BENZINE AND
MINERAL LUBRICANTS

J. FORMANEK

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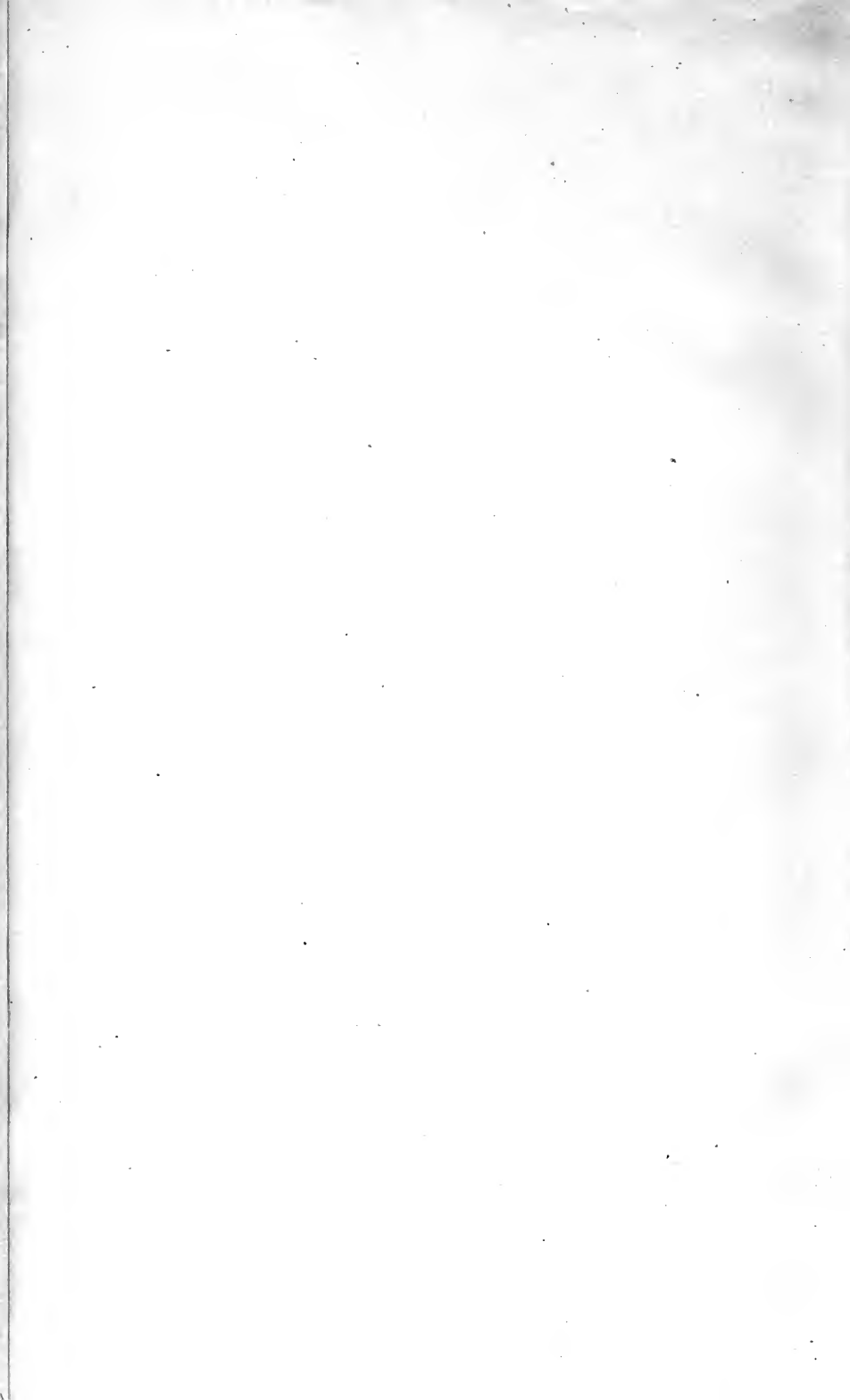
BENZINE AND
MINERAL LUBRICANTS

THEIR PRODUCTION, TESTING
AND USES

BY

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PUBLISHERS' NOTE

The German Edition was published in Berlin in 1918. Since that date Dr. J. Formanek has revised the work and added new matter, all of which is embodied in the present English Edition, bringing the subject up to date.

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PREFACE

Notwithstanding the various handbooks that have been published on the subject, the present work, which embodies the long experience of the author as a motorist and a chemist engaged in testing and reporting on motor fuels and lubricants, has become necessary.

The book itself has a two-fold purpose. On the one hand, it is intended to instruct motorists, owners of oil engines, motor engineers and all who have to do with benzole and benzene, in the importance, nature and scientific testing of these fuels, and at the same time show how they can be tested by simple means, and also be valued and economically utilised. On the other hand, it furnishes good advice to the chemist who is called upon to report on the substances used for working oil motors. With this object, brevity and comprehensiveness have been aimed at, rather than absolute exhaustiveness.

The composition and treatment of petroleum, coal tar and brown-coal tar have been treated briefly and only so far as is necessary to enable the reader to understand the subsequent chapters.

The author is indebted, for assistance in his work, to the motor department of the Erste Böhmisch-Mährischen Maschinenfabrik, Prague; the petroleum refineries in Kolin, Pardubicz and Kralupz; and to Mr. H. Bauer, manager of the Kolin refinery for revising several of the chapters.

Hints on any additional points which might be included in a future edition will be welcomed; and the author hopes that the book will fulfil its purpose and prove really useful.

<div align="right">J. Formanek.</div>

Prague.

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BENZINE AND MINERAL LUBRICANTS

CHAPTER I

INTRODUCTORY

So long as internal combustion engines were only used to a limited extent, pure and highly volatile benzine (petrol) could be obtained at a low price; but, of late years, the popularity of the motor-car and petrol engine has increased so rapidly that a scarcity of petrol has become unpleasantly apparent, in spite of importations from America and the East Indies. The Indian crude benzine at present imported into Europe contains only relatively small quantities of petrol; and the German production of this fuel from brown coal and by cracking petroleum distillates is small in quantity and low in quality. It therefore became necessary to draw upon the heavier and poorer grades of benzine—a circumstance highly agreeable to petroleum producers, who, in consequence of the increased demand for petrol, had only a small outlet for heavy benzine.

Another result of the growing scarcity of petrol was the employment of benzol as motor fuel; and when even the increased output of this substance proved insufficient, owing to the numerous other purposes for which it is in demand, recourse was had to alcohol and finally to petroleum.

At the same time, numerous mixtures of benzine, benzol, alcohol and petroleum were put on the market under various names, and not infrequently lauded in a manner not consonant with their merits.

In order to facilitate the ignition of these mixtures, various other, specially inflammable, ingredients were added, such as sulphuric ether, carbon disulphide, acetone, nitro compounds (*e. g.* picric acid), etc.; but few such mixtures

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have an efficiency equal to that of benzol, whilst still fewer
are comparable to petrol.

Petrol and benzine were usually—and are still mainly—
purchased on the basis of specific gravity.   The composition
of the product was taken on trust, no one giving it a thought,
the consumer being quite satisfied so long as the petrol had
a density not exceeding 0·700 and was easily ignited.

At present, however, specific gravity is no longer con-
sidered sufficient indication of the quality of petrol or other
fuels, because it does not afford any information as to quality
or properties.   Thus, for instance, a benzine of medium
gravity can be obtained by mixing light and heavy fractions,
or by adding a large proportion of gasoline to heavy benzine ;
but such mixtures cannot possess the same properties as a
natural product, of equal density, obtained by direct dis-
tillation of the raw material, these mixtures lacking the
middle fractions that are important for motor use, whilst
containing a large proportion of heavy fractions that are
difficult to vaporise in the carburettor.

Conversely, a mixture of benzol, of sp. ·gr. 0·885, with
petrol of sp. gr. 0·700, has the same density as a heavy
benzine, but makes a good motor fuel, because the benzol
itself is suitable for the purpose.

Mere determination of the density, moreover, will not
reveal the proportions of benzol and benzine in a mixture.
The fractions of American and Russian coming over at the
same range of temperature, 60–130° C., differ very consider-
ably in density, that of the former product being about
0·015 lower than the corresponding Russian fractions.
Similarly, the density of commercial benzols is of no par-
ticular value, and mostly serves merely for approximation,
it being quite possible, for example, to prepare mixtures of
benzol, toluol and xylol which will apparently pass the test
but have not the proper composition.

Moreover, the density and external appearance alone will
not reveal whether the product contains intentional or
natural additions which, though apparently unobjectionable,
may injuriously affect the parts of the motor after prolonged
use—for instance, a high content of carbon disulphide in
petrol or benzol.

It is therefore highly important that motor fuels should
be purchased entirely on the basis of their chemical com-
position and physical properties, and to classify them
commercially under definite corresponding names.   It is

also essentially necessary that, in the case of mixtures sold under names that do not indicate their composition, the substances of which they are composed should be stated, this being of special importance for the proper running of the engine.

In view of all these circumstances, the International Petroleum Commission in 1912 took up the question of standardising benzines according to origin, range of boiling points, etc.; but so far no agreement has been arrived at on the subject.

In looking through the recent literature on the testing of benzine, benzol and mineral lubricants for internal combustion engines, it will be noticed that there are, at present, no uniform and accepted testing specifications or agreed standards for judging these materials, of the kind that exist for other important industrial substances, although both benzine and benzol should be included in this category. For the most part we find only vague statements, sometimes incomplete and not corresponding to practical requirements, and quite insufficient for accurately judging these technical products.

It is only quite recently that writers have dealt with these materials—especially in the technical press—from the technical standpoint and on an economic basis in a far more thorough manner than heretofore; and even now no exhaustive method for the physico-chemical examination of these materials, with regard to their technical employment as a source of motive power, has been introduced.

It is true that a good deal of valuable matter in this connection is contained in the recent works of Engler-Höfer, Holde, Lunge-Berl, and others; but even these particulars do not entirely correspond to the requirements of practice and the actual state of affairs. Thus, for example, the following properties for motor petrol are specified in various books: sp. gr. 0·700–0·720; colourless and readily volatile, leaving no residue or greasy mark on paper after evaporation; constituents boiling above 100° C. not to exceed 5 per cent.; unsaturated or aromatic hydrocarbons, not over 2 per cent.; low range of boiling points. Medium benzine: of about 0·724 density, no constituents boiling above 110° C.; heavy benzine to have a range of boiling points between 80° and 150° C., etc.

These, and other requirements, however, are not fulfilled in practice, although they easily could be by a number of

petroleum and benzine refiners, who would find it to their own interest to do so on account of the preference which uniform quality would ensure, whilst the increased reliability in working would more than compensate any slight increase in price, which would be readily paid by users.

Commercial grades of benzine vary considerably, and—as will be seen from the Tables given later—contain constituents whose boiling points range from 24° C. to about 200° C.; but experience has shown that very low density is not essential for modern petrol motors.

The devising of analytical methods for determining the properties and establishing the requisite standards for motor fuels should be undertaken by chemists who also possess practical experience of motoring and are able to judge what can be beneficial or injurious to the motor, and what requirements, commensurate with moderate price, it is possible to expect refiners to fulfil.

Naturally, a chemist with practical motoring experience has a deeper and therefore more accurate insight into the connection between the properties of the fuel and the needs of the engine than an analyst pure and simple.

In this respect Dr. K. Dieterich was the first chemist and practical motorist to publish a valuable contribution on the analysis and valuation of petrol, benzol and motor spirit, supplemented by one on the differentiation and examination of light motor fuels and war substitutes. He showed that density alone should no longer form the standard of value, and he also recommended the adoption of uniform methods of physical and chemical examination, which are still lacking for petrol and motor benzol.

The author, who has also been a motorist for some years, has, more particularly of late—and primarily in his own interest—been engaged in the investigation of various commercial benzines, benzols, and lubricating oils, both from the physico-chemical and technical standpoint. The experience gained in this way, together with that already collected, is now placed before the reader, for practical application in testing and judging the materials used for operating internal combustion engines.

The present work is divided into three Sections, of which the first, or General Section, contains a brief description of the occurrence, composition and treatment of petroleum for the recovery of the several products; the Analytical Section deals fully with the composition, testing and valuing

of benzine, benzol and mineral lubricants, from the physical
and chemical standpoint; whilst the Technical Section
treats of the special properties, value and practical suitability
of the materials currently employed for operating petrol
engines, concluding with a chapter on the methods of storing
petrol and benzol so as to prevent risk of fire and explosion.

GENERAL SECTION

CHAPTER II

PETROLEUM : ITS COMPOSITION AND TREATMENT

HISTORICAL

MINERAL oil (petroleum, crude oil, naphtha, ropa), from which benzine, lamp oil (kerosene) and various lubricants are obtained, is a substance which was probably formed (in a manner similar to coal from vegetable remains) by the decomposition of animal remains under the influence of high temperature and pressure. It is true that there are various other views as to the origin of petroleum, but according to the researches of Engler, the one given above seems to be the most feasible.

Petroleum was known to the oldest civilised peoples, the Egyptians, Babylonians, Assyrians, Greeks and Romans, who used it for numerous purposes, such as heating, lighting, cementing, preserving, and also as a healing agent, etc. Nevertheless, even as recently as the Middle Ages, the employment of petroleum continued to be very restricted in extent ; and it was not until the nineteenth century that a commencement was made in treating it industrially on a large scale.

In 1854 the first attempts were made, in Pennsylvania, to produce petroleum by drilling down to the deposits in the depths of the earth ; and already in the 'sixties the production and treatment of petroleum had developed to such an unexpected extent that large quantities of the crude oil and its products were being shipped to Europe. In 1859 the first refinery was started in Baku, the centre of an important oil-field.

Mineral oil springs were known in Galicia in 1790, and the oil was used for a variety of purposes. In 1817, J. Hecker, on official of the Galician salt-mines, made the first experiments in public lighting, at Prague, with petroleum of his

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own production ; but it was not until 1855 that a large petroleum refinery was erected in Lemberg. In Roumania and Italy, also, the petroleum industry is quite a modern development ; and the treatment of mineral oil on a large industrial scale in Europe only became general in the early 'eighties.

Petroleum occurs in many localities throughout the globe, and occasionally over very large districts. In many places it rises spontaneously out of the ground, but for the most part only comes to the through surface borings, either in the form of a gusher (under the pressure of the gas accumulated above the oil underground), or else having to be pumped.

The most abundant deposits in Europe are those of Russia (Baku, Caucasia), Roumania (Campina, Bustenari, Baicoi, Moreni, etc.), and Galicia (Boryslaw-Tustanowice, Schodnica, Urycz, Nadworna, Krosno, etc., over an area of over 10,000 sq. kiloms.).

Smaller quantities are met with in Germany (Wietze in Hanover), Alsace (Pechelbronn), and Italy ; and the existence of petroleum has also been proved in nearly every other country in Europe.

North America possesses the most valuable and abundant oil-fields, in the states of Pennsylvania, Ohio, West Virginia, Indiana, Illinois, Texas, Oklahoma, California, Colorado, Canada, and Mexico ; and in South America there are considerable deposits in Venezuela, Peru, Argentina, Bolivia, etc.

In Asia, the largest oil deposits are found in the British and Dutch Indies (Burmah, Sumatra, Borneo, and Java), and Japan.

The greatest share in the world's production of petroleum is held by America and Russia, the Dutch East Indies coming next, followed in succession by British India, Roumania, and Galicia. The output in Germany is only small. In 1910 the aggregate production of petroleum amounted to 43,071,000 tons, increasing to 53,448,200 tons in 1914, and to 57,480,500 tons in 1915.

Composition, Properties, and Uses of Petroleum.

Petroleum is not a homogeneous substance, but consists essentially of a mixture of numerous hydrocarbons, composed of carbon and hydrogen in varying proportions.

As will be seen later, petroleum also contains other compounds (containing oxygen, nitrogen or sulphur), in addition to carbon and hydrogen.

The hydrocarbons are partly gaseous, and partly liquid or solid. Each class of hydrocarbon has its own particular specific gravity, which, however, is always lower than that of water. The liquid hydrocarbons boil at temperatures ranging from 18° to over 300° C.

The compounds occurring in petroleum are classified into the following groups in accordance with their chemical composition and properties :—

(1) *Saturated Hydrocarbons of the Methane Series, or Paraffins.* (General formula C_nH_{2n+2}).[1]—These hydrocarbons consist of various groups of carbon and hydrogen—CH_2 or CH_3—linked together in an open chain.

These compounds are said to be saturated because they cannot be induced to combine with any further atoms of hydrogen, even by the action of chemical reagents. They are also called " paraffins," after paraffin, which is a member of the series.

The simplest members are methane (CH_4) and ethane (C_2H_6 or $CH_3 \cdot CH_3$), which escape from the earth along with the oil and are used for heating or lighting.

Other gaseous and liquid hydrocarbons of this group present in petroleum are :—

Propane, $CH_3 \cdot CH_2 \cdot CH_3$, or C_3H_8.

Butane (normal and isobutane), C_4H_{10}, normal butane, for instance, being $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

Pentane (normal, iso and tertiary pentane), C_5H_{12}, normal pentane being $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

Hexane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$, or C_6H_{14}.

Heptane, C_7H_{16}.

Octane, C_8H_{18}.

Nonane, C_9H_{20}.

Decane, $C_{10}H_{22}$, etc.

From $C_{16}H_{34}$ onward these compounds are solid at ordinary temperature, and the most complex in composition is paraffin, or hexacontane, $C_{60}H_{122}$, which melts at 101° C.[2]

---

[1] C indicates a carbon atom, H a hydrogen atom, the letter n being an arbitrary whole number.

[2] The names of these compounds are derived from the Greek numerals, pentane, for instance, being from pente (five), because it contains five atoms of carbon; hexane from hex (six), because it has six carbon atoms; and so on. Paraffin is from the Latin " parum affinis," meaning inert or of low affinity for other substances.

The boiling points of these compounds increase with the complexity of the molecule. They are insoluble in concentrated sulphuric acid, and are not attacked thereby.

(2) *Unsaturated Hydrocarbons of the Ethylene Series, or Olefines.* (General formula C_nH_{2n}).—These are called unsaturated because they will take up more hydrogen under the influence of chemical agents.

The simplest member of the series is ethylene, $CH_2 : CH_2$, or C_2H_4. Others are : propylene, $CH_2 : CH \cdot CH_3$, or C_3H_6; butylene, C_4H_8, a-butylene, for instance, being, $CH_2 : CH \cdot CH_2 \cdot CH_3$; amylene, C_5H_{10}, etc.

In these compounds also the carbon atoms are linked in an open chain. They are only present in small quantities in petroleum, and are soluble in concentrated sulphuric acid.

(3) *Unsaturated Hydrocarbons with the General Formula,* C_nH_{2n-2}.—The lowest member of this series is acetylene, $CH : CH$ or C_2H_2. Isoprene, C_5H_8, diallyl, C_6H_{10}, etc., are also included.

Acetylene is the well-known illuminating gas obtained by suffusing calcium carbide (a compound of calcium and carbon) with water.

(4) *Unsaturated Hydrocarbons with the General Formulæ,* C_nH_{2n-4}, C_nH_{2n-6}, etc.—The carbon atoms are linked in an open or closed chain. To this group belong the terpenes, which, on being oxidised by air, cause the gumming or resinification of oils.

(5) *Saturated Hydrocarbons of the General Formula,* C_nH_{2n}: *Naphthenes* (cycloparaffins, polymethylenes), in which the carbon atoms are linked in a closed ring. Typical examples are : pentamethylene, or cyclopentane, $CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$;

hexamethylene, $CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$, etc.

The naphthenes form the transition stage to the aromatic hydrocarbons (*see* later), but resemble the paraffins more closely in their properties.

Most of the naphthenes may be regarded as cyclical polymethylenes, or cycloparaffins, with six and more carbon atoms, six of which hydrocarbons are of the ring type, but with single linkages, viz. : hexanaphthene, C_6H_{12}, or hexahydrobenzol (cyclohexane); heptanaphthene, C_7H_{14}; octanaphthene, C_8H_{16}, and so on.

The cycloparaffins are analogous to the hydrogenated aromatic hydrocarbons in constitution ; that is to say, they

have lost the double linkage of the benzol ring by the absorption of six additional hydrogen atoms, so that the linkage of the carbon atoms, though cyclical, is single. Thus, benzol, for example (C_6H_6), is transformed into hexahydrobenzol, C_6H_{12}, by taking up six atoms of hydrogen, the change being expressed by :— [1]

$$
\begin{array}{cc}
\underset{\substack{H\ H \\ HC\langle\substack{C=C \\ C-C}\rangle CH \\ H\ H}}{} &
\underset{\substack{H_2\ H_2 \\ H_2C\langle\substack{C-C \\ C-C}\rangle CH_2 \\ H_2\ H_2}}{}
\end{array}
$$
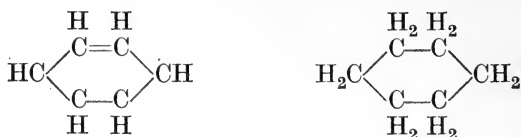
Even the highest members of this series form thick, semi-solid masses, being thus distinguishable from the saturated hydrocarbons of the methane series. In contradistinction to the olefines of the same formula, they are insoluble in concentrated sulphuric acid. They are present in large quantities in petroleum, especially Russian.

(6) *Hydrocarbons of the Aromatic Series.*—To this group belong benzol and the benzol derivatives, which consist of cyclically combined groups of carbon with hydrogen atoms. The simplest member is benzol, C_6H_6, the chemical structure of which is shown by :—

$$
\underset{\substack{H\ H \\ HC\langle\substack{C=C \\ C-C}\rangle CH \\ H\ H}}{} \quad \text{or, more simply,} \quad
\underset{\substack{H\ \ \ \ H \\ H\langle\ \ \ \rangle H \\ H\ \ \ \ H}}{}
$$
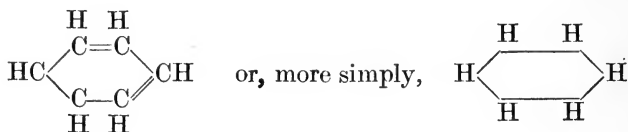
The group also includes toluol, $C_6H_5 \cdot CH_3$ (methylbenzol; the xylols (dimethylbenzols), $C_6H_4(CH_3)_2$, namely, ortho-, meta- and paraxylol [2]

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
\langle\rangle CH_3 & \langle\rangle CH_3 & \langle\rangle \\
\text{Orthoxylol.} & \text{Methaxylol.} & CH_3 \\
& & \text{Paraxylol.}
\end{array}
$$
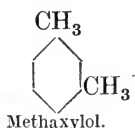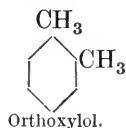
cymol, $CH_3 \cdot C_6H_4 \cdot C_3H_7$, etc.

[1] In chemistry, the composition of compounds is expressed—in addition to naming the elements and stating their numerical proportions—by figures (constitutional formulæ) illustrating the relative positions of the atoms or atomic groups.

[2] The terms ortho-, meta-, and para-, serve to differentiate the positions of the CH_3, or other groups, in the benzol ring.

These substances are colourless liquids, and in the pure state have an agreeable smell. They occur in varying quantities in petroleum, but are mostly obtained from gas- or coke-oven tar, as decomposition products of the dry distillation of coal.

These hydrocarbons are insoluble in water, but are rendered soluble therein by the action of concentrated sulphuric acid, which transforms them into other compounds. The nitro compounds important as explosives are obtained from these hydrocarbons by treatment with nitric acid.

This group also comprises naphthalene, $C_{10}H_8$, the constitution of which is represented by :—
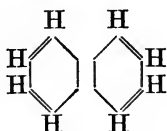
It consists of two juxtaposed benzol rings, and will be dealt with more fully later, in the Technical Section.

(7) *Sulphur and Sulphur Compounds.*—Sulphuretted hydrogen, carbon disulphide, thiophene and allied compounds, alkyl sulphides (methyl- and ethylsulphide), mercaptans. These bodies impart to petroleum an unpleasant smell which is difficult to eliminate. Lamp oil containing sulphur compounds gives off a smell of burning sulphur during combustion.

(8) *Nitrogen Compounds.*—Substances such as pyridin, containing nitrogen in addition to carbon and hydrogen, are mostly found in only very small quantities in petroleum.

(9) *Oxygen Compounds.*—These are of acid character, the most important belonging to the naphthenic series of acids, with the general formula $C_nH_{2n\ 1}\cdot CO_2H$ or $C_nH_{2n\ 2}O_2$. The chemical composition is allied to that of the oleic acid series, the percentage proportions of carbon, hydrogen and oxygen being the same in both cases; but the naphthenic acids are saturated compounds, and are therefore incapable of taking up any additional hydrogen atoms.

With alkalis the petroleum acids, like the fatty acids, form soaps, which, in consequence of the temporary scarcity of fats, have recently been employed by soapmakers, with satisfactory results.

To the oxygen compounds belong also the asphaltic and resinous substances which contaminate petroleum and are

the cause of its colour. The nature of these compounds has not yet been sufficiently investigated.

In point of chemical composition and properties, mineral oils differ to such an unexampled extent, according to locality, that no generally applicable classification on this basis has yet been successfully devised.   On the other hand, they can be divided into two main varieties on the basis of the manner in which they can be treated in refining (which depends on the paraffin content), namely :—

1. Oils high in paraffin.
2. Oils low in, or free from, paraffin.

The former class includes all the mineral oils whose high percentage (3–12 per cent.) of paraffin renders them suitable for the recovery of that substance.   They are mostly low in naphthenes.   To this class belong many of the American crude oils (Appalachian, Oklahoma, Kansas) ; certain Asiatic oils from the Sunda Islands (Java), British India (Upper Burma) and Tscheleken Island ; certain Roumanian oils (Campina—in part—Policiori, Glodeni) ; a few Galician oils (Boryslaw-Tustanowice, Mraznica, Schodnica) ; Grosny oil (Russia), and Pechelbronn oil (Alsace).

The oils low in paraffin are those containing at most about 1 per cent., and therefore incapable of yielding paying quantities of that substance.   This group includes the American oils from Texas, Louisiana, California, and Mexico ; certain Asiatic oils from the Sunda Islands ; most of the Russian oils (Balachany, Ssurachany, Bibi Eibat, Maikop) ; the Roumanian oils from Campina (part), Bustenari and Mareni) ; the West Galician oils from Potok, Krosno, Rogi, Harklowa, Kleinkowka, etc. ; the East Galician oils from Urycz, Bitkow, etc. ; and German oil from Wietze (Hanover).

Whilst the crude oils high in paraffin are generally lighter and poor in benzine, the somewhat heavier non-paraffin oils are mostly higher in benzine, and, by reason of their generally large proportion of naphthenes and low paraffin content, are specially suitable for the preparation of lubricating oils to stand low temperatures.   Those free from paraffin are also well adapted for the preparation of artificial asphaltum.

The constitution of the varieties of petroleum is divergent, and depends on their origin.

American Crude Oils—for example, those from Pennsylvania—consist almost exclusively of saturated hydrocarbons

(paraffins), some kinds containing but little actual solid paraffin, others a considerable amount. The crude oils of California, Texas and Ohio, however, contain in addition large quantities of aromatic hydrocarbons, such as toluol and xylol (but little benzol), and also naphthene compounds. In addition to paraffins, Texas crude contains naphthenes and sulphur compounds.

Russian Oils also differ in constitution according to locality. A few consist largely of paraffins, whilst others contain up to 80 per cent. of naphthenes, cyclopentane, cyclohexane, methylcyclohexane, etc., and small amounts of aromatic hydrocarbons, benzol in particular.

Galician Oils partly resemble American, and partly Russian, in constitution. According to the locality, they contain varying proportions of paraffins and naphthenes. Some crude oils are low, and others high, in paraffin, with, occasionally, considerable quantities of aromatic hydrocarbons, benzol, toluol, and xylol, as well.

Roumanian Oil approximates in constitution to Russian oil, containing on the one hand paraffins, and on the other naphthenes, together with olefines. A few of the crude oils also contain large proportions of aromatic hydrocarbons.

Indian, Javan, Bornese, and Japanese Petroleum contains, in addition to paraffins, considerable quantities of aromatic hydrocarbons; Sumatra oil having also a high content of olefines.

The proportion of benzine in crude oil varies with the origin. Galician oil (Bitkow) contains 3–35 per cent. of benzine boiling up to 150° C.; Russian (Baku) 5–10 per cent. boiling up to 150°; Roumanian, 4–25 per cent. boiling up to 150°; and Pennsylvanian, 10–20 per cent. boiling up to 120°.

