes. For lubricating oil the technique of the method is somewhat different (*vide* p. 203). The same method is sometimes applied to the treatment of paraffin wax, and it will be remembered that sulphuric acid is also used for the refining of ozokerite or natural wax.

Many sulphur-containing oils, however, do not readily yield sweet-smelling, marketable products by such a comparatively simple treatment. Numerous methods for treatment of such oils have been described, but comparatively few are in successful operation. Certain of these methods are directed to remove the sulphur from the crude oil. In many cases, such as, for example, the crudes of Mexico, rich in asphalt, of which sulphur is an essential or constitutional component, such a method would be inapplicable. The problem of desulphurizing the crude is, however, of relatively minor importance as there is no objection to the presence of sulphur compounds in a fuel oil or asphalt. A method applied to the crude oil is that designed by Frasch (*J. Ind. and Eng. Chem.*, vol. 4, p. 134). The sulphur rich crude oils of Canada and Ohio are distilled in a flat-bottomed cylindrical still in presence of copper oxide. The still is fitted with a vertical shaft carrying horizontal arms, to which hanging chains are attached. By this means the copper oxide is kept in suspension in the oil. After the bulk of the oil has distilled off, a further charge is added and the process repeated, and this may be carried out four or five times. The residue and the copper oxide are then pumped out through a filterpress, the copper oxide being thus separated off and regenerated by roasting. The same process is sometimes carried out in another way, the vapours of the distillate being made to traverse a cylindrical vessel in which revolves a steel brush, dipping into a mixture of heavy oil and copper oxide in the lower part of the vessel. The vapours passing through the teeth of the revolving brush are thus subjected to the copper oxide and so refined.

Another method in common use is that in which sodium plumbite is used. The benzine (or kerosene) is treated with a saturated solution of litharge (PbO) in strong caustic soda. A heavy black sludge is formed and the benzine remains black owing to the presence of suspended lead sulphide. A trace of flowers of sulphur is usually added, which completes the precipitation of the lead sulphide. After drawing off the sludge, the benzine or kerosene is washed with water. This process may be used in connection with the ordinary acid treatment.

Innumerable other methods of treatment have been devised. Colin and Amend (U.S. Pat. 723368 of March 24, 1903) recommend the use of an alkaline hypochlorite in presence of a catalytic agent, such as manganese dioxide. Dunstan (Eng. Pat. 139233) uses an alkaline hypochlorite and regenerates this electrolytically after use. H. A. Frasch (U.S. Pat. 525811 of 1894) also advises the use of a hypochlorite. Hall (Eng. Pat. 26756 of 1913) recommends the use of sulphur dioxide, followed by a distillation, claiming that a large amount of the sulphur is thereby converted into a form which may be easily removed by the ordinary methods.

The refining of shale oil benzines and cracked benzines presents difficulties owing to the presence of unsaturated hydrocarbons. Treatment with a dilute sulphuric acid (80 to 90 per cent.) often suffices to remove the more objectionable of these, particularly the diolefines which readily condense up to form resinous bodies. Brooks and Humphrey (*J.S.C.I.*, 1918, 316A) have investigated this question and have concluded that during the refining by sulphuric acid two actions take place simultaneously, viz. the olefines are partly removed and partly polymerized, neutral alkyl esters being formed at the same time. These latter and the polymerized products may remain in the oil, and account for the increase of specific gravity sometimes noticed in refining such benzines.

Methods of refining cracked benzines, dependent on the use of colloidal or absorbent substances have been proposed.

Hall (Eng. Pat. 12100 of 1917) proposes passing benzine vapours through fuller's-earth, kept at a temperature above the final boiling point of the benzine. The columns of fuller's-earth are kept at constant temperatures by means of oil baths, and the benzine vapours are passed through the columns in series. It is claimed that the issuing vapours when condensed have completely lost the odour characteristic of cracked spirit. The fuller's-earth appears to have the power of causing polymerization of the unsaturated hydrocarbons to take place, so that high boiling condensation products are formed which may be drawn off from the columns. The fuller's-earth in course of time loses its efficacy and needs regeneration, after which it can be reused.

The methods of refining above described are in the main applicable to kerosene also. The application of these methods, while producing a kerosene which is perfectly "sweet," may still yield a product of which the colour is not up to the required standard. The colour may readily be improved by mixing the kerosene with a small percentage of some decolorizing powder, and allowing the powder to settle out or filtering it off. Various decolorizing powders may be used for this purpose, *e.g.* animal charcoal, a bone black, the many varieties of fuller's-earth, *e.g.* the American floridin, the German frankonit and so forth. Certain types of bauxite also function well.

The action of these decolorizing powders is so erratic that general working rules cannot be laid down. Some powders in the case of certain kerosenes may act best in their ordinary air-dried state, some may work better if dried at 105° C., and others only if previously ignited. For any particular kerosene, powder A may be found better than B, yet for another type of kerosene, powder B may be found better than A. It is of the utmost importance, therefore, to examine thoroughly the effect of the possible powders on the kerosene in question before beginning operations.

It will generally be found that the animal charcoals are much more efficient (per percentage used) than are the fuller's-earths, but they are usually much too expensive. As a general rule, also, fuller's-earth works better if previously ignited or at least if previously dried at 105° C. Many of these fuller's-earths may be regenerated and reused, as is also the case with bauxite.

In the case of kerosene, the decolorizing powder may be introduced into the ordinary agitator, and the mixture run off into a settling tank. In order that the last traces of the powder may be removed, the kerosene should be filtered through paper in filter presses, or may be centrifuged by means of a Gee centrifuge.

The chemical treatment of lubricating oils and waxes are carried out on similar lines, certain necessary modifications being introduced.

The treatment of lubricating-oil distillates with sulphuric acid is usually carried out in an agitator constructed somewhat similarly to that used for kerosene. The agitators are usually of somewhat smaller capacity, of greater diameters, and less depth. They may be provided with steam coils for heating purposes. The agitation is invariably effected by means of air. Large percentages of acid up to 20 per cent. or more may be used, especially for the heavier oils. After agitation the mixture is usually run out into a settling tank of large diameter, in which the acid sludge may more easily separate out. This acid sludge, in the case of heavier oils, may be practically solid and may require digging out. The supernatant oil, after thorough settling, is drawn off and transferred to the soda agitator, where it is neutralized with white dilute caustic soda with gentle agitation and then washed. Great care must be taken with the neutralizing and washing as emulsions may form, the subsequent splitting up of which may give great trouble.

The colour and appearance of the finished oil will depend to a great extent on the thoroughness of the separation from the acid sludge. Inefficient washing of the soda treated oil will result in the presence of soaps in the finished oil. After thorough washing the oil is usually warmed and blown dry by passing air through it. This must be done at a temperature not too high, not exceeding 50° C., otherwise the oil may go off colour somewhat. Various modifications of this method have been suggested and are in operation, *e.g.* the use of sodium silicate in place of caustic soda, the use of lime or soda lime for neutralization in place of soda.

A great number of lubricating oils are, however, made without any acid and soda treatment at all. Such are the filtered cylinder oils, filtered neutral oils, and many others.

The filtration is effected through one of the decolorizing powders above mentioned. The operation is simple. The filtering powder, usually granulated and free from fine dust, is filled into a vertical cylindrical vessel, resting on filter cloth supported on horizontal grids. The filtering vessel is steam jacketed, and fitted with manholes or a removable bottom for extracting the powder after use. The heated lubricating oil distillate is allowed to percolate upwards through the filtering medium. The first fractions which pass through may be only slightly coloured, but the colour grows in depth as filtration proceeds. By collecting the filtered oil in separate vessels several grades may be produced. After the filtering has proceeded as far as is deemed advisable, the vessel is disconnected and allowed to drain. Benzine is then passed through the vessel in order to dissolve out the oil adhering to the fuller's-earth, this benzine being subsequently recovered by distillation. After thus washing the fuller's-earth, steam is passed through to remove the last traces of benzine. The vessel is then opened and the fuller's-earth removed for regeneration. The behaviour of the fuller's-earth should be investigated before use in order to find out the best conditions for use. The decolorizing action of fuller's-earth is doubtless a physical one, the asphaltic bodies being absorbed. Gurwitsch maintains that the fuller's-earth exerts a polymerizing action on the unsaturated compounds, an opinion shared by Hall (*vide* p. 202).

The method of refining by mixing with decolorizing powder is also applied to the manufacture of paraffin wax. This is described in Section D, dealing with that product.

The Edeleanu Process.—The above-mentioned processes for the refining of oils apply generally to the removal of small percentages of constituents (so-called impurities), the presence of which is considered objectionable. The kerosene fractions of certain crude oils, notably those of Borneo, and to a less extent those of Rumania, contain appreciable quantities of aromatic hydrocarbons, the presence of which renders the oil of relatively poor burning quality when used in ordinary lamps. (When, however, burned in lamps of suitable design such aromatic kerosenes can give excellent results.)

The problem in refining such oils is, therefore, that of removing a relatively large percentage of aromatic hydrocarbons. This could, of course, be done by sulphonation, but in this case the splitting up of the sulphonic acids formed and the regeneration of the sulphuric acid, are problems of great technical difficulty. The process designed by Edeleanu (U.S. Pat. 911553, Eng. Pat. 11140 of 1908) is a physical process in which the above-mentioned difficulties do not appear. This process depends on the use of liquid sulphur dioxide as a solvent for unsaturated and aromatic hydrocarbons. Naphthenes and paraffins are relatively insoluble in this reagent.

The principle of the process is simple. The kerosene to be treated is agitated with a large volume of liquid sulphur dioxide at a low temperature, say —10° C. Separation into two layers takes place, the lower being a solution of the aromatic hydrocarbons in liquid sulphur dioxide, the upper the naphthenes and paraffins, containing some sulphur dioxide in solution. These layers are separated and the sulphur dioxide is separated off by distillation, recondensed, and used over again. The sulphur dioxide works thus in a cycle, so that only working losses need be made up.

By the Edeleanu process also the sulphur-containing bodies occurring as impurities may also be removed.

Several large-scale plants operating by this method have been erected in Rumania and elsewhere. Edeleanu gives a full description of the working method in "Bulletin," *Am. Inst. Min. Eng.*, 1914, p. 2313.

The distillate is first dried by passing through filters filled with dry salt. It is then pumped through a cold exchanger, where it is cooled by the cold extract issuing from the mixing vessel. The distillate is then further cooled by passing through a distillate cooler, where it is cooled by a separate refrigerating system (not shown in the diagram). It then passes into the mixing vessel, where it meets the liquid sulphur dioxide which has likewise been cooled by the issuing refined product and in a special cooler by means of a refrigerating system not shown in the diagram.

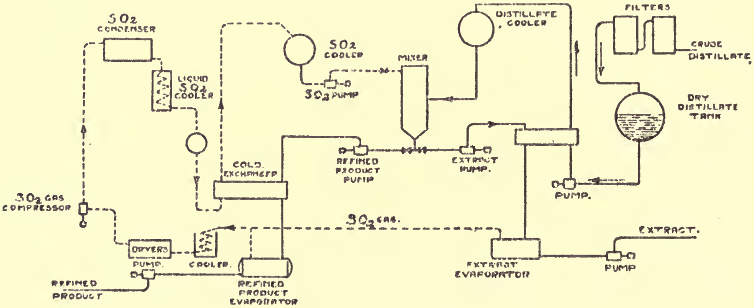

FIG. 38.—Working scheme of Edeleanu plant.

As the sulphur dioxide is admitted into the mixer, it is at first completely absorbed by the distillate. After a time, however, the mixture separates into two layers, the lower being the extract, a solution of the aromatic hydrocarbons in liquid sulphur dioxide ; the upper, the unaltered naphthenes and paraffins, containing some sulphur dioxide in solution, containing also, naturally, some proportion of aromatics unextracted, according to the conditions of working.

The extract is drawn off by the extract pump through the distillate cold exchanger to the extract evaporator, where it is heated by steam coils (not shown in diagram) ; the sulphur dioxide is returned to the system through coolers and dryers, and the extract, now free from sulphur dioxide, is pumped away.

The refined product is pumped out from the mixer through a cold exchanger, absorbing heat from the liquid sulphur dioxide in this case. The refined product then passes on to its evaporator, where the dissolved sulphur dioxide is driven off. The heating of the evaporators may be effected by the exhaust steam from the engine which drives the pumps and compressors. Only the bare outlines of the operation of the plant are described above.

In treating a Rumanian distillate of sp. gr. 0·820, 75 per cent. of a refined product of sp. gr. 0·803, and 25 per cent. of an extract of 0·869 were obtained. The loss of sulphur dioxide amounted to 0·56 per cent. reckoned on the distillate treated.

The oils extracted from the sulphur dioxide solution are very rich in aromatics and may find special applications as solvents or in other directions, or may be utilized as fuel, while the treated kerosenes, being free from aromatic hydrocarbons, are of excellent quality as illuminating oils for use with the ordinary types of lamp on the market.

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SECTION D.—THE MANUFACTURE OF PARAFFIN WAX AND LUBRICATING OIL

THE starting point for the manufacture of paraffin wax is the wax distillate obtained by the distillation of paraffin wax-containing crudes. The operation of the subsequent processes depends to a very great extent on the character of this distillate. This distillate is a mixture of wax and lubricating oil distillate, and both wax and lubricating oils are made therefrom. Unfortunately the conditions best for lubricating oil production are not those best for wax production, so that usually a compromise must be made, or perhaps resort may be had to redistillation. The less steam used in distilling, *i.e.* the higher the temperature and the greater the cracking, the more easily crystallizable the wax and the less viscous the character of the oil and vice versa. The extent to which the distillation may be carried is determined almost entirely by the nature of the crude oil. Some crude oils (*e.g.* Pennsylvanian) readily give up their wax on distillation, leaving as residue an oil relatively wax free. Such residues may indeed be used as "steam refined cylinder stocks." Others leave a residue which still contains much wax. This residue cannot be distilled further by the ordinary method employing steam, as the distillates which would be so obtained would contain high melting-point wax which would not crystallize or sweat well, perhaps owing to the highly viscous oil with which it would be associated. Such residues may be either burnt as fuel or distilled by the so-called cracking distillation method, *i.e.* without steam, right down to coke. As the paraffin wax existing in the crude oil cannot be separated off by means of filtration owing to its amorphous condition the oil must be distilled. The paraffin which distils over is crystalline and amenable to filtration. The methods adopted for working up the distillate containing paraffin wax vary with different crudes and in different refineries. In some cases the wax distillates are subjected to a sulphuric acid treatment and perhaps to a redistillation before being filtered, but in many cases this is not necessary.

In general, the method of extracting the wax adopted is that of filtering off the wax from the chilled distillate, and subsequently freeing it from oil by sweating, or by washing by solvents which dissolve the oil but not the wax, *e.g.* alcohol.

The wax distillate is "cut" from the distillation by using the congealing point as a guide, the points selected being based on previous works and laboratory experience for the particular oil.

The chilling of the distillates may be effected in various types of plant. That in general use in the United States is continuous in action, viz. the "Carbondale" type. This consists of a number of coolers made up each of two concentric pipes arranged one over the other horizontally. The wax distillate is pumped through the internal pipes, each of which is provided with a worm, passing through the set in series, while the cold brine is circulated through the annular spaces in counter-current fashion.

The cold brine is produced by one of the well-known types of refrigerating plant, usually with ammonia as working fluid. For details of the operation of such a plant the reader must be referred to standard works on refrigerating practice. The degree to which the wax distillate is cooled must depend on its wax content. If the wax content be high the operation may best be conducted in two or even three stages. In such a case the chilled distillate would be filtered, and the filtered oil further chilled; if the chilling were completely effected in one stage the chilled distillate might be too thick to handle.

As the formation of well-defined crystals is of importance because of the subsequent operations, and as the size of the crystals depends, not only on the material, but on the conditions of cooling, other types of cooler may be found more satisfactory in certain cases. A well-known type is the "Henderson" (Fig. 39). This is composed of a large rectangular vessel, which may have a capacity of 10 tons or more, divided up into a number of narrow compartments by hollow plates through which the cold brine circulates. A central shaft carrying scrapers very slowly revolves, scraping away the wax as it crystallizes on the surfaces of the hollow plates. A stirrer working in a channel along the bottom enables the pasty mass to be transferred to the suction of the pump. In another type of somewhat similar design, no scrapers are employed, so that the cooling is very slow. The dividing plates are in this case made tapering in section, so as to allow of the easy removal of the semi-solid mass.

The chilled wax distillate is then passed on by pumps to the filter-presses. These filter-presses are of the normal type, sometimes with square plates, more often with circular. The presses used in America are of massive construction—48 inches in diameter with 300 plates. These presses are fitted with hydraulic ends for closing the press tight, as pressures up to 300 lbs. to the square inch are sometimes employed in filtering the wax. Numbers of these presses are housed in one building, which must be kept cool and well insulated. It is usual to maintain the temperature in the filter-presses a degree or two above that of the chilled wax distillate, in order to ensure that no crystallization takes place in the presses (as this would tend to clog the filter-cloths).

When any one press is full and has been pumped up to full pressure, the supply of chilled distillate (which may be called by the convenient Galician term "gatsch") is cut off and the press is opened. The filter cakes fall out into a conveyer placed beneath the press and are conveyed to a melting-up tank outside the building.

In this way the wax distillate is separated into a "slack wax" filter cake and filter oil, this filter oil being naturally

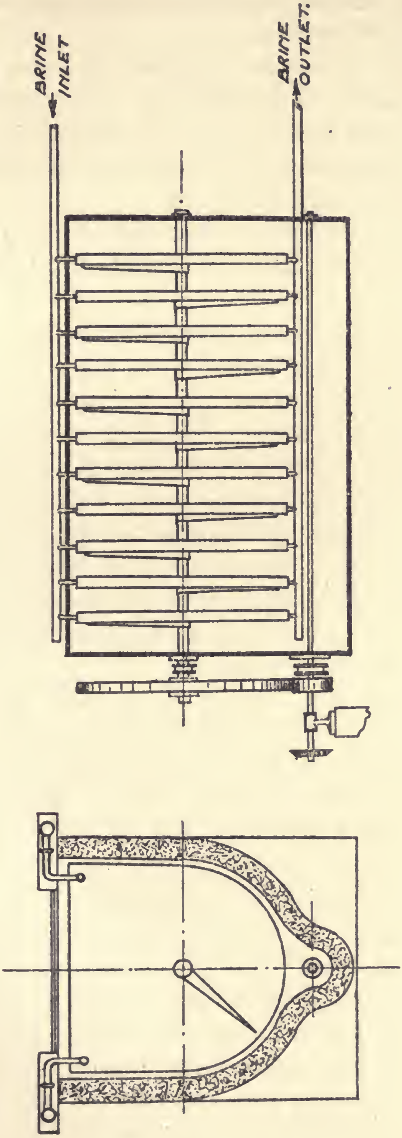


Fig. 39.—Henderson Cooler.

saturated with wax at the temperature of filtration. The slack wax may amount to about 20 per cent. of the gatsch pumped through the press.