The character of crude oil also varies with the origin; but most crude oils occur as a thick, yellowish-brown, dark-brown to brownish-black liquid, with a blue or green fluorescence and a peculiar—generally not unpleasant—smell, which, however, is disagreeable when the oil contains sulphur compounds. Pale yellow and very fluid crude oil is sometimes met with.

Petroleum is lighter than water, the density varying, according to the constitution, between about 0·700 and 0·960. It is quite insoluble in water; but itself contains small quantities of water, or occurs in admixture (emulsified) therewith.

The percentage composition of various petroleums is approximately :—

Carbon	.	.	.	79·5–88·7	per cent.
Hydrogen	.	.	.	9·6–14·8	,, ,,
Nitrogen	.	.	.	0·02–1·1	,, ,,
Sulphur	.	.	.	0·01–2·2	,, ,,
Oxygen	.	.	.	0·1–7·0	,, ,,

However, the carbon content is rarely less than 83 per cent. and seldom exceeds 86 per cent., whilst the hydrogen content almost invariably lies between 11 and 13 per cent.

Petroleum is used as fuel, either alone or along with solid fuels. When freed from mechanical impurities and water, it is employed as a fuel for Diesel engines, greasing railway axles, impregnating railway sleepers and timber generally, as a disinfectant, and, finally, for spraying road surfaces to prevent dust. For the most part, however, it is refined, for the preparation of petrol, benzine, lamp oil, gas and motor oil, lubricating oil, vaseline, paraffin, petroleum pitch, and oil coke.

The Treatment of Crude Petroleum

Crude oil was originally worked up into lamp oil and lubricating oils exclusively, the benzine long continuing, in many centres, to form a by-product for which there was no special demand, and which the refineries therefore endeavoured to get rid of in various ways. Up to about thirty years ago, the Bohemian refineries were offering benzine at the equivalent of about 1s. 6d. per cwt., and the producers in the Dutch East Indies burned it to waste, as an " unsaleable " product, on the shores of the Sunda Islands.

Until within the last twenty years the chief uses of benzine were for cleaning, burning in benzine lamps, making gasoline gas, and (heavy benzine) in the extraction of fats. However, since the application of the internal combustion (explosion) engine and the motor vehicle has developed to an unanticipated extent, benzine, in the form of " petrol," has become an extremely valuable and widely sought product.

The various integral constituents of petroleum are recovered from the crude oil by fractional distillation in special stills, the general practice being to separate the oil into four portions.

The first distillate, crude benzine, forms the raw material

for the recovery of petrol and benzine; the intermediate distillate is worked up into lamp oil; and the third distillate serves for the production of gas and fuel oils, lubricating oils, vaseline, and paraffin. The residue in the stills is either treated in the various ways hereinafter described, or else the distillation is carried so far that, finally, petroleum pitch, petroleum asphaltum, or petroleum coke, is left in the still.

Before the crude oil is admitted to the stills, it is usually preheated in a system of partly vertical, partly horizontal, cylinders, the heat of the vapours and residues from the stills being utilised for this purpose. At this stage considerable quantities of the more volatile constituents are expelled from the oil, and are condensed, the non-condensable gases (methane, ethane, propane, butane) and other light hydrocarbons, being collected, and either used for heating the stills, or else compressed.

The oil thus strongly preheated is then subjected to continuous distillation in batteries of ten to twelve stills, arranged in cascade, so that the oil fed into the highest still flows, after parting with its most volatile constituents, into the lower ones in succession, parting with progressively higher fractions in each. The intermittent system of distillation is now rarely employed.

The stills are heated by direct fire heat, and at the same time steam is admitted into the oil, to facilitate distillation.

The vapours disengaged in the stills condense, in part, in passing through the preheaters, and the remainder in a series of condensers—coils kept cool by a continuous flow of water.

The distillates issuing from the individual condensing coils are of approximately constant density in the continuous distillation process, and can therefore be conducted from the receivers into the corresponding storage tanks.

The Recovery of Benzine

The first fraction obtained in distilling crude oil—usually that boiling up to 150° C.—forms crude benzine,[1] which consists chiefly of the hydrocarbons pentane, C_5H_{12}, to nonane, C_9H_{20}; with decane, $C_{10}H_{22}$, to dodecane, $C_{12}H_{26}$,

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[1] Crude benzine is not collected as a single fraction, but is usually divided into light crude benzine (boiling up to 120° C.) and heavy (constituents boiling between 120° and 150°). Sometimes, too, a third and higher crude benzine is collected, chiefly for making varnish and " benzine."

in smaller quantities, together with naphthenes, C_5H_{10} to $C_{12}H_{24}$, and—according to the origin of the oil—unsaturated and aromatic hydrocarbons. It thus contains, in addition, bodies boiling above 150°, that pass over with the lighter members.

The crude benzine (containing hydrocarbons boiling up to 200° C.) is usually subjected to chemical refining with sulphuric acid and caustic soda (or carbonate), and then rectified by a second fractional distillation in column stills similar to those used in the spirit industry.

Sometimes the refining process is postponed and applied to the rectified products. The method of refining is the same as described in connection with petroleum products (see later).

The chemical refining is not infrequently omitted altogether, in which case the resulting commercial benzines are termed " rectified " benzines, to distinguish them from the " refined and rectified " qualities.

Unfortunately, the number and character of the fractions obtained in the rectification of crude benzine is highly divergent and arbitrary, usually depending, first of all, on the constitution of the crude oil, and then principally on the demand for the time being.

Galician crude benzine is generally treated so as to furnish the following products :—

CRUDE BENZINE

(a) *Light*   (b) *Heavy*

(1) Hydrür,
(2) Gasolene,
(3) Detergent benzine,   refined and recti-   (1) Safety lamp benzine,
(4) Safety lamp benzine,   fied   (2) Extraction   benzine
(5) Extraction benzine and   or rectified only.   and petrol,
        petrol,   (3) Benzine residue.
(6) Benzine residue (prim-
        ary).

The benzine residue is treated further to furnish :
(1) Varnish spirit,
(2) Turps substitute,   refined and rectified or only rectified.
(3) Petroleum benzine,
(4) Benzine residue (secondary), which is worked up into lamp oil.

The nomenclature of the benzine products is by no means uniform, different products being often called by the same name, and identical products by different names. Thus, in Russia, gasoline means the fraction 100–140° C. (sp. gr.

0·740–0·760), whereas in Austria the term is applied to a light benzine of sp. gr. 0·660–0·680 and boiling at 70–90° C.¹

In Austria, benzine is graded into :—

"Hydrür," sp. gr. 0·640–0·650 ; gasoline (ligroin) or petroleum ether, sp. gr. 0·660–0·680 ; detergent benzine, sp. gr. 0·698–0·705, or 0·690–0·700 ; motor spirit (petrol) of various grades, sp. gr. 0·680–0·700, 0·700–0·715, 0·715–0·725, 0·725–0·745, 0·745–0·755, 0·745–0·760, 0·750–0·760 ; varnish spirit, sp. gr. 0·760–0·770, 0·770–0·785 ; turps substitute (test benzine), sp. gr. 0·775–0·780, 0·780–0·785 ; petroleum benzine, sp. gr. 0·790–0·795.

In America, benzines are classified into :—

Zymogene (contains butane), sp. gr. 0·590 ; rhigolene (contains pentane), sp. gr. 0·625–0·631, b. p. 18–37° C. ; canadol (Sheerwood oil), sp. gr. 0·610–0·669, b. p. 37–50° C. ; naphtha (petroleum ether), sp. gr. 0·670–0·700, b. p. 50–60° C. ; petroleum benzine (gasoline, kerosol), sp. gr. 0·700–0·729, b. p. 60–80° C. ; ligroin, sp. gr. 0·722–0·737, b. p. 80–120° C. ; cleaning oil (turps substitute), sp. gr. 0·760–0·810, b. p. 120–150° C.

Zymogene, rhigolene, and hydrür can also be obtained by the direct distillation of petroleum, without rectification, the gases and vapours produced by the distillation being condensed in a compressor. Gasoline, too, can be prepared by direct distillation.

Zymogene, rhigolene, petroleum ether, and hydrür contain propane, butane and pentane. Gasoline contains pentane and hexane. The other grades of benzine contain chiefly hexane, heptane, octane, or cyclopentane, cyclohexane, and heptanaphthenes up to nonaphthene ; whilst the heavy kinds chiefly contain nonane and decane, or decanaphthenes up to dodecanaphthene.

Hydrür, gasoline, petroleum ether, zymogene, rhigolene and canadol are used for carburetting coal gas, for lighting purposes, extracting fats, as fuel for aircraft engines, gassing textiles, producing gas for industrial purposes and the laboratory (instead of coal gas), for manufacturing ice, dressing wounds in surgery, etc.

The heavy benzines, above 0·680, are used for heating, soldering, cleaning, as solvents in the rubber industry, in making perfumes and medicaments, as a turps substitute in making lacquers, in the manufacture of artificial silk, as solvents for rosin, phosphorus, and sulphur, in making cartridges, and especially as motor fuel.

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PREPARATION OF LIGHTING OIL

The second (middle) fraction—petroleum distillate—passing over in the distillation of crude oil between 150 and 300° C., has a density of 0·780–0·870, and is employed in the preparation of lighting or lamp oil. It is always refined with sulphuric acid and caustic soda, repeatedly washed with water, filtered through salt and sawdust to extract· the adherent water, and then constitutes lamp oil of varying quality (according to the method of fractionation); kaiser oil, standard petroleum, etc.

The refined oil is sometimes improved by adding a dyestuff, such as methyl violet or fluorene (soluble in oil),. to mask the yellowish tinge.   These adjuncts, however, are not always permanent, sometimes settling down to the bottom of the vessel and being identifiable by filtration through filter paper or wadding, to which they adhere.

Even the finest grades of lamp oil have a bluish flourescence (in contrast to benzine, which has none), though not to the same degree as the ordinary standard qualities. If necessary, this fluorescence can be removed by a-nitronaphthalene, aniline dyes, or " oxidised " oil of turpentine—which consists of oxygenated derivatives of that oil.[1]   In practice, however, this treatment is restricted to the lubricating oils (*q. v.*).

Lamp oil contains the paraffin hydrocarbons $C_{10}H_{22}$ to $C_{16}H_{34}$; not infrequently naphthenes, $C_{10}H_{20}$ to $C_{16}H_{32}$, and occasionally small quantities of benzol.   Its flash point is fixed by legislative enactment in most countries.   Its chief application is for lighting, inferior grades being used as motor fuel, for cleaning, etc.

PREPARATION OF LUBRICATING OIL

The residue (residuum, masut, astatki) left in the still after the removal of the crude benzine and crude lamp oil, and boiling above 300° C., is partly used as a fuel oil for steamships and locomotives, and also as a railway grease. For the most part, however, it is re-distilled in a second apparatus, the vacuum still, with superheated steam, the fractions passing over at certain definite temperatures being collected separately.   The employment of a vacuum enables

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[1] M. Riegel, *Chem. Ztg. Chem.-techn. Uebersicht*, 1917, p. 194.

the higher fractions to be recovered without appreciable decomposition.

In this way, provided crude oils poor in, or free from, paraffin, be taken, a variety of lubricating oils, ranging from highly fluid to semi-fluid consistency, can be obtained ; in some cases natural vaseline.

Natural vaseline is a mixture of readily fusible paraffin hydrocarbons from about $C_{16}H_{34}$ to $C_{20}H_{42}$, which melts at 35–45° C. Artificial vaseline, on the other hand, is a mixture of one part of ceresine (from ozokerite) and four of bleached, heavy mineral oil. It melts at 47° C.

Natural vaseline is a colourless or pale yellow mass, of the consistency of ointment, and is used for pharmaceutical and cosmetic purposes ; also as a lubricant and anti-corrosive for iron. It was formerly prepared exclusively from American petroleum.

The corresponding distillate from the mineral oils high in paraffin is paraffin distillate, which contains practically the whole of the paraffin of the crude oil, and from which latter it must be separated—mostly by artificial cooling—before the distillate can be further treated for the production of gas-, motor- and lubricating oils. This treatment consists in repeated fractional distillation (reduction or concentration) of the de-paraffined distillate, in special vacuum stills ; the gas oil, vaseline oil, spindle oil, engine oil and cylinder oil fractions, boiling at different temperatures, are recovered separately. In some cases only a portion of the oil is driven off in vacuum stills, the remainder being recovered, from the still residue, in a cracking still.

According to the manner in which the distillation has been conducted, the final residue in the still consists of :

1. A black, smeary residue—goudron—or
2. Petroleum pitch, or artificial asphaltum, or
3. Petroleum coke.

Distillation *in vacuo* and with superheated steam is not, however, practised in all refineries. In countries where the crude oil is low in benzine and lamp-oil fractions—for instance, in certain American regions—or where the crude oil is not suitable for the production of cylinder oil, intensive cracking is adopted in the first distillation of the crude oil, the heavy fractions being, as far as possible, transformed into lighter, lamp-oil distillates, without the use of a vacuum or steam.

With this object, the distillates from the large horizontal

still are passed into a column on a higher level, loosely filled with stones, etc., to present a large surface to the vapours. From this they are led through a dephlegmator column, composed of numerous vertical iron tubes, and thence into a condenser.

The large surface and atmospheric cooling effect in the two columns cause a considerable portion of the heavy vapours to condense and flow back into the still, where the renewed prolonged heating effects their extensive decomposition into light distillates. This process furnishes heavy benzine fractions and lamp oils of good burning properties.

All the heavy oil, containing paraffin, is distilled further, until nothing but coke remains.

Recovery of Paraffin

The crude paraffin distillates obtained in the treatment of crude oils high in paraffin, serve as the raw material for the recovery of paraffin, which is present in solution and is now almost exclusively obtained by crystallisation at artificially produced low temperatures down to $-20°$ C. Under these conditions, most of the paraffin separates out as a scaly, crystalline mass, which is freed from the accompanying oil in filter presses.

The paraffin taken out of the press is purified and freed from oil by recrystallisation or fractionation, the final traces of oil being eliminated by sweating. This process consists in slowly raising the crude paraffin scale to near melting point in steam-heated sweating chambers, so as to cause the oil to exude and leave the pure, hard paraffin behind. Finally, the paraffin is refined with sulphuric acid in the warm, and bleached by filtration through decolorising agents (see later, under " Purification ").

Pure, commercial paraffin is a bluish-white, alabaster, translucent, inodorous, crystalline mass, of sp. gr. 0·87–0·91. There are two chief grades : transparent, and milky or opaque, the difference between them consisting in the fact that the former is almost entirely free from oil, whereas the latter still contains a small quantity, which produces the milky appearance. Another classification divides paraffin into hard, melting above $50°$ C., and soft, melting at lower temperatures.

Paraffin finds numerous industrial applications, chiefly,

however, as a substitute for stearine and beeswax in the manufacture of candles.

The Chemical and Mechanical Purification of Petroleum Products

The chemical purification, or "refining," of the distilled petroleum fractions, by means of which refined benzine, lamp oil, refined oils, and paraffin are obtained from these intermediate products, is employed for the purpose of eliminating the semi-products accompanying the hydrocarbons in the crude oil, and also the unstable sulphur, nitrogen, and oxygen compounds formed during distillation, together with certain unstable unsaturated hydrocarbons present. The action of this chemical treatment is manifested in the elimination of the coloured, malodorous, and readily oxidisable constituents, whose unfavourable properties would make the oils more or less unsuitable for most of the purposes in view, and therefore adversely influence the quality of the products.

The agent best adapted, and most widely used for this purpose in practical working on the large scale is concentrated sulphuric acid, which either dissolves the said injurious compounds, or else transforms them into black, tarry masses.

The product to be refined is placed in iron vessels—agitators—with conical bottoms, and usually lined with lead, where they are intimately mixed—in two successive treatments—with 1 to 2 per cent. of concentrated sulphuric acid (about 66° Bé. strength), by compressed air forced in through a pipe that reaches nearly to the bottom of the agitator.[1] This treatment is known as acidification, or souring. After the air blast has been turned off and the mixture left to settle, the deposited sulphuric acid, which has carried down the impurities, is drawn off through a tap in the bottom. The black, resinous mass recovered along with the surplus dark and evil-smelling sulphuric acid (sludge acid) is known as acid tar or acid goudron.

The contents of the agitator are next washed with water discharged through a sprinkling or spraying device, in order

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[1] In the case of benzine, special mechanical stirrers are almost always used, in order to prevent loss by volatilisation, circulating pumps being more rarely employed.

to remove the bulk of the residual sulphuric acid and the sulphurous acid formed during the acid treatment,[1] the acid washings being thereafter drawn off and the product treated with about 0·05 per cent. of caustic soda lye [2] (about 2–4° Bé. strength), also in an air-blast agitator, in order on the one hand to precipitate as soaps the injurious organic acids present, and on the other to remove the final traces of sulphuric and sulphurous acids. This stage forms the alkali treatment.

When strongly smelling benzine is in question, the caustic soda is mixed with lead oxide, which dissolves in the lye and assists in the removal of impurities, sulphur compounds in particular. This treatment is mainly applied to cracked benzine.

After prolonged settling, the milky mixture of lye and accompanying soaps is drawn off, and the product is repeatedly washed with cold water (warm in the case of oil and paraffin), to eliminate the alkali completely.

Benzine and lamp oil are left to settle for a long time, and then—mostly, however, only in the latter case—slowly passed through a filter composed of alternate layers of sawdust and common salt ; whereas the heavy oils and paraffin are suitably heated, and clarified by prolonged treatment with a powerful air-blast.

Many distilled engine and cylinder oils, intended for special purposes, are simply freed from colouring and malodorous substances by filtration through decolorising agents, such as fuller's earth or Florida earth, though sometimes this treatment is preceded by refining. This method, which was first employed in America for treating lamp oils, engine oils and cylinder oils, is frequently used there as a complete substitute for refining with acid and alkali. One of its advantages consists in preventing the loss of oil resulting from resinification in the acid treatment. When the earth has absorbed so much resinous matter from the oil that its decolorising properties have disappeared, it is regenerated by a special process for use over again.

Of late, the ultra-violet rays have also been employed for bleaching and deodorising oils, by means of the so-called Uviol lamp—e. g. Schott mercury-vapour lamps with ultra-

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[1] This applies only to benzine and lamp oil, the other oils and paraffin being treated with alkali without any intermediate washing.

[2] Caustic soda is sometimes replaced by sodium carbonate, e. g., in refining benzine.

violet irradiation. This treatment causes certain changes in the oil, the author having found that the viscosity of a gas oil is raised from $1\cdot9°$ Engler to $2\cdot4°$ by the action of the ultra-violet rays for a period of fifty hours. The iodine value of this oil was lowered from $17\cdot4$ to $14\cdot2$, so that, apparently, some partial transformation of the unsaturated hydrocarbons into a saturated condition had taken place.

Paraffin is decolorised by means of various powders (ferrocyanide residues, bone black) or fuller's earth and bleaching earths (aluminium-magnesium hydrosilicates). During the past ten years, the alkali and decolorising treatments have mostly been combined in a single operation, by means of bleaching earths possessing suitable neutralising properties.

CLASSIFICATION AND USES OF LUBRICATING OILS

The various commercial lubricating oils may be classified, according to their external characteristics, into two main groups, viz. :—

I. Refined, chemically purified lubricating oils, and

II. Unrefined—not subjected to chemical purification.

Whereas the former are more or less decolorised, in accordance with the degree of chemical treatment sustained, besides being more or less transparent and inodorous—or only exhibiting a slight smell of mineral oil—the members of the second group can generally be recognised by their dark colour, decidedly unpleasant smell, and, in most cases, by complete opacity.

Each of these groups contains two sub-groups :—

(a) Distillate oils.

(b) Residue, or reduced, oils,

according as they have been prepared from distillates or reduction residues. These two sub-groups, also, are recognisable from their external features, the distillate oils being much the lighter in colour, whether refined or not, whilst, on the other hand, the residue oils always exhibit a less pronounced smell.

The commercial grades of lubricating oils may therefore be divided into :—

Refined distillate oils ;

Refined residue oils ;

Unrefined distillate oils, and

Unrefined residue oils.

Another system of classification is based on the uses of the oils :—

(1) *Vaseline Oils.*—These are thin and pale, and serve for the production of artificial vaseline and a variety of technical oils and fats ; also for lubricating sewing machines, cycles, etc. Their viscosity (*q. v.*) ranges from 2·8 to 5·0° E. at 20° C.

(2) *Compressor- and Refrigerating-Machine Oils.*—These are also very fluid and pale, and do not solidify except at very low temperatures, about −20° C. Their viscosity is 2·6–5·0° E. at 20° C.

(3) *Spindle Oils* are thin and pale, and are used for lubricating textile machinery, centrifuges, turbines, high-speed steam engines, cycles and sewing-machines. Viscosity 5–15° E. at 20° C.

(4) *Light Engine Oils.*—These are thick, and are used for oiling light shafting, dynamos, electromotors, centrifuges, fans and agricultural machinery. The viscosity is 9–25° E. at 20° C.

(5) *Heavy Engine Oils* are intended for large engines and heavy shafting with high loads. They are extremely thick, the viscosity being 25–50° E. at 20° C.

(6) *Motor Oils and Motor-car Cylinder Oils,* for gas engines, Diesel engines, petrol engines and motor-car cylinders. The motor oils have a viscosity of 12–77° E. at 20° C., and 3·5–8° E. at 50° C. ; whilst that of the cylinder oils is 20–85° E. at 20° C., and 4·5–12° E. at 50° C. The flash point ranges from about 185° to 230° C.

(7) *Steam Turbine Oils.*—An essential property of these oils is that of repelling water. Their viscosity is 9–13° E. at 20° C. ; but still more viscous oils, *e. g.* about 4–4·5° E. at 50° C., have occasionally proved satisfactory.

All the above oils are perfectly transparent in the refined state, and pale yellow, reddish-yellow, yellowish-red to dark red in colour.

(8) *Railway Axle and Locomotive Oils.*—These are dark-coloured lubricating oils, of low setting point for winter use, and have a viscosity of 4–7° E. at 50° C.

(9) *Cylinder Oils* are very thick, and like ointment at ordinary temperature. Their use is for oiling the cylinders of steam engines.

Other oils on the market are :—

(10) *Cleaning Oils.*—Thin, light-coloured oils, for cleaning machinery, and consisting of distillates boiling at about 280–350° C.

(11) *Gas Oils and Fuel Oils* (blue oil and Diesel engine oil) are the petroleum fractions coming over between the lamp oil and vaseline oil fractions; density, 0·83–0·93, b. p. 260–400° C. They are used, on the one hand, for making illuminating gas (hence their name), and on the other as fuel for Diesel engines and oil engines.

(12) *Transformer Oils*, for transformers and rheostats in electric power plants, in which they serve as cooling and insulating media. They have to be bad conductors of electricity, and must therefore be well refined. The viscosity is 5–9° E. at 20° C.

(13) *Water-soluble Mineral Oils*, for drilling, milling, cutting and polishing machines, form perfectly clear solutions or emulsions with water. They are prepared by dissolving lime-, soda- or ammonia soaps of the resinic or naphthenic acids, ammonia, benzine, or alcohol being sometimes acid, and serve as cheap lubricants.

(14) *Dust-laying Oils*, for laying dust on roadways or flooring. They consist of the cheapest mineral oils, crude oils, tar, or the like, or mixtures of these with water—magnesium chloride, calcium chloride solution, and emulsifying agents being employed (Westrumite). All these dust-laying oils should be free from smell. Mixtures of mineral oils with other cheap oils, fats or soap, are also used for the same purpose.

(15) *Froth Oils* are used for killing frothing in fermentation.

(16) *Compound Oils and Fats* are mixtures of mineral oils with animal and vegetable oils, fats and soaps.

Finally, there is the class of *Solid Greases*, so called because they retain a fairly high and uniform consistency even at high temperatures, and melt only above 70° C. They are used for greasing machine parts that are difficult of access, such as pinions, variable and differential gears, journals, chains, etc. These solid greases are prepared by stirring light or heavy mineral engine oils to a complete emulsion with 15–25 per cent. of lime- or magnesia soap and 1–7 per cent. of water. The water is essential for obtaining emulsification and uniform texture, anhydrous solutions of lime soaps in mineral oil becoming irregular in a very short time.

The lime soap, which is contained in a very finely divided state in the grease, is prepared from rape oil or beef tallow, or, in the absence of these, from rosin, mineral wax [1] or petroleum acids.

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[1] Mineral wax is obtained from certain varieties of brown coal or bituminous shale, by extraction with benzine or benzol under pressure.

The solid greases occasionally contain potash- or soda soaps, beef- or mutton tallow, graphite, etc. Compound greases, which are mostly used for marine engines, contain large quantities of hard (soda) soaps, in addition to vegetable oil or animal fat.

Solid greases consisting of paraffin, lime soap and soft soap, have recently come into the market.

Calypsol greases, of American origin, have recently made their appearance on the market. They are chiefly mixtures of mineral oils and hard or soft (alkali) soaps, the former being prepared from the solid fatty acids derived from tallow. The melting point of the greases is from 120° to 200° C.

Mixtures of wool fat, alkali soaps and graphite with mineral oils, form solid greases sold under various names. The fatty constituents of wool grease (suint) have a high viscosity and melting point.

The appended Table is a comprehensive diagrammatic scheme of the various stages in the treatment of a Galician petroleum (Boryslaw-Tustanowice) high in paraffin.

CHAPTER III

PRODUCTS analogous to petroleum benzine and lubricating oils are obtained from coal tar and brown-coal tar, and from the tars furnished by bituminous [1] shales and peat.

Coal tar is mainly produced in coking plants (coke-oven tar) and gasworks (gas tar), and also in the pig-iron industry (blast-furnace tar), as a by-product in the dry distillation of coal. Oil-gas tar and water-gas tar are less important.

Coal tar is a dark (mostly black), oily, sluggish to viscous mass, with a characteristic smell, usually recalling that of creosote. The density varies between 0·955 and 1·28, according to the origin of the tar, and generally exceeds 1.

The chemical composition also differs with the origin, the constituents including—in addition to ammonia water —light and heavy hydrocarbons of the aromatic series, benzol and its homologues, such as toluol, xylol, pseudo-cumol; naphthalene, azenaphthene, phenanthrene, anthracene, phenols (phenol and cresol); nitrogenous substances —chiefly pyridine bases, quinoline bases and carbazol; sulphur compounds, such as carbon disulphide and thiophenes; asphaltic substances, etc.

Crude, undistilled coal tar is used for firing gas retorts, impregnating timber, painting iron, making roofing felt, disinfection, etc.; but is mostly distilled and refined for the manufacture of a variety of products.

The crude distillation products of coal tar are :—

(1) Light Tar Oil (1–3 per cent.), distilling over up to 170° C. This is a yellowish to dark-brown liquid, of sp. gr. 0·910–0·950, consisting, to the extent of about 65 per cent., of hydrocarbons, benzol, toluol, xylols and pseudocumol; in addition to which it contains phenols (carbolic acid),

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[1] Bitumen (Lat. " pix tumens " = boiling pitch), in the strict sense, is native asphaltum, freed from earthy impurities, and soluble in carbon disulphide, benzol or carbon tetrachloride. In the wider sense, the name is applied to its artificial substitutes, such as petroleum pitch, coal-tar pitch, brown-coal-tar pitch, oil-gas-tar pitch, etc.

DIAGRAM I: TREATMENT OF BORYSLAW-TUSTANOWICE CRUDE OIL.

CRUDE OIL
Preheater
Petroleum still

Crude Benzine Light — Crude Benzine Heavy — Petroleum distillate — Paraffin distillate — Residue: Mazut — Oil still

Refining — Refining — Filtration

Crude Benzine Light — Refined Benzine Light or Heavy — Rectification — Benzine residue

Refined and rectified Benzene — **Refined petroleum**

1. **Residue** or 2. **Asphaltum** — **Asphaltum** — Paraffin distillate — Cracking still — **Gas for Heating** — (a) **Asphaltum** or (b) **Petroleum Coke**

Paraffin Plant
Dehydration
Crystallisation
Filter press

Paraffin distillate

Crude paraffin — Scale — Melting — Sweating

Fractionation or Recrystallisation

Intermediate products high in paraffin — Crude paraffin — Refining and decolorising — **White paraffin**

Paraffin distillate

Filtered oil
Concentration
Reduction still

Gas oil distillate — Vaseline oil distillate — Spindle oil distillate — Engine oil distillate — Reduced engine oil residues — Cylinder oils

Dehydration — Refining — Refining

Gas oil, Fuel oil — Vaseline oils — Spindle oils — Engine oils

Motor naphtha

pyridine bases, naphthalene, sulphur compounds (thiophene), paraffin and olefine hydrocarbons, and finally ammonia water, which passes over during distillation.

(2) Medium or Intermediate Oil (8–12 per cent.), the fraction 170–230° C., containing higher hydrocarbons (naphthalene), phenols (carbolic acid), and bases (pyridine).

(3) Heavy Tar Oil (6–10 per cent.), the 230–270° C. fraction, consisting mainly—in addition to hydrocarbons —of cresols and quinoline bases.

(4) Anthracene Oil (16–20 per cent.). In the ordinary way, this fraction would come over between 270° and 400° C.; but it is recovered by the aid of a partial vacuum or by means of superheated steam. It contains methylnaphthalene, anthracene, phenanthrene, and carbazol.

(5) Residue : Pitch (about 55 per cent.).

The distillates from coke-oven tar are very similar, but contain less benzol and phenol, and more anthracene.

Oil-gas-tar distillates, on the other hand, have a different composition, being usually free from phenols and low in pyridine bases. The benzol from this tar is high in olefines ; the intermediate oil is low in naphthalene ; and the heavy oils contain but little anthracene.

Intermediate between the distillates of oil-gas tar and coke-oven tar are those from blast-furnace tar, which more nearly resemble the distillates from brown coal.

The light tar oil is first freed from the accompanying ammoniacal liquor, and is then separated, by distillation, into the following three fractions :—

(1) Light benzol; (2) heavy benzol; (3) phenol oil.

Each of these fractions is refined and then redistilled.

The refining of crude (light and heavy) benzol consists in a preliminary washing with 10 per cent. caustic soda, which combines with the acid constituents (carbolic acid, cresols, etc.), followed by treatment with sulphuric acid (37·5° B.) to remove the pyridine bases (pyridine and its homologues). Next follows extraction with concentrated sulphuric acid (66° B.), which resinifies the impurities— cumarone and other unsaturated compounds.

The refined benzol is separated from the highly coloured acid tar, neutralised by washing with water and caustic soda, and subjected to fractional distillation in the same kind of apparatus as used for crude benzine, either pure or technical products (benzol, toluol, xylol) being obtained. The latter are largely sold as motor fuel, or are used in the

manufacture of dyestuffs, medicaments, explosives and saccharin, as also for carburetting water gas, as solvents in making rubber goods and varnishes, and as substitutes for oil of turpentine.

The medium oil is mixed with the residues from the distillation of the light oil, and treated in the same way. Since this oil contains about 40 per cent. of naphthalene, it is left to stand for some time, the naphthalene gradually separating out, whereafter it is filtered off in special presses and purified with sulphuric acid and by distillation. The oil is distilled, furnishing crude benzol (II), creosote oil and naphthalene oil. The crude benzol is refined in the same way as that from light oil, the creosote oil producing carbolic acid, and the naphthalene oil naphthalene. The residue is used as a disinfectant and impregnating material.

The heavy oil is partly used direct for impregnating timber, but is mainly treated for the production of phenol, cresols and naphthalene. The residue serves the same purposes as that from the intermediate oil.

The anthracene oil contains 25–30 per cent. of anthracene, which is recovered by leaving the oil to stand until the anthracene has separated out, and then putting it through the filter press. The resulting crude anthracene is usually purified by heating with pyridine, which absorbs the impurities.

The separated oil, which is known in commerce as carbolineum or avenarine, serves as a wood preservative.

The coal-tar oils are also employed as cheap lubricants or as motor fuel.

Crude phenolate liquors from refining the tar fractions are treated for the recovery of phenol (carbolic acid) and cresol. The basic constituents extracted from the tar fractions by sulphuric acid are treated for the recovery of pyridine and bases for denaturing alcohol. The acid tar furnishes cumarone resin, which serves as a shellac substitute.

The benzol content of coal tar amounts to 0·6–1·5 per cent., and, as experiment has shown, is less than one-tenth that present in the gases formed during the dry distillation of coal.

Hence, the bulk of benzol, toluol, and xylol is recovered from coke-oven gases and coal gas, by extraction with " wash oil "—a tar fraction, 90 per cent. of which comes over between 200° and 300° C.—in special apparatus. The operation is conducted on the counter-flow system (the

DIAGRAM II: TREATMENT OF COAL-TAR.

COAL TAR

DISTILLATION

Gas Liquor — First Runnings — Light Oil Distillation — Intermediate Oil — Heavy Oil — Anthracene Oil — Residue

Light Oil Distillation → Light Benzol, Heavy Benzol, Phenol Oil

Heavy Refining Naphtha Bases → Pyridine, Phenols, Naphthalene

Rectification → Benzol, Residue

Benzoles, Toluol, Xylol, Solvent naphtha.

Intermediate Oil → Crude Benzol, Creosote Oil

Heavy Oil → Wash Oil, Impregnating Oil, Motor Oil, Creosote Oil

Creosote Oil → Naphthalene Oil, Naphthalene

Naphthalene Oil → Impregnating Oil, Motor Oil

Anthracene Oil → Anthracene, Wood preservative, Motor Oil

Residue → Hard Pitch

wash oil and gas flowing in opposite directions), the benzol being extracted almost completely and recovered by steam distillation in column stills.   This crude benzol is refined and fractionated as described in the case of light tar oil.

The Del Monte process, in which coal is coked at 500–600° C.—as compared with 1000–1200° C. in the more rapid coke-oven process—furnishes a tar containing more aliphatic than aromatic compounds, and therefore more nearly resembling brown-coal tar than coal tar.

The appended Diagram II is a simple diagrammatic scheme of the treatment of coal tar.

CHAPTER IV

Tars are obtained by the dry distillation of brown coal, earthy bituminous coal, shale, and peat, in the same way as coal-tar is from coal.

As in the case of petroleum, these tars are treated for the production of benzine, lamp oil, cleaning oil, yellow oil, red oil, and gas oil, and especially for paraffin.

Brown-coal tar forms, at ordinary temperature, a buttery mass, which becomes fluid when slightly warmed, and is yellowish-brown to dark brown in colour, with dark green fluorescence, smelling of creosote and sometimes also of sulphuretted hydrogen.

This tar chiefly consists of saturated hydrocarbons, heptane (C_7H_{16}) to heptacosane ($C_{27}H_{56}$); unsaturated hydrocarbons; aromatic hydrocarbons, such as benzol and its homologues, phenols, cresols, and small quantities of naphthalene. Of these compounds, about 16 per cent. consist of paraffins, 31 per cent. of olefines (ethylenes), 4 per cent. of naphthenes, and 45 per cent. of aromatic hydrocarbons.

The tar obtained from bituminous shale contains about 42 per cent. of paraffins, 39 per cent. of olefines (ethylenes), 10 per cent. of naphthenes, and 7 per cent. of benzol. It is mainly produced in Scotland, Ireland, and America, and also in Thuringia and at Messel, near Darmstadt.

The first distillation of brown-coal tar yields the following crude products :—

(1) Light crude oil; (2) hard-paraffin distillate; (3) red products; (4) residue—asphaltum, pitch, or coke.

The light crude oil furnishes, on refining : (1) Brown-coal benzine; (2) photogene; (3) solar oil; (4) pale paraffin distillate; (5) solar paraffin distillate.

Brown-coal benzine has the sp. gr. 0·790–0·810, boils at 100–200° C. and consists chiefly of the hydrocarbons benzol, toluol, and xylol. It is used by itself or in admixture with petroleum benzine.

DIAGRAM III : TREATMENT OF BROWN-COAL TAR.

BROWN – COAL TAR

Distillation.

Light Crude Oil.

Brown-coal. Photogene. Solar-oil.
Benzine

Pale Paraffin Distillate.

Cleaning Oil.

Yellow Oil. Paraffin.

Solar Paraffin Distillate.

Lubricating Oil.

Paraffin.

Hard Paraffin Distillate.

Heavy Oil.

Crude Photogene.

Solar Oil.

Paraffin Distillate. Paraffin.

Gas Oil. Motor Oil.

Red Products Red Oil.

Residue.

Asphalt. Pitch. Coke.
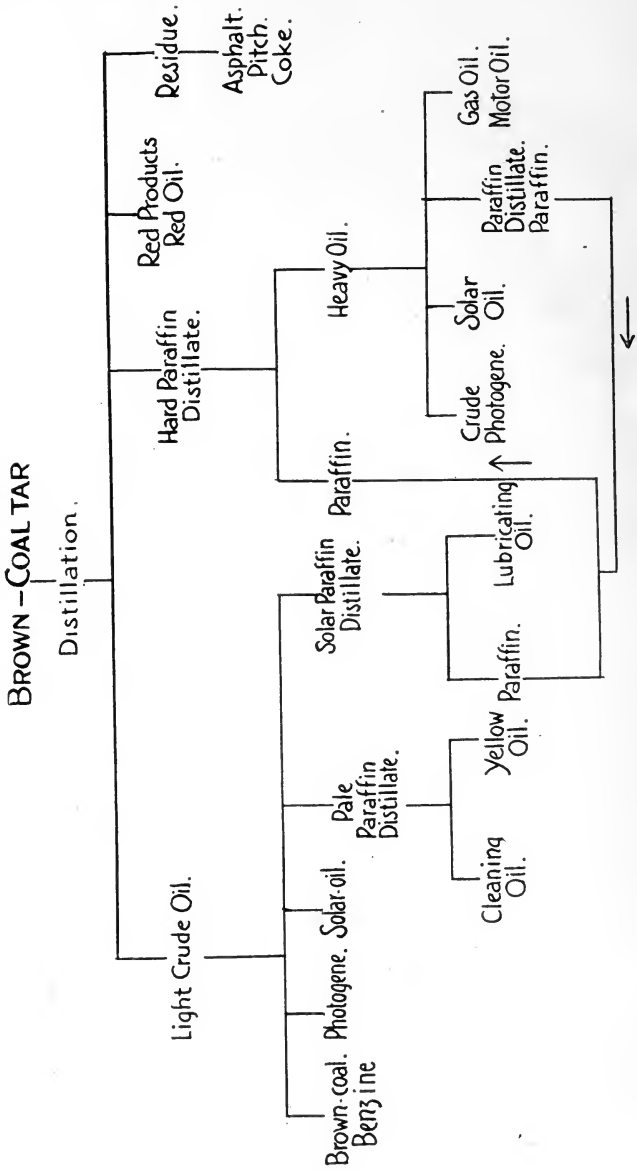
Photogene and solar oil have the sp. gr. 0·810–0·830, boil between 150° and 270° C., and serve as lamp oil or motor fuel.

The light-coloured paraffin distillate furnishes the cleaning oil and yellow oil used as lubricants.

The solar paraffin distillate is placed in a cooling chamber, where the paraffin separates out and is filtered off in the press, the residual oil finding employment as a lubricant.

The separation of the hard paraffin from the corresponding distillate leaves heavy crude oil, which, on distillation, furnishes crude photogene, solar oil, paraffin distillate, second-grade paraffin, and gas oil (for carburetting or motor fuel).

The most valuable product, however, is the paraffin, which is recovered and treated in the same way as that from petroleum.

Diagram III is a simple diagrammatic scheme of the treatment of brown-coal tar.

CHAPTER V

As a result of the extremely rapid extension of internal combustion engines, especially for motor-cars, a scarcity of petrol soon developed, and experiments were therefore made to produce petrol by artificial means—on the one hand from the heavy residues from petroleum and brown-coal tar, or the distillates from shale and peat, and on the other hand by transforming mixtures of various gases into liquid hydrocarbons of the petrol type by high temperature and pressure.

These investigations have enabled an artificial petrol to be placed on the market, which, however, is still greatly inferior to natural petrol in properties and efficiency.

As long ago as 1861, it was accidentally observed, in an American petroleum refinery, that the vapours of the higher hydrocarbons were changed into hydrocarbons of lower boiling point by contact with the heated walls of the still. This phenomenon was afterwards more thoroughly investigated, and for more than thirty years the cracking, or destructive distillation process has been practised in petroleum refineries. It was found that a gradual decomposition of the higher hydrocarbons into others of lower boiling point takes place even when the supply of heat is insufficient to maintain the normal course of distillation. These low-boiling vaporous products have sufficient tension to escape from the still, whereas the higher ones remain behind.

In this process, however, there must be sufficient free space above the oil in the still to ensure that only such vapours as possess sufficiently high tension will pass over into the condenser.

Decomposition of this kind proceeds in every normally operated distillation that requires the use of a high temperature; and therefore, when such decomposition is not desired, care is taken to minimise it by increasing the supply of superheated steam and reducing the pressure.

Whereas, in the ordinary method of distillation, without any extensive decomposition of the oil, and in which the sp. gr. of the distillate continually increases, the heat applied is consumed in vaporising the oil, and must therefore be increased as the boiling point rises, the splitting of the hydrocarbons in the cracking process absorbs a large portion of the heat applied.

In the former case—ordinary distillation—the heat has to perform physical work almost exclusively, but in the latter case its work is mainly chemical; and since, in equal intervals of time, equal quantities of hydrocarbons have to be decomposed and equally low-boiling products of equal composition produced, the amounts of heat supplied in each period must be uniform.

The classes of petroleum most suitable for destructive decomposition are those high in alkenes (ethane, olefines) and unsaturated hydrocarbons; whereas oils rich in naphthenes (polymethylenes, *i. e.* closed-chain hydrocarbons) are unsuitable, though even the closed-chain hydrocarbons undergo extensive decomposition if high temperatures (400–500°) and pressure be employed.

Destructive distillation is applied either to a suitable crude oil, or to the residue (residuum, goudron) left after distilling off the benzine, lamp oil, and certain oil fractions.

The cracking of residue is carried to such an extent in some works that only a coke-like residue (petroleum coke) remains in the still.

In those American refineries in which petroleum rich in alkenes is available for treatment, the cracking process is pursued to such an extent that nearly one-half of the lamp oil produced consists of hydrocarbons recovered by decomposition. In addition to this main (lamp oil) product, the process furnishes gaseous and low-boiling hydrocarbons. The former are either consumed for fuel or liquefied in compressors, whilst the low-boiling oils are mixed with crude benzine obtained by ordinary distillation. Owing, however, to the large percentage of unsaturated hydrocarbons, these oils are regarded as a troublesome by-product by the refiner, since only a comparatively small proportion can be added to the benzine.

Analogous to the cracking process is the so-called pyrogenic decomposition, the chief object of which is to obtain a preponderance of gaseous hydrocarbons and only a small quantity of the liquid kinds. The resulting gas is partially

liquefied by compressing at low temperature the resulting liquid ("hydrocarbon"), consisting mainly of aromatic hydrocarbons, with about 70 per cent. of benzol, the other 30 per cent. comprising toluol and higher hydrocarbons of the aliphatic series—especially ethylene. This "hydrocarbon" is used as a fuel for stationary engines. (The Pintsch works, Vienna, in making oil gas from special raw materials, obtain a hydrocarbon by-product which is used for engine fuel when refined; but the production is small, and the character of the oil has not been investigated.

In view of the considerable waste attending the cracking process, and the unsatisfactory yield and quality of the benzine obtained, many attempts have been made at improvement, and there are, at present, a number of processes for the production of artificial benzine, few of which, however, have proved successful in practice. The benzine made in this manner is dark in colour and malodorous, apart from which it contains large amounts of unsaturated hydrocarbons and resins, which liberate a good deal of carbon in burning.

Nevertheless, this benzine can be refined, so as to remove the colouring matters and much of the bad smell, though this treatment is attended with considerable additional waste.

Within the last few years, the cracking process has been considerably improved by Burton, and adopted, for the first time, by the Standard Oil Co. The improvement consists in distilling petroleum under a definite pressure and at definite temperature.

W. F. Rittmann is also said to have succeeded in improving the manufacture of artificial benzine on similar lines, by forcing petroleum vapours through iron pipes at a temperature of 450° C. and under a pressure of six atmospheres. At increased temperatures and pressures, benzol and toluol are stated to be obtained, which was also accomplished earlier by Nikiforow by heating petroleum in retorts.

Snelling is also reported to have treated paraffin and oil residues by a special process furnishing a "crude oil," from which a colourless benzine with only a slight smell was obtained.

MacAfee recently discovered that saturated hydrocarbons of low boiling point can be obtained by the action of aluminium chloride in the distillation of petroleum.

The Continental Caoutchouc and Guttapercha Co. have

patented a process in which benzine is prepared by heating petroleum of high boiling point in a still with a hydrocarbon-aluminium halide, or by passing the vapours of petroleum or oil distillate over porous masses impregnated with a hydrocarbon-aluminium halide acting as catalyst.

A substantially different product—a liquid similar to benzine—is obtained by heating a mixture of methane and ethylene, or acetylene, or a mixture of carbon monoxide and hydrogen, in the electric arc at a temperature of 2000° C. It has been found that the output of benzine can be considerably increased by the presence of porous substances, powdered metals, and metallic oxides; but the method does not seem to have made any headway in practice.

It is well known that hydrogen burns better than carbon, and is of far greater calorific power, 1 kilo. of hydrogen furnishing 28000 calories, as compared with 8040 from 1 kilo. of carbon. Consequently, the larger the quantity of hydrogen present in a hydrocarbon, the greater its heating value; and, for this reason, toluol and xylol burn better than benzol.

On this account attempts have been made in practice to enrich the hydrocarbons, high in carbon and low in hydrogen —such as benzol, toluol, xylol, naphthalene, etc.—with hydrogen, the only way to accomplish this, however, being to heat these hydrocarbons with hydrogen under pressure, in association with hydrogen iodide and phosphorus, or in presence of catalysts like spongy platinum, nickel oxide, etc.

In this manner benzol, C_6H_6, has been transformed into hexahydrobenzol, C_6H_{12}, and naphthalene, $C_{10}H_8$, into liquid decahydronaphthalene, $C_{10}H_{18}$, which compounds have lower boiling points than the originating materials, and burn more easily.

This method of introducing hydrogen into aromatic hydrocarbons is known as hydrogenation.

Ethyl alcohol, although its hydrogen content is high in relation to the carbon present, is of low heating value because two of its hydrogen atoms remain combined, in the product of combustion, with the oxygen in the original substance.

ANALYTICAL SECTION

CHAPTER VI

TESTING BENZINE AND BENZOL

The physical and chemical examination of benzine and benzol is preferably conducted in the following serial order :—

(1) External characteristics : colour, smell, filter-paper test.

(2) Specific gravity (density).

(3) Intermittent or fractional distillation.

(4) Evaporation test in watch-glass.

(5) Acidity.

(6) Behaviour towards sulphuric acid.

(7) Test for sulphur compounds.

(8) Test for aromatic hydrocarbons, especially benzol, and for unsaturated hydrocarbons in benzine.

(9) Test for unsaturated compounds in benzine and benzol.

(10) Determination of paraffin hydrocarbons in benzol.

(11) Water content.

Apart from these general tests, determinations are made of the coefficient of refraction and the setting point ; and, in special cases, of the flash and burning points, vapour tension, explosibility, and heat of combustion (calorific value).

In mixed fuels the proportions of ethyl and methyl alcohol, sulphuric ether, and acetone are also determined.

EXTERNAL CHARACTERISTICS : COLOUR, SMELL, FILTER-PAPER TEST

The substance under examination is poured into a test-glass, about 4 ins. long, which is placed on a sheet of white paper, and the liquid is observed from above in a good light. Benzine and benzol should be transparent, clear, and colourless. In countries where a distinction is

drawn between untaxed and taxed benzine, the former is coloured a reddish tinge with a Sudan dye.

Pure benzine should be free from fluorescence. The best way to detect any fluorescence that may be present is to place the benzine in a small glass standing on a piece of glossy black paper, and examine the liquid by reflected light.

For further examination a little of the benzine or benzol is dropped on to a sheet of white filter paper, where it is left to evaporate. At the same time the divergent and characteristic smell of the two liquids can be observed. The paper should be examined for any residue or grease-marks.

If no filter paper is available, a little of the liquid is poured on the palm of one hand, which is then rubbed with the other. The warmth thus generated hastens the evaporation, and the smell is more decidedly apparent than when filter paper is used, so that the differentiation between benzine and benzol is facilitated.

Impure benzine or benzol will leave a greasy feel on the hands, which will otherwise remain dry. Any moisture present in benzol will leave the hands damp.

This evaporation test on the hand appears more practical than the filter-paper test; but it is advisable to employ both.
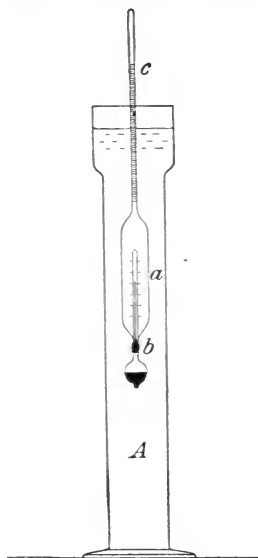
Fig. 1.

Specific Gravity (Density)

The specific gravity of liquids is tested in special apparatus at the standard temperature of 15° C. The instrument employed is the densimeter (aræometer, specific gravity instrument), which is of glass (Fig. 1) (preferably standardised) and consists of a float, a, to which is fused a thermometer, b, and a stem or spindle, c, which, in the case of benzine, is graduated from 0·680 to 0·780.

The benzine is poured into a test-glass, a, of convenient height and about 2 ins. wide, and cooled down to 15° C., the glass being then placed on a horizontal support.

The perfectly clean and dry densimeter is then lowered gently into the liquid, care being taken to maintain the standard temperature during the test.   At the end of about ten minutes, the sp. gr. is read off direct on the scale, at the level to which the liquid rises on the stem.   The instrument must be floating freely in the liquid, and not touching the sides of the test-glass.

If for any reason the benzine cannot be cooled down to the exact standard temperature, it will be necessary to correct the reading obtained, by adding thereto a mean figure of 0·0008 for each degree above 15° C., or subtracting the same figure for each degree below the standard temperature.

Example :—

Density recorded by the instrument at 20° C.	0·700
Correction for temperature : 0·0008 × 5	0·004
True sp. gr. at standard temperature (15° C.)	0·704

For a more exact temperature correction for individual densities, the following table, compiled by Mendeleeff for Russian oils, may be used :—

Density.	Correction per 1° C. difference in temperature.
0·700–0·620	0·00082
0·720–0·740	0·00081
0·740–0·760	0·00080
0·760–0·780	0·00079
0·780–0·800	0·00078

The above density determination will be sufficiently close for technical purposes.   The densimeter is handy, and can therefore be carried on the journey, in the course of which it is adapted to be very serviceable.

A more exact determination can be made by means of the Mohr-Westphal balance, or, better still, with a pyknometer with graduated neck.   This apparatus, however, is only used in the laboratory, where a chemical balance is available.

In determining the density of benzol, the same method is practised as for benzine, but as the former liquid is heavier, an instrument graduated from 0·800 to 0·900 must be used. The correction factor for temperature is also different, being, on the average, 0·00012 for each degree C. above and below the standard.

Intermittent or Fractional Distillation

1. *Fractional Distillation of Benzine.*—It has already been mentioned, in connection with petroleum and its composition, that benzine and technical benzol are not homogeneous substances, but mixtures of various compounds.

In order to obtain a clear idea of the composition of motor fuels, *i. e.* their proportions of the more and less volatile constituents, and thereby be enabled to compare different specimens of benzine and benzol, the liquids are subjected to analysis by distillation, and the percentage volume of the constituents passing over at given temperatures is measured. This process is known as intermittent or fractional distillation, because the various portions or fractions of distillate are collected separately.

Various forms of apparatus can be used for this purpose in the laboratory, and give different results according to the material, form, and size of the still used, the original quantity of material taken, the rate of distillation, and the arrangement of the condenser.   On this account, standardised forms of apparatus and methods are employed in carrying out the tests for commercial and Excise purposes.

In German and Austrian commercial laboratories, the Engler or Kissling apparatus is used, but another form is employed by the Customs authorities.   Even the first two differ in arrangement and dimensions; and different forms of apparatus are used in works laboratories in one and the same country.

Since only 100 c.c. of benzine are taken for a distillation test, the results may differ considerably, according as the Engler apparatus, without dephlegmator, or the Kissling apparatus, with dephlegmator, is used, especially when no attention is paid to the height of the barometer or to the temperature recorded by the column of mercury in the thermometer projecting from the still.

The Engler apparatus, as modified by Ubellohde and Holde, consists of a 150 c.c. fractionating flask (Fig. 2), mounted on a stand and surrounded by a screen.   A thermometer is secured in the neck of the flask, which is connected to a 2-ft. Liebig condenser.   The conventional dimensions of the flask are marked in millimetres in Fig. 2.

The flask is charged with 100 c.c. of the benzine under examination.   The initial boiling temperature is that recorded by the thermometer at the moment the first drops

of distillate appear at the mouth of the condenser. The distillation should be conducted in such a way that the distillate issues from the condenser at the rate of two drops per second.

The distillates are collected, at intervals of 10° C., in six test-glasses graduated to 0·2 c.c. and mounted on a rotary stand. If the fractions are not to be subjected to any further examination, the collector may consist merely of a 100-c.c. measuring glass graduated in 0·5 c.c., the volumes of distillate coming over being read off at the proper intervals in succession.

In distilling up to a given temperature limit, the corrections given in the following table must be made with regard to the temperature recorded by the projecting mercury filament of the thermometer, the figures being deducted from the temperature at which the distillate is to be collected, and the volume of distillate read off at the corrected temperature.
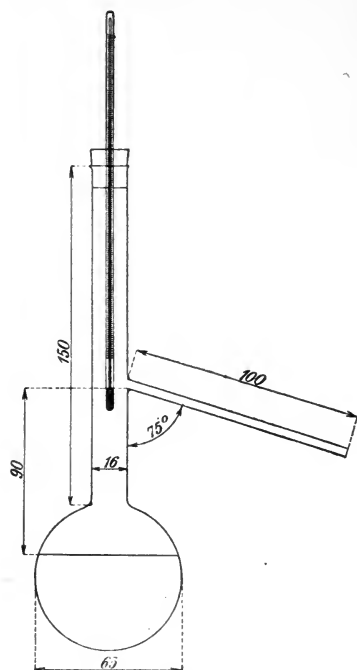
Fig. 2.

Recorded temperature. °C.	Correction. °C.	Recorded temperature. °C.	Correction. °C.
60	0·8	140	3·9
80	1·6	160	4·9
100	2·3	180	5·9
120	3·1	200	7·2

The end temperature of the distillation is that at which the bottom of the flask no longer shows any visible quantity of liquid.

For Customs and Excise purposes, the flask and condenser are of metal, and the apparatus is constructed to standard specifications.

The Kissling apparatus consists of a spherical flask, 100 mm. (4 ins.) in diameter, connected to a four-bulb dephlegmator tube 45 cm. (18 ins.) long, provided with a lateral reflux condenser tube. It therefore differs considerably from the Engler apparatus.

Allen and Jacobs [1] use an electrically heated 250-c.c. flask and a vertical condenser. The advantages of this apparatus are said to consist in the greater uniformity of the distillation, and in the avoidance of dephlegmation and consequent decomposition of the higher distillates.

For technical reasons, Dieterich proposed a method differing in some respects from the ordinary commercial one, namely, in the case of petrols and benzols for automobiles, to determine only the weight of the portions distilling up to 100° C., and that of the higher fractions, instead of measuring the fractions at intervals of 10° C.

With this object he weighed out 250 grms. of benzine into a 500-c.c. fractionating flask, and distilled until the thermometer indicated 85–90° C., the flask being then placed in a calcium chloride bath and distillation continued so long as any distillate came over at 100° C., this calcium chloride bath enabling the said temperature to be uniformly maintained.

After cooling down the flask and weighing, heating was continued over the naked flame (above 100°) until nothing but vapour remained in the flask, the end temperature being then read off.

By this means benzine is separated into two fractions, boiling up to and above 100° C. respectively, and the residual portion in the flask, the quality being judged from the results. Dieterich subsequently restricted the method to pure benzines, mixtures being excluded.

The objection to this method is that the calcium chloride bath is tedious and inconvenient to use; but the main point is that the distillation does not give adequate information for judging the benzine. The author's opinion is that, even when petrol alone is in question, dividing it into only three fractions cannot afford a sufficient idea of its composition.

As will be shown later, in the Technical Section, the benzine fractions between 60° and 120° C. are important for the development of motive power in the engine, whereas those between 40° and 60° C. mainly facilitate ignition, and

[1] U.S. Bureau of Mines Bulletin, 19, Washington, 1911.

those above 120° are of inferior value or less economical as a source of power.