The filter oil or pressed distillate, if from a first-stage chilling, is rechilled and refiltered, thus yielding another batch of filter cake of lower melting point; if from a final chilling it is reduced or concentrated in stills to the required viscosity to yield a lubricating oil.

The slack wax or filter cake is then melted up and pumped to the sweating house, where it is subjected to the sweating process.

Sweating is a process of fractional melting. The operation is carried out in sweating pans, erected in a sweating house. The sweating pans are shallow sheet-iron trays, 5 or 6 inches deep, fitted with false bottoms of coarse wire gauze. The bottom of the tray slopes from all sides toward the centre, from which point a draw-off pipe leads to a main draw-off pipe, passing to the outside of the house. Immediately beneath the wire gauze false bottoms lie a number of perforated steam pipes and just above the gauze are sometimes fixed a number of $\frac{3}{4}$-inch pipes, through which cooling water may be circulated.

The trays are first partly filled with water covering the gauze false bottoms. Melted slack wax is then floated on to the surface of the water until it forms a layer 3 to 4 inches thick and is then allowed to cool. When the wax has solidified, the water is run off, the cake of wax being thus allowed to rest on the gauze false bottom.

The house, containing a number of such trays, fitted up one above the other, is then closed up and slowly warmed by means of exhaust steam through steam pipes placed on the walls. As the temperature rises, sweating starts, the oil oozes out of the fine network of crystals, accompanied of course by much low melting-point wax. The process is controlled by watching the character of the wax flowing off and by examining the product as it lies on the trays.

When the process is judged to be complete, the wax lying on the trays being oil-free and of the correct melting point, the temperature of the house is quickly raised and live steam is blown in through the perforated pipes, so that the sweated wax on the trays is melted up, the effluent pipes being then diverted to the sweated wax tanks.

The slack wax is thus split up into sweated wax (which is now free from oil) and "foots oil" and "foots wax." The "foots wax" is resweated to yield wax of lower melting point, or it may be in part returned to the cool-house or even to the distilling bench.

The process of sweating is slow, usually taking from 24 to 60 hours according to the nature of the wax. The above-described apparatus, which is that in most general use, was first devised by Henderson in Scotland. A noticeable improvement is that patented by Pijzel. The sweating stoves are made movable so as to run on rails. The sweating house consists of a long tunnel heated by hot air, with a melting-out chamber at one end. The sweating pans enter at one end and are transferred through the tunnel by a series of stages as each finished stove is melted out. The considerable waste of heat involved in alternately cooling and heating the sweating house is thus avoided.

The actual control of the operation and the working details depend on many factors and must be worked out for each particular plant. Generally, several grades of wax of melting points say about 122°, 127°, 132°, and 140° F. will be made and perhaps, also, a very soft match-impregnating wax too.

The sweated wax should now be free from mineral oil, but will still contain some colouring matter. This may be removed either by refining or by filtration.

If the refining process be used the melted paraffin wax is agitated with a small percentage of concentrated sulphuric acid. The acid sludge is drawn off and the melted wax is then run down into a powder mixer. This is a cylindrical horizontal vessel fitted with paddles. In this vessel the wax, kept hot by means of steam coils, is agitated with a decolorizing powder, such as animal charcoal, potassium ferro-cyanide waste, some type of fuller's-earth or bauxite.

When the treatment is complete the whole is blown by compressed air through a cloth filter-press, to remove the bulk of the decolorizing powder, the last traces being removed by filtering through paper in a filter-press fitted with steam-jacketed plates.

Instead of treatment with acid and decolorizing powder, a filtration treatment may be adopted. The filter used is made of a vertical cylindrical steam-jacketed vessel, which may have a capacity of 1 ton or more of filtering medium. It is constructed with a removable bottom, so that the exhausted decolorizing powder may be removed. The melted wax is allowed to percolate through the filtering medium, which may be a fuller's-earth such as floridin, an animal charcoal or bauxite (Eng. Pat. 16617 of 1908). The filtering medium must not be too finely divided, otherwise filtration is too slow. It is usually ground to the fineness of coarse gunpowder. In some cases decolorizing powders act best after drying at 105° C., in some cases best after ignition. This point must be settled by experiment in the laboratory. As the wax filters through, the discoloration is removed, but as the powder loses its efficacy the issuing wax will begin to show a yellowish tint. At a certain point, therefore, the filtration must be stopped and the filter drained. The exhausted filtering medium is then removed and a fresh charge put in. After filtration the wax is finally filtered through filter-presses with paper, and is then run off into moulds and allowed to cool. It may also be cooled by being allowed to flow in a thin film on to the surface of a rotating cylinder cooled internally by water, from the surface of which it is peeled off by a fixed knife-edge and packed directly into barrels.

The actual details of the method to be employed in working up any particular crude for wax must depend upon the crude itself and upon local conditions.

The paraffin wax crudes of the United States of America, contain, as a rule, about 2 to 3 per cent. of wax, Galician oils about 5 to 6 per cent., while some of the oils of Burmah and Borneo contain up to 10 per cent., or more.

As an example the following scheme of working up a crude oil may be given :—

This crude yielded on distillation—

Crude benzine	14 per cent.
,, kerosene	41 ,,
Gas oil	3 ,,
Wax distillate	37 ,,
Coke	3 ,,

The wax distillate was worked up in the manner set out diagrammatically below.

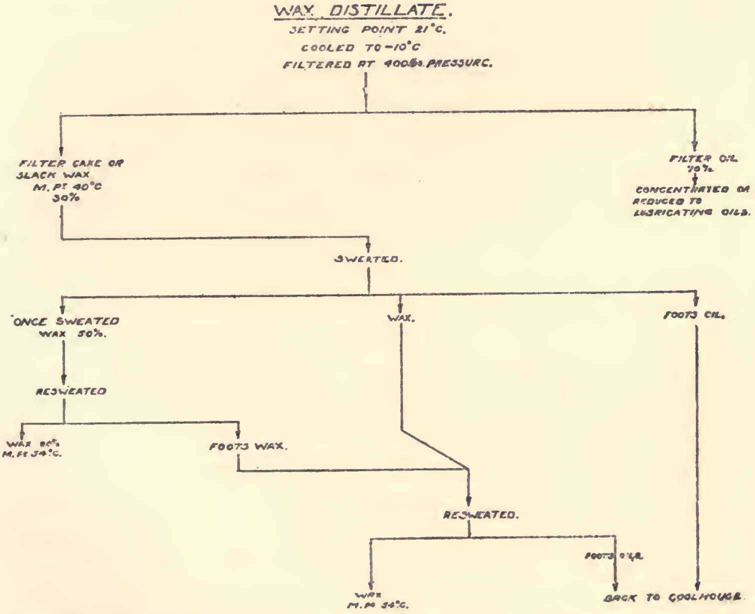


FIG. 40.—Scheme for operating a wax plant making one grade of wax only.

This represents an ideally simple case. In many cases several grades of wax of different melting points are made.

Variations of the method are innumerable and must be worked out to suit each case. In some cases the foots oil is returned to the cool-house for rechilling, in others it is redistilled, in some cases it may be pumped to liquid fuel. Paraffin wax is also extracted from materials other than crude petroleums. The shale oils of Scotland, for example, yield about 2 per cent. of rather low melting point (45/46° C.) wax. The shale oils of New South Wales also yield paraffin wax, as do in general most shale oils. Tars from the distillation of wood, especially beech, also yield paraffin wax; in fact, this is the material from which paraffin wax was first made. Lignite and the peculiar mineral substance pyropissite (*vide* p. 151) are worked up in Germany and yield considerable quantities of paraffin wax, as distinct from the montan wax already alluded to (*vide* p. 150). As, in the case of such tars produced by distillation, the paraffin wax exists in the crystalline form, it can be directly separated from the tar, topped to remove the lighter fractions, by the usual crystallizing method.

Several processes of extracting paraffin wax depending on the relative solubilities of wax and mineral oils in various solvents, *e.g.* alcohol of various strengths, acetone, ethyl acetate, etc., have been devised (*e.g.* German Pats. 123101, 140546, and 149347), but these methods are not used to any extent. Alcohol will dissolve all the oils, resins, and creosotes present in such tars. The tar is dissolved in ten times its weight of 90 per cent. alcohol in an autoclave at 80° C. and the solution cooled. The paraffin wax crystallizes out and may be separated off by centrifuging.

The manufacture of **lubricating oil** is intimately connected with that of paraffin wax, as in many cases lubricating oils are made from the oils resulting from the filtering off of the wax from wax distillates. Lubricating oils are also manufactured from naphthenic or asphalt base oils, in which case the removal of wax by filtration is unnecessary.

It is often held, though by no means proved, that lubricating oils derived from paraffin wax base oils are of better quality than those derived from naphthenic or asphalt base crudes.

Lubricating oils may be divided roughly into two classes, residual and distillate oils. Residual oils are those which result from the concentrating down by distillation of certain types of crude oil. A naphthenic oil free from paraffin and not rich in asphaltic material may be concentrated down to make a low-grade black oil, such as an axle oil, which need not have a high flash-point or good colour. Such oils may also be used for the manufacture of dark greases.

Certain types of paraffin-wax-bearing crude oil of the Appalachian fields yield as a residue after the other products, including the wax, have been distilled off, a so-called "*steam-refined cylinder stock*." The distillation is carefully carried out at as low a temperature as possible (preferably in vacuo) with ample steam. The distillation is carried on until the flash-point of the residue rises to from 500° F. to 700° F.; 600° F. steam refined stock being the grade in general use. With these crudes the asphaltene content is so low that these residues, which have exceptionally high flash-points, may be used as cylinder oils for steam cylinder lubrication. With other types of crude oils the residues so produced would contain too much wax, or be too rich in asphaltenes, or have too low a flash-point, and so be of relatively inferior quality. These steam-refined cylinder stocks may be filtered through decolorizing powders or animal charcoal, the asphaltenes being thus removed, so that a fine-looking oil, reddish-brown by transmitted, green by reflected, light results. Such oils are known as "*filtered cylinder oils*," and are much valued as such and for blending purposes. Such filtered cylinder oils may, however, still contain a little paraffin wax. This may be removed by dissolving the oil in light benzine, chilling the mixture, and removing the separated wax by means of a Sharples centrifugal machine; the benzine is then distilled off and a filtered cylinder bright stock then remains.

Similar cylinder oils may be manufactured by the concentration of lubricating oil distillates. Russian crudes, for example, may be distilled down to "astatki," or thick fuel oil, lubricating-oil distillates being produced. These lubricating-oil distillates may be concentrated down to cylinder oils of flash-point about 400° F.

This concentration is carried out in an ordinary fire-heated still, the temperature being kept down as low as possible by means of copious use of steam. The distillation or "reducing" is carried on until the tests of the residue have the required values. This reduction is best effected in vacuo, the quality of both distillates and reduced stock being thus improved.

The lighter varieties of mineral lubricating oils are all distillates which may or may not have been reduced to grade by concentration, or which may be straight distillates, or perhaps blends of several distillates.

The material used may be either a distillate from naphthene base crude oils, such as those of Russia, Texas, and California, or a filtered "press oil" obtained by filtering off the paraffin wax from a well-cooled wax distillate obtained from wax or mixed base crude oils, *e.g.* certain of those of Pennsylvania or Mid-continent fields.

When the distillates have been distilled or concentrated to the required viscosity, they must be refined. In some cases these oils are refined before pressing out the wax, in other cases the refining is the last treatment to which they are subjected.

In United States practice the lighter wax distillates are called "neutral oils" or "spindle distillates."

The pressed distillate after reducing to grade is filtered through a decolorizing medium, and does not receive an acid treatment. The resulting oil is termed a "neutral oil." Such neutral oils may be termed "non-viscous" or "viscous" according to their viscosity.

The chemical treatment of lubricating oil by means of sulphuric acid is carried out in agitators of the usual type, the temperature of the oil being kept as low as conveniently possible in regard to fluidity.

In order to economize plant the settling out of the acid sludge is usually allowed to take place slowly in shallow settling tanks of large diameter. When the acid sludge has settled out completely the oil is transferred to the soda agitators, where it is gently warmed and neutralized with caustic soda, being subsequently well washed by sprays of water, and finally dried by the blowing through of air. The process of refining of lubricating oils, particularly the neutralizing and washing, is difficult, as emulsions often form with great readiness, and these may be difficult to split up.

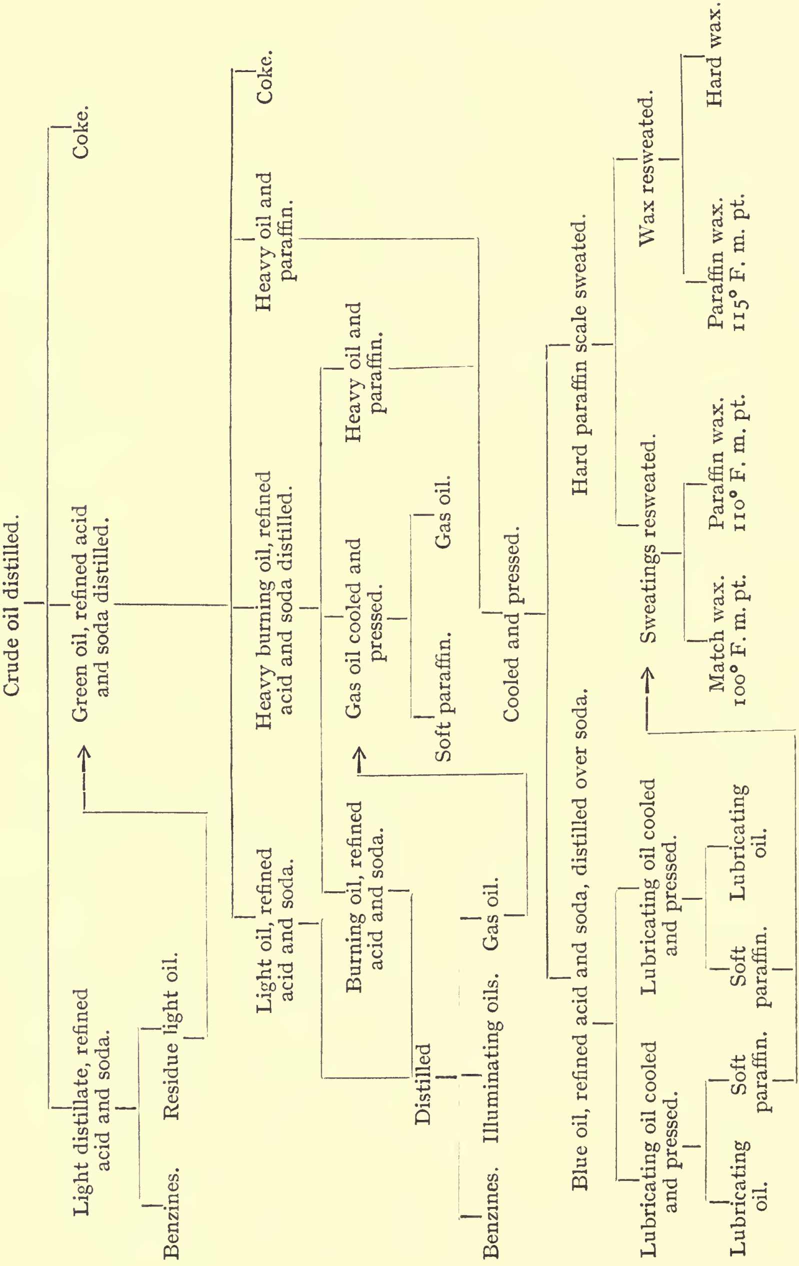
The splitting of such emulsions is usually effected by the addition of dilute acid, and subsequent re-treatment by soda after good settling out of the dilute acid layer. The addition of small quantities of oleic acid during the soda treatment may also assist in preventing the emulsification, and the addition of salt water may sometimes break up an emulsion once formed.

Sodium silicate in a solution of specific gravity about 30 Be. may also be used in place of soda, the precipitated silica perhaps assisting by carrying down impurities mechanically.

Many other methods of refining have been proposed for which *vide* Engler-Hofer, "Das Erdol," vol. 3, pp. 522, 527.

No general rules can be laid down, as the detailed method of treatment of any oil depends on the nature of the oil. The losses incurred by refining in this way are high, amounting to as much as 20 per cent. or more in particular cases.

As the general plan of the working up of a shale oil into wax and lubricating oils may be more complicated than that of a petroleum crude, a scheme of working up a Scotch shale oil (*vide* "The Oil Shales of the Lothians," *Mem. Geol. Survey, Scotland*) is herewith given :—


Crude oil distilled.
Light distillate, refined acid and soda.
Green oil, refined acid and soda distilled.
Coke.
Benzines.
Residue light oil.
Light oil, refined acid and soda.
Heavy burning oil, refined acid and soda distilled.
Heavy oil and paraffin.
Coke.
Burning oil, refined acid and soda.
Gas oil cooled and pressed.
Heavy oil and paraffin.
Distilled
Soft paraffin.
Gas oil.
Benzines.
Illuminating oils.
Gas oil.
Cooled and pressed.
Blue oil, refined acid and soda, distilled over soda.
Hard paraffin scale sweated.
Lubricating oil cooled and pressed.
Lubricating oil cooled and pressed.
Sweatings resweated.
Wax resweated.
Lubricating oil.
Soft paraffin.
Soft paraffin.
Lubricating oil.
Match wax. 100° F. m. pt.
Paraffin wax. 110° F. m. pt.
Paraffin wax. 115° F. m. pt.
Hard wax.

It must be again emphasized, however, that every oil to be worked up must be treated on its own merits, and the best method for that particular case must be devised.

The various grades of mineral lubricating oil made and their properties will be described under the section dealing with applications of petroleum products.

"Perotlatum," also known as petroleum jelly, petroleum ointment and vaseline (the trade name of the well-known product made by the Cheeseborough Co.), is a product defined in the United States pharmacopœia as "a mixture of hydrocarbons chiefly of the methane series obtained by distilling off the lighter and more volatile portions from petroleum and filtering the residue."

It may be prepared from the residues from the distillation of certain paraffin wax base crude petroleums, the concentration being carried to the necessary extent. Many paraffin-rich crudes will, however, not yield a suitable product. It may also be made from the "rod wax" which accumulates in the pumps of certain wax crude wells (Mabery, *Proc. Am. Acad.*, 1904, p. 349), and from the bottom settlings (B.S.) of the same type of oil.