For these and other reasons, which will be discussed later, the author has selected the golden mean, and fractionates benzine with the aid of a dephlegmator, collecting separately the fractions 20–40°, 40–60°, 60–80°, and so on, until evaporation is almost complete, the residue being weighed after the apparatus has been cooled down.

The apparatus used is the following :—

The heating device consists of a ("Silund")[1] plate heated by an electric current of 4 ampères 120 volts, and provided with metal rings like a water bath (these rings are not supplied with the plate). A fine-adjustment resistance is connected up in the heating circuit, to enable the temperature to be more accurately controlled. Electric heating is preferable to gas, because it enables the bottom of the flask to be heated in a more uniform manner.

The distillation is effected in a 500-c.c. Jena flask, with a dephlegmator tube ground into the neck. An accurate thermometer is ground into the upper end of this tube so that the upper end of the mercury bulb is exactly on a level with the lateral delivery tube of the dephlegmator. The thermometer is constructed so that the interval between the graduations (1° C.) is exactly 1 mm., and that the 25° mark is just above the top of the dephlegmator (the 45° mark in the case of heavy benzines).
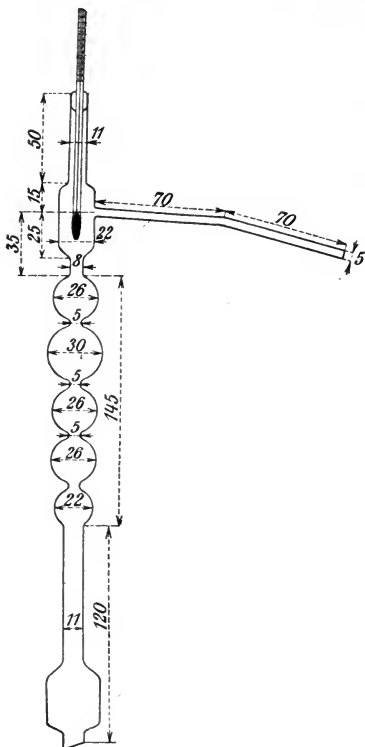
The dephlegmator tube has five bulbs of different sizes and a cylindrical enlargement at the point of attachment

Fig. 3.

_____
[1] Siemens-Schuckert-Werke.

to the delivery tube, as shown (with the dimensions) in Fig. 3.

The reflux condenser provided in the Glinski apparatus and that of Kissling, with dephlegmator, for distilling light oils, is omitted, the author having found, by repeated experiment, that, provided the following precautions be observed, the difference in the results with and without a reflux condenser is within the limits of experimental error.
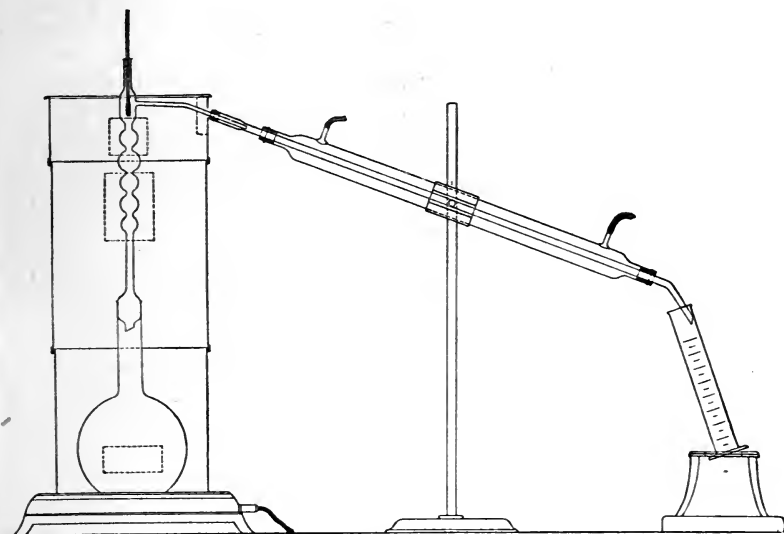
FIG. 4.

In the case, however, of heavy benzines, it is preferable to use the dephlegmator tube with reflux condenser, like that shown in Fig. 4, because, otherwise, an excess of liquid collects in the bulbs of the dephlegmator.

Instead of being ground in, the dephlegmator tube and thermometer may be inserted in cork stoppers, but the cork must be of very best quality and brushed over with a thick pulp of linseed meal and water, otherwise the benzine vapours will escape through the pores and be largely lost. To obviate this tedious manipulation, and because the corks must, in any case, be changed after two or three experiments, it is preferable to grind the tube and thermometer in, as already mentioned.

The dephlegmator is connected to a Liebig condenser,

the outside shell of which is 60 cm. long and the inner tube 85 cm. long. The receivers consist of measuring cylinders (50–100 c.c.) graduated in $\frac{1}{2}$ c.c., these being changed for each fraction.

While the fractions are coming over below 100° C., there is no need to protect the apparatus against cooling ; but when the thermometer rises above that point, the whole apparatus should be surrounded by a shield. Otherwise the dephlegmator bulbs will be overcharged with benzine, the distillation becoming irregular and giving erroneous results.

In distilling off the high fractions, an excessive reflux of the condensate from the dephlegmator bulbs into the hot liquid in the flask may result in a partial cracking of the higher fractions into lighter hydrocarbons.

Both the still and dephlegmator must also be protected against draughts, in order that the uniform ebullition of the benzine may not be disturbed, and that fluctuations of the thermometer may be prevented in any event, especially when the temperature approaches the upper limit for the fraction in course of collection.

For this purpose the author uses three shields of thin, flexible steel, 14 cm. in diameter, bent round so as to leave a gap on one side. The lower shield, which protects the flask, is 12 cm. high, the middle one 24 cm., and the top one 11 cm. high.

These last two shields are to protect the dephlegmator, the one being slipped into the others so as to rest on small lugs attached thereto. In putting them into position, the shields are sprung open a little, so as to enable them to slip over the flask and the dephlegmator, the resilience of the metal causing them to resume their shape automatically.

Each shield is provided with two diametrically opposite mica windows, through which the progress of the distillation in the apparatus can be conveniently observed. The top shield extends above the delivery tube of the dephlegmator.

In distilling heavy benzines, the opening in the top shield is covered with a thin sheet of asbestos, provided with a hole for the stem of the thermometer.

Fig. 4 shows the whole apparatus with the shields in position. The apparatus is supplied by the firm F. Zahradnik, Prague.

The distillation of benzine is performed in the following manner :—

Four or five lumps of pumice, or a couple of glass capillaries, are placed in the flask, to prevent the bumping of the liquid when boiling. The flask is weighed empty, and again after being charged with 300–350 c.c. of benzine, the actual weight of benzine to make up this volume being ascertained by determining the specific gravity beforehand. For example, the weight of benzine of sp. gr. 0·720 will be : $300 \times 0·720 = 216$ grms.

The use of a larger quantity of benzine for the distillation test will, it is true, prolong the operation, but, on the other hand, will reduce the possible amount of error in calculating the results to 100 c.c.

The charged flask is next connected to the condenser, one of the above-mentioned measuring cylinders being used as a receiver.

The flask is heated somewhat strongly at first, until the liquid begins to boil, whereupon the heating is interrupted for about a minute, and is then applied with gradually increasing intensity until uniform gentle ebullition sets in.

As soon as the first drops begin to fall from the condenser, the temperature is read off on the thermometer, and distillation is carried on at the rate of two drops of condensate per second. When the upper limit of temperature for the fraction draws near, the heating is reduced so that only one drop per second comes over. At the instant the limit temperature is reached, the receiver is replaced by another, and distillation is again accelerated in the same way as before.

When 100° C. is attained—or, if necessary, earlier—the shields are slipped over the apparatus in turn, without interrupting the distillation; but at the same time—or preferably a little earlier—the heating must be correspondingly moderated. The need for the shields begins as soon as the lower bulbs of the dephlegmator commence to fill with benzine, or when the distillation of the higher fractions slows down—although the heating is maintained—as already described.

When inspection of the flask through the lower mica window shows that nearly all the benzine has been driven off, heating is continued carefully until the flask is free from liquid and appears to be full of fumes. At this moment the final temperature is read off on the thermometer, and

4

the heating is stopped at once to avoid breaking the flask.

The flask is now allowed to cool down, and the weight of the residue is ascertained. The weight is referred to volume, on the basis of the specific gravity (from the table of standard fractions) of the fraction next above that corresponding to the final temperature (see p. 57). This calculation is quite sufficient for technical analyses.

The volumes of distillate in the various measuring cylinders, read off at 15° C., are calculated to percentage volumes, and the sum of the distillates and residue should amount to 100. If the loss exceeds 1 per cent., there has been some leakage in the apparatus and part of the benzine has escaped. It is therefore advisable, as a check, to determine the quantity of the residue in each test.

In ordinary distillation it is perhaps impossible to prevent small losses, especially with light benzines, small quantities, with dissolved gases, always escaping with the air in the apparatus, at the commencement of distillation, in spite of the most careful cooling.

In order to prevent these losses, it would be necessary to connect the receiver up gas-tight and place it in communication with a washing bottle containing a weighed quantity of benzol to absorb the uncondensed benzine vapours.

The atmospheric pressure may also affect the results of the distillation test.[1] The higher that pressure, the smaller the volume of benzine passing over, at a given temperature, in comparison with that given off in distillation at the standard pressure (760 mm.) under which water boils at 100° C. Conversely, the lower the pressure, the larger the amount of distillate obtained.

Thus Kissling states that the following percentage volumes of distillate were obtained from a light benzine under varying conditions of atmospheric pressure :—

| | Atmospheric pressure. | |
	760 mm.	730 mm.
Up to 60°C.	20	23
70	53	58
80	82	85
90	94	95
100	97	97

[1] R. Kissling, *Chem. Ztg.*, 1908, p. 695; Ubellohde, *Zeits. angew. Chem.*, 1906, p. 1155.

According to Scheller, a benzine of sp. gr. 0·6848 gave the following values in vol. per cent. :—

| | Atmospheric pressure. | |
	714·5 mm.	760 mm.
Up to 50°C.	16·0	14·0
60	42·2	40·8
100	93·0	92·0
125	97·0	97·0

So long as the atmospheric pressure does not vary by more than 5 mm., either way, from the standard, Kissling considers that it can be neglected; but when the variation is greater, the fractions must be collected at limits of temperature corresponding to the difference between the boiling point of water at standard pressure and at the actual pressure for the time being. In other words, a correction must be made for pressure, the fractions being collected in accordance with the result.

The following table gives the boiling point of water at different barometer readings :—

Barometric pressure. mm.	B.P. of water. °C.	Barometric pressure. mm.	B.P. of water. °C.
735·85	99·1	754·57	99·8
738·50	99·2	757·28	99·9
741·60	99·3	760	100·0
743·83	99·4	762·73	100·1
746·50	99·5	765·46	100·2
749·18	99·6	768·20	100·3
751·87	99·7	771·95	100·4

With the same object, Fuss designed a thermometer with a sliding scale, the 100° mark of which is adjusted to the actual boiling point of water for the time being.

The correction for the boiling point of benzine on the basis of that of water is not accurate, because benzine presents a mixture of different compounds. On this account the correction for benzine must be determined by direct experiment, though the method described is sufficient for practical purposes.

A. Scheller [1] recommends the Bunte pressure regulator, which is connected, air-tight, to the receiver; but this device only excludes the influence of atmospheric pressure on the distillation in the case of pressures below 760 mm., and must

[1] *Chem. Ztg.*, 1913, p. 917.

be arranged differently for those above that figure. Moreover, the arrangement is not practical, since it sets up difficulties in the way of changing the receivers.

In scientific work and when dealers specify benzine fractions of definite character, the atmospheric pressure has to be taken into account, since otherwise different results would be obtained by the chemists representing both parties to the transaction.

As can be gathered from what has been stated above, the differences in the amounts of the fractions at pressures other than the standard only begin to assume any importance when the difference in pressure is considerable, as in the examples cited, where the margin amounts to 30–45 mm.

Comparison of the two foregoing tables also shows that the differences in the amounts of benzine fractions passing over at a given temperature under different conditions of pressure are the smaller in proportion as the boiling point of such fractions is higher.

The author also has distilled one and the same benzine at different atmospheric pressures, the following values being obtained :—

Fractions.				Mean atmospheric pressure.		
				775·0	758·5	743·4 mm.
60– 80 °C.	.	.	.	1·3	1·5	1·9
80–100	.	.	.	35·7	36·1	36·6
100–120	.	.	.	39·1	39·5	40·0
120–140	.	.	.	13·9	14·1	14·1

These figures show that when the atmospheric pressure differs but slightly from the normal, the differences in the results are so slight as to be permissible in the case of technical analyses, and that, consequently, there is no need to make any correction for pressure in distillation tests so long as the pressure does not vary by more than 15 mm., either way, from the standard (reduced to zero C. and sea-level). In accurate work, moreover, a correction must be made for that portion of the mercury column that extends above the vapours, though, in commercial analyses, this correction is neglected.[1]

By plotting the progress of fractional distillation, marking

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[1] For the corresponding correction in the distillation of benzine, see H. Schütter, *Chem. Ztg.*, 1915, pp. 177, 187 and 202.

the temperature at intervals of 20° C. as abscisses, and the volumes of distillate as ordinates, the distillation or fractionation curve (boiling curve) is obtained. Such curves illustrate the constitution of the benzine, and enable the proportions of the constituents passing over up to a given temperature to be determined, the form of the curve indicating whether the constitution of the benzine is uniform or otherwise.

Fig. 5 gives the curves corresponding to the types of benzine set out in Table III, viz. a light benzine, No. 3 (A), a medium benzine, No. 5 (B), and a heavy benzine, No. 8 (C).
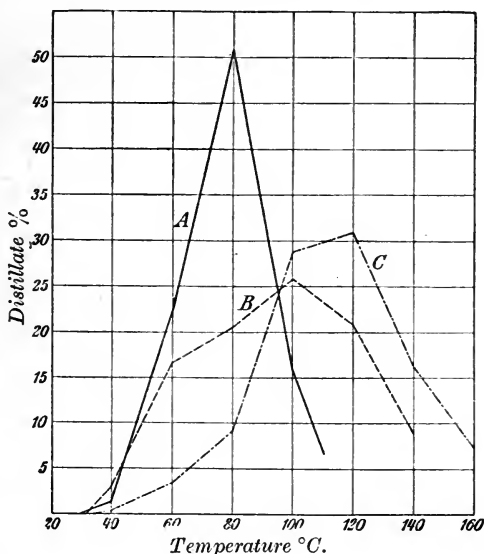
Fig. 5.

Various commercial benzines were distilled in the above described manner at a pressure approaching that of the normal atmosphere, the results being given in Tables I, II, and III as percentages by volume.

Table I relates to benzines from Galician crude oil, Table II to commercial benzines Nos. 1–7 from Roumanian crude, and a commercial benzine, No. 8, from Mexican oil. The results of benzol distillations are added for comparison; but since benzol boils at 80·5° C., the fractions 60–80° and 80–100° were collected together.

TABLE I.—BENZINE FROM GALICIAN CRUDE

Fraction °C.	Sp. Gr. of Standard fractions	No. 1 Sp. Gr. 0·696	No. 2 Sp. Gr. 0·5990	No. 3 Sp. Gr. 0·700	No. 4 Sp. Gr. 0·701	No. 5 Sp. Gr. 0·708	No. 6 Sp. Gr. 0·738	No. 7 Sp. Gr. 0·740	No. 8 Sp. Gr. 0·742	No. 9 Sp. Gr. 0·744
– 40	0·6524	1·6	14·0	2·0	11·5	7·0	0·3	—	0·1	0·5
40– 60	0·6593	30·6	21·0	20·0	16·0	14·5	7·1	0·5	2·0	1·5
60– 80	0·7005	29·0	24·0	61·0	34·6	37·7	12·2	2·1	7·6	9·5
80–100	0·7351	27·2	13·5	10·0	17·0	18·9	32·5	33·2	27·8	23·0
100–120	0·7495	8·3	15·0	3·5	12·7	10·3	21·0	40·7	37·7	32·0
120–140	0·7625		6·0	1·5	4·1	4·7	16·0	16·0	17·6	15·5
140–160	0·7738	2·7	3·0	1·6	2·0	3·3	6·5	5·0	5·9	11·0
160–180	0·7872		1·5		1·7	2·7	3·5	2·2	1·0	4·5
Over 180 (Residue)			1·5							2·0
		99·4	99·5	99·6	99·6	99·1	99·1	99·1	99·7	99·5

Fraction °C.	No. 10 Sp. Gr. 0·746	No. 11 Sp. Gr. 0·754	No. 12 Sp. Gr. 0·756	No. 13 Sp. Gr. 0·760	No. 14 Sp. Gr. 0·762	No. 15 Sp. Gr. 0·765	No. 16 Sp. Gr. 0·768	No. 17 Sp. Gr. 0·769	Benzol No. 1 Sp. Gr. 0·878	Benzol No. 2 Sp. Gr. 0·878	Benzol No. 3 Sp. Gr. 0·881	Benzol No. 4 Sp. Gr. 0·885
– 40	0·6	—	0·2	—	—	—	—	—	—	—	—	—
40– 60	2·9	0·2	0·7	0·2	—	—	0·1	0·1	—	—	—	—
60– 80	7·4	2·8	3·3	2·4	6·4	3·0	2·0	0·3	96·6	82·5	97·0	77·0
80–100	28·9	11·4	17·4	11·4	34·4	14·5	9·5	8·1	1·6	10·0	2·9	16·5
100–120	31·0	36·8	22·9	25·8	31·1	32·5	23·0	14·3		4·3		5·3
120–140	16·0	33·8	25·8	29·6	16·4	28·3	22·5	29·0	1·6	1·6		1·0
140–160	6·2	11·2	16·6	17·1	6·0	16·2	18·0	24·9		1·3		
160–180	3·0	2·8	7·9	9·2	5·2	4·6	13·0	17·0				
Over 180 (Residue)	3·5		4·5	4·0			12·0	5·5				
	99·5	99·0	99·3	99·7	99·5	99·1	100·1	99·2	99·8	99·7	99·9	99·8

TABLE II

Benzine	Rectified 1	Rectified 2	Rectified 3	Light Crude 4	Rectified 5	Heavy Crude 6	Petro-leum 7	Mexican 8
Fraction °C.	Sp. Gr. 0·679	Sp. Gr. 0·721	Sp. Gr. 0·722	Sp. Gr. 0·744	Sp. Gr. 0·759	Sp. Gr. 0·766	Sp. Gr. 0·774	Sp. Gr. 0·726
Up to 40	4·3	0·2	—	—	—	—	—	0·2
40–60	45·5	12·2	—	0·5	—	—	—	1·3
60–80	31·2	27·5	41·5	9·9	0·7	1·5	—	12·0
80–100	14·2	33·0	43·8	29·3	77·7	17·0	5·5	21·7
100–120	4·2	19·0	14·3	24·0	45·5	25·5	28·2	32·3
120–140		5·5		18·5	27·0	22·5	22·8	18·0
140–160				9·2	12·2	16·1	20·6	12·0
160–180	0·4	2·6	0·3	5·8	2·8	9·9	11·2	2·4
Residue . .				2·7		7·3	11·6	
	99·8	100·0	99·9	99·9	99·9	99·8	99·9	99·9
Aromatic and unsaturated hydrocarbon Vol. %	2·0	—	5·6	9·6	13·2	14·4	16·3	6·9
Bromine value	4·5	—	6·0	23·7	12·3	22·3	28·0	23·3

Table III gives the composition of types of light, medium, and heavy benzines supplied to the author by various refiners. This table also gives the times of evaporation; setting points; tests for benzol with dracorubine and indanthrene dark blue BT; percentage content of unsaturated hydrocarbons; degree of purification, and coefficients of refraction. These tests will be described later.

In order to obtain a foundation for subsequent observations and considerations, the author distilled 100-kg. samples of light, medium, and heavy Galician benzine, collecting the distillates at intervals of 20° C., and fractionating these with the dephlegmator already described until fractions boiling within definite temperature limits were obtained.

In this way fractions were prepared between 24° C. and 220° C., those above the latter temperature being disregarded as being present only in insignificant quantities in benzine. The fractions collected at intervals of 20° were classed as standard fractions.

The object of this method was not to isolate from the benzines chemical entities (pure hydrocarbons) which are already sufficiently well known and described, but only fractions boiling within definite limits, with a view to ascertaining their properties as a basis for subsequent comparative consideration.

TABLE III

Fraction °C.	Sp. Gr. of Standard Fractions	Light Benzine			Medium Benzine				Heavy Benzine		
		1	2	3	4	5	6	7	8	9	10
		Sp. Gr.			Sp. Gr.				Sp. Gr.		
		0·681	0·683	0·698	0·709	0·720	0·724	0·739	0·742	0·753	0·762
		Boiling begins at			Boiling begins at				Boiling begins at		
		30° C.	26° C.	30° C.	31° C.	32° C.	36° C.	34° C.	35° C.	39° C.	75° C.
-40	0·6324	8·6	6·3	1·3	1·2	2·9	0·3	4·0	0·3	0·2	—
40–60	0·6593	42·4	43·0	25·6	23·7	16·7	1·1	4·3	3·3	0·7	—
60–80	0·7005	20·1	40·3	50·3	28·7	21·0	56·0	12·5	9·0	0·9	0·6
80–100	0·7351	20·5	4·0	16·0	28·2	25·8	35·9	14·5	29·0	3·7	1·7
100–120	0·7495		2·6		11·5	21·0	5·3	21·2	31·0	55·0	25·8
120–140	0·7625					9·0		22·9	16·5	36·4	38·7
140–160	0·7738	8·2[1]	3·2	6·0[2]	6·7[3]		1·2	12·5	7·1	1·3	26·0
160–170	0·7851					3·1		5·2	2·8	1·2	5·3
over 170 (residue)								2·7			1·7
		99·8	99·4	99·2	100·0	99·5	99·7	99·8	99·0	99·4	99·8
Spontaneous evaporation		42 m. no residue	54 m. no residue	1 h. 20 m. no residue	1 h. 42 m. no residue	3 h. 6 m. no residue	2 h. 34 m. no residue	7 h. 45 m. very little residue	5 h. 40 m. slight residue	9 h. 35 m. slight residue	15 h. 17 m. slight residue
Evaporation assisted by aspiration		38 m.	49 m.	55 m.	1 h.	1 h. 30 m.	1 h. 12 m.	4 h. 8 m.	3 h. 58 m.	7 h. 45 m.	10 h. 0 m.
Solidification point		-147° C.	-148° C.	-142° C.	-135° C.	-126° C.	-125° C.	-130° C.	-120° C.	-100° C.	-95° C.
Coefficient of refraction		1·3905	1·3880	1·3924	1·3968	1·4043	1·4055	1·4187	1·4173	1·4221	1·4265
Dracorubine test		slightly reddish	slightly reddish	slightly reddish	slightly reddish	slightly reddish	slightly reddish	pale pink	faint pink	faint pink	pale pink
Indanthrene dark blue test		faint pink	faint pink	faint pink	faint pink	faint pink	faint pink	pink	pink	pink	pink
Sulphuric acid test (degree of purification)		pale yellow	pale yellow	pale yellow	pale yellow	pale yellow	pale yellow	brown	yellow	brown	brown
Aromatic and unsat. hydrocarbons. Vol. '1.		6·0	4·0	7·5	4·0	7·6	6·0	14·0	10·3	11·0	15·1

[1] Up to 110° C, 7·4; at 110° C, 0·8.

[2] Up to 116° C, 3·9; at 116° C, 2·1.

[3] Up to 138° C, 3·9; at 138° C, 3·5.

The benzine fractions were also—as described in the Technical Section—employed for experiments in the carburettor and in the motor itself.

The following constants were determined in these standard benzine fractions : specific gravity ; spontaneous evaporation ; evaporation assisted by aspirating the air ; coefficient of refraction, and setting point ; all of which will be dealt with later.   The values obtained are grouped in the following Table :—

Fraction °C.	Sp. Gr. at 15 ° C.	Setting point° C.	Coefficient of refraction at 15° C.	Spontaneous evaporation	Evaporation assisted by aspiration
20–40	0·6324	–203	1·3608	35 min.	29 min.
40–60	0·6593	–198	1·3735	51 min.	60 min.
60–80	0·7005	–185	1·3941	1 hr. 36 min.	1 hr. 55 min.
80–100	0·7351	–170	1·4100	4 hrs. 11 min.	3 hrs. 47 min.
100–120	0·7495	–151	1·4189	9 hrs. 18 min.	5 hrs. 41 min.
120–140	0·7625	–139	1·4268	21 hrs. 0 min.	10 hrs. 49 min.
140–160	0·7738	–127	1·4334	31 hrs. 30 min.	16 hrs. 24 min.
160–180	0·7872	–112	1·4398	167 hrs. 13 min.	—
180–200	0·7962	–104	1·4445	—	—
200–220	0·8072	–93	1·4500	—	—

The boiling points of the principal hydrocarbons occurring in Galician, Russian, and Roumanian benzine are appended for comparison :—

Pentane	. C_5H_{12}	36° C.	Cyclopentane	. C_5H_{10}	51° C.
Hexane	. C_6H_{14}	69	Cyclohexane	. C_6H_{12}	81
Heptane	. C_7H_{16}	98	Heptanaphthene	. C_7H_{14}	100
Octane	. C_8H_{18}	125	Octonaphthene	. C_8H_{16}	119
Nonane	. C_9H_{20}	151	Nononaphthene	. C_9H_{18}	135
Decane	. $C_{10}H_{22}$	173	Isodecanaphthene	. $C_{10}H_{20}$	151
Undecane	. $C_{11}H_{24}$	197	Undecanaphthene	. $C_{11}H_{22}$	180
Dodecane	. $C_{12}H_{26}$	215	Dodecanaphthene	. $C_{12}H_{24}$	196

To ascertain how far the densities of the fractions obtained by distilling benzine correspond to these of the standard fractions, the sp. gr. of the individual fractions was determined in numerous analyses.

The following Table shows a fair degree of concordance on the whole, complete agreement being precluded by the fact that the standard fractions were obtained by repeated distillation.   Nevertheless, the density of the standard fractions can be employed in approximate calculation, or for comparison in the technical analysis of benzine, without

it being necessary to determine the density of the individual fractions of the benzine specially. As will be seen later, the densities of the standard fractions are also important in the examination of mixtures.

Fraction. °C.	Sp. gr. of standard fractions	Sp. gr. of fractions of analysed benzines			
40–60	0·6593	0·6586	0·6598	—	0·6566
60–80	0·7005	0·7004	0·7000	0·6977	0·7030
80–100	0·7351	0·7388	0·7382	0·7324	0·7350
100–120	0·6495	0·7514	0·7469	0·7480	0·7510
120–140	0·7625	0·7597	0·7625	0·7590	0·7610
140–160	0·7738	0·7748	0·7734	0·7720	—
160–180	0·7872	0·7846	—	—	—

2. *Fractional Distillation of Benzol.*—The determination of the limits of boiling point of commercial benzol was performed with a Bannow-Krämer-Spilker apparatus (Fig. 6), consisting of a 150-c.c. spherical copper flask, *a*, with slightly
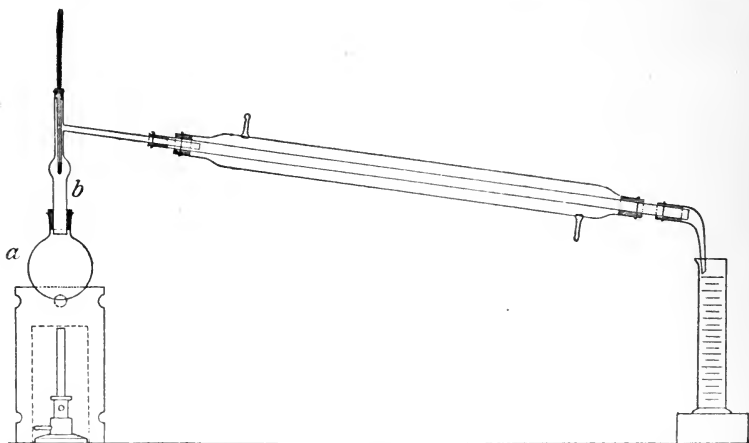

Fig. 6.

flattened bottom and 66 mm. in diameter. Into the slightly tapered neck (25 mm. long, 22 mm. wide at the top and 20 mm. at the base) of the flask is inserted a tube, *b*, 14 mm. wide, 150 mm. long, and provided with a 30-mm. bulb, which tube houses a standardised thermometer, so that the mercury bulb extends into the middle of the tube bulb.

This thermometer is 7 mm. thick and is provided with an adjustable scale.

For 90 per cent. and 50 per cent. benzol (commercial No. I and II) the scale is graduated in $\frac{1}{2}°$ C., and for pure benzol and pure toluol in $\frac{1}{10}°$ C.

The flask is heated with an ordinary Bunsen burner of about 7 mm. nozzle, surrounded by a metal shield which has a small door and two rows of four ventilation holes, 10 mm. from the top and bottom edges. An asbestos plate with a circular 50-mm. opening is placed on the shield and supports the flask.

The tube surmounting the flask is connected with a Liebig condenser, with a tube 800 mm. long and 18 mm. wide, and mounted obliquely so that the delivery end is 100 mm. lower than the intake. The receiver is a 100-c.c. measuring glass, graduated in $\frac{1}{2}$ c.c.; and the distillate is allowed to flow down the side. In order to obtain comparable results, the foregoing conventional dimensions of the apparatus must be strictly maintained.

As in the distillation of benzine, the prevailing atmospheric pressure must be taken into consideration when it differs appreciably from the normal.

According to Lenders (*Chem. Industrie*, 1889, p. 169), the correction for pressure, when an ordinary thermometer is used, is obtained in one or other of the following ways :—

(1) In order to reduce pressures between 720 and 780 mm. to 760, there must be added to, or deducted from, the results :—

for 90 per cent. benzol, 0·033 per cent.
,, 50 ,, ,, 0·077 ,,

per millimetre.

(2) For the same limits of pressure, in distillations conducted at 100° C., the addition to, or subtraction from, 100° will be :—

for 90 per cent. benzol, 0·0453° C.
,, 50 ,, ,, 0·0461 ,,

per millimetre.

Example.—If 90 per cent. of a 90 per cent. benzol distil over up to 100° C., with an atmospheric pressure of 740 mm., the percentage of distillate at 760 mm. would be :—

$$760 - 740 \ = 20 \text{ mm.}$$
$$20 \times 0·033 = 0·66 \text{ per cent.}$$
$$92 - 0·66 \ = 91·34 \text{ per cent. at } 100° \text{ C.}$$

On the other hand, according to (2) :—

$$760 - 740 = 20 \text{ mm.}$$
$$20 \times 0\cdot0453 = 0\cdot906° \text{ C.,}$$

to be subtracted from 100° C., so that, in distilling under these conditions, the value of distillate should be read off at 99·1° C., instead of at 100°.

According to Bannow, the distillation is rendered independent of the height of the barometer by placing 100 c.c. of distilled water in the flask and distilling over about 60 c.c., the boiling point of the water being noted, or the 100° point on the thermometer being adjusted.[1] The apparatus is then dried, the flask charged with 100 c.c. of benzol, and the distillation regulated so that two drops per second fall from the condenser. The first drops falling into the receiver give the initial boiling point.

In distilling commercial benzols, the fractions collected up to 100° C. are measured, the percentage boiling above 100° being calculated from the difference. Heavy commercial benzols contain no fractions up to 100°, and therefore in their case the higher fractions are measured.

The benzol under examination is classified according to the proportion distilling over up to 100° C.

Another method of testing benzol is to continue the distillation until 90 per cent. (90 c.c.) have passed over, and noting the initial and final temperatures. The distillation is not continued to the limit, because decomposition occurs in the final traces.

Simple distillation, which is sufficient for an approximate evaluation of benzol, does not, however, furnish any conclusions on the actual composition of the sample. Therefore if the quantitative composition of a commercial sample, expressed as benzol, toluol, and xylols, is to be ascertained, a fractional distillation within suitable boiling-point limits must be performed.

Various apparatus are employed for this purpose, the most usual one being the Krämer & Spilker cylindrical copper flask, 110 mm. wide and 150 mm. in height, with domed bottom, and topped· with a Lebel-Henniger bulb tube 60 cm. long. The amount of benzol taken is 1 kilo.;

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[1] With a thermometer adjusted in this manner, the boiling-point of pure benzol will be 80° C., and that of pure toluol 110° C., the state of the barometer being immaterial provided it does not vary during the experiment.

and the thermometer, arrangement of condenser, and rate of distillation are the same as given above. The distillates are collected in tared flasks and weighed, the following fractions being taken :—

Pure benzol :—.

up to 79°	first runnings
79–81	benzol
remainder	final runnings.

90 per cent. and 50 per cent. benzol :—

up to 79°	first runnings
79–85	benzol
85–105	intermediate fraction
105–115	toluol
remainder	xylols.

By repeating the fractionation, fairly pure benzol, toluol, and xylols are obtained ; but it is difficult to effect any exact separation of these hydrocarbons by this means.

For 90 per cent. benzol, a single fractionation is usually sufficient ; but with benzols containing a larger proportion of toluol and xylols, the individual components must be fractionated a second, and even a third, time, since toluol raises the boiling-point of the benzol—toluol mixture.

The first fraction is collected up to 85° C. ; the second between 85° and 115° ; and the third at 115–145°. Each of the three is then re-distilled separately, individual fractions being collected at the aforesaid temperatures, and all those of the same temperatures united and re-distilled.

A benzol containing 48·7 per cent. of benzol gave, on the first distillation :—

up to 85° C.	19·7 per cent. benzol,
85–115	70·2 ,, ,, benzol and toluol,
115–145	10·0 ,, ,, xylol and toluol.

The second distillation furnished the fractions :—

up to 85° C.	50·5 per cent. benzol,
85–115	47·5 ,, ,, toluol (benzol)
115–145	1·2 ,, ,, xylol (toluol).

The results set forth in Table IV were obtained by fractionating benzols with the apparatus described on p. 46. For simplicity, the fractions were only collected up to 85°, at 85–115°, and 115–145°, the first runnings and the intermediate fraction (85–105°) being left out of consideration. The fractionation was repeated twice.

TABLE IV

Benzol	1	2	3	4	5	6	7	8	9
		90%				50%		30%	0%
Fraction °C. Sp. Gr.	0·883	0·881	0·884	0·878	0·878	0·875	0·870	0·870	0·865
Up to 85° C. (benzol)	96·0	95·0	93·0	88·1	55·8	50·5	34·0	1·5	—
85–115° (toluol and benzol)	4·0	4·6	1·5	11·7	37·4	47·5	64·6	85·3	71·0
115–145° (xylol and toluol)	—	—	1·7	—	5·2	1·2	1·0	12·2	26·8
Remainder	—	—	3·5	—	1·5	0·5		0·8	2·5
	100·0	99·6	99·7	99·8	99·9	99·7	99·6	99·8	100·3
Free evaporation	3 h. 50 m. very small residue	4 h. 10 h. small residue (naphthalene)	7 h. 0 m. residue (naphthalene) about 0·1%	5 h. 30 m. very small residue	6 h. 30 m. small residue	9 h. 30 m. small residue	11 h. 0 m.	12 h. 30 m. very small residue	15 h. 45 m.
Evaporation by aspiration	20 h. 50 m.	3 h. 20 m.	4 h. 0 m.	3 h. 30 m.	4 h. 15 m.	5 h. 20 m.	6 h. 40 m.	8 h. 15 m.	10 h. 5 m.
Setting point	+ 2·5° C.	+ 2·5° C.	+ 1·8° C.	+ 2·0° C.	− 10° C.	− 18° C.	below − 60° C.	below − 60° C.	below − 60° C.
Coefficient of refraction	1·5012	1·5030	1·5010	1·4995	1·5000	1·4965	1·4942	1·4942	1·4932

This table also contains particulars relating to free and accelerated evaporation, setting points, and coefficients of refraction, which will be dealt with later.

Evaporation Test on Watch Glass

When different benzines or benzols are left to evaporate spontaneously, it is found that the time required for a given volume varies. This length of time depends on the composition of the sample, the lower the boiling-points of the constituents the higher the rate, and vice versa.

This behaviour, however, affords only an approximate idea of the quality of the substance.

The evaporation test, though already recommended by Kissling, was first employed by Dieterich in the preliminary examination of fuels. According to his proposals, 10 c.c. of benzine or benzol are measured out into a watch glass, 10 c.c. in diameter and 1 cm. deep, placed on a sheet of black paper, in a room perfectly free from draughts and having a temperature of about 20° C. (permissible limit of variation 16–20° C.). The liquid is allowed to evaporate spontaneously, and the time occupied is noted down; a note being also made whether the evaporation is uniform, or takes place more quickly at first and more slowly towards the end, and whether any odoriferous, oily or other residue is left.

This evaporation process is primarily influenced by the temperature of the room in which it is performed, and also by the pressure and humidity of the atmosphere. It may also be affected by the presence of heavy vapours above the test sample in the glass. For these reasons, the tests must always be conducted under identical conditions, if comparable results are to be obtained.

Unless the evaporation is unduly prolonged, the time factor does not affect the sample; but in the case of heavy benzines and heavy benzols, which evaporate slowly, it may happen that the temperature of the room fluctuates considerably, especially when the test has to be begun in the evening in order to finish the following day. Precautions must therefore be taken to keep the temperature within the prescribed limits—which is not always easily effected. Moreover, apart from this consideration, the unduly protracted evaporation test is inconvenient and wearisome.

On this account the author accelerates the evaporation by aspirating the air overlying the benzine in the following manner. The watch glass is mounted on a 15-cm. square slab of cork, a glass funnel, 12–13 cm. inside diameter, being mounted above the watch glass, at a distance of 2 mm. from the slab. This funnel is connected, by a rubber tube, with an air meter or gas meter, and the air is aspirated, by means of a suitable device, so as to pass 10 litres per minute through the funnel. In this way the benzine vapours forming above the watch glass are removed, thereby facilitating the evaporation of the benzine (or benzol).

In order to enable the time of evaporation of different benzines or benzols to be compared under these conditions, the specified volume of aspirated air and a temperature of about 20° C., must be maintained in all cases.

Of course, only results obtained by spontaneous evaporation, or by accelerated evaporation, alone, are capable of relative comparison.

The author has also tried evaporation *in vacuo*, but the time was not appreciably shortened, because, under excessive aspiration, the benzine and benzol cool down too far, thus retarding the evaporation. In view of the necessary prolonged and inconvenient operation of the vacuum pump, the simpler aspiration method described above appears preferable and more practical.

The results of such evaporation tests on different benzine fractions are given in Table III. The times are much shorter than those required for spontaneous evaporation, except in the case of the fractions 40–60° C. and 60–80° C. The longer time taken in these two instances is attributable to the considerable cooling of the benzine by the accelerated evaporation, and the consequent retardation of the process. The succeeding fractions, on the other hand, evaporated much faster by aspiration. This peculiarity of the fractions 40–80° C. is important in considering the vaporisation of benzine in the carburettor (see Technical Section).

From Tables III and IV it will be seen that the difference in the rate of evaporation with and without aspiration is slight for the light benzines, but that aspiration accelerates the operation considerably when heavy benzines and benzols are in question.

This assisted evaporation is not on a par with the vaporisation in the carburettor, since in this latter case the benzine

is not only evaporated, but also, to some extent, carried off by the rapid flow of air. This point will be dealt with more fully in the Technical Section.

ACID CONTENT

To ascertain whether the refining process has completely freed a benzine from sulphuric or sulphurous acid, about 10 c.c. of the sample are shaken up, in a test glass, with $2\frac{1}{2}$ c.c. of dilute litmus solution, which should turn neither red nor blue, but remain neutral (violet-blue coloration).

The acid test may also be performed with a 1 per cent. aqueous solution of ethyl orange, which, in presence of acid, turns from orange yellow to red. For the test, 2–3 drops of the reagent are added to 10 c.c. of distilled water.

Still more sensitive to acid than either of these two reagents is alkali blue 6B (Höchst), 0·01 grm. of which is dissolved in 100 c.c. of pure ethyl alcohol, the blue solution being treated with one drop of $\frac{1}{100}$-normal caustic soda, which turns it red. A few cubic centimetres of this solution shaken up with the benzine will acquire a blue coloration if any acid be present in the latter. This test will also reveal any organic acids—originating in the raw material —which have no action on ethyl orange or litmus. The best plan is to make tests with alkali blue, and also with litmus or ethyl orange. Benzol is tested in the same way.

BEHAVIOUR TOWARDS SULPHURIC ACID

The coloration obtained when a liquid fuel is mixed with concentrated sulphuric acid affords an idea of the degree of purity resulting from the refining process.

Ten c.c. of benzine are gently shaken up in a flask with 5 c.c. of sulphuric acid of sp. gr. 1·53 (50° Bé., or 62·5 per cent. acid) for three minutes, the acid being then allowed to settle down and its colour observed.

For commercial benzols I and II, pure benzol, toluol, and xylol, the following sulphuric acid test is recommended : 5 c.c. of the benzol, etc., are well shaken for eight minutes with 5 c.c. of concentrated sulphuric acid, in a clear-glass 15-c.c. flask, the colour being then compared with that of solutions of potassium bichromate—0·01, 0·05, 0·1, and 0·15 per cent. strength) in 50 per cent. sulphuric acid. For this purpose

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5 c.c. of each of these solutions are placed in clear-glass flasks of uniform size, and covered with 5 c.c. of purest benzol.

This test is unsuitable for commercial benzols III–VI, because the results obtained vary according to the use for which these benzols are intended.

In examining mixed liquid fuels, the sulphuric acid must be added slowly, owing to the risk of the mixture becoming strongly heated and spirting, especially when it contains sulphuric ether, alcohol or acetone, all of which themselves react with sulphuric acid and also acquire coloration as well as the acid.

Testing for Sulphur Compounds

The qualitative examination for sulphur compounds (carbon disulphide, alkyl sulphides, thiophene, mercaptans) in benzine and benzol is generally performed with silver nitrate.

About 10 c.c. of the benzine, etc., are thoroughly shaken up in a test glass with 3 c.c. of an alcoholic ammoniacal solution of silver nitrate,[1] and warmed for several minutes in hot water. When any sulphur compound is present, the liquid acquires a brown to black colour due to pre-cipitated silver sulphide.

Carbon disulphide is revealed by the following test : The benzine or benzol is treated with one-fourth its volume of 25 per cent. alcoholic caustic potash solution and gently warmed with repeated shakings. If carbon disulphide be present, potassium xanthate is formed, and the subsequent addition of a few drops of an alcoholic ammoniacal solution of nickel chloride will give a brownish-red coloration. This test is sensitive for less than 1 per cent. of carbon disulphide.

Another successful test is that of Votocek, in which benzine or benzol is mixed with an equal volume of 25 per cent. alcoholic caustic potash, treated with 3–4 drops of aniline, shaken and gently warmed. A few drops of very dilute, freshly prepared sodium nitroprusside solution are then added, and the whole is stirred up. In presence of carbon disulphide a violet coloration is obtained.

The quantitative determination of carbon disulphide in benzol and benzine is effected, according to Frank, by

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[1] Prepared by dissolving 0·1 grm. of silver nitrate in 10 c.c. of alcohol, and carefully adding concentrated ammonia until the precipitate first formed is re-dissolved.

thoroughly mixing 50 grms. of the benzine, etc., with 50 grms. of alcoholic caustic potash (11 grms. of potassium hydroxide to 90 c.c. of absolute alcohol) in a separating funnel, and leaving the whole to stand for several hours at room temperature. The mixture is then shaken up with 100 c.c. of water, which dissolves out the potassium xanthate formed by the reaction between the potash and the carbon disulphide.

The aqueous solution is drawn off, and the benzol is shaken up again several times with more water. The aqueous solutions being united, an aliquot part is measured off and neutralised with acetic acid, being then titrated with a standardised solution of copper sulphate [1] until a drop, transferred on a glass rod to a sheet of filter paper imparts a reddish-brown coloration to an adjacent drop of potassium ferrocyanide solution at the plane of contact. The end point of the reaction can also be approximately identified by the agglomeration of the initially finely divided precipitate of copper xanthate.

The above quantity of 50 c.c. of caustic potash suffices for a content of up to 5 per cent. of carbon disulphide; but if the proportion be higher, as for example in benzol first runnings or in mixed fuels, either more potash or less test substance must be employed.

The total sulphur in benzine or benzol is determined, quantitatively, by the Heussler-Engler method. The benzine or benzol is burned in a special apparatus, and the liberated gases, containing sulphur dioxide from the combustion of the sulphur compounds in the liquid, are collected in an alkaline solution of bromine, which oxidises the sulphur dioxide to sulphuric acid, the latter being then determined quantitatively and calculated to sulphur. The combustion apparatus used has been improved by K. Schenk (*Chemiker Zeitung*, 1914, p. 83 ; see also F. Schulz, *Petroleum*, Vol. 8, 1913, p. 585).

Testing Benzine for Aromatic Hydrocarbons (especially Benzol) and Unsaturated Hydrocarbons

The determination of aromatic and unsaturated hydrocarbons in benzine is important, because they do not burn

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[1] 12·475 grms. of pure crystallised copper sulphate are dissolved in water to make 1 litre. 1 c.c. of this solution corresponds to 0·0076 grm. of carbon disulphide.

so well as the latter and are therefore liable to alter its properties.

The quality of a benzine is consequently dependent on the amount and character of the aromatic and unsaturated hydrocarbons it may contain. The author therefore strongly recommends that, in addition to fractional distillation, a quantitative (as well as qualitative) determination of these hydrocarbons should be undertaken, this being important and essential for judging the benzine correctly.

According to Holde, the qualitative examination for aromatic hydrocarbons should be performed with a specially prepared asphaltum—purified with benzol of sp. gr. 0·70–0·71—which is insoluble in benzine, but dissolves to a brown solution in benzol. If, therefore, a small quantity of this finely-powdered asphaltum be stirred up in benzine and filtered off, the filtrate will be colourless in the event of the benzine being free from any considerable proportion of benzol; otherwise it will be yellow or brown. By this means it is stated that down to 5 per cent. of benzol can be detected in benzine. However, the preparation of the asphaltum is a rather troublesome matter, and moreover the test is not sufficiently delicate.

Another test is based on the fact that technical benzol contains about 0·6 per cent. of thiophene, which gives a blue coloration when slightly warmed with a solution of isatin in concentrated sulphuric acid, whereas benzine free from benzol and thiophene remains colourless. The test is, however, unreliable, if not altogether unsuitable, because an ordinary benzine or benzol not infrequently acquires a greenish, or even brown, coloration, when tested in this way.

The author, on investigating this phenomenon, has found that the failure of the test is due to impurities in incompletely refined benzine, the sulphuric acid itself turning yellow to brown, according to the character of the benzine; and this coloration masks the blue formed by the isatin reaction.

The author has tried to distil off the fraction containing the benzol, up to 100° C., in order to eliminate the thiophene, which boils at 84° C.; but the distillate gave only a greenish-brown coloration under the isatin test. Consequently, the unsuitability of this test is due to the benzine containing substances capable of colouring sulphuric acid, together with other impurities.

Liebermann's reagent—nitrososulphuric acid or amyl nitrite and sulphuric acid—also gives unsatisfactory results with motor benzines (petrol).

For this reason Dieterich employed, for the detection of benzol in benzine, a dyestuff, dracorubine (a mixture of the dracoresinotannol esters of benzoic and benzoylacetic acids), prepared from palm dragon's blood and used in the form of test paper. This dracorubine is insoluble in pure, cold benzine, but gives a dark red solution with benzol, toluol, and xylol (both of which are always present in technical benzols).

Dieterich, therefore, proposes to detect the presence of benzol in benzine by placing four strips of dracorubine paper and 30–35 c.c. of the benzine in a stoppered clear-glass cylinder, and leaving the whole to stand all day, or all night, at room temperature. After another shaking the test papers are taken out, and the colour of the liquid is examined by placing a sheet of white paper under and behind the glass. If the benzine contains even only 5 per cent. of benzol, it will be stained a faint pink.

The test paper is dried, and examined for colour and pliability.

The author has found, from repeated trials, that the dracorubine test is fairly sensitive; but care is necessary in forming an opinion from the coloration produced, inasmuch as dracorubine forms a deep red solution with ethyl, methyl, and amyl alcohol, sulphuric ether, carbon disulphide, acetone, and chloroform, all of which, except chloroform, may be present in benzine and benzine substitutes. Consequently when the test gives positive results the benzine must be examined for the presence of these substances.

For the detection of alcohol or acetone in benzine, Dieterich employs the so-called dracorubine capillary test.[1]

The Dieterich tests suggested to the author the idea that some of the readily accessible, cheap commercial dyestuffs might be suitable for the same purpose; and he has discovered such in the (Badische) vat dyestuffs : indanthrene dark blue BT and indanthrene violet RT, both in powder. These give better results than dracorubine.[2]

[1] K. Dieterich : *Die Untersuchung und Prüfung der leichten Motor-betriebsstoffe*, 1916, pp. 19, 44.

[2] Pure indanthrene dark blue BT, which is prepared from benzanthronequinolin by fusing with potash, is no longer on the market ; and it does not dissolve in benzol. The present commercial variety consists of a mixture of indanthrene dark blue BO and indanthrene violet RT, the

Indanthrene dark blue BT (" dark blue BT ") and indanthrene violet RT (" violet RT ") appear to be practically insoluble in standard benzine (*i. e.* pure benzine of sp. gr. 0·695–0·705, boiling at 65–95° C., and free from unsaturated and benzol hydrocarbons), only a scarcely discernible pink tinge being observable in a thick stratum of the liquid. They are, however, soluble in benzol, toluol, xylol, carbon disulphide, and chloroform, giving a bluish-red colour with yellow fluorescence. The benzol solution of blue BT has more of a reddish cast, and that of violet RT more bluish. The former being the brighter, the author uses blue BT.

Both dyestuffs are considerably less soluble in ether and acetone. Blue BT is only very slightly soluble in ethyl alcohol, giving a faint pink coloration, which after a time turns yellow with green fluorescence; whilst violet RT is almost insoluble in this alcohol. Methyl alcohol has but a very slight solvent effect on either, and the solutions, on prolonged standing, become yellowish with green fluorescence. Both blue BT and violet RT are insoluble in amyl alcohol.

Blue BT is almost insoluble in petroleum and in French, German, and Swedish oil of turpentine. Violet RT is only very slightly soluble, giving a bluish-violet coloration.

Owing to their low solubility in alcohols, ether, acetone, and oil of turpentine, and their greater power of staining benzol, both dyestuffs present a great advantage over dracorubine.

When blue BT is added to benzine containing 10 per cent. of ether and 10 per cent. of alcohol, the mixture, although becoming pink, gradually turns almost colourless, with a yellow tinge. If violet RT be used, the pink is persistent.

If the benzine contains 5 per cent. of carbon disulphide, either blue BT or violet RT will give a faint pink coloration, a decided pink only appearing when the carbon disulphide amounts to 10 per cent. Both carbon disulphide and ether,

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former of which is prepared by fusing benzanthrone with potash, whilst the other forms a chlorine derivative of indanthrene dark blue BO.

Since indanthrene dark blue BO is only slightly soluble in benzol, the coloration of the latter is due to the chlorine derivatives of that dyestuff. The absorption spectrum of the benzol solution of blue BT consists of three bands : the chief one being situated at 549·0, and the subsidiary bands at 190·0 and 510·0. In the benzol solution of violet RT, the principal band is at 586·5, and the subsidiary bands at 541·5 and 500·5.

Whilst there are other suitable commercial dyestuffs, those just named are the best. There are also other coloured compounds which might be used, but their preparation is a rather troublesome matter, even for the chemist.

in association with benzine, are therefore far less soluble in these dyestuffs than in dracorubine.

Blue BT and violet RT are stable dyestuffs; their solutions do not alter on exposure to air and light, decoloration taking place only on exposure to the direct rays of the sun, to which violet RT is less sensitive than blue BT. Dracorubine, on the other hand, alters gradually in the air, and gradually loses colour in diffused light.

The test with either blue BT or violet RT is performed in far less time than the dracorubine test. For example, benzine with 5 per cent. of benzol takes twelve hours to acquire a faint pink tinge with dracorubine, whereas fifteen minutes only are needed with either blue BT or violet RT, the coloration being, moreover, far more distinct, and the test therefore more delicate.

The test for benzol is carried out in the following manner :—

About 0·05 grm. of the dyestuff (as much as will go on the point of a knife) is added to 20 c.c. of the benzine in a stoppered glass flask, the mixture being well shaken up and left for two hours with occasional inversion. The benzine is then filtered off into a narrow cylinder of clear glass, to a depth of 10 cm. and examined from above and sideways, the cylinder being placed on a sheet of white paper.

If the benzine be free from benzol, the 10-cm. stratum will show a barely discernible pink tinge; but when only 2 per cent. of benzol is present, a decided pink will be observed, which increases progressively with the proportion of benzol, until, with 25 per cent., a very deep shade is obtained.

Table III gives a comparison of the colorations produced by dracorubine and blue BT in various benzines, together with the percentages of aromatic hydrocarbons present.

Since both blue BT and violet RT are stable dyestuffs, an approximate estimate of the amount of benzol present in benzine can be made by comparing the coloration of the test sample with that of a benzine containing a known percentage of benzol. An even better way is to make a colorimetric determination of the benzol.

In order to ascertain what minimum percentage of benzol or aromatic hydrocarbons can be detected, colorimetrically, in benzine, and what is the shortest time needed for the test, the author carried out further investigations, on the one hand with pure benzine treated with known additions

of benzol, and on the other with ordinary commercial benzines, the aromatic and unsaturated hydrocarbons in these latter being determined by the Krämer-Böttcher method.

The standard test liquid employed was a benzine containing 7·0 per cent. of aromatic hydrocarbons, this liquid being mixed with the above quantity of dyestuff (blue BT), and filtered at the end of two hours. Comparative tests with the Zeiss colorimeter gave the following results :—

Added benzol per cent.	Benzol revealed by colorimeter	
	After 2 hrs.	After 24 hrs.
2·0	1·4	1·5
4·0	4·2	4·2
6·0	5·8	6·2
8·0	7·4	7·4
9·0	8·2	8·4
11·0	10·2	10·3
13·0	13·9	13·9
15·0	14·1	14·8
20·0	19·6	19·9

The commercial benzines referred to in Tables I and III gave :—

						Aromatic hydrocarbons.	Revealed by colorimeter.
Table	I,	No.	1	.	.	3·6	3·2
,,	III,	,,	2	.	.	4·0	3·5
,,	,,	,,	6	.	.	6·0	5·7
,,	,,	,,	7	.	.	14·0	15·1
,,	,,	,,	8	.	.	10·3	8·8
,,	,,	,,	9	.	.	11·0	10·0
,,	,,	,,	10	.	.	15·1	14·0

It follows from these data that the colorimetric determination of aromatic hydrocarbons can be effected in two hours by means of blue BT, and that the resulting values agree fairly well with those of the Krämer-Böttcher method. The blue BT method is therefore suitable for the rapid determination of benzol and aromatic hydrocarbons in general. Care is needed to see that the test sample and check solution should be left in contact with the reagent (blue BT or violet RT) for the same length of time, and that the undissolved dyestuff should be removed by filtration.

Another method for the qualitative and quantitative determination of benzol in benzine is based on nitration with fuming nitric acid, the action of which is to transform benzol—and also toluol and xylol—into the characteristic nitro-compounds.

For the qualitative test, about 10 c.c. of the benzine are mixed in a 200-c.c. flask with a ten-fold volume of a cooled mixture of 1 part concentrated sulphuric acid and 2 parts fuming nitric acid, and left for an hour with occasional gentle inversion, being suitably cooled to check the violence of the reaction. The mixture is afterwards gently warmed in the water bath, so long as brown nitrous fumes continue to come off and until the product has become pale yellow. If benzol be present, the oily supernatant layer will be yellow and the liquid will smell like oil of bitter almonds.

The quantitative determination is performed in a special apparatus.[1]

In testing for benzol by nitration, it should be borne in mind that benzine itself, and especially the heavy kinds, may also contain aromatic hydrocarbons which undergo nitration at the same time. There are also hydrogenated hydrocarbons (naphthenes), which—e. g. hexahydrobenzol —are transformed into nitrobenzol by oxidation with nitric acid and nitration.

Hence, even if the nitration test gives positive results, this does not prove that benzol has been intentionally added to the benzine; and, moreover, even many light benzines sometimes contain small quantities of benzol from the raw material, according to origin and degree of refining.