The residues or "reduced oils" from certain crudes are filtered through animal charcoal or some form of fuller's-earth in steam-jacketed filters, the first runnings being collected and steamed to remove any earthy smell due to the fuller's-earth. The rod wax or crude oil B.S. may be similarly distilled to the right concentration and then filtered.

Another variety of petrolatum is made by the addition of paraffin wax of low melting point to lubricating oils filtered to a fine colour. Such petrolatums are, however, not so homogeneous and separate out crystalline paraffin.

Liquid Petroleum or Medicinal Oil is a product which is to all intents and purposes a highly refined lubricating oil. Oil of a suitable viscosity is treated with successive treatments of oleum, neutralized and filtered through fuller's-earth. The treatment is very drastic and the refining losses very heavy. The product is quite odourless, tasteless, and colourless. The hydrocarbons which are present in petrolatums are all undoubtedly of a saturated type. In the types of petroleum derived from residue no crystalline hydrocarbons are present, the solid members being probably similar to those found in ozokerite or natural mineral wax.

Lubricating Greases.—These are made in great variety, a petroleum oil forming the basis of the majority. They are composed in the main of two constituents, a soap and an oil, the soap usually being formed during the manufacture of the grease. Calcium and sodium soaps are generally used, but certain greases contain potassium and aluminium soaps. Moreover, some greases contain fillers such as graphite, French chalk, mica, etc. Many varieties of oils and fats are used, such as palm oil, tallow, resin oil, anthracene oil, and petroleum residual oils.

The plant used for the manufacture of greases is simple, consisting merely of (*a*) a melting and boiling pot for melting up or heating the fat or oil, (*b*) a mixing vessel with steam-jacketed walls and arrangements for stirring. The constituents of the grease are introduced into the boiling pot and heated for several hours, the contents then being run down into the mixing vessel, where they are thoroughly incorporated. Fats proper or fatty acids may be used for grease making, in the former case the glycerin remaining in the grease.

A cup or motor grease may be made by the incorporation of about 6 per cent. of hard tallow soap into an engine oil, or alternately by boiling up tallow, and finely divided slaked lime free from grit with the necessary proportions of the selected mineral lubricating oil.

The so-called "fibre greases" are made by using caustic soda in place of lime. "Rosin greases" are made by boiling lime with rosin oils; "black greases" by the use of mineral residual oils. A product termed "mineral castor oil," which contains an aluminium soap, is used for the lubrication of agricultural machinery. A soap stock is made by making first a sodium soap and treating this with alum solution. The aluminium soap is then dissolved in a quantity of mineral oil and the clear soap stock so obtained is mixed into further quantities of mineral lubricating oil to make the various grades of "mineral castor" required. Innumerable types of greases are manufactured and sold; an enumeration of the various formulæ used for compounding would serve no good purpose here.

Cutting Oils.—A special product which should have good lubricating properties and a high specific heat is required for lubricating cutting and drilling tools, as an important function of such a lubricant is the cooling of the cutting edge. The so-called water soluble oils are, therefore, largely used for this purpose. Water soluble oils are usually mineral oils held in suspension by soaps, alkalies, or sulphonated oils. These oils should be readily miscible and form a stable emulsion with water so that they may be circulated and used over and over again.

Oleic acid is saponified with soda, the solution concentrated and mixed with alcohol, and then with a mineral oil. The naphthenic acids extracted during the refining of mineral oils may be used for the purpose of making the soaps for these soluble oils. Sulphonated castor oils are also used for this purpose.

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SECTION E.—THE MANUFACTURE OF FUEL OILS, RESIDUAL OILS, AND ASPHALTS FROM CRUDE PETROLEUMS

THE manufacture of fuel oils from various crudes is a comparatively simple operation, the *modus operandi* depending on the nature of the crude oil and the type of fuel oil to be produced. There are a number of crude oils, particularly of the naphthene base type, which yield a residual fuel oil, of low viscosity after the distillation off of the benzine and kerosene fractions.

Such fuel oils may be of low cold test, liquid at temperatures well below 0° C. These oils easily fulfil the conditions of the British Admiralty specification and may in many cases be used as diesel oils even for marine engines.

Crude oils of other types which contain asphalt in greater quantity yield, as a residue after distillation off of the benzine and kerosene fractions, a fuel oil of greater viscosity and higher cold test. Such an oil, while a perfectly satisfactory fuel, may not conform to Admiralty specification. Other crudes, *e.g.* the asphaltic crudes of Mexico, after only the benzine fractions have been topped off, yield a residue which is too viscous for use as fuel without special heating and burning arrangements. Such crude oils are, however, valuable as sources of asphalt.

In distilling such crudes down to asphalts of the required specification, quantities of gas oil distillate are obtained, which distillate may be used directly as a diesel fuel oil, or as a diluent for thinning down supplies of a too thick fuel oil. Other types of crude oil yield a wax residue which may be distilled to coke in a coking still, yielding wax distillate and wax tailings, which, on filtration, yield an oil which may be used as fuel.

Fuel oils may thus be divided into two categories—(*a*) distilled fuel oils, *i.e.* gas or solar oils, which being distillates are free from any residual asphalt, and which therefore form high-class oils for diesel and semi-diesel engines, and which may be used as a basic material for cracking—either to gas for enriching illuminating gas, or to motor spirits (*vide* Section F); and (*b*) residual fuel oils which may be used for diesel engine fuels in some cases, and as furnace oils in all cases.

Of similar nature are the residual oils used for road spraying (road oils), and those used for thinning down asphalts (flux oils), which are merely residual oils which must conform to certain specifications as regards viscosity, flash-point, etc., and which, therefore, must be made from certain selected crudes. The manufacture of all such oils may be carried out in the ordinary type of still, or in a plant of the tubular retort type, it being merely a question of distilling off sufficient distillate to obtain a residue of the required character.

Asphalts are manufactured from certain types of crude oil which contain little or no paraffin wax. Certain crudes which are free from wax contain, however, little asphalt, and may thus best be used for liquid fuel manufacture. Most native asphalts are much too hard for most purposes, particularly for road work, and so must be softened by the addition of flux oil. Asphalts made from certain types of crude petroleum can, however, be made to any degree of hardness by controlling the distilling process.

The best asphalts are produced from certain crude oils of Mexico and California. Certain crudes of Texas, Venezuela, Trinidad, and elsewhere also yield good asphalts.

The process of manufacture consists in distilling down to the required concentration under certain conditions. To obtain the best qualities of asphalt, the avoiding of cracking is necessary; consequently distillation to asphalt is always carried out with the assistance of copious supplies of steam blown into the still during distillation, the distilling temperature being kept thus as low as possible.

This distillation is usually conducted in very large stills, worked periodically; it may also be carried out in a continuous bench of stills, the control being effected by examination of the residue rather than of the distillate. The distillates may be gas or lubricating oils, according to the grade of asphalt which is being made. An objection to this mode of distillation is the length of time to which the asphalt is subjected to a high temperature.

It may also be made by one of the topping-plant type of tubular stills. In this case the asphalt is subjected to the necessary temperature for distillation for a very much shorter period. Overheating of an asphalt during manufacture is indicated by the difference in solubility in carbon bisulphide and carbon tetrachloride. This difference for a well-made asphalt should not exceed 0·5 per cent.

The temperature of distillation may also be kept down by distilling in a high vacuum plant, a method which produces asphalts of very good quality.

The grade of asphalt is usually defined by the penetration test, *i.e.* the depth to which a standard needle (No. 2 sewing needle) under a load of 100 grammes will sink into the asphalt at a definite temperature (77° F.) in 5 seconds. Grades of penetration varying from 200 to 40 are usually made for road work. Harder asphalts are also sometimes made for certain purposes.

Blown Asphalts.—Large quantities of asphalt are also made by the blowing process. As far back as 1865 it was known that asphaltic substances were susceptible to the action of oxidizing agents, which produced products of greater viscosity. In 1894 a patent was granted to Byerley for "blowing" petroleum residual oils by means of air. The action which takes place appears to be a condensation, hydrogen being removed from two molecules as water, the molecules then condensing up.

The blowing process is carried out in large stills, the larger, the easier the control. The oil or asphalt to be blown is heated up to a temperature between 200° and 230° C. Copious supplies of air are introduced by means of a large number of perforated pipes placed in the bottom of the still. As the oxidation proceeds, sufficient heat is developed to render external heating necessary; indeed, care must be exercised to prevent the temperature rising too high. As the oxidation proceeds the melting point of the asphalt rises, the penetration decreases, and the ductility falls off very rapidly. In this way heavy road oils or liquid asphalts may be blown to asphalts of high melting point. These asphalts, if produced from a moderately hard asphalt to start with, may be brittle and hard; if produced from a liquid asphalt containing much oil, may be tough, pliable, and leathery in nature. The quality of the blown asphalt may thus be varied considerably by varying the basic material, and to some extent also by varying the conditions of blowing.

During the blowing process, vapours are given off which may be condensed and used as fuel oil.

The blowing process has several advantages:—

(1) The yield of asphalt from a given petroleum residual oil is greater than that obtained by distillation methods.

(2) Certain crudes which would yield little or no asphalt by distillation will yield asphalts of good quality by blowing. Naturally, the more asphaltic the nature of the crude the less blowing necessary.

(3) Blown Asphalts are less susceptible to temperature changes than are those made by distillation. The process, however, is of longer duration. Much care must be taken in the manufacture of blown asphalts, particularly when they are made from crudes poor in asphalt. When made from mixed base petroleums they are likely to present a greasy surface, owing to the presence of paraffin wax. In general, blown asphalts are characterized by lack of ductility, and if overblown, or blown at too high a temperature, they will contain excess of carbenes and even free carbon. The fusing point of a blown asphalt will generally be found to be higher than that of a residual asphalt of the same penetra-

tion. The subject of blown asphalts is treated in detail in Abrahams' book on "Asphalts and Allied Substances," p. 287 (D. van Nostrand Co.).

Vulcanized or Sulphurized Asphalts may be made by treating with sulphur, the sulphur apparently affecting the condensation (with liberation of sulphuretted hydrogen) just as does oxygen. The product is similar in character to an air-blown asphalt.

Sludge asphalts may be obtained from the sludge acids resulting from the treatment of kerosenes and lubricating oils. These sludges are boiled with water until all the acid separates and leaves a heavy residuum. This is then washed with water and heated to the required consistency by the injection of superheated steam. Sludge asphalts are characterized by a high content of sulphur and oxygen, and high solubility in aromatic free petroleum spirit (sp. gr. 0·645). They do not withstand the weather as well as do the blown and residual asphalts, and are at present of comparatively little importance.

There are many other varieties of asphalt of minor importance, such as **wurtzilite asphalt** or **kapak**, which is made by the distillation of wurtzilite under pressure. This is characterized by high melting point and great toughness, being somewhat similar to blown asphalts.

A great variety of somewhat similar bodies, properly termed "pitches," are manufactured by the distillation of such substances as stearine, cotton seed, wool grease, etc., being obtained as by-products from the refining of vegetable oils and greases, etc., a description of which lies beyond the scope of this book.

GENERAL REFERENCES TO PART VII., SECTION E.

Abrahams, "Asphalts and Allied Substances." D. van Nostrand Co.

Kohler and Graefe, "Natürliche und künstliche Asphalte." Vieweg und Sohn.

SECTION F.—CRACKING AND HYDROGENATING PROCESSES

THE extraordinary rapid growth of the automobile industry has given rise to a constantly increasing demand for benzine, which, so far, has been met by the petroleum industry. The motor spirit of twenty years ago consisted almost entirely of the most volatile fractions of crude oil. Products boiling completely below 120° C. were common. As the demand increased, and as carburettors were improved, the volatility of the benzine decreased. In consequence of the great demand present-day motor spirits are much less volatile and include fractions of higher boiling point. Final boiling points of 220° C. are not uncommon; indeed, in the United States of America benzines of final boiling point 230° C., or even higher, are on the market.

It has long been realized that, by the ordinary means of distillation, a sufficient yield of benzine cannot possibly be obtained in the future from the available supplies of crude oils. Efforts have consequently been made to increase the yield by resort to cracking methods, *i.e.* methods of converting hydrocarbons of high boiling point into those of low boiling point.

As far back as 1861 an American stillman accidentally noticed that high boiling-point hydrocarbons, at high temperatures, *e.g.* when distilling without steam, cracked, yielding hydrocarbons of lower boiling point. In 1863 Breitenlohner passed the vapours of heavy mineral oils through red-hot tubes, obtaining volatile oils, hydrogen. and coke. In 1865 Young took out a patent (Eng. Pat, 3345 of 1865) for increasing the yield of burning oil by distilling under pressure. In 1866 Vincent, Richards and others (Eng. Pat. 616 of 1866) patented a process by which the vapours partly condensed and dropped back into the hot residue, thus facilitating cracking. In 1871 Thorpe and Young (*Proc. Roy. Soc.*, vol. 19, p. 370, vol. 20, p. 488, vol. 21, p. 184) described the formation of hydrocarbons of the paraffin and olefine series, by heating paraffin wax under pressure. In 1889 Redwood and Dewar (Eng. Pat. 10277 of 1889, 13016 of 1890, 5971 of 1891) patented a process for cracking by distilling and condensing the vapours under pressure.

Since that time, hundreds, even thousands, of patents have been granted for cracking processes of one kind or another, a fact which indicates the importance of the subject. The fact that up to the present no really satisfactory cracking process has been devised indicates the difficulty of the problem.

The theoretical side of the subject has been by no means completely investigated. The factors influencing the cracking of any particular heavy oil must be numerous, and their study complicated by the difficulty of getting any information as to the chemical nature of hydrocarbons of high boiling point. The number of bodies taking part in the reaction may be great, as also the number of bodies formed.

In general, cracking may be said to be a splitting up of complex molecules, or a reaction between complex molecules, of such a nature that simpler molecules and also more complex molecules are formed. As the percentage of hydrogen in the molecules of low molecular weight is higher than in the molecules of high molecular weight, the formation of low molecular weight molecules must be accompanied either by liberation of carbon, or by formation of molecules of higher molecular weight.

The chief difficulty in most cracking processes is indeed the separating out of solid carbon which clogs up the plant. It is quite open to doubt how far this material is really carbon, how far it is really composed of carbon compounds of high molecular weight.

The reactions are further complicated by the fact that unsaturated hydrocarbons and even hydrogen are often formed. The temperature at which noticeable cracking takes place depends on the nature of the oil, and the influence of the temperature on the rate of cracking is very marked.

F. W. Padgett (*Chem. and Met. Eng.*, 1920, p. 521) gives the following data showing the influence of temperature on the cracking of paraffin wax :—

Temperature in still in ° C. ..	417	432	437
Illuminating oil produced % ..	25·4	37·0	33·5
Hydrogen produced %	0·3	0·9	3·0
Saturated hydrocarbons produced %	74·3	62·1	63·5

By slight changes in the working temperature the character of the cracking may be considerably altered. Standinger, Endle, and Herold (*Ber.*, 46, p. 2466), and Zanetti (*J. Ind. and Eng. Chem.*, vol. 8, p. 20) among others, investigated the effect of temperature in the case of particular hydrocarbons. As a general rule it may be taken that (1) temperatures up to 500–600° C. yield chiefly mixtures of paraffins and olefines; (2) temperatures about 700° C. yield olefines, diolefines, and aromatic hydrocarbons with smaller quantities of paraffins; (3) temperatures about 1000° C. yield permanent gases and heavy oils rich in aromatic hydrocarbons.

Pressure is another important factor, the general effect of pressure being to enable reactions to take place at lower temperatures, especially reactions of the nature of polymerization.

As a general rule the unsaturated hydrocarbons and the paraffins are least stable towards heat, the aromatics most so. Padgett (*loc. cit.*) suggests the following type reactions:—

(1) $R-CH_2-CH_2-CH_2-R \rightarrow R-CH=CH-CH_3+RH$
(2) $R-CH_2-CH_2-CH_3 \rightarrow RH+CH_2=CH_2+C+H_2$
(3) $R-CH_2-CH_2-R \rightarrow RCH_3+C+RH$

As olefines doubtless occur in many crudes, particularly in the fractions of high boiling point, the following type of reaction may occur :—

(4) $R-CH=CH_2 \rightarrow RCH_3+C$.

Olefines may also crack in this way—

$R-CH_2-CH_2-CH=CH-R \rightarrow RCH=CH-CH=CH_2+RH$

yielding diolefines, a class of hydrocarbons which are certainly present in many cracked distillates.

Further, at high temperatures particular reactions which give rise to the formation of aromatic hydrocarbons take place, as exemplified in the cracking processes of Hall and of Rittman.

The real problem awaiting solution is the conversion of heavy asphaltic residues into volatile products. So far only the cracking of heavy distillates, such as gas oil, has met with any measure of commercial success. The formation of coke when cracking such a distillate is naturally less than would be the case if a residue were cracked.

The chief difficulty in the way of commercial cracking is this formation of coke. The coke deposits on some part of the surface through which the heat is transmitted to the oil, and this gives rise to overheating of the metal in this place, with its consequent burning through. Should this happen in the case of a plant under pressure a disastrous accident may ensue.

Cracking processes may be divided into the following classes :—

(*a*) Distillation without steam at ordinary pressures.
(*b*) Distillation or heating under pressure.
(*c*) Heating the oil in the vapour phase.
(*d*) Hydrogenating methods.
(*e*) Various other methods.

(*a*) A mild form of cracking by carrying out the **distillation** of crude oil **without the assistance of steam** is in everyday use. In the case of certain crude oils an increased yield of illuminating oils is so obtained. In distilling for paraffin wax, a less viscous distillate is obtained by distilling without steam. This is due to slight cracking. Even in the ordinary processes of distilling lubricating oils with steam a slight yield of low-flash distillate is obtained. When distilling certain mixed base oils down to coke in the usual refinery practice considerable cracking takes place. This is also the case when distilling crude oils derived from the distillation of shale. In fact, it is the rule that a certain amount of cracking cannot be avoided, however carefully distillation be conducted.

(*b*) **Distillation in the Liquid Phase under Pressure.**—As above mentioned, numerous patents have been taken out, but few of these processes have found any technical application.

The Burton process is very extensively used in the United States, gas oil being the basic substance usually treated. This gas oil is distilled in a cylindrical still under a pressure of 4 to 5 atmospheres and the distillates are condensed under the pressure generated in the still (U.S. Pat. 1049667, January 7, 1913). The operation is carried out in a still of the ordinary type, specially strengthened to withstand the internal pressure. The vapours are led to an ordinary condenser the outlets from which are closed by valves, so that the condensation takes place under pressure. The product obtained has a decided odour and is of a light yellow colour, which can be removed by refining. It is claimed that by working at this pressure the product consists largely of paraffin hydrocarbons. If the condensation is not carried out under pressure, considerable quantities of olefines are found in the distillate.