In general, unsaturated and aromatic hydrocarbons are determined by the Krämer-Böttcher method, by absorption in sulphuric acid, as follows [2] :—

Twenty-five c.c. of benzine and 25 c.c. of a mixture of 80 parts (vol.) of concentrated and 20 of fuming sulphuric acid are placed in a fairly strong 75-c.c. flask, the neck of which, about 50 cm. long, is graduated in $\frac{1}{10}$ c.c., the mixture being well shaken for a quarter of an hour. Continuous energetic shaking, preferably in a machine, is essential to prevent considerable divergence in the results of the tests. At the end of half an hour, concentrated sulphuric acid (not the above mixture) is added until the upper layer of oil is driven up into the tube; and after the expiration of an hour, the volume is read off at intervals

[1] See Lunge-Berl : *Untersuchungsmethoden*, III, p. 500; also Holde : *Kohlenwasserstofföle*, p. 62.

[2] For other quantitative methods, with formaldehyde and sulphuric acid, or with liquid sulphur dioxide, see Engler-Höfer : *Das Erdol*, IV, p. 21.

until there is no further reduction in the quantity of the hydrocarbons.   The percentage volume of absorbed hydro-carbons is calculated from the difference between the initial and final volume.   In presence of more than 13 per cent. of unsaturated hydrocarbons, however, the method is stated to be inexact.

In the author's laboratory the above flask has been successfully replaced by the Bunte burette (Fig. 7) as used for gas analysis, this affording the advantage that the absorbent sulphuric acid can be easily renewed as required, so that hydrocarbons in excess of 13 per cent. can also be estimated.

In operating with this burette, the sulphuric acid is first drawn in from below, a partial vacuum being then produced in the burette by means of the pump. The measured volume of benzine, being introduced into the funnel, will run down into the cylinder on the tap being gradually opened.   Before shaking is begun, the volume of benzine in the burette must, of course, be carefully read off on the scale.
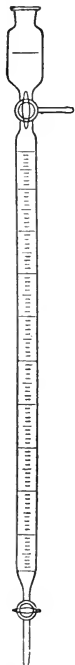
DETERMINATION OF UNSATURATED COMPOUNDS IN BENZINE AND BENZOL

In certain circumstances, unsaturated compounds will absorb bromine and iodine, as well as hydrogen, and will decolorise these agents, whereas pure benzine (freed from unsaturated compounds), benzol, or toluol will remain coloured for some time when treated with bromine water or iodine solution.

The behaviour towards bromine is utilised, in the case of commercial benzols I and II, pure benzol, and toluol, to check the extent to which they have been refined, i. e. how far they have been freed from the resinifiable substances (cumarone, indene) capable of forming additive compounds with bromine. This behaviour may also be employed as an approximate test for the purity of benzine.   The method is inapplicable to the higher benzols, such as xylol, pseudo-cumol, etc., the higher benzol homologues not being completely inert towards bromine.

In the examination of benzine and benzol, bromine water is replaced by a deci-normal solution of potassium bromide and potassium bromate, from which bromine is liberated

Fig. 7.

by the action of sulphuric acid, in accordance with the equation :—

$$5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3Br_2 + 3H_2O.$$
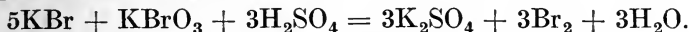
The titrating solution is prepared by dissolving 9·9180 grms. of pure potassium bromide and 2·7836 grms. of pure potassium bromate in 1 litre of distilled water.   One c.c. of this solution corresponds to 8 mgrms. of bromine.

With this solution, 5 c.c. of benzine (or benzol) are titrated in a glass-stoppered flask (after addition of 10 c.c. of 20 per cent. sulphuric acid) by continuous agitation for five minutes, until, after standing for a quarter of an hour, the benzine remains orange, and a drop let fall on freshly-prepared zinc-iodide starch paper immediately gives a blue stain. The titration is duplicated, the first test being taken as a preliminary.   The purity of the benzine or benzol is judged from the amount of bromine consumed in saturation, expressed in milligrams per cubic centimetre of test liquid.

This method, proposed by Krämer & Spilker, is, however, attended with certain defects.   In the first place, it has been found that a considerably larger quantity of the titrating solution is consumed when the test is made in the light than in the dark.   For instance, with 5 c.c. of light benzine mixed with 10 c.c. of potassium bromide-bromate solution :—

4·40 c.c. of the solution were consumed in 30 min. } when shaken in the
4·75   ,,   ,,   ,,   ,,   45 ,,   }   light,

whereas the consumption was only 1·75 c.c. in twenty hours, in semi-darkness without agitation.   In the case of a standard benzine, entirely free from unsaturated and aromatic hydrocarbons, the consumption of bromide-bromate solution per 5 c.c. of benzine was only 0·03 c.c. in the dark, as compared with 3·9 c.c. in the light.

. Another drawback of the method is that the end point of the bromine reaction must be ascertained by the inaccurate spotting method.

In collaboration with Dr. J. Knop, the author has modified the method as follows : A 50-c.c. flask, with ground-glass stopper, is charged with 5 c.c. of benzine or benzol, 10 c.c. of 20 per cent. sulphuric acid, and exactly 10 c.c. of deci-normal potassium bromide-bromate solution, this quantity being sufficient for most tests.

The liquid must be coloured a brownish-yellow by liberated bromine;   otherwise larger quantities of the

bromide–bromate solution must be taken, especially in the case of impure benzols.

The flask is closed at once, wrapped in brown paper, and shaken in an agitator for half an hour, experience having shown this time to be ample.

If no agitating machine is available, the test mixture is left in the dark for twenty-four hours without shaking.

A simultaneous blank experiment should be made without benzine, to standardise the bromide–bromate solution.

Both samples are then treated with 5 c.c. of 10 per cent. potassium iodide solution and 10 c.c. of water; and, after adding freshly-made starch solution, the iodine liberated by the bromine is titrated with thiosulphate solution (assisted by shaking) until the blue solution is decolorised. Any blue tinge reappearing is neglected.

From the difference in the volume (cubic centimetres) of thiosulphate solution consumed in the two experiments, the amount of bromine (equivalent to the iodine) consumed by the benzine is ascertained by calculation, and is expressed in percentage, by weight, of the benzine (or benzol).

Example.—Five c.c. of benzine were treated with 10 c.c. of potassium bromide–bromate solution as described above. On titration the liquid consumed 9·85 c.c. of thiosulphate solution, and the check sample 9·10 c.c. The titre of the thiosulphate solution was 7·996 mgrms. (roughly 8 mgrms.) of bromine per 1 c.c.

The difference: $9·85 - 9·10 = 0·75$ c.c., multiplied by $8 = 6$ mgrms., gives the weight of bromine absorbed by the 5 c.c. of benzine. The sp. gr. of the benzine being 0·730, the bromine value is: $6 \div (5 \times 0·730) = 1·64$.

Another and simpler method of determining the purity of benzine and benzol is by titration with potassium permanganate. The following method has been worked out in the author's laboratory, and is being further investigated.

Five c.c. of benzine or benzol are placed in a 150-c.c. flask (with plain glass stopper), which is wrapped in black paper and has been rinsed out with dilute permanganate solution and distilled water. Twenty c.c. of 20 per cent. sulphuric acid and 50 c.c. of $\frac{1}{50}$-normal permanganate solution are added, and the whole is shaken continuously for thirty minutes. If the solution becomes decolorised, more permanganate solution must be taken.

Simultaneously with this test, the permanganate solution is standardised with $\frac{1}{50}$-normal oxalic acid.

The test liquid is then titrated back with $\frac{1}{50}$-normal oxalic acid.

The number of cubic centimetres of permanganate solution consumed for oxidation gives the number of milligrams of oxygen, and, by further calculation, the bromine value.

It is found that the bromine value determined in this way coincides well with that given by the bromide–bromate method.

The purity of the benzine or benzol can, of course, also be judged from the " oxygen value " (number of milligrams of oxygen consumed per 1 grm. of sample).

Example.—Five c.c. of benzine were treated with 50 c.c. of $\frac{1}{50}$-normal permanganate solution and 20 c.c. of 20 per cent. sulphuric acid, and, after shaking for half an hour, titrated with $\frac{1}{50}$-normal oxalic acid. The solution consumed 34·8 c.c. of this acid. The titre of the permanganate solution having been ascertained to correspond to 53·2 c.c. of $\frac{1}{50}$-normal oxalic acid per 50 c.c., 1 c.c. of the oxalic acid = 0·94 c.c. of the permanganate solution, and therefore : 34·8 × 0·94 = 32·7 c.c. of $\frac{1}{50}$-normal permanganate solution.

The difference : 50 − 32·7 = 17·3 c.c. of permanganate solution as consumed by the benzine.

Since 1 c.c. of $\frac{1}{50}$-normal permanganate corresponds to 0·16 mgrm. of oxygen, and the sp. gr. of the benzine was 0·711, the consumption of oxygen was therefore :—

$$17\cdot3 \times 0\cdot16 \div 5 \times 0\cdot711 = 0\cdot778 \text{ mgrm.}$$

As 1 c.c. of $\frac{1}{50}$-normal permanganate corresponds to 1·598 mgrm. of bromine, the bromine value is therefore 7·78, or ten times the oxygen value.

In this case the bromine value by the bromide–bromate method was 7·12.

Perfectly pure benzine (free from unsaturated and aromatic hydrocarbons), and also pure benzol, do not decolorise the permanganate solution.

The Hübl-Waller and the Wijs iodine solutions are not very suitable for benzine and benzol, the iodine absorption taking too long.

The disagreeable smell of imperfectly refined benzine is sometimes masked by small additions of oil of turpentine, pine oil, etc.

To detect oil of turpentine in benzine, the following method has been proposed in the literature :—

The benzine is treated with one drop of a dilute solution

of bromine in benzine, and shaken. In the absence of turpentine the brown coloration due to the bromine persists unaltered for some time; but in presence of turpentine the brown colour disappears at once or after standing a little while.

The author has demonstrated, by repeated experiments, that this test is not decisive in the case of motor spirit, which nearly always contains—especially if imperfectly refined or unrefined—aromatic and unsaturated hydrocarbons which decolorise bromine, either at once or in a short time (see following Table).

Since these compounds absorb |iodine, in the cold, far more slowly than bromine, iodine solution is a better means of detecting oil of turpentine; but a certain degree of caution is needed, because many kinds of benzine may also contain compounds which absorb iodine rapidly, and therefore decolorise it even in the absence of oil of turpentine.

If one drop of Hübl-Waller solution [1] be added to 5 c.c. of a benzine containing oil of turpentine and shaken, the pink coloration vanishes in a relatively short time, whereas, under similar conditions, a pure benzine will still remain coloured after half an hour.

The results of tests on a number of refined and unrefined benzines, with bromine and iodine, by the method described above, are given in the following table. In each case, the unsaturated and aromatic hydrocarbons were determined by the Krämer-Böttcher method (p. 73) for comparison.

This Table shows that iodine solution, even in the absence of oil of turpentine, may be decolorised in less than thirty minutes; see Nos. 10, 12, and 16. The sample No. 12 had an unpleasant smell and was also unrefined.

The decoloration is probably due more to the aliphatic unsaturated hydrocarbons present than to aromatic hydrocarbons.

The rate at which iodine is decolorised in presence of oil of turpentine depends on the compounds, capable of decolorising iodine, originally present in the benzine.

Experiments were made by adding 0·1 per cent. of oil of turpentine, and then iodine solution, to different benzines. On the other hand, one drop of iodine solution was added to the benzine, and, as soon as the coloration disappeared,

---

[1] 2·5 grms. of iodine and 3 grms. of mercuric chloride are each dissolved in 50 c.c. of 95 per cent. ethyl alcohol, the solutions being filtered, united, and treated with 5 c.c. of HCl (sp. gr. 1·19).

0·1 per cent. of turpentine was added, followed by another drop of iodine solution.

Benzine. No.	1	2	3	4	5	6	7	8
Refining	Unrefined	Refined	Refined	Refined	Refined	Refined	Refined	Refined
Sp. gr.	0·671	0·687	0·693	0·705	0·720	0·725	0·730	0·740
Aromatic and unsaturated hydrocarbons	1·9	3·7	5·5	4·0	3·8	7·0	6·8	12·4
Bromine de-coloration in	1½ h.	immediately.						
Iodine de-coloration in	48 h.	3 h. 10 m.	2 h. 30 m.	5 h. 10 m.	2 h. 55 m.	1 h. 45 m.	4 h. 10 m.	2 h.

Benzine. No.	9	10	11	12	13	14	15	16
Refining	Unrefined	Refined	Un-refined	Un-refined	Un-refined	Refined	Refined	Un-refined
Sp. gr.	0·740	0·740	0·748	0·750	0·755	0·756	0·760	0·761
Aromatic and unsaturated hydrocarbons	17·6	12·3	9·8	11·6	11·3	11·6	13·5	12·8
Bromine de-coloration in	at once		35 m.	at once	5 m.	at once		
Iodine de-coloration in	40 m.	3 m.	24 h.	imme-diately	24 h.	55 m.	2 h. 30 m.	22 m.

As can be seen from the following table, the decoloration in the second series was sometimes faster and sometimes slower than in the first; and taking all the results into consideration, this method for detecting oil of turpentine must be regarded as merely indirect and uncertain.

Benzine. No.	1	2	3	4	5	6	7
Refining	Un-refined	Refined	Refined	Un-refined	Un-refined	Refined	Refined
Unsaturated and aromatic hydro-carbons	1·9	5·5	6·8	9·8	11·3	11·6	10·8
0·1 % turpentine; iodine solution decoloration in	3 h. 40 m.	1 m.	1 h. 33 m.	1 h. 26 m.	2 h.	11 m.	8 m.
Iodine solution, followed by 0·1% turpentine and iodine solution; decoloration in	3 h. 40 m.	1 h. 59 m.	3 h. 14 m.	3 h. 43 m.	1 h. 34 m.	15 m.	5 m.

The bromine and iodine values have been recommended for the quantitative determination of oil of turpentine; but it will be evident, from the above, that they are unsuitable for benzine.

DETERMINATION OF PARAFFIN HYDROCARBONS IN BENZOL

The quantitative determination of paraffin hydrocarbons in benzol or toluol is principally undertaken when the density of the sample is below the usual level of the commercial article (see p. 99).

Krämer and Spilker give the following method for this purpose :—

Two hundred grms. of benzol (toluol) are shaken up with 500 grms. of fuming sulphuric acid (20 per cent. anhydride) in a one-litre separating funnel for a quarter of an hour, taking care to prevent heating, and are then left for two hours. The acid is then drawn off and the experiment repeated twice with similar quantities of the same acid.

The united acid (1500 grms.) is slowly run into a three-litre flask containing the same weight of powdered ice, the flask being shaken and the temperature kept from rising above 40° C. The contents are then distilled, over a naked flame, into a 100-c.c. separating funnel, until, in addition to the small residue of oil, 50 c.c. of water have passed over, by which means any still dissolved or mechanically disseminated paraffin hydrocarbons are recovered from the liquid.

After the water has been drawn off, the oil obtained is united to that originally drawn off, and the whole liquid is repeatedly shaken up with 30 grms. (each time) of fuming sulphuric acid of the above-mentioned composition.

The residual oil is washed with small quantities of distilled water and weighed.

The number of grammes, divided by two, gives the percentage weight of paraffin hydrocarbons in the sample.

Since, however, this method gives not only the paraffin hydrocarbons in the benzol, but also other substances which are not sulphonable or destroyed by fuming sulphuric acid—such as naphthenes and carbon disulphide—the results are only approximately correct.

In order to obtain accurate figures, the carbon disulphide (if any) present in the hydrocarbons after treating the

benzol with sulphuric acid, must be determined and then subtracted (p. 66).

WATER CONTENT

Neither benzine nor benzol is miscible with water. If the former be shaken up with water, separation always occurs, the water settling down at the bottom of the vessel, whilst only a small quantity is absorbed by the benzine. Benzol, on the other hand, is capable of taking up a relatively larger amount of water.

The qualitative test for water in benzol is to add a few fragments of sodium or calcium carbide, and stir. If water is present, small bubbles of hydrogen or acetylene will be given off. Any more extensive liberation of gas points to an admixture of diluted alcohol.

The sodium test is the more accurate of the two.

For quantitative determinations the Hoffmann-Marcusson method, by distillation with xylol, is employed; but, for motor spirit, whether benzine or benzol, there is no particular interest in carrying out this examination.

COEFFICIENT OF REFRACTION

The coefficient of refraction, also termed index or exponent of refraction (n), also affords useful aid in the identification of organic compounds.

The determination of this coefficient is based on the following phenomenon.

When a ray of monochrome light passes from one substance into another, e. g. from air into glass, in an oblique direction, a portion of the light is reflected, and the remainder is deflected from its original direction. The ratio between the sine of the angle which the impinging ray makes with the vertical at the point of entry (angle of incidence), and the sine of the angle between the deflected (refracted) ray and the same vertical, is termed the coefficient of refraction.

Since the coloured rays going to make up white light have different angles of refraction, and since the refraction is also dependent on the temperature, the aforesaid ratio is determined for a ray of yellow light at 15° C., the coefficient of refraction being expressed as n_{D15}, in which n denotes a coefficient of refraction, $_D$ yellow light and $_{15}$ the temperature in degrees C.

6

The coefficients of refraction are ascertained by means of a special optical instrument, the refractometer; and the method of measurement is based on the observation of the total reflection on the surfaces of a flint-glass prism from which the light passes into the substance under examination.

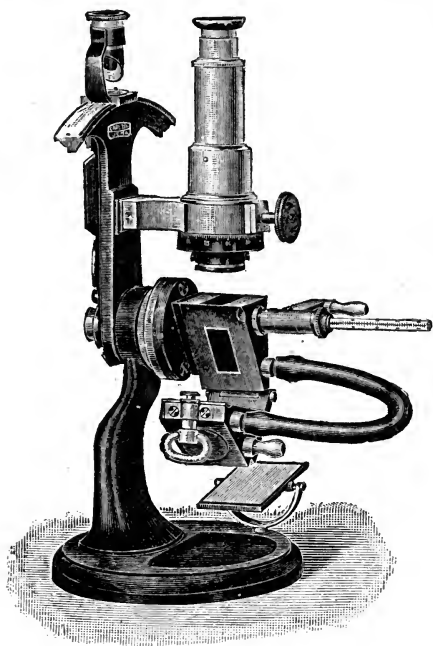The Zeiss refractometer illustrated in Fig. 8 consists principally of a double Abbe prism which is intended to contain the liquid, and is adapted to be rotated on a horizontal axis by means of an alhidade. The limits of total reflection are observed through a telescope, to which is connected a graduated sector on which the coefficients of refraction are read off.

For the examination of benzine and benzol the prism must be adapted to be attempered, and the instrument arranged for daylight illumination. The scale should be graduated between n_D 1·300 and n_D 1·6500. As full instructions for use are supplied with each instrument, they need not be discussed here.

FIG. 8.

As is the case with other substances, an increase in the density of hydrocarbons is accompanied by an increased coefficient of refraction; and this property also is utilised for the identification of petroleum and oils, the method of determination being effected easily and with small quantities of substance.

Investigations of this kind on petroleum, oils, lacquer benzines, and turpentine substitutes have been recorded by Holde and Lunge; and Engler–Höfer's work on petroleum gives the coefficients of refraction of various hydrocarbons and individual fractions of various origin.

Apart from Dieterich's work already alluded to, however, the literature is lacking in any particulars on the examination of motor spirit (benzine or benzol). That worker examined a number of samples and found considerable divergence in the coefficients of refraction of different kinds of benzine, the values ranging from n_D 1·37027 to 1·42857 at 15° C. Similar differences have been observed by the present author.

Since pentane and hexane have a low coefficient of refraction, whilst the higher hydrocarbons, such as heptane, octane, the olefines, etc., have a high index (at 14·8° C., that of hexane is 1·3780; octane, at 15·1° C., 1·4007; decane, at 14·9° C., 1·4108), it follows that light benzines, containing a larger proportion of pentane and hexane, will have a low refraction index; whereas the heavy benzines, containing larger amounts of higher hydrocarbons, will have a higher index. Consequently, this property may be utilised to advantage in the preliminary examination of benzines.

Technical benzols have, at 15° C., a coefficient of refraction of 1·49954 to 1·51069, according to the proportions of toluol and xylol present. At the same temperature, the refractive index of technical benzols is 1·5150; that of toluol being 1·4962, and xylol 1·4915 (orthoxylol, 1·5064; metaxylol, 1·5007; paraxylol, 1·4969).

The high refractive index of benzol enables it not only to be differentiated from benzine, but also, in some cases, to be detected therein.

For example, if a benzine with the refractive index 1·3964 be mixed with different quantities of benzol, the index will be increased as follows :—

5 per cent. of benzol to				.	.	.	1·4014
10	,,	,,	,,	.	.	.	1·4063
15	,,	,,	,,	.	.	.	1·4110
20	,,	,,	,,	.	.	.	1·4161

This instance shows that the index of refraction alone is not always sufficient to detect an addition of benzol, since it is only when the index rises above 1·430 that the purity of the benzine can be suspected.

If, however, an unusually high index of refraction is found, further examination must be undertaken to see whether the cause is really benzol or some other substance, such as petroleum or carbon disulphide, the last-named having a very high coefficient of refraction.

The naphthalene occasionally present in impure benzol increases the index of refraction, as may be seen from the following data relating to a benzol with the index 1·6017 at 15° C.

0·5 per cent. of naphthalene increased the reading to					.	1·6024
1·0 ,,	,,	,,	,,	,,	.	1·5031
2·0 ,,	,,	,,	,,	,,	.	1·5041

The appended list gives the coefficients of refraction, at 15° C., of a number of substances which may be present in benzine, benzol, or benzine substitutes :—

Methyl alcohol	. . 1·3302	Ordinary petroleum. .	1·4591
Sulphuric ether	. . 1·3570	Crude petroleum (semi-	
Acetone	. 1·3608	product) . . .	. 1·4659
Ethyl alcohol, 99% .	. 1·3630	German turpentine . .	1·4611
,, ,, 96% .	. 1·3641	French ,, . .	1·4695
,, ,, 90% .	. 1·3660	Swedish ,, . .	1·4738
Amyl alcohol . . .	1·4070	Carbon disulphide . .	1·6295
Pure petroleum (" Kaiser " oil)	. 1·4466		

The refractive indices of individual benzine fractions are given in the table on p. 57, from which it can be seen that the index increases with the boiling point and density.

FLASH POINT AND BURNING POINT

If benzine be gradually warmed from a very low temperature, in a closed vessel, it vaporises, a mixture of vapour and air being formed above the surface of the liquid. At a certain temperature the vapour tension of the benzine is so high that, in contact with a small flame, the mixture of air and vapour ignites with a slight detonation, the flame being extinguished immediately. The temperature at which this occurs is known as the flash point, or, according to Strache,[1] the lower flash point.

On the benzine being warmed still further, an explosive mixture is again formed, the explosibility at first increasing to a maximum and thereafter receding in proportion as the quantity of benzine vapour increases and that of the air in the mixture diminishes; until finally, at a certain temperature, the mixture will ignite without exploding, there being too much benzine and too little air present. The same condition occurs at all higher temperatures.

[1] *Zeitschrift des Oesterr. Ingenieur und Architekten-Vereines*, 1915, Nos. 52 and 53.

The point at which the mixture ceases to explode on ignition is termed by Strache upper flash point; whilst the point at which the mixture will ignite (without exploding) and continue to burn is known as the burning point.

Both the flash point and burning point are determined by means of the Abel-Pensky petroleum tester. In determining the flash point the inner vessel of the apparatus, filled with benzine, is immersed in a mixture of solid carbon dioxide and alcohol, and is thus cooled to about − 50° C. This being done, the vessel is taken out of the freezing mixture and wrapped in a cloth. The temperature now gradually rises, and the benzine is tested, in the same way as petroleum, until the small igniting flame, tilted downwards into the vessel by means of clockwork, just ignites the inflammable mixture above the surface of the benzine, the resulting flame giving a slight detonation and going out at once. The temperature at which this occurs is the (lower limit of) flash point.

The lid of the tester is then taken off, and the thermometer is secured in the apparatus by a clamp. The benzine continues to become warmer until a point is reached at which the benzine ignites on contact with the flame and continues to burn. This is the burning point.

The upper limit of flash point is ascertained by placing benzine at room temperature in the Abel-Pensky tester and cooling it by degrees until the mixture of air and vapour just reaches the explosive limit, which is recognised by a slight detonation on the application of the test flame.

There is no need to describe the use of the Abel-Pensky tester, since full instructions are issued with the apparatus.

The upper limit of flash point does not coincide exactly with the burning point, because the former is determined by gradually cooling the benzine and is therefore liable to fluctuation; but in any case the two points are close together.

What has been said with regard to benzine also applies to benzol.

Solidification, Setting, and Turbidity Points

The determination of the solidification or freezing point is particularly important in the case of benzols, because they solidify above zero C., and therefore may give rise to trouble if used as motor fuel in winter.

The different grades of benzine freeze only at much

lower temperatures; but nevertheless the determination of the freezing point is also of interest and may help as a preliminary indication of quality.

In the case of benzol, about 5 c.c. of the sample are placed in a test glass, which is equipped with a suitable thermometer and plunged into a vessel of pounded ice or a suitable cooling mixture, such as ice and common salt (see Solidification Point of Lubricating Oils). The liquid is slowly stirred with the thermometer, to prevent super-cooling; and as soon as the liquid has changed to a solid, white, crystalline mass, the solidification point is read off on the thermometer.

Since commercial benzols contain toluol and xylols which freeze considerably below zero C.—whereas the benzol itself solidifies above that temperature—the latter solidifies first; and for this reason the point at which the *entire mass* freezes is taken as the solidification point.

The test is performed in the same manner with benzine, liquid air being used as the refrigerant. For this purpose the liquid air is syphoned into a transparent Dewar flask, so that the progress of solidification can be observed. The test glass is lowered slowly into the liquid air and is lifted out at intervals in order to prevent too rapid cooling. Since mercury freezes at $-39°$ C., a pentane thermometer must be used, this liquid requiring a temperature below $-200°$ C. for congelation. The test liquid is kept stirred with the thermometer until the latter is prevented from moving by the crystalline mass of solidified benzine, where-upon the solidification point is read off.

Pure benzol solidifies at $5.5°$ C., but motor benzol, which contains varying amounts of toluol and xylol, is the more difficult to freeze in proportion as these are present in larger quantities. Thus, for example, 90 per cent. benzol, which contains about 80–90 per cent. of benzol, freezes at $1.5-3°$ C., whilst 50 per cent. benzol (40–50 per cent. of benzol) does not solidify until about $-10°$ to $-20°$ C.

Pure toluol solidifies at $-88°$ C.; paraxylol at $13°$ C.; metaxylol at $-54°$ C.; orthoxylol at $-28°$ C.; but technical xylol, which is a mixture of the last three compounds (70–85 per cent. of metaxylol) solidifies only at $-115°$ C. This is an interesting example of a mixture having a far lower solidification point than any of its components.

The solidification points of various commercial benzols are given in Table IV.

No precise details of the solidification point of the benzines is to be found in the literature, Holde, for example, merely assuming that a benzine of sp. gr. 0·65–0·67 solidifies below − 160° C.

The author has made numerous determinations of the solidification point of various benzines and benzine fractions, the results of which, in the case of Galician benzine, are given in the Table on p. 57.

It will be seen that the fraction 200–220° C. freezes at − 93° C., and the fraction 24–40° C. at − 203° C. It is therefore evident that the solidification point falls with the density and boiling point and therefore depends on the composition of the benzine. The higher the boiling points of the components the earlier congelation sets in, and vice versa.

The solidification points of various benzines are given in Table III.

The distillate obtained next in succession to benzine, from pure crude petroleum free from paraffin, solidifies between about − 70° C. and − 90° C.; and the still higher (paraffin-free) distillates between about zero and − 25° C.

To obtain accurate readings, the thermometer is observed as cooling progresses; and it will be found that the temperature either remains constant at a certain point for some time, or even rises a little, after which a fall is again recorded. This stationary or recalescence point is the true solidification point. In performing these determinations a correction must be made for the temperature of that portion of the mercury filament that projects above the liquid (see pp. 52 and 126).

In addition to the solidification point, benzol, petroleum, and lubricating oils are often tested for their setting and turbidity points.

The setting point is that temperature at which the test liquid, contained, to a depth of about 3 cm., in a test tube 20 mm. wide (inside) immersed in a cooling liquid, will no longer flow when the tube is taken out and tilted. The turbidity point is the temperature at which the liquid becomes cloudy in cooling.

At solidification point the liquid is completely solid, whereas at setting point it forms a thick pulp from the deposition of solid particles. The setting point and turbidity point are also influenced by the composition of the oils the various components of which separate out at

different temperatures. Thus, for example, the turbidity point of a crude petroleum containing paraffin was — 12° C.; the setting point —25° C., and the solidification point —55° C.

The following list of solidification points of various substances, some of which are used as fuel or as adjuncts thereto, is given for comparison :—

	° C.		° C.
Ethyl alcohol, 90% [1] .	— 108	Acetone	— 88
,, ,, 97% .	— 118	Petroleum [2] (crude distil-	
Methyl alcohol (technical)	— 89	late, containing paraffin)	— 58
Sulphuric ether (technical)	— 122	Petroleum (refined, no par-	
Carbon disulphide . .	— 89	affin)	— 85

CALORIFIC VALUE

The calorific value of the various benzines is only determined in special cases, since it varies within very narrow limits (11160–11225 cal.). In the case of mixed fuels, however, this determination is necessary.

The calorific value can be calculated, from the ultimate analysis, by the Dulong formula :—

$$H_n = \frac{8100C + 29000(H - \frac{O}{8}) + 2500S - 600W}{100}$$

referred to water vapour at 20° C.; but this formula gives incorrect values for liquid fuels, and therefore the calorimetric method is employed, the Junkers calorimeter or Berthelot–Mahler bomb being used.

With the Junkers calorimeter, a weighed quantity of benzine is vaporised in a simple gasifier, and is completely burned in a lamp situated in a specially constructed vessel traversed by a flow of water. The products of combustion give up the whole of their heat to the water; and by measuring the volume and increased temperature of the water that has passed through the calorimeter during the combustion of the benzine, the calorific value is found by the formula : $H = \frac{v}{b} t \, 1000$, in which H is the calorific value of 1 kg. of the fuel, v is the volume of water collected (litres), b the weight (grms.) of fuel consumed, and t the difference in temperature.

[1] Pure, 99 per cent. ethyl alcohol solidifies at — 130° C.
[2] Pure, paraffin-free petroleum (Kaiser oil) solidifies at — 90° C.

The results obtained in this way represent the higher (gross) calorific power, referred to liquid water as the final product of the combustion of hydrogen. Since, however, in combustion in motors, the water vapour is not condensed, deduction has to be made of the 600 cal. (per kg. of water) that would be liberated on condensation, in order to obtain the lower (nett) calorific power. The volume of water of combustion is determined by collecting this water in a small measuring vessel, multiplying the number of cubic centimetres by 60 and subtracting the product from the gross calorific value.

The Junkers calorimeter is suitable for all fuels that volatilise completely up to 250° C.; but for others the Berthelot–Mahler bomb must be used.

According to the Berthelot-Mahler method, the weighed quantity of benzine is introduced into a steel combustion vessel, or bomb, which, after being screwed down air-tight, is filled with oxygen under a pressure of 25 atmospheres. The bomb is then submerged in a specially arranged water tank, and the fuel charge is ignited by an incandescent electric wire. The heat of combustion is transmitted to the water, and is calculated from the rise in temperature and the weight of the water, certain corrections being made.

The calorific value determined in this manner is also the gross value; and, in order to obtain the nett value, deduction must be made of the amount of heat in the water formed during the test (see above), the quantity of this water being ascertained from the ultimate analysis of the fuel.

The Junkers calorimeter is the simpler to handle, and since it gives accurate results, has found extensive application in practice.

Vapour Tension

Vapour tension is the increase of pressure occurring in the dry air contained in a vessel when a liquid is evaporated therein.

The determination of vapour tension is important in the storage of benzine and benzol. For this purpose a standardised glass tube, about 15 mm. wide and 90–100 cm. long, closed at one end and graduated in millemetres, is carefully filled with mercury (freed from air by boiling), the open end of the tube being then closed by a finger and the tube arranged vertically in a trough of mercury. Any

bubbles of air adhering to the glass sides must be carefully expelled, by tilting and raising the tube before erection.

When the tube is upright, a barometric vacuum is formed, the height of the column of mercury (h) being then measured.

To carry out the test, a definite quantity of benzine or benzol is admitted into the mercury tube, from below, out of a completely filled thin tube provided with a glass stopper, the mercury tube being, meanwhile, tilted so that it is completely filled with mercury—otherwise it might be broken by the force of the upwardly projected particles of the metal.

In the vacuum the benzine vaporises, and the vapours depress the column of mercury. After standing for two to three hours, according as the benzine is light or heavy, the height of the mercury is read off (h'). Some unevaporated benzine should remain above the mercury in order to reproduce storage conditions, in which liquid and vapour are present together in the tank, etc.

The vapour tension is equal to the difference between h and h', less the correction due to the pressure of the liquid benzine present (this value being expressed by its equivalent in mercury).

Thus the true vapour tension, expressed in millimetres on the mercury scale, is

$$H = h - \left(\frac{h' + h2 \cdot s}{13 \cdot 6}\right)$$

wherein $h2$ is the height of the unvaporised benzine, and s its sp. gr.

The vapour tension *in vacuo* thus determined is the same as in air, since, according to Dalton's law, each gas component in a mixture exerts the same pressure as if it were present by itself in the given space.

The storage temperature of benzine being between zero and 15° C., there is no need to take the vapour tension of the mercury into account.

The vapour tension increases considerably with the temperature, and the temperature of the experiment must therefore be carefully noted.

When the vapour tension of benzine at storage temperature has to be ascertained, the measuring tube is surrounded by a water-jacket of glass, through which water of the desired temperature is passed; or, when possible, the determination is made in the storage chamber itself.

Since benzine and technical benzol are mixtures of various hydrocarbons, their vapour tension at a given temperature will vary according to their composition (quality).

The tension of the saturated vapours is closely connected with the boiling point, the liquid boiling at the temperature at which the tension of its saturated vapours is equal to the external pressure. Thus, benzine, for example, always boils at the temperature at which the vapour tension is equal to the atmospheric pressure.

Explosive Mixtures of Benzine (Benzol) Vapours and Air

The liability to explosion of mixtures of benzine (benzol) vapours will be fully dealt with in the Technical Section.

The explosive character of such mixtures is tested in an explosion pipette, in which the mixture is ignited over mercury by means of an electric spark.

The mixture is prepared in varying proportions, by introducing a definite quantity of benzine or benzol into a gasholder of known capacity filled with air, and, after the liquid has completely evaporated, transferring the mixture to the explosion burette, where it is ignited.

By means of a series of experiments, conducted at the same or at definite temperatures, the relative proportions needed to form an explosive mixture have been ascertained. In order to obtain comparable results, the tests must always be performed under the same conditions, because, as will be seen later, the explosive limits depend on a number of circumstances, especially on the vapour tension which (and consequently the volume occupied by unit weight of benzine) differs with the quality of the substance.

Detection of Ethyl- and Methyl Alcohol, Sulphuric Ether, and Acetone in Fuel Mixtures

Benzine, benzol, and mixtures of the two may intentionally contain—in addition to petroleum—additions of spirit (aqueous alcohol), wood spirit (technical methyl alcohol), sulphuric ether, carbon disulphide, and technical acetone.

According to the purpose in view, the detection of these substances may be performed either on the fuel itself, or

preferably on the products passing over between 40–66°, 60–80°, and 80–100° C. during fractional distillation. If the object of the test is merely to reveal ethyl- and methyl alcohol and acetone, it is advisable to shake samples of the 60–100° fractions gently with a little water, separate the layer of benzine (benzol) and employ the aqueous extract (which will contain any of the above three substances that may be present in the distillate) for the test.

An increased sp. gr. of the distillate in comparison with that of the standard fractions (q.v.) indicates an addition of extraneous substances.

If the fuel contain carbon disulphide, this will come over in the fraction 40–66° C., its boiling point being 46° C. When the fuel or distillate is shaken up with water, the carbon disulphide, being insoluble therein, will remain in the benzine or benzol.

Since the sp. gr. of carbon disulphide at 15° C. is 1·271, it considerably increases the density of the 40–66° fraction. Reference may be made to the method already described (p. 66).

Any sulphuric ether that may be present will be chiefly found in the fraction up to 40° C., since it boils at 35° C. Its sp. gr. being 0·720 at 15° C., it also increases the density of that benzine fraction. Sulphuric ether can be recognised by its smell, but still better by agitating the sample with water, in which it partially dissolves, imparting its characteristic odour thereto. Sulphuric ether also gives the iodoform reaction described later.

Petroleum boils between about 150° and 300° C., and forms the final fraction on distillation. It betrays its presence by the high sp. gr. and its fluorescence.

Preliminary Test for Ethyl- and Methyl Alcohol

The dyestuff fluoresceine, or uranine (the sodium salt of resorcinphthalein), serves as a preliminary test, 5 c.c. of the fuel—which may also contain benzine, benzol, sulphuric ether, carbon disulphide, or acetone—being placed in a dry test glass and shaken up with a few milligrams of this dyestuff. If either ethyl- or methyl alcohol be present, the sample will quickly acquire an orange-yellow colour and a powerful green fluorescence. Any other dyestuff that is soluble in alcohol, but insoluble in the other substances, will also do, Ostwald, for instance, recommending Victoria

blue. Fluoresceine is, however, preferable because its fluorescence increases the delicacy of the test.

DETECTION OF ETHYL ALCOHOL

(1) *Iodoform Reaction.*—Three c.c. of the distillate—or preferably the aqueous extract therefrom—are treated with 3-5 c.c. of dilute caustic potash (1:20) until the reaction is strongly alkaline. The mixture is then gently warmed to 50-60° C., and a dilute solution of iodine (1 grm. of iodine in 50 c.c. water with 4 grms. of potassium iodide) is added, with moderate agitation, until the mixture is decidedly yellow, whereupon it is left to settle, an aqueous layer separating out. If ethyl alcohol be present, the bottom aqueous stratum will deposit yellow crystals of iodoform (with its characteristic smell), either at once or after a time. When the distillate itself is employed as test sample, it should not be shaken too strongly, since iodoform is soluble in benzine or benzol; though, even then, it can be recognised by its penetrating smell.

Acetaldehyde, sulphuric ether, acetic ether, acetone, etc., also give the iodoform reaction; and the same product will also be formed if technical methyl alcohol be present along with ethyl alcohol, since ordinary wood spirit is also contaminated with acetone and small quantities of aldehydes.

Consequently, the iodoform reaction is not a definite proof that ethyl alcohol is present, and the following confirmatory tests will be required.

(2) *Berthelot's Benzoyl Chloride Reaction.*—About 5 c.c. of the sample are treated with two drops of benzoyl chloride, shaken up, and, after a few minutes, treated with caustic potash solution (1 : 10) until strongly alkaline. In presence of ethyl alcohol, the pleasant odour of ethyl benzoate will become apparent. This odour, however, may be masked by the smell of benzol or other aromatic substances in the sample.

(3) *Acetaldehyde Test.*—This test consists in transforming the ethyl alcohol into acetaldehyde and identifying the latter. With this object, 1 c.c. of the test sample is treated with 1 c.c. of pure sulphuric acid, followed by the gradual addition of 20–25 c.c. of a 1 per cent. solution of permanganate of potash and a sufficient quantity of cold-saturated oxalic acid solution (and another 1 c.c. of sulphuric acid, if necessary) to decolorise any excess of permanganate.

The resulting acetaldehyde is then tested with Jean's reagent, 2 c.c. of the liquid being treated with a few drops of a freshly prepared 1 per cent. solution of sodium nitroprusside, a few drops of phenylhydrazine, and (drop by drop) 1 c.c. of 50 per cent. caustic soda solution. In presence of acetaldehyde the liquid acquires a red coloration.

Instead of using permanganate, the oxidation of the alcohol can be effected by the repeated immersion of a superficially oxidised glowing copper spiral in the test liquid. The advantage of this arrangement is that the test liquid is not contaminated with manganese salts, and that the oxidation is effected quickly.

DETECTION OF METHYL ALCOHOL

(1) *Formaldehyde Test.*—This test is based on the oxidation of methyl alcohol to formaldehyde, and identifying the latter.

Two c.c. of the distillate, or aqueous extract therefrom, are oxidised with a glowing copper spiral as just described. The formaldehyde formed when methyl alcohol is present, is detected by its characteristic penetrating smell. It may also be identified by treating five drops of the liquid with twenty drops of concentrated sulphuric acid and a few grains of morphine (Kenntman's reagent), or with a few drops of a fresh 5 per cent. solution of pyrogallol, in a porcelain dish. If methyl alcohol has been present, the morphine test will give, sooner or later, a violet to deep violet coloration; pyrogallol a chocolate-brown.

(2) *The Denigès Fuchsine Bisulphite Reaction.*—One c.c. of the test substance is mixed with 5–10 c.c. of a 1 per cent. solution of permanganate, with addition of 0·5–1 c.c. of pure, concentrated sulphuric acid. The oxidation will be complete in two to three minutes, whereupon any coloration due to surplus permanganate can be removed by 1 c.c. of sulphuric acid and cold-saturated oxalic acid solution. The decolorised liquid is treated with 5 c.c. of fuchsine bisulphite solution (1 per cent. aqueous solution of fuchsine decolorised with sodium bisulphite solution). In presence of methyl alcohol the liquid assumes a decided violet colour after about 15 minutes.

In this manner, methyl alcohol can be detected in presence of ethyl alcohol, since the acetaldehyde produced by the oxidation of ethyl alcohol does not give the red

colour reaction with fuchsine bisulphite in a strongly acid solution.

(3) *Resorcine Reaction.*—The test sample (about 3 c.c.) is oxidised with a glowing copper spiral, and the liquid is treated with one drop of a 0·5 per cent. solution of resorcine, concentrated sulphuric acid being then carefully introduced underneath.   In presence of methyl alcohol a rose-red zone is formed at the plane of contact (Mulliken Scudder, *Amer. Chem. Journ.*, Vol. XXI, p. 267).

(4) An indirect test for methyl alcohol is based on the presence of acetone in crude wood spirit, the fuel being tested for acetone as described later.   A negative result will justify the assumption that no crude wood spirit has been added to the fuel.

DETECTION OF ETHYL- AND METHYL ALCOHOL JOINTLY

(1) The test sample is oxidised by the copper spiral method, or the Denigès permanganate method, the excess of permanganate being eliminated with oxalic acid, and the resulting aldehydes being distilled over.

The first fraction will contain any acetaldehyde present, which gives a deep red coloration with Jean's reagent; whereas formaldehyde comes over later and gives a greyish-blue or greenish coloration with this reagent.

Since, however, acetone also gives a red colour reaction with sodium nitroprusside and caustic soda, this test cannot be employed for ethyl alcohol when acetone is present.

(2) The test liquid is oxidised by the copper spiral method, and when cold, a portion is treated with one drop of a fresh 10 per cent. solution of nitroprusside and one drop of piperidine solution.   In presence of ethyl alcohol a blue coloration is obtained.

The other portion of the sample is boiled for one minute, and when cold, is treated with one drop of carbolic acid, concentrated sulphuric acid being slowly poured down the side of the test glass.   When methyl alcohol has been present, a red ring is formed at the zone of contact (Gianbatista Franceschi).

DETECTION OF ACETONE

(1) One c.c. of the fraction 40–80° C., or the aqueous extract therefrom, is treated with an equal quantity of

caustic soda solution and six drops of fresh sodium nitro-prusside solution (1 : 50).   If acetone is present, a red coloration is produced; a violet being obtained after the alkaline liquid has been carefully supersaturated with acetic acid.

(2) Two c.c. of the distillate (or aqueous extract) are treated with a few drops of orthonitrobenzaldehyde and a little caustic soda.   With acetone the liquid is coloured by the resulting indigo blue (Baeyer's reaction).

CHAPTER VII

JUDGING THE QUALITY OF BENZINE AND BENZOL

In judging the quality of benzine and benzol, the following points should chiefly be borne in mind :—

Colour, smell, evaporation test on filter paper and on the watch glass, fractional distillation, neutrality, presence of sulphur compounds, behaviour towards indanthrene blue BT, content of aromatic and unsaturated hydrocarbons (and paraffin hydrocarbons in benzol).

Preliminary Tests.—Specific gravity, behaviour towards sulphuric acid, test for water content, coefficient of refraction, and setting point.

In connection with storage and use in motors, the flash point and explosion risk, vapour tension and calorific value, are also of importance.

EXTERNAL CHARACTERISTICS : COLOUR, SMELL, TEST ON FILTER PAPER

Pure benzine and benzol should be transparent, limpid, and colourless, and have a mild and not unpleasant smell.

With good refining, the smell of benzol should be agreeably aromatic ; but unrefined or badly refined benzol has a disagreeable, sharp smell, sometimes even empyreumatic.

A disagreeable smell indicates badly refined products, or an addition of substances that have not originated in petroleum or coal-tar.

In addition to oil of turpentine, the bad smell of benzine and benzol is sometimes masked with nitrobenzol, which, however, can be detected by its aroma of bitter almonds, especially when the benzine is rubbed on the open palm. Chemical tests for nitrobenzol will be mentioned in dealing with the testing of lubricating oils.

Benzine should not exhibit any fluorescence ; if it has a

blue sheen, this may be due to brown-coal products, or, in the case of mixed fuels, to petroleum.

The absence of fluorescence, however, is no proof that such products are not present, since, as already mentioned, the fluorescence can be masked by suitable means.

When poured on to filter paper, pure benzine or benzol should evaporate readily, leaving neither smell, residue nor grease-spot behind. Other properties being equal, the purity of benzine or benzol is in direct ratio to the rapidity with which it evaporates.

Heavy benzines or impure benzols leave a residue, or a greasy stain, of more or less unpleasant smell, which only disappears slowly if at all. Impure benzol sometimes leaves a scaly residue consisting of naphthalene, which can be recognised by its peculiar smell (see also the watch-glass test on p. 105).

SPECIFIC GRAVITY

The specific gravity serves for comparing different kinds of benzines and benzols, to ascertain whether a benzine (purchased, for example, *en route*) is light or heavy; and for referring weight to volume and vice versa.

As mentioned in the Introduction, benzines are classified, according to density, into light, medium, and heavy, which classification was adopted in Table III.

Dieterich classed as light benzine (Class A) all those of sp. gr. 0·650–0·700; as medium (Class B), those of sp. gr. 0·701–0·730, and as heavy (Class C), those of sp. gr. 0·731–0·760 and over.

On the basis of the composition of commercial benzines, as given in Tables I and III, it is, however, advisable to raise the upper limit of the medium benzines, and to group motor spirit into : light benzine, sp. gr. 0·680–0·700 (benzine of sp. gr. 0·650–0·680 is the so-called petroleum ether); medium benzine, sp. gr. 0·701–0·740, and heavy benzine, sp. gr. 0·741–0·770.

An exact delimitation of the benzines according to density is, nevertheless, impracticable and indeed useless, since the boiling points form the sole proper criterion. It may happen, for example, that a benzine which, on the basis of density, would be classified as medium, must be regarded, from its composition, as light, and vice versa. It would be better, as already mentioned, to classify benzines according to their coefficient of refraction (see p. 81).

Particular importance attaches to the determination of the sp. gr. of individual benzine fractions in connection with the examination of mixtures of benzine with other fuels.

If the resulting values do not coincide with those already given for the standard fractions, the presence of added substances may be concluded.

The most frequent additions to benzine are : benzol, alcohol, wood spirit, and acetone. Benzol has the sp. gr. 0·884 and boils at 80·5° C. ; 94 per cent. alcohol, sp. gr. 0·812, b. p. 79° C. ; wood spirit, sp. gr. 0·796, b.p. 66° C. ; acetone, sp. gr. 0·800, b.p. 56° C.

Since the sp. gr. of the standard fractions 40–60°, 60–80°, and 80–100° C., in which these substances may occur, does not exceed 0·735, whereas benzol, alcohol, wood spirit, and acetone are of considerably higher density, the sp. gr. determination of individual fractions affords a hint as to the presence of extraneous substances ; and if the results exceed 0·735 to any considerable extent, the character of the individual fractions must be established by chemical examination.

Commercial benzols are also judged by their sp. gr. Some of these marks have densities that are fixed by convention in accordance with the normal composition of the benzols (see p. 103). The determination of the sp. gr., however, also affords some indication of purity, for if the sp. gr. of a commercial benzol be found considerably lower than corresponds to its normal composition, the presence of an increased proportion of paraffin hydrocarbons may be suspected (see p. 80). In benzol I and II, a higher sp. gr. indicates carbon disulphide ; and in Nos. III–VI insufficient refining (see pp. 74 and 92).

Pure benzol has the sp. gr.			.	.	.	0·883–0·885
Toluol	,,	,,	,,	.	.	.	0·870–0·871
Xylol	,,	,,	,,	.	.	.	0·867–0·869

A table of the sp. gr. of commercial benzols and motor benzol is given on p. 103.

JUDGING AND CLASSIFYING BENZINES AND BENZOLS FROM THE DISTILLATION TEST

I. *Benzines*

As has been stated in connection with the treatment of petroleum, the benzines are chiefly differentiated into those used for : lighting and heating ; extraction and dissolving ;

cleaning; motor spirit; and finally substitutes for varnish and oil of turpentine.

Each kind of benzine requires to have definite properties in order that it may be perfectly adapted to its purpose. These properties are set forth below in connection with the various kinds.

(1) *Benzines for Lighting and Heating* (Ligroin, gasolene, miners' lamp spirit).—These vary according as they are for use in open or closed lamps. A benzine for lighting should not smoke in the lamp, and should therefore be refined, rectified, and free from benzol. The sp. gr. should be 0·660–0·729, and the constituents should all be volatile between 60° and 100° C.

Benzines from brown-coal tar or coal-tar are unsuitable, being very smoky.

Benzines for generating gas in laboratories, for soldering, gassing, etc., should also comply with the same conditions.

(2) *Benzines for Extraction or Dissolving* also differ according to the purpose they are to serve. For example, a benzine for the extraction of fats should volatilise between 90° and 100° C. (maximum 110° C.), or contain only small quantities volatilising outside these limits.

(3) *Benzine for Cleaning Fabrics, etc.*, should be free from fats and not have any unpleasant smell; and therefore must be refined and rectified. If used in open vessels it may contain fractions up to 150° C., the losses by evaporation being thereby reduced.

(4) *Motor Benzine* (*Petrol*). — There are about seven different kinds of motor spirit, ranging in sp. gr. from 0·680 to 0·760. The properties required differ according as the spirit is to be used for aeroplanes, motor-cars, or motor lorries, the sp. gr. for aircraft spirit being 0·680–0·700, and motor-car spirit 0·680–0·740; whilst heavy kinds—0·740–0·760 and over—are used for lorries and stationary engines, the cost being the decisive factor.

The above figures do not constitute any hard-and-fast limits, since both light and heavy benzines can be very well used for motor-cars.

Motor spirit can only be judged approximately from the density, the relative proportion of the component benzine fractions being the most reliable guide, for the reasons set forth below.

Reference to the details given in Tables I and II will show, in the first place, that commercial benzines contain

constituents with boiling points ranging from 24° to above 200° C. (the last-named, however, only in small quantity).

It will also be evident from the tables that the condition laid down in some text-books that motor spirit should not contain more than 5 per cent. of constituents boiling above 100° C., is not complied with by any light benzine, and even less so by medium benzines; notwithstanding which, all these, and even the heavy kinds, are quite suitable for motor fuel even in winter, provided the carburettor and engine be properly arranged (see Technical Section).

For these reasons, and on the basis of the numerous analyses that have been made of benzines, up to 10 per cent. of constituents boiling above 100° C. must be permitted for light benzines, with the proviso that not more than 6 per cent. boils at above 120° C.

Medium benzines may be allowed 30–40 per cent. of constituents boiling above 120° C., but not more than 10 per cent. boiling above 140° C., whilst heavy benzines should not contain more than 50 per cent. boiling above 140° C., and not more than 20 per cent. boiling above 160° C.

Dieterich has proposed that light benzine should contain not more than 10 per cent. boiling above 100° C., with 125° C. as the final boiling point, the figures being 30 per cent. and 140° C. for medium benzine, and 75–80 per cent. and 165–170° C. for heavy benzine. However, from the composition detailed in Tables I and II, such low end boiling points as these cannot be stipulated.

When the method of determining individual fractions is adopted, the estimation of the end boiling point is of no practical value, since even light benzines contain small quantities of still higher fractions. The actual quantity of such fractions is, however, a decisive factor, and therefore no final boiling points have been given in the tables.

The particulars in the tables also show the importance, in connection with judging the quality of motor spirit, of a knowledge of the relative proportions of the various fractions, and that a mere statement of the total quantities of constituents boiling up to and over 100° C. respectively is inadequate for this purpose, since samples of approximately equal densities and containing about the same total amount of fractions up to 100° C. may, nevertheless, contain very different proportions of intervening fractions.

Thus, for example, benzines No. 7 of Table I and No. 7 of Table II, are of nearly the same density (0·740 and 0·739),

and contain nearly the same percentage (35·8 and 35·3) of constituents up to 100° C.; notwithstanding which the individual fractions up to 100° C. differ considerably. Moreover No. 7, Table III, contains 20·4 per cent. of fractions above 140° C., as compared with only 7·2 per cent. in No. 7 of Table I, the latter, however, being much richer in the fraction 80–100° C., which, as will be explained in the Technical Section, is of importance as regards economical working.

If, now, these two benzines were judged solely according to their percentage of constituents boiling up to and above 100° C., they would be classed as about equal, whereas, on the above basis, No. 7, Table I, is decidedly better than No. 7, Table III. This judgment is confirmed by the more rapid evaporation (6½ hours) of the former, its lower solidification point (− 148° C.) and lower coefficient of refraction (1·4160) than No. 7 of Table III.

This example also shows that the density alone is an insufficient criterion of the quality of a benzine.

(5) *Varnish and Turpentine Substitutes.*—The benzines for these purposes should have a mild, pleasant smell and be good solvents of rosin; and they should not evaporate more quickly or slowly than oil of turpentine. If the evaporation is more rapid, the rosin will be insufficiently dissolved; and if more slowly, the resulting varnishes will only dry gradually and incompletely.

The limits of boiling point of these benzines should be about 150–180° C. (the limits for oil of turpentine are 155–175° C.), although some turpentine substitutes on the market furnish constituents between 90° and 240° C. on distillation.

Benzine to replace oil of turpentine should have a sp. gr. of about 0·780–0·785 at 15° C., although densities of as low as 0·760 are met with in commercial grades for this purpose. The flash point should be 24–28° C., and in any case be above 21° C.

Of late benzine has been replaced, for extraction and turpentine substitutes, by carbon tetrachloride (CCl_4) or trichlorethylene (C_2HCl_3), which, though not inflammable, are poisonous and corrode metals.

II. *Benzols*

Commercial benzols are principally judged by the quantity distilling over up to 100° C., and by their density.

On this basis the following classification has been established :—

Works Nomenclature.	Commercial Name.	Limits of Boiling Pt.			Sp. gr. 15° C.
Com. benzol I	90% benzol	up to 100°,	90%		0·880–0·883
,, ,, II	50% ,,	,, 100°,	50		0·875–0·877
,, ,, III	0% ,,	,, 100°,	0		0·870–0·872
,, ,, IV	—	,, 130°,	30		0·872–0·876
,, ,, V	Solvent naphtha I	,, 130°,	0		0·874–0·880
,, ,, VI	,, ,, II	,, 145°,	0		0·880–0·910
,, heavy benzol	Heavy benzol	,, 160°,	0		0·920–0·945
Pure benzol	80–81 benzol	95% boilg. within 0·8°			0·883–0·885
Benzol free from thiophene	—	,, ,, ,,			0·883–0·885

In addition to the above commercial brands, there is a so-called 30 per cent. benzol.

Commercial 90 per cent. benzol (I) implies a benzol of which at least 90 per cent. distils over up to 100° C., at 760 mm. pressure, the usual yield being 90–93 per cent. In the case of 50 per cent. and 30 per cent. benzol, the corresponding amounts of distillate are obtained up to 100° C.

The benzol marked 0 consists entirely of toluol and xylols,[1] and has no constituents boiling below 100° C. Solvent naphtha is the term also applied to the fractions passing over between 120° and 170° C. The 50 per cent., 30 per cent., and 0 benzols have been off the market for some time, and are only supplied to order.

Another method of judging benzol is by distilling 90 c.c. from a sample of 100 c.c. and determining the limits of boiling point.