Other processes have been designed, operating with tubular stills and retorts. These have the advantage that relatively small quantities of oil are in the plant at one time. Fleming uses a vertical still, claiming that coke deposits much less readily on vertical walls. Many devices for protecting the bottoms of cracking stills have been devised, *e.g.* that of Coast (U.S. Pat. 1345134 of June 29, 1920) in which a protective layer of molten alloy kept in circulation is used.

(*c*) **Cracking in the Vapour Phase.**—When working with a two-phase, liquid, and vapour system, conditions are limited by the fact that for any particular temperature the corresponding definite vapour pressure must be employed. Therefore, to attain the high temperatures required, correspondingly high pressures must be employed. Moreover, temperature and pressure cannot be varied independently of each other. With a single-phase vapour system this objection disappears.

Several processes operating on the principle of heating the vapours instead of the oil, have met with some measure of commercial success. For example, Hall (*J.S.C.I.*, 1915, p. 1045) designed a process which is in operation at present.

The oil to be cracked, a heavy kerosene or gas oil, is first preheated and then passed through a cracking coil, which may be heated up to 600° C. This coil is of small diameter (1 inch) and of great length (over 300 feet). The products are pumped through at high velocity, little or no coke being deposited in the tubes. The vapours are then allowed to expand suddenly into a vessel of large diameter filled with packing rings, the temperature being consequently reduced to about 325° C. Quantities of carbon separate out in this vessel. The vapours are then passed through a dephlegmator where the less volatile constituents separate out, the rest of the vapours being then passed through a compressor working up to five or six atmospheres. The product is then condensed in the ordinary way. By working at higher temperatures aromatic hydrocarbons have been produced by the Hall process, the loss by formation of non-condensable gases being in this case, however, excessive.

Another example of a process of this type is that of Rittman (*Bulletin* 114, U.S. Bureau of Mines, 1916). The Rittman furnace consists of a battery of vertical cracking tubes of diameter up to 10 inches and 12 feet in length. The vapours of the gas oil to be cracked are heated in these tubes at pressures up to 6 or 7 atmospheres, and temperatures from 600° to 700° C. according to circumstances. These tubes are provided with a central cleaning rod and are connected at their lower ends to a tar pot. An attempt was made to utilize this process for the manufacture of benzene and toluene during the war, but no measure of success was attained.

In other forms of plant for cracking in the vapour phase superheated steam is introduced. For example, Greenstreet (Eng. Pat. 16542, July, 1912) forces a mixture of oil and steam through a cracking tube 1½ inches diameter and 100 feet in length, heated to a cherry-red heat, under considerable pressure. Greenstreet claims that in this way, mainly paraffins and olefines are produced.

(*d*) **Hydrogenation Methods.**—The classic researches of Sabatier and Senderens on the catalytic effect of nickel in accelerating hydrogenation has given rise to the modern industry of hardening fats. Numerous attempts have consequently been made to apply this process to the hydrogenation of petroleum products. Hydrogenation by means of steam has also been tried by various inventors, so far, however, with little measure of success.

Bergius has carried out pioneer work on hydrogenation at high pressures. He claims that heavy mineral oils may be transformed into low boiling products by treatment with hydrogen at 400° C. under a pressure of 100 atmospheres. Under these conditions no coke is formed, and the amount of uncondensable gases is less than in the case of a cracking process (*Zeit. angew. Chem.*, 1921, p. 341). He claims that even coal can be so treated to yield large percentages of oil. The possibilities of such a process are very fascinating and foreshadow the eventual manufacture of petroleum products from waste vegetable matter. The technical difficulties, however, of working at such high pressures are very great.

Day (U.S. Pat. 826089, July, 1906) claims to hydrogenate unsaturated hydrocarbons by bringing them into contact with hydrogen and a catalyst such as palladium or hydrogen at high pressure. No satisfactory method of hydrogenation of petroleum hydrocarbons, however, has so far been developed.

(*e*) **Various other Methods.**—The well-known use of aluminium chloride for effecting syntheses in organic chemical research work has suggested its application in this case also, Friedel and Craft having themselves tried the effect of this reagent on petroleum oils. They showed that not only a synthetic action, but also a disruptive action, may be effected. Egloff and Moore particularly have investigated these reactions (*Met. and Chem. Eng.*, 1916, p. 340). McAfee (*Trans. Am. Inst. of Chem. Eng.*, 1915, p. 179) has studied the possible application of the method and has patented a process (U.S. Pat. 1235523, July, 1917) for which he claims that he obtains a substantially complete conversion of higher-temperature boiling petroleum oils into lower-temperature boiling oils. He operates the process by passing chlorine into the oil, containing finely divided aluminium in suspension. The chlorine is evolved mostly in the form of hydrochloric acid gas which can be recovered. A conversion of the higher boiling oils into benzine is claimed. The oil during the process must be kept in agitation, and moisture and sulphur compounds must be rigorously excluded. The recovery of the aluminium chloride would present a somewhat difficult problem.

Attempts have also been made to bring about cracking by submitting oil vapours to silent electrical discharges. Cherry, Robertson, and others have suggested such methods.

A very full account of the various methods which have been proposed is given in "Gasoline and other Motor Fuels," by Ellis and Meigs (D. van Nostrand Co.), to which the reader may be referred for further information on this interesting, but, so far, incompletely worked out subject.

SECTION G.—REFINERY WASTE PRODUCTS—THEIR REGENERATION AND UTILIZATION

IN connection with various refinery processes, particularly the chemical treating and filtration, various products result which are too often allowed to run to waste. Even in the case of crude oil itself much emulsion, commonly called B.S., accumulates at the bottom of the storage tanks. This material, which may contain large percentages of oil, was at one time allowed to run to waste, or was burnt. It is now usually treated, either by the electric dehydration process, or by means of the super-centrifuge. Both these processes have been described in Part III., Section D.

From the distillation of crude oil and more particularly from cracking operations, quantities of gas or light vapours are evolved. These consist partly of condensable, partly of non-condensable gases, and in the case of gases from cracking operations, usually contain quantities of olefines.

The condensable gases are usually absorbed in modern refineries by means of some form of gas absorber or scrubber, the non-absorbable gases being led to a gasholder and eventually used as fuel. In certain cases the gases from cracking stills contain propylene, which is absorbed in sulphuric acid. This, on subsequent treatment with steam, liberates propyl alcohol, which is utilized in admixture with benzine as a motor spirit. This is analogous to the preparation of alcohol from the ethylene in coal gas by means of the Bury process (*Chemical Age*, August 28, 1920).

Very large quantities of sulphuric acid sludge result from the treatment of light oils, lubricants, and paraffin wax. Much attention has been given to the recovery or utilization of these acid sludges, in many cases, however, with little success. The character of the acid sludge depends naturally on the character of the oils which have been treated.

In many cases the acid sludge is merely diluted with water. This causes a quantity of oil to separate out, which is skimmed off or absorbed in a heavy oil and used as fuel. The diluted acid cannot usually be reconcentrated successfully as it still contains organic matter in solution, so that on concentration reactions take place resulting in the evolution of sulphur dioxide and the separation out of carbonaceous matter which clogs up the concentrating plant. In many cases it pays to purchase fresh acid rather than concentrate the waste.

In the case of acid sludges which result from the treatment of lubricating oils, they may be treated with live steam, the oils which separate out being mixed with petroleum residues and used as fuel. If the material separating out from the sludge is of an asphaltic nature it may be incorporated with lime and used as an asphaltic waterproof material (Baskerville, *J.S.C.I.*, March 15, 1920) (*vide* also "Sludge asphalts," p. 228).

The diluted acid is in some cases neutralized with lime and the precipitated calcium sulphate removed. The solution then contains calcium sulphonates which may be salted out by calcium chloride. These calcium sulphonates yield sulphonic acids from which soaps may be prepared. As the calcium and magnesium sulphonates are soluble in water, soaps made from these sulphonic acids will produce good lathers with sea water (Divine, U.S. Pat. 1330624).

The sludge obtained from the treatment of lubricating oils may, after dilution and removal of the diluted acid, be incorporated with liquid fuel or thin asphalt to make a hot-neck grease. The diluted acid, freed from oily matters, may be concentrated down and then allowed to flow into a retort kept full of concentrated acid through which a current of air is blown. The organic matter is thus destroyed and the acid vapours given off may be condensed and concentrated (Ger. Pat. 221615, June 19, 1909). Much work still remains to be done before the problem of the recovery of the waste sulphuric acid can be really satisfactorily solved.

Quantities of waste soda sludge from the treating of petroleum distillates also result. These sludges contain, in addition to much free soda, sodium naphthenates. These may be obtained by concentrating down the lye and salting out with common salt. The naphthenates (soaps) separate out and may be freed from excess of water. These soaps can be used as low-grade soaps, but they have an objectionable odour. The naphthenic acids themselves may be liberated by the addition of sulphuric acid. They may be used as antiseptics, timber preservatives, solvents for varnish, resins, and as substitutes for turkey red oil.

Markownikoff has shown that these naphthenic acids belong to a group with the general formula $C_nH_{2n-2}O_2$, being carboxylic acids of the hydrocarbons of the naphthene series. Several of the lower members of the series, *e.g.* $C_6H_{11}COOH$, sp. gr. 0·950, b. pt. 216 °C., have been isolated. (N. Chercheffsky, "Les Acides due Naphte." Paris, Dunod et Pinat.)

From the filtration and treatment of lubricating oils, kerosenes and paraffin wax by means of fuller's-earths, much impregnated powder is obtained.

In the case of powders from the treatment of kerosene, the material is first treated with water. This causes the bulk of the absorbed oil to separate out. The oil is used as fuel. The sludge powder is then dried and regenerated by being passed through one of the ordinary type of roasting furnaces.

The black powder obtained by the filtration of lubricating oils is usually first treated with benzine. The benzine solution is then concentrated down, the residue furnishing a low-grade lubricant, the benzine being distilled off, condensed and re-used. The resulting powder is then roasted.

The powders left after the treatment of wax are either extracted by benzine, or steamed out, the latter being the cheaper process. The wax-free powder may be again regenerated by roasting.

The lead sulphide sludge obtained as a by-product from the treatment of oils by means of the sodium plumbite process is usually returned to the lead smelters.

Automobile lubricating oils after use may be easily cleaned and reconditioned by filtration and washing with sodium carbonate solution, any dissolved benzine being removed by evaporation. Such reconditioned oils may be re-used with complete satisfaction (W. F. Parish, paper read before *Am. Chem. Soc.*, Rochester, 1921).

PART VIII.—THE CHARACTERS AND APPLICATIONS OF PETROLEUM PRODUCTS

[The characters and applications of the naturally occurring gases, solid bitumens and pyrobitumens, and the mineral waxes have already been dealt with, *vide* Parts II., V. and VI. The characters and applications of the manufactured products will be dealt with in this part.]

SECTION A.—BENZINES

THE volatile liquid products are utilized chiefly as motor fuels and as solvents. Relatively small quantities find special applications, *e.g.* the most volatile fractions may be used as refrigerants. Light benzines boiling completely below 100° C. are used for carburetting air to make the so-called air gas or petrol gas, often used for lighting country houses far removed from coal-gas works.

Quantities of special boiling-point benzines are used for the extraction of oils from seeds. The range of boiling point required varies according to the type of extraction plant in use. Benzines of boiling point ranges 80° to 100° C., 90° to 110° C., and 100° to 120° C. are in common use. Such benzines should be well fractionated and well refined to get rid of any constituents of strong odour. A special range of boiling point is demanded for such benzines in order to exclude both the light volatile fractions, which would bring about high working losses, and the higher boiling-point constituents which would not be readily evaporated from off the extracted oil solution (Shrader, "Solvent Extraction in the Vegetable Oil Industry," *Chem. and Met. Eng.*, vol. 25, p. 94).

Quantities of benzine, sometimes of special boiling-point range, are used as solvents for rubber in the manufacture of fine rubber goods.

Very large quantities of heavy benzine, or rather light kerosene, are used under the names of "white spirit" or "mineral turps" in the manufacture of paints, varnishes, and so forth. In order to comply with regulations such white spirits are distilled to have flash-points over 73° F. The final boiling point varies according to requirements, grades boiling between 140° C. and 200° C., and others with final boiling points up to 250° C., are on the market.

The bulk of the light petroleum distillates under the names of motor spirits, petrols, benzines, naphthas, and gasolines are consumed as motor fuels.

The subject of the efficiency of a motor fuel, and the factors on which this depends, is one which has received much attention during the last two or three years. It is a subject of great importance, as the urgent necessity for economy in fuel consumption is being brought to the fore owing to the rapid increase in the output of motor vehicles, the rate of increase of which at the present time tends to exceed that of increase of the petrol supplies. This demand for motor spirits has of late years increased so enormously that at least 90 per cent. of the production of light petroleum fractions is used for this purpose. The following figures illustrate this :—

Year.	Total consumption in U.S. of motor spirit in automobiles in millions of U.S. gallons (approx.).	Production of motor spirit in U.S. in millions of U.S. gallons (approx.).
1911	250 *i.e.* 31·2 per cent. of	800
1913	450 ,, 37·5 ,, ,,	1200
1915	850 ,, 48·5 ,, ,,	1750
1917	1750 ,, 62·5 ,, ,,	2800
1919	3400 ,, 85 ,, ,,	4000
1920	3900 ,, 82 ,, ,,	4750

In consequence of this ever-increasing demand strenuous efforts have been made to increase the production of motor spirit in every way possible. This has been effected in the main in three ways : (1) by increasing the yield obtained from the crude, (*a*) by improvement in refinery methods, (*b*) by alteration of quality; (2) by increasing production of gasoline extracted from natural gases; and (3) by the production of gasoline made by cracking processes.

The changes in quality of the gasoline produced in the United States is indicated by the increase in the final boiling point, which has taken place in spite of improved methods of refining.

Year.	Percentage distilling to 100° C.	Final boiling point °C.
1915	40	185
1917	30	200
1919	25	220
1920	22	230

The following table gives the production of gasoline in the United States from natural and casing-head gas (Dykema, U.S. Bureau of Mines, *Bulletin* 76):—

Year.	Gasoline produced, U.S. gallons.	Average yield per 1000 cu. ft. of gas.	No. of plants.
1911	7,425,800	3·00	176
1912	12,081,200	2·60	250
1913	24,060,800	2·43	341
1914	42,652,600	2·43	386
1915	65,364,700	2·57	414
1916	103,492,700	0·496	596
1917	217,884,100	0·508	886

In 1914 the production of gasoline by cracking amounted to little more than 1 per cent. of the total output; in 1920 this figure had increased to nearly 5 and is steadily increasing.

The characters of a motor spirit depend on both its physical properties and chemical composition. In countries where benzine is sold by volume, the specific gravity is naturally a factor of some importance, as it determines the weight of fuel per gallon or litre.

The point of prime importance to the user is the obtaining of the maximum work for the money expended. The calorific value of the motor fuel per unit volume is thus of great importance in countries where motor fuels are sold by volume.

The calorific value per unit weight of the paraffins is higher than that of the naphthenes, which is in turn higher than that of the aromatic hydrocarbons. The specific gravities of these three classes of hydrocarbons (in the case of the members in most general use as motor spirits) vary in the other direction. As a result of this the calorific value per unit volume is largest in the case of the aromatic hydrocarbons.

Hydrocarbon.	Sp. gr.	B.Th.U.'s per lb.	B.Th.U.'s per gallon.
Heptane (paraffin)	0·688	19,400	133,470
Hexahydrobenzene (naphthene)	0·776	18,900	140,660
Toluene (aromatic)	0·884	17,660	153,640

If, therefore, the high specific gravity of any motor fuel is caused by the presence of naphthenes and aromatics and not of paraffins of high boiling point, the high specific gravity is a decided advantage.

Specific gravity alone is utterly useless as a criterion of quality for obvious reasons. A mixture of light benzine and kerosene, quite unsuitable as a motor fuel, may have the same specific gravity as a good homogeneous benzine of reasonable boiling range. A sample of motor benzol, an excellent fuel, may have a specific gravity higher than that of a light paraffin gas oil. Unfortunately, owing to the fact that the motor fuels first on the English market were of the paraffin type, the idea that low specific gravity was a criterion of quality became deeply rooted in the minds of the motoring public, a mistaken idea which dies very hard.

The range of boiling point is a character of more importance. The fuel must contain sufficient light fractions to render it sufficiently volatile to enable starting up the engine at ordinary winter temperatures without unreasonable difficulty. The degree of ease with which any engine can be started depends as much or more on the engine as on the fuel, the design of the induction system having very much influence. However, for a definite engine, the ease with which a fuel will start up depends on two factors, (*a*) the range of air mixtures over which the fuel will burn, and (*b*) its volatility. As regards the burning range, all petroleum motor spirits are similar. Only mixtures of air and benzine vapour, containing between 2 and 5 per cent. approximately of the latter, are explosive. Alcohol, on the contrary, has a much larger range, viz. from 4 to 14 per cent.

The volatility of a fuel depends on its composition, not only on the percentage of any particular volatile hydrocarbon, but on the relative quantities of the less volatile fractions too. In a rough way, volatility may be taken as measured by vapour pressure, but as the conditions under which evaporation take place in a vapour pressure apparatus and in an internal combustion engine (the relative proportions of vapour and liquid being so different) differ so greatly, conclusions drawn from vapour pressure determinations may be quite erroneous. The following table gives the vapour pressure of various fuels at 0° C. :—

Fuel.	Vapour pressure in mm. at 0° C.
n-pentane	183
n-hexane	45
n-heptane	11·5
Benzene	26
Toluene	9
Cyclohexane	27·5
Ethyl alcohol	12

The following table gives the boiling-point ranges of a number of motor spirits and their vapour pressures :—

Fuel.	Sp. gr. 15° C.	Distillation test, boiling up to					Final boiling point.	Vapour pressure at 0° C.
		80° C.	100° C.	120° C.	140° C.	160° C.		
1	0·782	2	18	55	83	96	165	28 mm.
2	0·725	12	55	82	93	98	160	55 ,,
3	0·704	27	67	86	95	—	152	70 ,,
4	0·760	—	15	66	89	97	165	19 ,,

Ricardo, in a series of articles in the *Automobile Engineer*, February to August, 1921, has dealt with this subject among others. He finds that the rise of temperature brought about in the induction pipe of a standard engine, run under standard conditions with heat supplied to the air induction pipe at a standard rate, gives a measure of the volatility of a motor fuel. This figure involves latent heat as well as vapour pressure.

The upper end of the range of boiling point is in some respects of great importance. If the motor fuel contain fractions of too high boiling point, then a certain amount of condensation will take place on the cylinder walls, and the high boiling fractions so condensed will gradually find their way past the pistons into the crank-case, where they will dilute the engine oil. This will sooner or later give rise to bearing trouble. With a motor spirit of too high final boiling point it will be found necessary to change the lubricating oil more frequently. A final boiling point of 220° C. may be taken as permissible, although many motor spirits on the market, particularly in the United States, have final boiling points exceeding this. The high final boiling point is the chief objection to benzol-kerosene mixtures as motor fuels.

Of very much greater importance, however, is the question of the efficient burning of the fuel in the motor, as on the efficiency depends the fuel consumption per brake horse-power hour, a question of the greatest importance to the user and to the world at large. It is in this connection that the chemical composition of the fuel plays such a very important part.

The efficiency of an internal combustion motor, assuming that the working fluid is a perfect gas, is given by the formula

$$E = 1 - \left(\frac{1}{r}\right)^{\gamma - 1}$$

γ being the ratio of the specific heats of a gas.

r being the compression ratio, *i.e.* the ratio of the volume of the cylinder at the bottom of the stroke to that at the top. As, however, a mixture of benzine vapour and air is not a perfect gas, this expression must be modified. Tizard and Pye (*Automobile Engineer*, February, 1921) have found that the expression $E = 1 - \left(\frac{1}{r}\right)^{0{\cdot}258}$ gives the correct values.

It can be seen from this formula that the efficiency of an internal combustion engine varies with the compression ratio—

Compression ratio.		Air cycle efficiency.
4 : 1	.. .. ..	42·56 per cent.
5 : 1	.. .. ..	47·47 ,,
6 : 1	.. .. ..	51·16 ,,
7 : 1	.. .. ..	53·98 ,,

Experiments carried out in a special variable compression engine by Ricardo, gave the following actual figures for indicated thermal efficiency :—

Compression ratio.		Actual indicated thermal efficiency.		Efficiency relative to air cycle efficiency.
4 : 1	..	27·7 per cent.	..	65·0 per cent.
5 : 1	..	31·9 ,,	..	67·1 ,,
6 : 1	..	35·3 ,,	..	68·8 ,,
7 : 1	..	37·5 ,,	..	69·6 ,,

The advantage of using an engine of high compression ratio is thus obvious.

The influence of the chemical composition of the motor fuel here comes particularly into play.

The maximum compression ratio and therefore maximum efficiency at which a particular internal combustion engine can be run is limited in practice by the fact that when this reaches a certain value dependent on the particular fuel, detonation (the knocking or pinking of the motorist) sets in, and this, if allowed to continue, soon brings about preignition with consequent loss of power. When detonation occurs in practice, the throttle must be partially closed, which is tantamount to lowering the compression ratio of the engine, or the spark must be retarded, either of which means loss of efficiency.

This subject has been investigated fully by Ricardo (*loc. cit.*), who examined the behaviour of various fuels and as far as possible pure hydrocarbons in a special engine, the compression ratio of which could be varied and set to any particular value even during the running of the engine. These investigations proved very decisively one point, namely, that of the three types of hydrocarbons found in petroleum motor fuels, the aromatic hydrocarbons showed least tendency to detonate, the paraffins most, the naphthenes occupying an intermediate position. The following table gives a list of some fuels examined and the maximum compression ratio at which they could be used without excessive detonation in the experimental engine :—

Fuel.	Highest usable compression.
Toluene	7·85
Ethyl alcohol	7·50
m-xylene	7·40
Benzene	6·90
Cyclohexane	5·90
Cycloheptane	5·90
n-Hexane	5·25
n-Heptane	3·75
Ether	2·95

The next table gives the chemical composition of certain typical fuels examined by Ricardo, together with the maximum compression ratios at which they could be used in that engine :—

Fuel.	Sp. gr. 15° C.	Composition by weight.			Highest usable compression ratio.
		Paraffin, per cent.	Aromatics, per cent.	Naphthenes, per cent.	
1	0·782	26	39	35	6·0
2	0·767	10·2	4·8	85	5·9
3	0·760	38	15	47	5·35
4	0·727	61	8·5	30·5	5·25
5	0·704	80·5	4·3	15·2	5·05
6	0·718	63·3	1·7	35·0	4·85

Ricardo has also shown that the heats of combustion per unit volume of the air-fuel mixtures (in the correct proportions for complete combustion) show little variation for all volatile hydrocarbon fuels.

Fuel.	Calorific value, B.Th.U.'s per lb.	Relative heats of combustion per unit vol. of air-fuel mixture giving complete combustion.
Hexane	19,390	46·0
Heptane	19,420	46·06
Benzene	17,460	46·9
Toluene	17,660	46·9
Cyclohexane	18,940	46·08
Kerosene	19,100	46·14

The practical result of this is that in an engine of such low-compression ratio (and therefore low efficiency) that any hydrocarbon fuel could be used therein without detonation, the relative efficiencies of all such fuels would be about the same.

This is borne out by the following results :—

Fuel.	Sp. gr. 15° C.	Minimum consumption per I.H.P. hour.	
		Lbs.	Pints.
1	0·782	0·432	0·442
2	0·767	0·425	0·443
3	0·760	0·422	0·445
4	0·727	0·421	0·463
5	0·704	0·414	0·471
6	0·718	0·415	0·462

If, however, the minimum consumptions per I.H.P. hour are compared at the maximum compression ratios at which the fuels can be used, then the effect of the increase of efficiency so obtained is most marked.

Fuel.	Sp. gr. 15° C.	Highest usable compression.	Minimum compression per I.H.P. hour.	
			Lbs.	Pints.
1	0·782	6·0	0·393	0·402
2	0·767	5·9	0·389	0·405
3	0·760	5·35	0·407	0·428
4	0·727	5·25	0·410	0·451
5	0·704	5·05	0·412	0·469
6	0·718	4·85	0·422	0·471

The practical value of these results lies in the fact that a motor spirit, rich in paraffins and poor in aromatics and naphthenes, will detonate in the average engine when the spark is fully advanced and the throttle open. It is, therefore, advantageous even in engines of low-compression ratio to use motor spirits rich in aromatics and naphthenes if obtainable. In the case of aeroplane engines, where efficiency is of such great importance, which are usually therefore of high-compression ratio, only motor fuels of low paraffin content can be used.

The motor spirits marketed in different localities show much variation in quality, this being largely due in the first place to the character of the crude oils from which they are manufactured. The specific gravity may vary much, according to chemical composition and boiling-point range. Spirits composed mainly of volatile paraffin hydrocarbons may have specific gravity as low as 0·680. Spirits relatively rich in aromatic and naphthene hydrocarbons may have specific gravity 0·760 or more (pure benzene sp. gr. 0·884). The initial boiling point (the determination being carried out in an Engler flask of standard dimensions, under standard conditions) may be as low as 30° C. or as high as 60° C. The percentage boiling below 100° C. usually varies between 10 and 70 per cent. The final boiling point lies usually between 160° C. and 200° C., but is occasionally as low as 130° C. and often as high as 230° or 240° C. As the method of testing of motor spirits is so well described in various works, this subject will not be dealt with here, but a few words on the interpretation of the results will not be out of place. The specific gravity must be interpreted in connection with the boiling-point range and chemical composition. A high specific gravity with components of normal boiling-point range would indicate presence of naphthenes and aromatics. The boiling point or distillation test would show up the presence of excessive quantities of the very volatile casing-head gasolines or the presence of constituents of too high boiling point.

Tests are usually carried out to show that the spirit has been adequately refined and is free from appreciable contamination with organic sulphur compounds which impart to it an objectionable odour. As the majority of the tests are of an empirical nature, there is great diversity of method, but steps are being taken to unify and standardize methods.

GENERAL REFERENCES TO PART VIII., SECTION A.

Dean, "Motor Fuels," *Jour. Franklin Inst.*, 1920, p. 269.

Ellis and Meigs, "Gasoline and other Motor Fuels." D. Van Nostrand Co., New York.

Formanek, "Benzine and Mineral Lubricants." Scott, Greenwood and Son.

Pogue, "Economics of Petroleum," chapter ix. J. Wiley and Sons, New York.

SECTION B.—KEROSENES, ILLUMINATING OILS, ETC.

THE distillates which come off after the benzine fractions and before the gas-oil fractions, are worked up into kerosenes. There is no hard-and-fast line of demarcation between benzine on the one hand and gas oil on the other. At one time, when benzine was practically a by-product of no value, as much as possible of the low boiling constituents was included in the kerosene, with the result that this product had almost invariably a low flash-point as near the legal limit (73° or 76° F.) as might be. Nowadays, however, as improved motor engines can deal with less volatile benzines the tendency is to include part of the lower boiling constituents of what was formerly made into kerosene, in the benzine fraction. The removal of these lighter fractions from the kerosene, has brought about the necessity for the removal of a balancing quantity of heavier fractions of higher boiling point (which now go into gas oil). Kerosenes nowadays have thus a higher flash-point and a narrower boiling-point range than was formerly the case, so that an improvement in the quality of the kerosene generally marketed has thus been effected.

Kerosene was at one time the mainstay of the petroleum industry. As a cheap illuminant it has been aptly termed "one of the greatest of all modern agents of civilization." The recent great developments in automobile engineering and the increased use of liquid fuels, and to a less extent asphalts, have forced kerosene to take a back seat.

This is well illustrated by the following table :—

Year.	Kerosene production expressed as percentage of crude oil treated.
1899	58
1904	48
1909	33
1914	24
1916	14
1918	13·3
1920	12·7

(Pogue, "Economics of Petroleum").

The above figures refer to the United States only, but may be taken as indicating the position generally. In 1899 kerosene represented 60 per cent. of the value of the total petroleum products ; in 1920 only 14 per cent.

Kerosenes show great variation in quality according to (*a*) the nature of the crude oil, (*b*) the method of distillation, and (*c*) the method of refining.

The quality of the kerosene from the point of view of an illuminant can only be spoken of relatively to the type of lamp used. With the ordinary type of lamp, kerosenes composed largely of paraffin hydrocarbons (other things being equal) give the highest candle power ; those composed mainly of naphthenes do not burn so well and those rich in aromatics will burn only with a smoky flame. With certain suitable lamps, however, kerosenes rich in aromatics will give higher candle power than those rich in paraffins. For vaporizing lamps, on the other hand, all types behave well.

The method of distillation, or rather the cutting of the distillates, may be effected so as to produce various grades. For example, in the United States, it is usual to manufacture two grades, one by taking a cut from the middle fractions of the distillate, and one by mixing the lighter and the heavier cuts together. The former naturally gives a finer and more homogeneous product, although the specific gravity of the latter may be the same.

The method of refining is important, as products of fine colour (the so-called water white) are in demand. For kerosenes used for signal lamps and so forth, which demand efficient burning over long periods, carefully refined products are necessary; for native lamps of simple construction, on the other hand, poorly refined grades serve quite well. The majority of kerosenes now in the market have specific gravities varying from 0·780 to 0·825 or more. Flash-points are nowadays about 40° C. (Abel Pensky test), but may be as high as 65° C. The low limit for flash-point for various countries varies much, ranging from 24° C. to 45° C. or more. The boiling-point range usually extends from 150° C. to 300° C., as determined by standard Engler flask. The colour varies from a distinctly yellow tint to nearly colourless.

The following table gives analyses of a few types of kerosenes marketed, from which the considerable variation in properties may be noticed :—

Kerosene.	Sp. gr. 15° C.	Flash-point °C.	Percentage boiling in Engler flask (vol.) up to °C.				
			175	200	250	275	300
A	0·783	39	23	65	97	100	—
B	0·804	43	7	34	75	90	96
C	0·807	53	—	15	66	85	92
D	0·814	48	—	16	67	85	89
E	0·815	69	—	3	60	85	96
F	0·818	31	30	55	85	93	98
G	0·820	36	15	32	68	82	91
H	0·828	36	18	52	93	98	—

Kerosene.	Average candle power in Hinks' duplex lamp to 90 per cent. consumed.	Consumption per candle-power hour in grams.
A	36	1·86
B	30	1·95
C	16	3·87
D	20	3·64
E	27	2·20
F	18	3·3
H	21	3·9

The qualities of a kerosene must be considered in relation to the purpose for which it is to be used. Kerosenes are used chiefly for illuminating purposes in wick-fed lamps, but are also largely used as motor fuels for types of internal combustion engines fitted with vaporizing devices, and for semi-diesel motors, and to a much less extent for other purposes of minor importance such as insecticides and flotation oils.

For illuminating purposes the kerosene should have a normal range of boiling points. The final boiling point should not much exceed 300° C., as the higher boiling-point constituents are lacking in capillary power and do not flow well up the wick, especially as the level of the kerosene in the container falls. Constituents of too high boiling point also tend to bring about charring of the wick. The kerosene should contain no foreign matter, should be composed entirely of hydrocarbons, should contain no acids or products of careless refining, and should be quite free from ash. The colour is usually considered a point of some importance, but this is largely a matter of taste.

From the point of view of a fuel for internal combustion motors, kerosenes have lower calorific powers per unit weight than benzines derived from the same crude oil. If purchased by the unit of volume, however, the advantage lies with the kerosene, owing to the preponderating effect of the specific gravity.

	Sp. gr.	B.Th.U.'s per lb.	B.Th.U.'s per gallon.
Kerosene	0·810	18,900	153,000
A motor spirit ..	0·705	19,130	134,900

It would appear, therefore, that kerosene is the more efficient motor fuel when purchased by the unit of volume. It must be remembered, however, that the detonation point of kerosenes is much lower than that of benzines generally, as a consequence of which they can be used only in engines of low-compression ratio, *i.e.* of low efficiency.

Moreover, the absorption of the kerosene by the lubricating oil is of much greater consequence than in the case of benzines. However, owing to its low price, compared to that of benzine, it is economical in practice, being much used as a motor fuel for vaporizing engines used in propelling small boats and for small land power plants.

Emulsions of kerosenes are much used as insecticides for spraying fruit trees. The kerosene may be emulsified by dissolving a soap in warm water and adding to it kerosene in small amounts with vigorous stirring. Whale-oil soap is a good material for the purpose. Pure kerosene delivered by an efficient atomizing jet may however be used.

SECTION C.—GAS OILS

THE so-called gas oils are distillates from petroleum or shale oils intermediate in character between kerosene and light lubricating oils. They may be made from any type of crude, either as direct distillates or as by-products from some subsidiary operation. For example, as a residue from the redistillation of a heavy kerosene distillate, as a filter oil from the filtration of cooled wax distillates, as a distillate from the concentration down of lubricating oil distillate, and as a distillate from the destructive distillation of an oil down to coke.

Gas oils form a loosely defined class of products, as is to be expected from the fact that their main use is as fuels for certain types of internal combustion motors, for thinning down viscous residual oils, as a basic material for most cracking processes, for gas enriching and for many purposes of minor importance, such as insecticides and so forth.

As fuel oils the flash-point must lie above the usual legal limits, 65° C. or 80° C. as the case may be. The viscosity of gas oils is always so low as to give no trouble in this respect. Their calorific value will depend somewhat on the nature of the crude from which they have been manufactured, as the hydrogen/carbon ratio is not constant. The variation is, however, comparatively slight. The average net calorific value of a gas oil may be taken as 9800 to 10,200 calories. The specific gravity of gas oils may vary from 0·850 to 0·920, the percentage boiling below 300° C. may vary very considerably from a few percentages to 70 or more. Gas oils being distillates should contain no asphaltic matter insoluble in petroleum ether of sp. gr. 0·645, and should leave only a very small percentage of coke (say 0·5 per cent.) on being distilled to dryness in a crucible. (This test should be carried out under definite conditions as laid down by Conradson.)

Gas oils are rarely used as fuels for direct combustion under boilers or in furnaces, as thicker residual fuels serve this purpose equally well and are cheaper. They are, however, largely used in internal combustion motors of the semi-diesel type in land installations, and in diesel engines of the marine type. Diesel engines will burn residual fuels with success, but as more frequent cleaning of the valves is then necessary, gas oils find more favour for marine use where long periods of running without enforced shut-downs are necessary.

The following table gives a few representative analyses of various gas oils :—

Gas oil.	Sp. gr. 15° C.	Flash-point. P.M. °C.	Per cent. boiling up to °C.		Gross calorific value. Calories per gram.
			250°	300°	
A	0·848	85	6	52	10,980
B	0·860	66	18	56	10,900
C	0·863	73	13	57	11,000
D	0·865	75	12	48	10,600
E	0·895	65	15	46	—

Oils derived from the distillation of coal tars may also be used for diesel engines, but as their ignition temperatures are lower engines when running on such oils are usually fitted with a pilot ignition jet, by means of which a little petroleum oil is injected into the cylinder immediately before the main charge of tar oil in order to act as a primer. The calorific value of such tar oils is about 20 per cent. lower than that of petroleum gas oils owing to the presence of oxygenated bodies such as the higher homologues of phenol.

Tar oil for diesel engine use should comply with the following specification :—

1. Must not contain more than 2 per cent. of solid constituents insoluble in xylene.

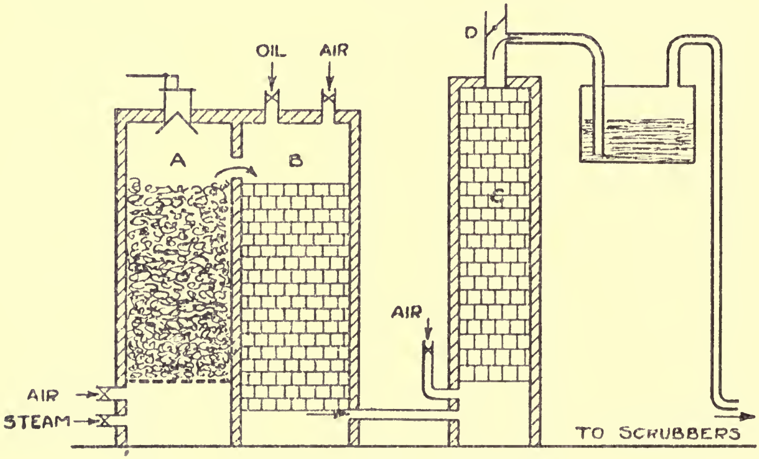
2. Ash must not exceed 0·08 per cent.
3. Water not to exceed 2·5 per cent.
4. Coking value not to exceed 3 per cent.
5. The oil must be a distilled product.

A few typical analyses of tar oils are given herewith (Moore, "Liquid Fuels for Internal Combustion Engines").

Oil.	Sp. gr. 20° C.	Gross calorific value. Calories per gram.	Flash-point closed. Gray.	Sulphur per cent.	Tar acids.
Horizontal retort tar oil ..	1·049	9191	93° C.	0·65	14
Vertical retort tar oil ..	1·016	9189	88° C.	0·49	28
Blast furnace tar oil	0·903	9992	70° C.	0·28	23

The tar oils usually employed for diesel engine work are the creosote and anthracene oils. The naphthalene and anthracene may be removed, but there is no necessity for this procedure as it is an easy matter to keep the oil liquid by warming the feed tank.

Gas oils are also extensively used for the making of gas for the enriching of water gas, which is now so largely used to supplement coal-gas supplies. The plant used for this purpose consists of four parts, viz. the generator, carburettor, superheater, and scrubber. The operation of such plants is always intermittent. During the "blowing period" air is blown through the coke in the generator A (Fig. 41), so as to allow partial combustion; secondary air is also admitted into the carburettor B, which is filled with checker brickwork, the combustion of the gases being here completed. The heated gases then pass into the superheater C, where the temperature may be controlled if desired by admission of extra air. The products of combustion then pass into the stack by the valve D. When the generator and carburettor are both thoroughly well heated and the temperature of the superheater brought up to about from 650° to 700° C., the air supply is shut off, steam is blown into the generator and the valve D closed so as to direct the gases through the scrubbers to the gas-holders. The "blue" gas, a mixture of carbon monoxide and hydrogen thus formed on passing through the carburettor, comes into contact with a spray of gas oil, which is there vaporized. On passing through the superheater, the oil vapours are cracked into permanent gases, a certain amount of tar being also formed. As the temperature falls owing to the reaction between steam and carbon being endothermic, at a certain point it is necessary to stop the process and revert to blowing again in order to restore the temperatures of the generator, carburettor, and superheater. As a general rule the blowing period occupies from three to five minutes, the gas-making period from two to four.



LOWE WATER-GAS PLANT

FIG. 41.

Gas oil is also used for the manufacture of illuminating gas which is used alone, *e.g.* for lighting railway carriages. For the making of gas for such purposes, the gas oil is allowed to drop slowly into retorts made of cast iron kept at a moderately red heat.

In practice it has been found that for gas-making purposes gas oils derived from paraffin base petroleums are best, as they give the maximum yield of gas. Those containing unsaturated straight chain hydrocarbons are less efficient, and those containing aromatics in quantity very much less so.

GENERAL REFERENCES TO PART VIII., SECTION C.

Diesel Engine Users Association reports.

Moore, " Liquid Fuels for Internal Combustion Engines." Crosby, Lockwood and Son.

Schenker, " Combustibles pour Moteurs Diesel." Dunod, Paris.

SECTION D.—FUEL OILS

FUEL oils derived from petroleum and shale oils show great variation in character according to the nature of the crude from which they are derived, and the method of manufacture. If oils derived from coal and low-temperature tars be included, the variation in character is even greater. Fuel oils may be divided broadly into two main classes, viz. distilled and residual oils.

The distilled oils include the gas or solar oils, which from a fuel point of view are generally similar in character from whatever type of crude they be manufactured. These distilled fuel oils have been dealt with in the last section.

Residual Fuel Oils are produced in the main from asphaltic or naphthenic base crudes, being in many cases merely the residues left after the benzine and kerosene fractions have been " topped " or " skimmed " off. Many such crudes yield 80 per cent. or more of fuel oils, whereas the wax or paraffin base crudes, which are usually more completely worked up, yield, as a rule, only from 10 to 40 per cent.

There are no hard-and-fast or even generally accepted specifications to which fuel oils must conform, as in the case of the lighter constituents of petroleum. Regulations generally demand a minimum flash-point of 65° or 80° C., but are not exacting in other respects.

The properties to be looked for in a liquid fuel depend to a great extent on the purposes for which and the conditions under which it is to be used. Residual fuel oils may be used in many cases as diesel oils, particularly for land installations where the plants run intermittently, opportunities for frequent cleaning being thus afforded. Even the most viscous asphaltic fuels may be used with satisfaction in diesel engines, indeed coal tars may so be used, but the preference is given naturally to distilled oils of the gas-oil type. Many diesel oil users specify a maximum coking value of about 4 per cent., a figure which excludes many residual oils, the coking values of which may be as high as 10 per cent. or more. Tars, moreover, usually contain varying percentages of free carbon according to the method of manufacture, from about 3 per cent. for low-temperature up to 20 per cent. for high-temperature tars. A coal tar suitable for land diesel engine use might have a specification, sp. gr. below 1·12 ; ash, below 0·08 per cent. ; water less than 2 per cent. ; free carbon, not above 6 per cent. ; coke value, not above 10 per cent. ; calorific value, at least 9100 calories (*J.S.C.I.*, September 15, 1919).

Liquid fuels for furnace use may, however, be allowed much greater latitude in properties. A practical difficulty arises from the high asphaltic (and/or wax) content of many fuels bringing about a high viscosity and congealing point. If arrangements can be made for heating the oil then pumping difficulties disappear. Perfect combustion can in all cases, however, be attained if the temperature of the fuel oil fed to the burners is sufficiently high. Specifications for liquid fuels are often laid down by large consumers and government departments, limiting the viscosity, sulphur content, and so forth.

The British Admiralty, for example, demand a viscosity not exceeding 1000 seconds Redwood II. at 0° C., a flash-point of 80° C. and a sulphur content not exceeding 3 per cent. The United States navy limit the specific gravity to the range 0·85 to 0·96, the sulphur content to not exceeding 1·5 per cent., and the viscosity to not exceeding 140 seconds Saybolt Furol at 70° F. (21·1° C.). They also demand a calorific value of not less than 10,000 calories per gram. taking 10,250 as the standard and paying a bonus or deducting a penalty as the fuel oil supplied has a calorific value above or below this value. France demands a minimum flash-point of 93° C. and Italy 100° C. for fuel for naval use.

The characters of a few residual fuel oils taken at random given herewith, will illustrate the great diversity of character of these oils.

Fuel oil.	Sp. gr. @ 15° C.	Visc. R. I. @ 100° F.	Flash-point °C.	Sulphur per cent.	Gross calorific value. Calories per gram.
Texas ..	0·889	74	105	0·6	10,800
Persia ..	0·899	150	88	1·5	10,550
Borneo ..	0·913	41	80	0·1	10,500
Texas ..	0·917	204	99	—	10,700
Trinidad ..	0·947	450	86	—	—
Mexican ..	0·955	1360	71	2·9	10,450
Mexican ..	0·961	2500	75	3·7	10,210
Venezuela ..	0·963	5000	83	2·4	10,200
Texas ..	0·973	4850	86	0·9	10,400

A very complete list of fuels and their properties is given in the *Mechanical World* for April 2, 1920, to which the reader is referred.

The various **tars** derived from the distillation of coals under various conditions and of lignite, peat, wood, etc., may also be used as liquid fuels. For diesel engine use they cannot compare with the petroleum fuels. The difficulty of ignition may be overcome by the use of a pilot jet as described under tar oils (p. 258), but the presence of free carbon in such tars is a severe handicap, as this gives rise to much trouble with the exhaust valves. The removal of the free carbon from such tars is difficult and hardly an economic proposition. The relatively high ash content also militates against their successful use.

When tars are used in furnace work the objections mentioned above naturally largely disappear. The high specific gravity of the tars makes the separation of water difficult, and the low calorific value must always remain an objection, which, however, may be nullified by price of the tars in relation to fuels of higher calorific value.

Analyses of several types of tars are herewith given (Moore, " Liquid Fuels for Internal Combustion Engines ").

Tar.	Sp. gr. @ 15° C.	Elementary Analysis.			Ash.	Coke.	Net calorific value. Calories per gram.	Free carbon per cent.
		C.	H.	S.				
Horizontal retort ..	1·180	91·5	5·2	0·5	0·20	24·0	8645	18·2
Vertical retort ..	1·089	88·0	6·8	0·6	0·03	6·1	8664	1·7
Simon-Carvè coke oven	1·090	88·1	5·6	0·2	0·07	6·0	9261	traces
Low temperature carbonization	1·058	85·8	8·1	0·09	0·11	8·2	8776	2·2
Water gas ..	1·054	92·2	6·8	0·6	trace	18·7	8647	6·8
Blast furnace ..	1·172	89·5	5·75	0·84	0·36	23·4	8288	9·5

Methods of Burning Liquid Fuels.—Liquid fuels are usually burnt under furnaces by one of three methods, the choice of method depending upon conditions, viz. (*a*) injection or atomizing by means of steam, (*b*) by means of compressed air, (*c*) by means of pressure only. Atomizing jets may be divided into three main groups: (1) those in which the atomizing is effected by the simple impact of a stream of oil and air or gas, (2) those of the injector type, and (3) those of the direct spray type, in which no spraying agent is employed, the oil being merely forced under pressure through a suitable jet. Innumerable forms of burner have been devised (Report of the United States Liquid Fuel Board, 1904), the description of which lies beyond the scope of this work. The **steam injection** system is very simple and is much used for land installations. An objection to this system is the fact that about 6 per cent. of the steam raised is used for spraying the liquid fuel For this reason this arrangement is rarely if ever installed in sea-going vessels. The **compressed air** system is not much used as the installation of auxiliary compressor plant is necessary. For small installations or where compressed air is available this method of injection is useful, as it is very easy to manipulate. The **pressure jet** system is the most economical in practice, the steam required for pumping and heating the oil amounting to only about 2 per cent. of that generated. The system may be applied to even the thickest and heaviest oils provided that the oil is heated to a sufficiently high temperature before injection. If this temperature be too low incomplete combustion with production of much smoke results.

The **advantages presented by burning liquid fuels in place of coal** are very great. The calories per unit weight are considerably greater in the ratio of approximately 1·6 to 1, so that with certain prices the actual number of calories per unit cost may be greater. If, however, this is not the case, there are so many collateral advantages on the side of oil that the higher cost per calorie is usually more than completely counterbalanced. Among such advantages may be enumerated the following: Less room required for storage; less difficulty and cost in transport and handling; more uniformity in fuel; absence of ash, cleaning of furnaces and costs of removal of ashes thus being avoided; less wear and tear on the plant; greater efficiency of the boilers, resulting in lower maintenance costs, and lower capital outlay for a definite steam-raising capacity, or increase in capacity for an existing plant; greater flexibility and easier control in running, and very much reduced labour charges, not to mention such minor advantages as absence of smoke and general cleanliness.

When applied to marine use further advantages result in: the superior evaporative power per unit weight of fuel carried, thus ensuring greater radius of action, or less weight of fuel necessary for a given voyage, thus allowing more cargo space, and ease of bunkering and consequent saving of valuable time.

Nevertheless, to quote Beeby Thompson, "From an economic point of view, the burning of oil under boilers can only be regarded as a wanton waste of the world's resources, as each pound of oil consumed under boilers is capable of yielding four or five times the power if applied in accordance with modern methods," *i.e.* in internal combustion engines.

As liquid fuel presents such numerous advantages over coal, particularly for sea-going vessels, the world's shipping is rapidly turning to the use of oil, indeed the world's navies have already adopted it as their standard. Whereas 10·5 per cent. of the world's shipping tonnage in 1918–19 used oil fuel under boilers, 16·3 per cent. used it in 1919–20 (*The Naval Annual*, 1920–21, London, p. 180). During the last few years bunkering stations in great number have been constructed by the leading oil companies, so that now ample supplies are ensured at numerous points on the great trade routes throughout the world.

GENERAL REFERENCES TO PART VIII., SECTION D.

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Brewer, "Efficient Handling of Fuel Oil," *Power*, 1921, January–March.

Dunn, "Industrial Uses of Fuel Oil." Technical Publishing Co., San Francisco.

Moore, "Liquid Fuels for Internal Combustion Engines." Crosby, Lockwood and Son.

North, "Oil Fuel." C. Griffin and Co.

Sothern, "Oil Fuel Burning in Marine Practice." Munro and Co., Glasgow.

SECTION E.—PARAFFIN WAX

ALTHOUGH paraffin wax cannot be regarded as one of the main products of petroleum it is, nevertheless, produced in large quantities, not only in the United States, where production for 1920 amounted to 152,000 tons, but also in the East Indies, Burmah, Rumania, Galicia, Mexico, and elsewhere. It is, moreover, produced in quantities from shale oil, as in Scotland, and from the distillation of lignite in Thuringia.

Paraffin wax, together with ceresin and montan wax, finds its chief use for the manufacture of many articles for which otherwise the more expensive bees- or other wax would be used. In many cases, too, new industries involving the use of paraffin wax, have been developed. A good example of the replacement of beeswax by paraffin is afforded by the "batik" industry in Java. Fabrics are dyed by the natives by first covering the portions of the surface which are not to be dyed by a layer of batik wax, applied in the melted state by hand, by means of a very small kettle, and then immersing the material in the dye. After dyeing, the wax is removed by hot water and used again. Beeswax was at one time almost universally used for this industry, but it has been largely replaced by substitutes composed in the main of paraffin wax, blended with such substances as carnauba wax, montan wax, japan wax, resins and the like. Many such varieties of vegetable or animal wax substitutes are made. Paraffin wax also enters largely into the composition of polishes for floors, leather, etc. Large quantities are used in the electrical industries for insulating purposes, often directly, often in admixture with resin, tallow, etc., for cable work. The use of paraffin wax for waterproofing paper for packing purposes, for making jam pots and the like, is now the basis of a considerable industry. It is so used in the making of washable wall-papers, for waterproofing cartridges, in the waterproofing of chrome leather. It also plays an important part in the waterproofing and finishing of textile fabrics. For making rainproof material, a solution of paraffin wax in benzine or other volatile solvent is sprayed on to the cloth. In conjunction with ceresin and soap, together with starch and filling material, it is used for glazing certain fabrics by hot calendaring. It is also used in laundry work for imparting a high gloss to collars, etc.

It is also used as a convenient base for many ointments for medical use in admixture with wool fats and oils, and in quite another direction for surgical use as a dressing to exclude air and even in place of plaster of Paris for splints. For many other minor purposes such as manufacture of crayons, sealing waxes, etc., quantities are used.

By far the largest quantities, however, are used for the manufacture of candles, nightlights and the like. Candles are made by casting in moulds made of an alloy of tin and lead, the wick being placed *in situ* before running in the wax. These moulds are grouped together in machines which may contain 200 or more moulds. Candles may be made of pure paraffin, but it is usual to employ mixtures, because pure paraffin has a tendency to stick to the moulds, and, moreover, candles of pure paraffin soften too readily on exposure to only moderate temperatures. Stearine, a mixture of stearic and palmitic acids prepared by the splitting of certain fats, is mostly used for this purpose, grades of melting point 55° C. being usually selected. Mixtures of stearine and paraffin have always melting points lower than those of the constituents, but in spite of this they stand up better to heat and less readily become plastic. The real advantage of adding stearine is this stiffening effect. The white marble-like appearance caused by the addition of stearine is of minor importance; nevertheless, attempts have been made to imitate this by the addition of small percentages of such substances as β-naphthol. Candles may be coloured by the use of certain aniline dyes which are slightly soluble in paraffin wax or stearin, *e.g.* methyl violet, malachite green, quinoline yellow, and so forth. Although the quantities used are so minute, colourless candles always burn better.

The wick plays a very important part, and great care must be bestowed on its manufacture. A wick must be "self-snuffing," *i.e.* it must bend over so as to project into the outer oxidizing atmosphere of the flame, and must be impregnated with certain chemicals to enable it to burn to a light powdery non-coherent ash. The former is attained by weaving the wick with one set of strands under greater tension than the others, the latter by impregnating the wick with such salts as potassium chlorate, ammonium nitrate, ammonium phosphate. In addition to being used for the direct manufacture of wax matches, paraffin of low melting point, about 47° C. is used for impregnating the tips of wooden matches.

GENERAL REFERENCES TO PART VIII., SECTION E.

Campbell, "Petroleum Refining." C. Griffin and Co.
Graefe, "Die Braunkohlenteer-Industrie." W. Knapp, Halle.
Gregorius, "Mineral Waxes." Scott, Greenwood and Son.
Lamborn, "Modern Soaps, Candles, and Glycerin." Crosby, Lockwood and Son.
Scheithauer, "Shale Oils, and Tars." Scott, Greenwood and Son.

SECTION F.—LUBRICATING OILS

THE subject of lubrication generally, and more particularly that of the relation between the chemical and physical properties of an oil and its practical lubricating value, is one of great difficulty. Much has been written on the subject, but there is a great lack of concrete fundamental data, so that the basic problems are still far from being solved.

Up till quite recent times, lubrication presented no difficult problems. Vegetable oils and fats were used, sperm oils for light-running machinery, rape, castor, and lard oils for heavier work, and tallow for the heaviest. As modern high-speed machinery developed and as the demand for lubricating oil increased, mineral lubricating oils began to come into use, naturally first by blending with sperm and other fatty oils. Thus according to Parish (*Chemical Age*, New York, 1922, p. 61), the lubricating oil business developed along most complicated lines, so that " in a decade the lubricating practice of the world was one jumbled mass of dissociated facts due to the practice of producing a comparatively few number of oils at the refinery and of compounding, mixing, and branding an immense and complicated number of oils, many of them finally being used for the lubrication of the same class of machinery, as, for instance, high-speed machinery working under about the same mechanical conditions, but being lubricated with a great number of different kinds of compounds and mixtures sold under a multitude of names, all descriptive of the machine on which the oil was intended to be used." In this manner the lubricating-oil trade developed, and in this manner it exists to-day. There is, however, a tendency to improvement.

The futility of present methods is being recognized, the number of brands is being reduced and efforts are being made to study the problems and acquire data of real value. With the modern developments of machinery new lubricating problems have arisen, such as the lubrication of superheated steam cylinders, and internal combustion engines of various classes. Such special conditions call for certain types of oil regarding which a good deal of empirical knowledge has been accumulated. In all cases of lubrication the design and condition of the surfaces to be lubricated play much the most important part. Bearings of the Michell type are so nearly perfect that the character of the oil used is of quite secondary importance.

The physical property most generally considered in relation to lubricating value is the *viscosity*. In the case of lightly loaded spindles running at high speed the viscosity or internal friction of the oil is the factor of prime importance, so in dealing with such cases there is little difficulty. In the case of heavily loaded bearings, however, the problem is one of the capability of the oil of forming a thin film and of maintaining this film without breaking down under conditions of great stress.

According to Langmuir the spreading of the oil in a film only one molecule thick depends on a definite chemical attraction between the metal and the oil. According to this view unsaturated compounds should be better lubricants than saturated. This is, in fact, borne out by the work of Wells and Southcombe on the effect of the addition of small percentages of fatty acids to mineral lubricating oils (*J.S.C.I.*, vol. 39, p. 51T). This has led to efforts to correlate the lubricating power of an oil with its surface tension relative to metals, a difficult problem which has not yet been successfully attacked. Holde (*Chem. Ztg.*, 1921, p. 3) states that mineral lubricating oils have on the average lower surface tensions than fatty oils. He takes the product of the surface tension of an oil in air with the cosine of the angle of contact as a measure of the affinity of an oil for the metal to be lubricated. He also confirms Wells' and Southcombe's observations.

Oils derived from petroleum have largely replaced the vegetable and animal oils once generally used. Mineral oil lubricants can be manufactured in great variety, ranging from the thinnest spindle oils more limpid than sperm oil to the thickest oils more viscous than castor. The viscosities of mineral oils fall off more rapidly with increase of temperature than do those of fatty oils, this phenomenon being much less marked, however, at temperatures over 40° C. (Archbutt and Deely, "Lubrication and Lubricants," p. 191). The more viscous the oil, the more marked is the change of viscosity with temperature. Woog (*Comptes rendus*, 1921, p. 303) found (cryoscopically) that the mean molecular volume of a fatty oil was much less than that of a mineral oil of the same viscosity.

Of the chemistry of mineral lubricating oils little is known. They consist of hydrocarbons of high molecular weight, consequently the difficulty of isolating any group of individuals and still more so of elucidating their constitution is very great. Marcusson (*Chem. Ztg.*, 1911, pp. 729, 742) holds that the constituents to which mineral oils chiefly owe their lubricating power are those which do not react with formaldehyde and sulphuric acid. Mabery ("Composition of Petroleum and its Relation to Industrial Use," *Am. Inst. of Min. and Met. Engineers*, February, 1920) states that hydrocarbons of the general formula C_nH_{2n-4} form the constituents of the best lubricants it is possible to prepare from petroleum, and that heavy petroleums of an asphaltic base contain these hydrocarbons in large proportion, and lighter varieties in small amounts. He also concluded that hydrocarbons of the series C_nH_{2n+2} had a low lubricating value, and that the lubricating hydrocarbons from Pennsylvania petroleums consisted mostly of the series C_2H_{2n} and C_nH_{2n-2}. Aisinmann (*J.S.C.I.*, 1895, p. 2812) states that the lubricating oils of Baku are composed mainly of naphthenes and olefines, but this has been disputed.

Unsaturated hydrocarbons constitute 20 to 40 per cent. of most lubricating oil distillates. They can be and often are removed by treatment with concentrated sulphuric acid, as in the ordinary process of refining. Certain unsaturated hydrocarbons and asphaltic resins, which are probably mainly responsible for gumming and carbonization of oils, should be removed, but it is open to question as to whether the sulphuric acid treatment does not also remove desirable unsaturated constituents.

The saturated constituents are probably naphthenic and polynuclear in structure, but it is possible that isoparaffins, too, possess lubricating properties. Of the influence or even presence of aromatic hydrocarbons in lubricating oils practically nothing is known.

The influence on the viscosity of lubricating oils of their chemical composition has been studied by Mabery and Mathews (*J. Am. Chem. Soc.*, 1908, p. 992), who showed that a low hydrogen content is related to a high viscosity. Dunstan and Thole (*J.I.P.T.*, 1918, p. 191) consider that "a lubricating oil should contain a certain proportion of unsaturated hydrocarbons, as large a proportion as is compatible with not too much susceptibility to oxidation, polymerization, gumming, and reactivity."

Mineral lubricating oils from the point of view of manufacture fall into two main groups, (*a*) residual oils, and (*b*) distillate oils.

(*a*) The residual oils may be further divided into two classes: (1) the black axle oils which are unfiltered and untreated, made from either naphthene or paraffin base crudes by concentrating down to the required viscosity.

Typical analyses of such oils are—

	A.	B.	C.
Specific gravity at 15° C. ..	0·896	0·952	0·955
Flash-point, P.M. °C.	230	233	190
Fire test °C.	280	270	220
Viscosity, Engler, at 50° C. ..	21	24	35
,, ,, at 100° C. ..	3·3	2·7	3·3

(2) The cylinder stocks made from certain paraffin wax base crude oils, notably those of the Appalachian fields. These cylinder oils, which are largely used for steam cylinder

lubrication and for blending with distillate oils for motor cylinder and other uses, are characterized by high flash-points, and by a good viscosity curve, *i.e.* a relatively less falling off of viscosity with increase of temperature, than that evidenced by other classes of oils. They appear on the market as **steam-refined cylinder stocks** and as **filtered cylinder stocks,** the latter being obtained from the former by filtration through some form of fuller's-earth.

Typical analyses of cylinder stocks—

	A.	B.	C.	D.
Specific gravity at 15° C. ..	0·890	0·902	0·884	0·892
Flash-point P.M. °C. ..	265	280	240	260
Fire test °C.	324	320	300	315
Viscosity, Engler, at 50° C.	27	29	17·5	—
,, ,, 100° C.	4·1	4·1	3·2	—
,, Redwood I. at 100° F.	—	—	—	1800
,, ,, at 200° F.	—	—	—	144

(*b*) The great majority of mineral lubricating oils belong to the second category. The manufacture of these oils has already been described. They may be further subdivided roughly into two classes, viz. (1) those derived from paraffin wax base oils, (2) those derived from naphthenic base oils, but as crude oils vary so greatly oils of all grades intermediate between these two types are found. These two classes of oil differ to some extent in their properties. For oils of the same viscosity the specific gravity of the naphthenic oil is the higher, and the flash-point the lower. Moreover, oils of the naphthenic type show a greater falling off of viscosity with increase of temperature (Fig. 42).

It is generally held that the more gentle gradient of the viscosity curves of the oils derived from paraffin base crudes is a point in their favour, but this view is by no means proved.

The viscosities of all lubricating oils at high temperatures, say 200° C., approximate very closely to each other. The differences in viscosity of various oils are more marked the lower the temperature (Fig. 43).

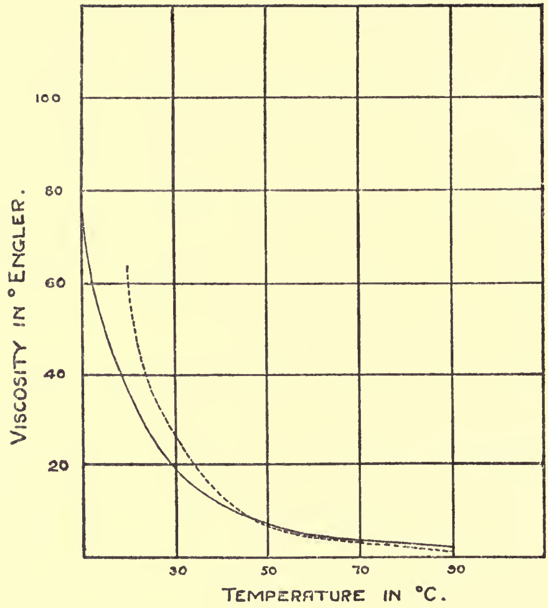

Fig. 42.—Curves showing relation of viscosity to temperature for lubricating oils: from paraffin base crudes ———; from naphthene base crudes ....

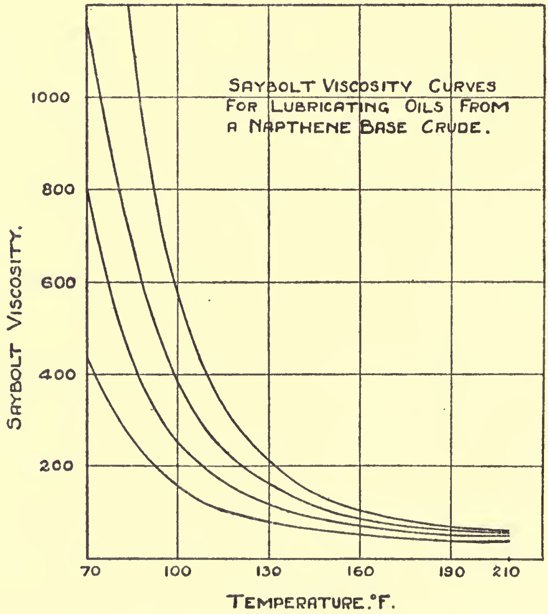

Fig. 43.—Curves showing relation of viscosity to temperature for four oils of the same type.

The **specific gravity** of lubricating oils is a property which has no direct significance. Indirectly, however, it indicates the origin of the oil, as for any definite viscosity at temperature $t°$ the specific gravities of oils derived from the paraffin wax base crudes are lower than those of oils from naphthene base crudes.

The **flash-point** of a lubricating oil is usually specified. This property perhaps has some significance, as an unduly low flash-point might indicate careless fractionation or possibly overheating during distillation with the result that cracking had taken place. This latter might be taken to indicate instability of the oil at high temperatures, and therefore the unsuitability of the oil for certain classes of work. In general, however, the flash-point has no intrinsic significance. As is the case with specific gravity it may indicate the origin of the oil ; on the contrary, it undoubtedly bears some relation to the volatility of the oil, or the loss by evaporation at high temperatures, but if such a factor be of importance, then it is much better to carry out a specific test on this point rather than rely on inferences drawn from the flash-point.

In the case of oils to be used for the lubrication of internal combustion engines a test which could indicate the degree of resistance to carbonization in the cylinder would be of value. Unfortunately, no such test, which gives reliable figures which may be interpreted in terms of actual practice, is known. The nearest approach to such a test is perhaps the **coking test** as carried out by the **Conradson** method (*J. Ind. and Eng. Chem.*, vol. 4, p. 903).

Garner (*J.I.P.T.*, 1921, p. 98) expresses the opinion that " the rapid carbonization of oil, *i.e.* the coking value, will be a more important factor in the testing of lubricating oils for internal combustion engines than the gradual carbonization at lower temperatures," basing this opinion on the supposition that the major part of the oil which gets into the combustion space is in the form of a fine spray. This is very much open to doubt. Certainly the Conradson test does not give reliable indications as to the ease of carbonization in many cases (*Circular*, Bureau of Standards, U.S.A., No. 99, "Carbonization of Lubricating Oils"). It is quite possible that the so-called carbon deposits which form on the pistons of automobile engines are due to cracking of the lubricating oil, but they may also be due to oxidation. Waters has devised a test (Bureau of Standards, *Scientific Papers* 1532160, *Technologic Papers* 4273, and *Circular* 99) based on oxidation, but so far this test also has not yielded results comparable to those obtained in actual practice.

The **ash** of lubricating oils for use in internal combustion engines should naturally be as low as possible. Distilled oils should yield no appreciable ash and filtered residual cylinder oils should not yield more than 0·02 per cent., although higher figures than these are often found.

Pure mineral oils should be free from **soaps,** the presence of which may indicate inefficient washing after the refining process. The presence of such soaps may give the oil a stringy character, which is usually objected to by buyers, although it does not necessarily impair the lubricating qualities of the oil. In certain cases, indeed, aluminium oleate is added to increase the consistency, and soaps are normal constituents of greases. Oils containing soaps will more readily emulsify with water than will pure mineral oils. For many purposes, particularly in the case of forced feed systems of lubrication as in the case of turbines, an oil which will resist emulsification, *i.e.* which has a good **demulsibility**, is necessary.

For general lubricating work a very large number of lubricating mineral oils are made, and the number is still further increased by blends with fatty oils. For a few specific purposes oils of special character are required. For the general lubrication of **marine engines** heavy mineral oils, blended with from 20 to 30 per cent. of a blown vegetable oil such as rape, are usual.

For **automobile cylinder** lubrications blended oils, containing filtered cylinder stock but no fatty oils, are used. Such oils should be resistant to carbonization, but a means of satisfactorily measuring this property in the laboratory is still to be devised.

For **air compressors** oils resisting oxidation must be selected and for **refrigerating machines** naturally oils of low cold test.

Oils for **turbines** should be pure mineral oils free from any trace of organic acid, so that they resist emulsifying with water. A type of oil not strictly a lubricant, but similar in character, which may be noticed here is **transformer oil.** Transformer cases are filled with oil, as oil is a better conductor of heat than air, and so dissipates more quickly the heat generated, and for good insulation purposes. The requirements of a good transformer oil are—

(1) It must have a good dielectric strength. It should not break down at less than 22,000 volts when tested between the flat surfaces of two parallel discs 1 inch diameter and $\frac{1}{10}$ inch apart; or not less than 40,000 volts when tested between two 12·5 mm. spheres 5 mm. apart.

(2) It must be quite free from moisture, as this causes very serious falling off in the dielectric strength. As little as 0·005 per cent. of water will reduce the breakdown voltage by 50 per cent.

(3) It should have a low viscosity, about 8° Engler at 20° C. or 2·5° Engler at 50° C.

(4) It should be pale in colour consequent upon intensive refining.

(5) It must be pure mineral oil neutral in reaction.

(6) It should have a high fire test, over 170° C.

(7) It should be resistant to oxidation, *i.e.* should give a good "sludging test."

This "sludging" is one of the main troubles. The sludge always contains oxygen. A sludging test has therefore been designed based on the behaviour of the oil when oxygen is bubbled through it for several hours under fixed conditions.

A special type of lubricating oil is **medicinal oil.** This is nothing more or less than a highly refined oil of moderate viscosity. Various specifications for this product have been drawn up by the pharmacopœia of various countries. The specific gravity usually lies between 0·870 and 0·920 at 15° C. The oil must be colourless, odourless, and tasteless, have no fluorescence, be neutral in reaction, leave no ash on ignition, must separate no paraffin wax at 0° C., and must show only a slight colour after shaking for five minutes with twice its volume of a mixture of nitric and concentrated sulphuric acids in the proportions of three to one. The viscosity should be about 300 Saybolt at 100° F. (16° E. at 20° C., 105 R.1 at 100° F.).

GENERAL REFERENCES TO PART VIII., SECTION F.

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Thomsen, "Practice of Lubrication." McGraw Hill Book Co.

SECTION G.—ASPHALTS

IN the early days of the industry the crude oils first worked in America were of the paraffin base type. Those of the European and Asiatic fields later developed, though largely of naphthene base, contained relatively little asphalt, so that the distillation residues were liquid and suitable for fuel. Only comparatively recently did the heavy Mexican crudes with their large asphaltic content appear on the scene. Strangely the ever-extending use of light petroleum fractions for motor transport has brought about a demand for the heaviest constituents, viz. the road oils and asphalts. The necessity for good roads which can stand up to modern heavy traffic, and the superiority of petroleum asphalts for this purpose is being generally recognized. Moreover, the general tendency of the coal carbonizing industry towards vertical and even low-temperature retorts, renders the coal tar available less suitable than formerly for road-making purposes.

By far the most important application of the asphalts is in connection with road making or paving in one form or another. The application of the naturally occurring asphalt-impregnated rocks for road surfacing has already been described, as has also the application of the naturally occurring asphalts of Trinidad and Venezuela, together with the petroleum residual asphalts for the same purpose (Part V., Section B).

Some idea of the extent to which asphalts are used may be gleaned from the following figures: The total consumption of asphalt of all kinds in the United States for 1919 was 1,443,289 tons. About 86 per cent. of this was manufactured from petroleum; native asphaltites and pyrobitumens were responsible for 2·3 per cent., and natural asphalts from Trinidad and Venezuela for 6·7 per cent. (Hubbard, *Chemical Age*, New York, August, 1921). It is estimated that the asphalt used in the United States for road construction alone during 1921 amounted to 634,000 tons. The present annual consumption of asphalt for the roofing industry in the United States is estimated at 625,000 tons, so that these two outlets alone account for nearly 90 per cent. of the total consumption.

Apart from road construction, asphalts are used in connection with the following: impregnated fabrics for roofing, flooring, waterproofing and insulating purposes, also paints, varnishes, japans, pipe-dipping compounds, acid-resisting compounds, etc., etc.

In the manufacture of "roofing felt" two distinct operations are necessary, viz. "impregnation" and "surfacing." For impregnating, a material of penetration not more than 60 at 77° F. and melting point from 100–160° F. (ring and ball method) is usually employed. Native or prepared asphalts, also products such as wood-tar pitch, rosin pitch or fatty-acid pitch, may be used, fluxed if necessary to the required consistency by means of soft asphalts or flux oils. Such impregnating mixture should naturally have a flash-point well above the working temperature for impregnation, which may be as high as 200° C. It should also contain a large percentage soluble in 0·645 petroleum ether (malthenes). For surfacing or for cementing together several layers of impregnated fabric into a composite sheet, similar mixtures, but of a somewhat higher melting point and consistency are used. Such mixtures should possess the following characters: penetration from 10 to 50 at 77° F., melting point not below 160° F. (ring and ball), low volatility and high flash-point (as above). The weather-resisting properties are apparently improved by the admixture of fatty substances, also of opaque material such as graphite or lampblack, which act as absorbers of the actinic rays.

The action of "weathering" on asphalts has been studied by Hubbard and Reeve (*J. Ind. and Eng. Chem.*, vol. 5, p. 15) and Lewis (*J. Ind. and Eng. Chem.*, vol. 9, p. 743). They find that the changes consequent on weathering are due to evaporation, oxidation to form oxidized products, elimination of hydrogen by oxidation, and polymerization. Exposure to weather has the following effects: the penetration, melting point, flash-point and fixed carbon content all increase, while the ductility, adhesiveness, solubility in carbon bisulphide and in 0·645 petroleum spirit all diminish. This is in agreement with the gradual change known as inspissation, the action of which in nature is inferred from the relations of the natural asphalts to the asphaltites and pyrobitumens.

The impregnated fabrics are manufactured simply by running the material through a bath of the melted impregnating material. Roofing felt will absorb about 130 per cent. by weight of asphalt. The surface of the finished material, after treating with the surfacing coat, may be further coated with talc, sand, or even fine pebbles according to taste. For a full description of the method of manufacture of roofing felt, asphalt shingles and their applications, the reader is referred to Chap. XXV. of Abrahams' excellent book on "Asphalts and Allied Substances" (D. van Nostrand Co.).

Asphalt saturated felt is also used as a "substitute for linoleum," in which case it merely acts as a support for a layer of the linoleum composition on the upper surface. Impregnated cotton fabric is also largely used for "damp-proof courses" in buildings. "Insulating papers" are also largely made by impregnating suitable papers with asphalt mixtures as used for roofing felt, also with other petroleum products, such as paraffin wax and cylinder oils. Such papers are used for insulating refrigerator vans, ice chests, etc., also for electrical purposes. Insulating tape is made in a similar way.

Asphalt enters into the composition of "pipe-dipping mixtures," used to protect iron or steel piping which is liable to exposure to damp soil containing corrosive salts, and to electric currents. The dipping mixture used must be durable and tough and adhere well to the metal. The pipes to be dipped are heated to about 200° C., and then immersed in a bath of the asphalt at the same temperature. On withdrawal, they are heated or baked before cooling. A number of "bituminous paints and varnishes" are on the market and are used for a variety of purposes, such as waterproofing walls, protecting wood and metal surfaces, etc. Bituminous paints are merely solutions of asphalt in suitable solvents, which on evaporation leave the asphalt distributed over the surface. Bituminous varnishes contain also vegetable drying oils which contribute to the drying and hardening of the film, as in the case of ordinary oil paints. The so-called "mineral rubber," is also a petroleum product. The best grades consist of mixtures of blown asphalt and gilsonite, the gilsonite being usually mixed with the asphalt before the blowing operation. These mineral rubbers are used for incorporating into natural rubber with which they are masticated. C. O. North (*Chem. and Met. Engineering*, 1922, p. 253) has investigated this subject and has found that mineral rubber when mixed in in proportions from 3 to 15 per cent. has a beneficial effect on the properties of the rubber. In proportions greater than 15 per cent., however, it affects the rate of recovery of the rubber.

GENERAL REFERENCES TO PART VIII., SECTION G.

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PART IX.—THE TESTING OF PETROLEUM PRODUCTS

As the subject of the testing of petroleum products is fully dealt with in numerous books and publications, the description of detailed methods here would serve no useful purpose. It is proposed, therefore, merely to present a few general considerations on the subject together with a few data dealing with the relation of several of the instruments in general use to each other.

The tests applied to petroleum products fall at once into two categories, (*a*) those which are applied according to the methods of exact chemical analysis, and (*b*) those which are applied by means of apparatus of specified dimensions operated in a specified manner.

Under the former heading fall such determinations as elementary organic analysis, percentage of sulphur, the determination of certain physical constants, solubilities, and so forth. Under the latter heading fall all the determinations of the values of such properties as flash-point, viscosity, distillation range, colour, illuminating power, melting point, penetration, ductility, and the like.

The fact that the bulk of the determinations usually carried out are of such an empirical nature has brought about a position of chaos in this respect. Co-operation between large firms and between petroleum organizations in various countries has been practically non-existent, with the result that there are almost as many instruments in use for testing flash-points, for example, as there are countries. Prior to the great war an International Petroleum Congress had been formed, one of the aims of which was the standardizing of methods of testing, but this organization has unfortunately become defunct. The subject has, however, recently received the attention of the American Society for Testing Materials, a society which has already done much work, and is now also receiving the attention of the recently formed Standardization Committee of the Institution of Petroleum Technologists in this country. If these two bodies work together, a much desired uniformity in testing methods may be brought about (Brame, Presidential address to *Inst. of Pet. Tech.*, March, 1922). Until this much-to-be-desired state of affairs results, a few words dealing with the subject generally may not be out of place.

Of the determinations which fall in the first category mentioned above little need be said. The usual physical constants can be determined with accuracy by the usual methods. Even in the expression of such a simple and important constant as specific gravity there is, however, no uniformity. In America the arbitrary Béaume scale is used. In other countries there is often much confusion as to whether the specific gravity is referred to water at 15° C., 60° F., or 4° C. This may lead to disputes in the determination of the weights of cargoes of oil. Moreover, the figures used as coefficients for converting the specific gravity at any temperature t° to the standard temperature of reference are neither accurately determined nor even generally agreed. The elementary chemical analyses may be made in the usual way. Sulphur may be estimated by the calorimeter bomb, and in the case of light products, such as benzines and kerosenes, may be accurately estimated by one of the methods based on burning the oil in a current of air, absorbing the resulting sulphur dioxide and estimating it as sulphate or otherwise (Lomax, *J.I.P.T.*, 1917, p. 19; Bowman, *J.I.P.T.*, 1921, p. 334; Esling, *J.I.P.T.*, 1921, p. 83).

Methods of estimating the percentage of the various chemical compounds or even classes of hydrocarbons present in a crude oil or even in a light distillate are by no means reliable and yield only approximate results. Olefines may be estimated by removal by sulphuric acid, by bromine or iodine absorption, or by reaction with potassium permanganate, but all these methods give unsatisfactory results (Chavanne and Simon, *Comptes rendus*, 1919, pp. 70, 111; Lomax, *J.I.P.T.*, 1917, p. 22; Bowrey, *J.I.P.T.*, vol. 3, p. 287). The question of determining the percentage of aromatic, naphthene, and paraffin hydrocarbons in a motor spirit is one of importance. Perhaps the best and simplest method so far evolved is that of Tizard and Marshall (*J.S.C.I.*, vol. 40, p. 20T) (*vide also* p. 26). While this method gives reliable values for the aromatics, the values indicated for naphthenes are approximate only. In the case of products containing compounds of high molecular weight, methods are even less satisfactory. Asphalts are examined according to their solubility in various chemical solvents, and the existence of bodies termed asphaltenes, carbenes, malthenes, etc., is thereby inferred. The figures so obtained are doubtless of some value, as they can be correlated with variations in the method of manufacture and, moreover, give useful indications as to the origin of the product. How dependent these values are on conditions is well exemplified by the work of Mackenzie (*J. Ind. and Eng. Chem.*, 1910, p. 124), who showed that the amount of carbenes found largely depends on the exposure to light during the estimation.

When methods of the second category are considered, very great diversity, both in apparatus and methods of testing, are at once obvious. In the case of the examination of benzines for **range of boiling points** several methods have been largely used. Among these may be mentioned the Engler and the Ubbelohde, with their many modifications. In the case of the Engler test, the flask and its contents are weighed, and after distillation to a definite temperature, the contents are again weighed, the percentage distilling up to that temperature being determined by the loss of weight. The distillation in this case is interrupted at the temperature in question, and after the flask has been allowed to cool somewhat, heat is again applied until the temperature of the vapour again reaches the point in question. This operation is repeated several times (usually three). This method differs fundamentally therefore from the Ubbelohde method in general use in that the distillation in the latter case is carried on continuously, the percentages boiling over up to any definite temperatures being expressed in volumes. The Engler method usually yields results about 5 per cent. higher than those given by the Ubbelohde method, in distilling to 100° C. The liability to personal error in the Engler method is great, moreover, as the percentage distilling over is determined by loss of weight and not by measuring the distillate collected, the very volatile gaseous or noncondensable fractions which would otherwise be lost are included. Something is, of course, to be said on both sides of this question. Lomax (*J.I.P.T.*, 1917, p. 7) gives figures comparing the Engler and Redwood methods, this latter method being to all intents and purposes identical with the Ubbelohde method (except in so far as the method of determining the initial boiling point is concerned).

	Redwood.	Engler.	Redwood.	Engler.
Percentage to 100° C.	5	11	8	16
,, to 125° C.	60	65	61	67
,, to 150° C.	89	90	90	93
Final boiling point	176	175	176	174
Time for test (minutes)	50	90	55	90

A form of apparatus used in France, not only for benzine but also for kerosene and fuel oils, is the Luynes-Bordas. It consists of a copper retort of special design enclosed in an iron casing, connected to a metal water-cooled condenser. In the case of benzine the thermometer is immersed in the vapour, but when distilling kerosene or fuel oils it is placed in the liquid. As compared with the Ubbelohde test for benzine the lower fractions distil at slightly higher temperatures and the higher fractions at slightly lower temperatures. The figures given below illustrate a comparative test with the two types of apparatus :—

Volume distilled over (per cent.).		Luynes Bordas at temperature °C.	Ubbelohde at temperature °C.
5	..	72·6	67·3
20	..	87·5	84·8
45	..	104·7	106·9
55	..	113	115·2
90	..	158·3	160·4
95	..	175	175·5

The apparatus is very sensitive to changes in the rate of distillation. With kerosene the distillation results of the two methods show greater divergence. The method of Ubbelohde as modified by the American Society of Testing Materials (E. W. Dean, Bureau of Mines, *Technical Paper* 166), may be recommended for general adoption.

The determination of the **flash-point** of kerosenes is a subject which has received much attention. In the British Empire the Abel method is the standard, on the Continent the Abel-Pensky modification is used, the personal factor of the Abel apparatus being eliminated by the use of a clockwork device. In the United States several flash-point testers are in use such as the Tagliabue closed cup, the Foster and the Elliot. Allen and Crossfield have recommended a modified Abel-Pensky apparatus (Bureau of Mines, *Technical Paper* 49). Taking the Abel-Pensky as a standard, the Tagliabue closed cup gives results 3° C. higher; the Foster 6° C. higher, and the Elliot 5° C. lower. The German type of Abel-Pensky gives results 3·7° F. higher than the Abel. In France the Luchaire type of flash-point tester is in general use.

For the testing of **colour** many forms of instruments are in use. They may be divided roughly into two classes, (*a*) those which match the tint of a definite thickness of oil with various standardized coloured glasses, (*b*) those which match the tint of a standard coloured glass by varying the thickness of the layer of oil looked through. To the former class belong the instruments of Lovibond and Wilson, to the latter those of Saybolt and Stammer. For detailed descriptions of these instruments the reader may be referred to Campbell's "Petroleum Refining for Lovibond," Kansas City Testing Laboratory, *Bulletin* 14 for Saybolt, and to Holde, "Die Untersuchung der Mineralöle und Fette," for Stammer. The Lovibond instrument is also supplied with a fine range of glasses of yellow and red tints, in addition to the standard glasses for kerosene; the Stammer has the advantage that the thickness of the column of liquid under observation may be varied either way as often as required.

The trade terms used to designate the colours of kerosenes are Water-white, Superfine-white, Prime-white and Standard-white. These terms have unfortunately not precisely equivalent values on different instruments.

Fig. 44 shows at a glance the comparative readings of the four types of instrument mentioned. Francis (*Nat. Pet. News*, June 10, 1921, p. 34) gives a useful comparison between the Saybolt and Lovibond instruments, and compares this latter type also with the Union Petroleum Colour Standards

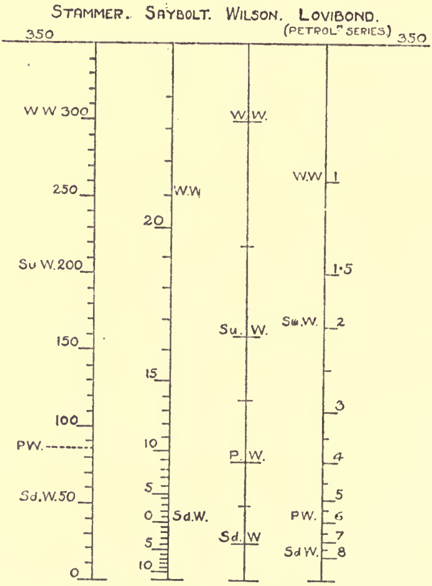

FIG. 44.—Comparative colorimeter readings, using benzine and kerosene.

and colorimeter used in the United States for the testing of lubricating oils.

There are also numerous types of instruments in use for determining the **flash-points** of heavy oils, fuels, lubricating oils and so forth. The order of accuracy of these instruments is not so great as those used for flash-points at lower temperatures, but the need for accuracy is not so great. The type in most general use is the Pensky Marten; the Cleveland open cup and the Gray tester are in use in the United States.

The influence of water on the flash-point must be noted, as unless the oils to be tested are dry, errors of as much as 20° F. in the flash-point may be made, the wet oil giving the higher value. The presence of 1 per cent. of water usually renders the determination impossible. Even with dry oils, successive determinations by the same observer may differ by as much as 7° or 8° F.

A large number of instruments have been designed for the testing of **viscosity.** Owing to the great range of viscosities to be determined, varying from that of a light spindle oil to that of a heavy cylinder, thick fuel or flux oil, one instrument of any type cannot well cover the whole range. For the more viscous oils, therefore, special types have been designed. There is, however, great lack of co-operation in this matter; not only do the instruments in use in different countries differ, but even the mode of expressing the results obtained.

The *absolute viscosity* of an oil is "the force which is required to move a unit area of plane surface with unit velocity relative to another parallel plane surface from which it is separated by a layer of the oil of unit thickness" (Herschel, U.S.A. Bureau of Standards, *Technologic Paper*, No. 100). The unit of absolute viscosity is termed the "poise."

$$F = \frac{\mu a v}{a}$$

F being the force in dynes required to slide two parallel plates, each of area *a* square centimetres, over one another at a velocity of v centimetres per second, when separated by a layer of oil of absolute viscosity μ and thickness a centimetres.

The absolute viscosity of water at 20° C. is 0·01005 poises. *Specific viscosity* is the ratio between the absolute viscosity of the substance and that of the absolute viscosity of water at the same temperature. In practice, however, the absolute viscosity of water at 20° C. is taken as the reference figure.

The absolute viscosity of an oil is determined in practice by the capillary tube method (Archbutt and Deely, "Lubrication and Lubricants," p. 155). For commercial use, however, relative viscosities only are usually required and these are determined by a number of different instruments, most of which depend upon the measurement of the time of flow of a definite volume of the liquid through an orifice of definite dimensions under definite conditions of temperature and head. The instruments in most general use are the Engler on the Continent, the Redwood in England, and the Saybolt in the United States. For very viscous oils a special Redwood Admiralty type, usually known as Redwood II. possessing a much larger orifice is in use in England, and a Saybolt Furol instrument in the United States. Descriptions of these instruments are given in most of the books dealing with the testing of petroleum products, *e.g.* Battle, "Industrial Oil Engineering," Griffin and Co. These instruments give values which are approximately proportional to actual viscosities particularly when oils of high viscosity are examined. When mobile liquids are examined the rate of flow depends by no means entirely on the viscosity, as it is influenced by the necessary increase in kinetic energy of the liquid, while flowing through the nozzle, which naturally impedes the flow. This kinetic effect, however, becomes negligible when the viscosity of the liquid exeeds about 10° Engler at the testing temperature. As a consequence of this kinetic effect, conversion factors for translating the reading of one type of commercial viscosimeter into the equivalent reading of another type are not constant, but vary somewhat with the viscosity of the oil.

With this reservation a table can be drawn up giving the relative values of viscosities as determined by the various instruments, at the same temperature. In order to calculate the viscosity of an oil on another instrument at a different temperature, a knowledge of the viscosity curve showing the relation of viscosity to temperature for that particular oil would be necessary.

The following figures may be taken, therefore, only as a rough guide :—

Engler seconds.	Redwood I. seconds.	Saybolt seconds.
56	21·5	32·4
66	34·6	39·3
75	39·8	45·5
85	45·7	52·5
100	54·3	63·0
130	71·7	83·5
160	89·1	104·4
200	111·9	131·6
250	140·3	165·5
300	168·5	198·8
350	197·0	233·2
400	225·5	266·5
500	282·0	334·0
600	339·0	400·0

The factors for converting Saybolt to Engler will thus be seen to vary from 1·73 for an oil of about 1° Engler to 1·50 for an oil of about 10° Engler (1° Engler equals approximately 53 seconds, but varies somewhat with different instruments).

As approximate values the conversion factors for Redwood I. to Redwood II. may be taken as 0·091 and for Saybolt to Saybolt Furol as 1·05 (Herschel, *loc. cit.*). The readings of the commercial instruments can be converted into absolute viscosities by the formulæ given by Herschel (U.S. Bureau of Standards, *Circular* No. 112).

Absolute viscosity

$$= \text{Sp. gr.}\left(0{\cdot}00213 \text{ Saybolt} - \frac{1{\cdot}535}{\text{Saybolt}}\right)$$
$$= \text{Sp. gr.}\left(0{\cdot}00147 \text{ Engler} - \frac{3{\cdot}74}{\text{Engler}}\right)$$
$$= \text{Sp. gr.}\left(0{\cdot}00260 \text{ Redwood} - \frac{1{\cdot}715}{\text{Redwood I.}}\right)$$

The calculation of the viscosities of mixtures of oils is almost impossible unless the two oils used are of viscosities very slightly different, a case seldom met with in practice. Viscosity numbers are not additive figures. The influence of the lower viscosity oil is always much greater than would be expected. This subject has been investigated by Dunstan and Thole ("The Viscosity of Liquids," p. 39), Espy ("Petroleum," 1919, p. 27), Herschel (Bureau of Standards, *Tech. Paper* 112), and others. A summary of their work may be found in Hamor and Padgett, "The Examination of Petroleum," p. 357.

The tests usually applied to the heavy asphaltic products of petroleum are largely of an even more empirical nature than those above described. Two types of **penetrometers** are in use, that of Dow and that of the New York Testing Laboratory, but both operate on the same principle, and give practically the same results under similar conditions.

Several methods are in use for the determination of the **melting point** of asphalts. As such substances gradually soften and have no definite melting point any test must be quite empirical. A comparison of the chief methods is given in *Chem. and Met. Engineering*, 1919, p. 81. The ring and ball method gives consistent readings, but the personal error may be large. The Kramer and Sarnow method gives less consistent results and is complicated in operation. This test gives results from 15° to 25° F. lower than those given by the ring and ball method.

The **total bitumen** is given by the solubility in carbon bisulphide. Any organic matter insoluble in carbon bisulphide is often erroneously termed free carbon. It may be free carbon in some cases, but it must be remembered that the kerotenes, the chief components of asphaltic pyrobitumens, are insoluble in carbon bisulphide. The amount insoluble in petroleum ether (sp. gr. 0·645) is usually determined, those constituents which are soluble in this solvent being termed **malthenes.** As the solvent powers of petroleum ethers depend on their chemical composition (aromatics and naphthenes being better solvents than paraffins), it is as well to use only petroleum ether composed entirely of paraffins. The constituents which are insoluble in petroleum ether are often termed **asphaltenes,** but it is better to restrict this term to the constituents insoluble in alcohol or alcohol-ether mixture. The constituents of some asphaltites which are soluble in carbon bisulphide, but insoluble in carbon tetrachloride are termed **carbenes.** Carbenes are not found in petroleum asphalts unless they have been overheated during manufacture. The presence of more than 0·5 per cent. of carbenes should be regarded with suspicion.

Several methods are used for the determination of the **melting point** of paraffin wax. Although this is quite a definite point as compared with the melting point of an asphalt, the various methods give considerably divergent results. The British method and the continental method (Shukoff) are similar in principle. A thermometer is immersed in a quantity of the melted wax and the cooling curve is drawn. At the point of crystallization the latent heat evolved by the crystallizing wax causes a break in the curve, so that the thermometer remains stationary for a short time. The temperature at which this occurs is taken as the setting point. The American method is more empirical. A thermometer of standard dimensions is placed with three-quarters of its bulb immersed in melted wax contained in a bowl 3¾ inches diameter. The temperature is noted when a film of solid wax extends from the sides of the bowl to the thermometer. The American method gives results 3° F. above those given by the British method.

Numerous other tests, some of value, many of little or no value, are employed. For details of these the reader must be referred to one of the many books dealing specially with this subject.

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