The commercial benzols are also characterised by the limits of distillation temperature of 90 per cent. of the liquid, and by the density of the whole sample (see preceding table). Thus 90 per cent. of the total volume is distilled over from :—

Commercial benzol	I	between	80°	and	100°	C.
,,	,,	II	,,	85	,,	120	,,
,,	,,	III	,,	100	,,	120	,,
,,	,,	IV	,,	120	,,	145	,,
,,	,,	V	,,	130	,,	160	,,
,,	,,	VI	,,	145	,,	175	,,
Heavy commercial benzol		,,	160	,,	190	,,

Though this simple classification is sufficient for ordinary purposes, in some cases, e.g. disputes, it is necessary to

[1] Technical xylol contains 70–75 per cent. of metaxylol, 20–25 per cent. of paraxylol, and 10–15 per cent. of orthoxylol, according to the origin of the raw material.

know the quantitative proportions of benzol, toluol, and xylols, which must be ascertained by fractional distillation.

Under this treatment normal commercial benzols furnish the following average figures :—

	90%	50%	Pure.
		Benzol.	
First runnings (up to 79° C.) .	1·0	0·3	0·5
Benzol (79–85° C.) . . .	78·8	18·3	(79–81° C.) 98·0
Intermediate fraction (85–105° C.)	10·0	47·5	
Toluol (105–115° C.) . . .	8·0	23·7	Final runnings 1·2
Xylol	2·0	10·0	
Loss	0·2	0·1	Loss 0·3

Krämer and Spilker give the following composition for the commercial benzols :—

90% benzol	84 benzol	13 toluol	3 xylols
50% ,,	43 ,,	46 ,,	11 ,,
0% ,,	15 ,,	75 ,,	10 ,,

These figures may vary to some extent, being merely approximate values depending on the character of the tar from which the benzol is recovered.

Since toluol is of lower sp. gr. (0·870) than benzol (0·884), the commercial benzols II, III, and IV are lighter than No. 1.

It is quite possible to prepare mixtures of benzol, toluol, and xylol which apparently comply with the test figures and still are not of the proper composition.

Thus, for instance, 90–93 per cent. of the following mixtures will boil up to 100° C. :—

Benzol 82 per cent., toluol 18 per cent.
Benzol 90 per cent., toluol 5 per cent., xylol 5 per cent.
Benzol 82 per cent., toluol 15 per cent., xylol 3 per cent.

The last one, however, alone corresponds to normal commercial benzol I.

Since benzol, toluol, and xylol differ in price, it is a matter of some importance to know which of them is present in a commercial benzol; and from the table already given (p. 62), it can be seen that commercial benzols vary in composition, some 50 per cent. benzols containing less than 50 per cent., whilst some 30 per cent. benzols contain very little.

For motor-car purposes the most important is 90 per cent. benzol, which is sold as motor-car benzol and should contain about 80–94 per cent. of benzol. However, as this grade solidifies in the neighbourhood of zero C., the benzols employed for winter use are higher in toluol and xylols,

e. g. 50 per cent. benzol, or mixtures of benzol and benzine (see Technical Section).

Watch Glass Evaporation Test

The quicker and more uniformly a fuel evaporates, and the smaller the residue it leaves, the better.

Dieterich gives the time required for the spontaneous evaporation of light and medium benzine as up to $2\frac{1}{2}$ hours; good heavy benzine maximum 4 hours. According to this authority, 90 per cent. benzol evaporates in $3\frac{1}{2}$ hours, heavy benzol in over 4 hours.

Light benzines evaporate quickly and leave no residue; medium benzines more slowly (and sometimes irregularly), with a small residue that volatilises with difficulty; heavy benzines evaporate slowly, leaving an oily residue that volatilises with great difficulty.

The relative evaporation of the various classes of benzine are given in Table III, according to which light benzine takes about $1\frac{1}{2}$ hours, medium benzine $1\frac{1}{2}$–7 hours, and heavy benzine about 6–15 hours. With accelerated evaporation light benzines take up to about 1 hour, medium 1–4 hours, and heavy kinds about 4–10 hours. Ninety per cent. benzol takes about 4–6 hours, and 50 per cent. benzol over 6 hours, these times being shortened, in accelerated evaporation, to 3–4 hours and over 4 hours respectively. Mixtures of benzol and alcohol naturally take longer, the latter evaporating at a slower rate.

Neutrality

Pure benzines always have a neutral reaction, as have also the benzols; and it is only in exceptional cases that heavy benzines are slightly acid. An acid reaction is attributable to imperfect refining.

Mixtures of benzol and alcohol may occasionally have an alkaline reaction, owing to the alkaline nature of the agents (pyridine bases) used for denaturing the spirit.

The presence of crude acetone (acetic alcohol) in a fuel may impart an acid reaction, because acetone not infrequently contains small quantities of free acetic acid.

Behaviour to Sulphuric Acid

A refined benzine that is completely volatile below 150° C. should not impart any coloration to sulphuric acid (50° B.);

but this requirement cannot be completely satisfied in the case of motor spirit (petrol), and it is therefore necessary to tolerate a pale yellow coloration of the acid in the case of light benzine, pale brown with medium, and brown with heavy benzines. Like all other tests for the degree of refining, the sulphuric acid test gives no definite information, since many unrefined, but rectified, benzines leave the acid nearly colourless, whilst, conversely, even light, refined benzines may give a coloration.

The accompanying table gives the degree of coloration furnished by a number of refined and unrefined benzines in the sulphuric acid test.

Benzine No.	1	2	3	4	5	6	7	8
Sp. gr. . . .	0·671	0·681	0·693	0·705	0·730	0·748	0·755	0·756
Refining . .	unref.	refined.	refined.	refined.	refined.	unref.	unref.	refined.
Sulphuric acid .	almost colourless.	pale yellow	pale yellow	light yellowish.	light yellowish.	light yellowish.	light yellowish.	pale yellow.
Aromatic and unsaturated hydrocarbons	1·9	6·0	5·5	4·0	6·8	0·8	11·3	11·6

In the case of 90 per cent., 50 per cent., and motor benzol, the coloration of the sulphuric acid should not be darker than that of a solution of 0·05–0·15 grm. of bichromate of potash in 100 c.c. of 50 per cent. sulphuric acid (see p. 65).

Pure benzol and pure toluol should not colour the acid at all. In the case of xylol, the coloration may correspond to that of a 0·2 per cent. solution of bichromate.

Mixtures of benzol and fuel alcohol or wood spirit always stain sulphuric acid a strong yellow to yellow-brown, due to impurities in the two spirits. Crude acetone in the fuel gives a yellow to red-brown coloration. In such cases, of course, no conclusions can be drawn as to the purity of the benzol.

SULPHUR COMPOUNDS

Light benzines should not give any colour reaction with an ammoniacal solution of silver nitrate; medium benzines merely a weak brownish tinge; whilst heavy benzines may give a brown to black turbidity.

Pure benzine contains only very small fractions of 1 per cent. of sulphur as sulphur compounds. The benzines from brown-coal tar usually give a turbidity with the above reagent; whilst commercial benzoles always give a black precipitate, being invariably accompanied by sulphur compounds, carbon disulphide, and thiophene (see Technical Section).

Benzol contains only a few tenths per cent. of sulphur as sulphur compounds, rarely amounting to 1 per cent. Ninety per cent. benzol usually contains 0·2–1·0 per cent., 50 per cent. benzol 0–0·5 per cent. of carbon disulphide. Commercial benzols III–VI are free from this latter compound.

AROMATIC HYDROCARBONS (ESPECIALLY BENZOL) AND UNSATURATED HYDROCARBONS

Commercial motor benzines, even when refined, contain varying proportions of benzol and other aromatic hydrocarbons.

The quantitative determination of these hydrocarbons may be preceded by a preliminary test with indanthrene dark blue BT, or indanthrene violet RT.

With indanthrene dark blue BT a pale pink tinge is permissible in the case of light benzines; up to pink with medium benzines, and even a red with heavy benzines (with an increasing content of aromatic hydrocarbons). Table III gives a comparison of the colorations produced by dracorubine, and blue BT with various benzines, together with the content of aromatic hydrocarbons in the latter.

The permissible percentages of aromatic and unsaturated hydrocarbons are : light benzines, up to 6 per cent. ; medium benzines, up to 15 per cent. ; heavy benzines, maximum 20 per cent.

UNSATURATED COMPOUNDS IN BENZINE AND BENZOL

Pure benzine, freed from unsaturated compounds, has a bromine value of about 0·5; that of properly refined commercial grades being, in general, 5–10, and that of impure, unrefined or imperfectly refined samples 20 or more.

For 90 per cent. and 50 per cent. benzols, the bromine value is 8, rarely attaining 14; but with imperfectly refined samples it may reach 50.

Pure benzol and pure toluol will give a colour reaction with

as little as $\frac{1}{10}$th c.c. of potassium bromide–bromate solution or permanganate solution, the coloration persisting for some time.

Commercial xylols will consume, within a few minutes, about 2·5 c.c. of the bromide–bromate solution, and considerably more after a time.

Paraffin Hydrocarbons in Benzol

Ninety per cent., 50 per cent., and 0 benzols contain only a few tenths per cent., maximum 1 per cent., of paraffins. Toluol as a rule contains none, but xylol not infrequently has up to 3 per cent. of paraffin hydrocarbons.

Coefficient of Refraction

The coefficient of refraction of light benzines at 15° C. is approximately 1·3700–1·4000; medium benzines, 1·4001–1·4200; heavy benzines, about 1·4201–1·5110 (see Table III); motor benzols, 1·4990–1·5110 (see Table IV). On this account benzine can be easily distinguished from benzol, though the presence of benzol in benzine is not always revealed by this coefficient. Nevertheless, the determination of the coefficient of refraction is occasionally of good service in the analysis of mixtures.

For example, a mixture of 2 parts benzol and 1 part alcohol will have a coefficient of refraction 1·4601 at 15° C.; whereas that of " benzolin," a benzine substitute compounded of alcohol, benzol, and carbon disulphide has the considerably higher coefficient 1·4781.

" Etol," another benzine substitute—a mixture of 25 parts petroleum, 50 parts alcohol, and 25 parts ether—whilst having a refraction index of 1·3865, was betrayed by its high sp. gr., 0·787, showing it to be at least not a benzine adapted to serve normally as a motor fuel.

Although the determination of the coefficient of refraction does not, in itself, afford a clear idea of the actual worth of the sample, it nevertheless forms one of the preliminary tests for determining the quality of different benzines.

If, for example, the benzines 1 and 2 in Table III be compared, one might assume, from their relative densities, that No. 1 is the better quality; but the coefficient of refraction shows the contrary, and is lower in No. 2 because this

latter contains double the quantity of fractions boiling between 60° and 80° C.

A similar instance occurs in the case of No. 7 (sp. gr. 0·739, refraction index 1·4187) and No. 8 in the same table (sp. gr. 0·742, refraction index 1·4173), and No. 7 of Table 1, which gave, on examination, the density 0·740 and the refraction index 1·4160 at 15° C.

In No. 7 of Table III and No. 7 of Table I, the density and the percentage volume of distillates up to 100° C. are almost identical (35·3 and 35·8 per cent.), only the co-efficients of refraction being different. This difference is explained by the relative amounts of the different fractions in the two benzines : No. 7 of Table I consisting almost entirely of middle fractions (80–140° C.), whereas No. 7 of Table III contains all the fractions, and especially a large proportion of constituents boiling above 140°.

Consequently No. 7 of Table I is decidedly preferable to No. 7 of Table III, although both were sold as medium.

The low coefficient of refraction of No. 8 of Table III is explained by the fact that this benzine contains 14·5 per cent. more than No. 7 of fractions passing over between 80° and 100° C., and has also a smaller proportion of constituents of higher boiling point.

The determination of the coefficient of refraction is of particular importance when it is desired to ascertain, without carrying out a fractional distillation, which of several samples of benzine of approximately equal density is distinguished by a particular quality, for example, a high proportion of the most volatile fractions. Nevertheless, in order to furnish an accurate judgment, the distillation test is indispensable.

Flash Point and Ignition (Burning) Point

According to Strach, the lower flash point of light and medium benzines lies between about −30° and −20° C., and the upper between about −5° and 10° C. The figures are higher for heavy benzines ; and the flash point of benzol and toluol is below 21° C.

Generally speaking, a rise in the density and boiling point of benzine corresponds to higher upper and lower flash points ; but, since the flash point depends very largely on the content of dissolved gases (methane, ethane, propane,

butane), some benzines of relatively high density may nevertheless have a low upper flash point.

The determination of the flash point is an important matter both for the motorist and in connection with the safe storage of benzine and benzol. This question is treated in the chapters on Benzine and Storage.

The ignition (burning) point of benzine and benzol, on the other hand, is less frequently tested.

SOLIDIFICATION POINT

The solidification point of motor benzines depends on their composition. The lighter the benzine, the lower the solidification point; for example, about $-135°$ to $-170°$ C. for light benzines, about $-125°$ to $-150°$ C. for medium grades, and about $-95°$ to $-120°$ C. for heavy benzines (see Table III).

The solidification point of commercial benzols varies with the toluol and xylol content; that is to say, the higher the proportion of these constituents, the lower the solidification point, 90 per cent. commercial and motor benzols solidifying between 3° and 1° C., whilst benzols containing toluol and xylol solidify at about $-10°$ to $-25°$ C., or even lower (see Table IV).

CHAPTER VIII

MACHINE parts are nowadays lubricated almost exclusively with mineral oils, which, however, are occasionally mixed with vegetable fats or oils, or with tar oils, and more rarely with animal fats and oils or rosin oils.

For specific purposes use is made of either individual oil fractions or residues, or else of mixtures of these in order to obtain the desired properties such as viscosity, flash point, density, etc.

As already mentioned in the Chapter on Petroleum, mineral oils are hydrocarbons of the aliphatic series, whilst vegetable fats and oils are compounds of fatty acids with alcohols, *e. g.* compounds of palmitic, stearic, and oleic acids with glycerine. The animal fats and oils also belong to the same group; but rosin oils and tar oils are aromatic hydrocarbons.

Vegetable oils are obtained by pressing crushed vegetable seeds or fruits, or by extracting these with benzine, carbon disulphide, or chlorinated hydrocarbons. To this class belong : rape oil, linseed oil, olive oil, cottonseed oil, poppy oil, etc.

Animal fats are recovered by boiling or extracting fatty animal tissues, or these tissues are separated, by pressing, into oil and residue (*e. g.* press tallow). Bone oil, train oil, tallow, etc., are in this category.

Tar oils are prepared from coal-tar and brown-coal tar ; rosin oils by the dry distillation of rosins.

Oils and fats are used for lubricating machine parts in order to minimise the friction between two moving metal surfaces, *e. g.* between a bearing and a shaft or journal. The capacity of oils to reduce this friction is mainly dependent on their adhesion to metallic surfaces and on their cohesion.

The property of adhesion enables the minutest particles of the lubricant to stick, more or less, to the frictional

surfaces and to hold them apart, so that only the particles of oil, and not the metallic surfaces, slide over one another.

The greater the adhesion of an oil, the more effectual is the separation of the frictional surfaces and therefore the smaller the friction. The degree of adhesion also determines the resistance offered by the lubricant to the expulsive pressure exerted by the axle or piston, and therefore the extent to which the oil is forced out of the bearing or cylinder. The higher the adhesion, the thicker the layer of oil between the frictional surfaces, and therefore the smaller the friction between them.

Cohesion, or the mutual tenacity of the particles of oil, is expressed by the internal friction of the oil particles themselves : the lower the cohesion, the smaller this friction. The cohesion, too, influences the thickness of the layer of oil between the frictional metal surfaces.

In general, it may be said that the lubricating value of a lubricant is the greater in proportion as the adhesion is higher and the cohesion lower. Opinions on the causes of the higher or lower lubricating properties of the oils are not yet reconciled ; it has not yet been established with certainty whether the lubricating value depends on the internal friction alone or on other properties of the lubricant.

One thing, however, is certain, namely, that the effective value of a lubricant is affected by a variety of other factors, such as the speed of the revolving shaft, the pressure on the frictional surfaces, the material of the bearings, the character of the frictional surfaces, etc.

The viscosity of a lubricant is related to the aforesaid properties. It constitutes a specific property and may be defined as the resistance offered by the minute particles of the lubricant to relative sliding movement ; that is to say, the viscosity represents the internal friction of the lubricant. It is independent of the density of the oil, for light oils may have a higher viscosity than heavy oils ; but, like the density, it varies with temperature, diminishing as the latter rises.

Mineral oils for lubricating machine parts must possess certain physical and chemical properties, according to their intended purpose. On this account, in addition to the colour, transparency, consistence, and smell, the following characteristics are chiefly determined : viscosity, flash and burning points, solidification and melting points, neutrality (including acidity and alkalinity), asphaltum

and rosin content, tar and tarification values, or coke and coking values, content of rubber soap, and of vegetable and animal tar and rosin oils.

When desired, the following may also be determined : density, water content, ash constituents, impurities, paraffin, ceresine, and graphite, degree of refining, vaporisation, coefficients of expansion, refraction, and optical rotation (specific rotatory power).

The paraffin, or ceresine content is seldom needed; in fact only when the origin of the oil has to be ascertained, or in special cases of dispute.

Oils are also sometimes tested, for lubricating power, in testing machines which enable the coefficient of friction (*i. e.* the frictional resistance per unit pressure and speed) to be determined. Owing to the differences in the construction of these testers, however, the results obtained with one type of machine cannot be correlated to those of other machines, nor can they agree very closely with those obtained in practice.

Coefficient of Expansion

The coefficient of expansion expresses the fractional extent to which a given volume expands during a rise of 1° C. in temperature. It serves for reducing the densities determined at different temperatures to the standard temperature of 15° C. (see later), and also for ascertaining the increased volume occupied by an oil when heated, for example, during storage or transport. For instance, if an oil occupies a cubical space equivalent to 100 units at 15° C., and its coefficient of expansion is 0·0007 per 1° C., the space it occupies at 20° C. will be : $1000 + 5 \times 0·0007 \times 100 = 100·35$ units.

The coefficient of expansion varies inversely with the density; the higher the latter, the smaller the expansion. For thin oils, between 20° and 78° C., it amounts to 0·00072–0·00076, and for viscous oil to 0·00070–0·00072. In the case of mineral lubricating oils of equal viscosity but different origin, the coefficient of expansion differs with the chemical composition.

Specific Gravity

The determination of the specific gravity (density) is of minor importance in the case of lubricating oils, though it

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serves, in commerce, for comparing or identifying samples, or for classifying oils of known origin.

The determination is usually carried out with a special densimeter, or more accurately with the Mohr-Westphal balance or a pyknometer, in the same way as for benzine (*q. v.*).

The correction for reducing the sp. gr. to standard temperature (15° C.) is a mean value of 0·00068 per 1° C. for thin mineral lubricating oils, and 0·00075 for viscous or vaseline-type oils.
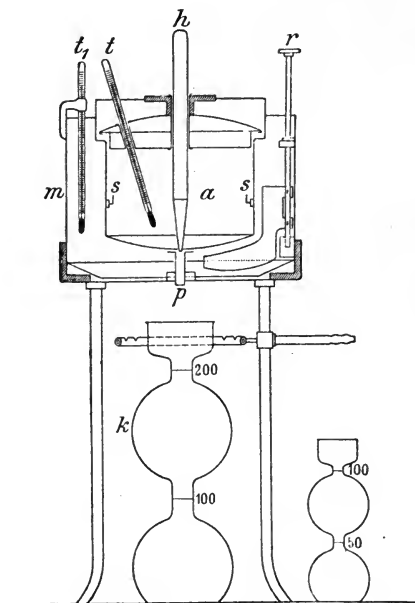

FIG. 9.

VISCOSITY

The viscosity is usually measured by the rate at which a liquid oil issues from a narrow tube, in a special apparatus known as a viscosimeter, or viscometer.

Although the values obtained in this manner do not correspond exactly to the internal friction of liquids, or bear any definite relation to the real viscosity of the oil, they nevertheless constitute conventional values which are comparable if obtained under identical conditions.

Various forms of apparatus are used for this purpose, that employed in Austria being the Holde or Ubellohde modification of the Engler viscosimeter. The chief difference consists in the heating arrangements, the Engler-Holde apparatus having a closed heating bath, and the Engler-Ubellohde apparatus, which is rather taller, an open bath.

The viscosity is determined by measuring the time required for a given quantity of the oil at a given temperature to issue from a vessel of known capacity through a narrow delivery tube, and comparing the result with the time taken by an equal quantity of water at 20° C. under the same conditions.

The viscosity being dependent on the temperature, the determination is usually performed at 20° or 50° C—sometimes at 100° C.—according to the use and viscosity of the oil under examination.

The Engler-Ubellohde viscosimeter (Fig. 9) consists essentially of a circular, gilt-lined metal vessel, a, provided at the bottom with a platinum tube or nozzle, p, which can be closed by a wooden pin, h. The vessel is fitted with a cover, through which is inserted a suitable thermometer, t, and is surrounded by a metal jacket, m, serving as a water bath to maintain a uniform temperature in the inner vessel. This bath is provided with a thermometer, t', and a stirrer, r. The shape and dimensions of the viscosimeter are prescribed by an official specification and must be rigidly adhered to.

Specification.			Tolerance ±
Internal diameter of vessel, a . . .		106 mm.	1·0 mm.
Height of cylindrical portion of a up to marks s		25 ,,	1·0 ,,
Distance of marks above lower orifice of nozzle, p		52 ,,	0·5 ,,
Capacity up to marks		240 c.c.	4·0 c.c.
Diameter of nozzle, p {top . . .		2·9 mm. }	0·02 mm.
{bottom . .		2·8 ,, }	
Length of p		20 mm.	0·1 ,,
Dimensions of external portion of p . length	3·0 ,,		0·3 ,,
extl. diameter	4·5 ,,		0·2 ,,

The inner vessel is so arranged that of the 240 c.c. of water it holds, 200 c.c. can escape within 50–52 seconds—otherwise the apparatus is unsuitable for the purpose in view.

In making the thermometers for use with the apparatus, the corrections for the projecting portion of the mercury column are taken into consideration, so that the corrected temperature can be read off direct. These thermometers must be officially standardised.

The measuring flasks may be standardised either according to delivery capacity or—as in the case of oil testing—charging capacity (dry flask).

In carrying out the determination, the viscosimeter is carefully washed out, first with sulphuric ether, then with ethyl alcohol, and finally with distilled water. It is next placed on a level plate, and the delivery nozzle is closed with a wooden pin, which can only be used for the water test and must be carefully cleaned. The inner vessel is filled with distilled water, at 20° C., to a little above the mark points, s, which serve on the one hand to indicate the 240-c.c. level, and on the other to show—when flush with the surface

of the liquid—that the apparatus is properly arranged. The outer vessel, serving as the water bath, is charged with water at 21° C.

The proper measuring vessel having been placed underneath the nozzle, the wooden pin is withdrawn and the water is allowed to run into the measuring vessel until it reaches the 200-c.c. mark, whereupon the nozzle tube—which is quite full of water—is re-closed by the pin.

The water in the flask is returned to the viscosimeter and allowed to drain for one minute ; and the pin is carefully eased so that a single drop of water appears at the orifice of the nozzle and remains in suspension there.

The water level is next adjusted accurately to the level of the marks by removing the surplus with a pipette ; whereupon the water temperature in the inner vessel is brought to exactly 20° C., and at the same time the flask k is placed underneath the nozzle so that the latter is concentric with the neck of the flask.

When the apparatus is ready for the test, the wooden pin is completely withdrawn (the surface of the water being undisturbed), and the number of seconds required for exactly 200 c.c. of water to flow from the vessel into the flask is determined by means of a chronograph (or a good watch).

This determination is repeated until the difference between three successive readings does not exceed 0·5 second and the values do not successively diminish.   When this result has been attained, the apparatus is cleaned, as already described, and the experiment is repeated for three more readings. If the results agree with those of the first series, they are taken as correct—otherwise a third series will be necessary. The mean of the last six readings is taken to the nearest half second.

In this manner, the water reading of the viscosimeter is ascertained, and need only be re-determined at intervals of about two months (not after each viscosity test).   If the apparatus has been properly constructed, the water reading should be 50–52 seconds.   For precise determinations the room temperature should be about 20° C.

The oil tests should be carried out in the same way as those for the water reading, the viscosimeter being first cleaned with a piece of filter paper, rinsed out with benzine, wiped out again with a soft, fine cloth, and the delivery nozzle cleaned out with a probe of filter paper.

If the oil under examination is dark or turbid, it is passed

through a sieve of 0·3 mm. mesh; and if thick, is first slightly warmed. Any water contained in the oil must be removed by agitation with calcium chloride and filtration. About 250 c.c. of the prepared oil are then transferred to a glass beaker and gradually warmed until the oil temperature reaches 20° C., the water bath being in the meantime filled with water at 20° C. and kept at that temperature.

A dry measuring flask, provided with a 200-c.c. mark, is placed exactly under the nozzle of the apparatus—which is closed by a different wooden pin from that used in the water test—and the warmed oil is poured into the inner vessel, as far as the marks, and is stirred with a glass rod, the cover being then put on the vessel.

In view of the expansion of the oil when heated, the precise adjustment of the oil level in the vessel should be deferred until the oil is approximately at the temperature of the experiment. This should be reached as quickly as possible, and thereupon the wooden pin is slightly eased to allow the delivery tube to fill with oil. The pin is then drawn out quickly and the time counting commenced, the reading being taken when the oil reaches the 200-c.c. mark in the flask.

During the test, the oil temperature is kept at exactly 20° C., by adding warm or cold water to the bath as required and keeping it well stirred. The water temperature must not vary by more than tenths of a degree.

The viscosity at 50° C. is determined in the same manner, the water bath, however, being heated either with a gas burner or electrically.

When, as is less frequently the case, the viscosity is measured at 100° C., a sufficient amount of glycerine—10–12 per cent. according to the atmospheric pressure—must be added to the water to enable a corrected bath temperature of 100·8–101° C. to be attained, so that the oil in the inner vessel may be at 100° C. For such determinations, a Holde apparatus, with enclosed bath, must be used, because, with an open bath, the delivery tube is liable to be overheated under these conditions.

If the oil is turbid from the presence of paraffin or pitch in suspension, the viscosity determinations at 20° C. are liable to considerable fluctuation arising from the circumstance that variations in temperature prior to the experiment may cause the particles of paraffin (which have melted at the higher temperatures) to be imperfectly separated by

a brief cooling—or, if the temperature drop has been large, the granules of paraffin will increase in size and therefore will not redissolve immediately on the temperature being raised again. With such oils the viscosity readings may vary by as much as 6—8 per cent. either way ; and for this reason it is advisable to repeat the test with another portion of the same oil that has previously been warmed to 100° C. for ten minutes ; and also with a portion of the sample that has been cooled to − 15° C. for an hour.

If, however, the viscosity of such an oil is measured at 50° C., this preliminary treatment is unnecessary, since at that temperature all the particles of paraffin or pitch will be dissolved or melted.

The viscosity of the oil under examination is expressed by dividing the time reading for the oil by the water reading of the apparatus at 20° C., the quotient forming the so-called Engler value, indicated by the suffix E. (thus 10° E. implies 10° Engler).

In the case of thick oils, the viscosity determination is a somewhat protracted operation ; and in many cases the available sample is too small for the full volume to be tested. When this is the case, smaller quantities may be measured, e. g. 50 or 100 c.c., a corresponding measuring flask being used. For thick oils, the vessel is charged with 240 c.c., but only 50 c.c. are collected for the reading. However, since the oil issues under a higher pressure at the start than prevails later, the times occupied for the issue of 20, 50, and 100 c.c. respectively bear no definite relation to that for 200 c.c., and the value for the latter must be calculated from the other readings. This is done by multiplying the reading for 20 c.c. of oil by 11·95 ; that for 50 c.c. by 5·02, and that for 100 c.c. by 2·352.

Ubellohde has compiled tables for the Engler viscosimeter from which the viscosities for 50, 100, and 200 c.c., for a water reading of 50–52 seconds, can be taken direct.

Where only a small sample of oil is at disposal, the whole is placed in the viscosimeter and a reading, at 20° C., is taken for an aliquot part, the result being referred to 200 c.c. by the aid of the following factors given by Gans for a given quantity of oil, e. g. 45 c.c.

Volume of oil in vis-									
cosimeter	.	.	25	45	45	50	50	60	120	c.c.
Volume discharged	.	10	20	25	20	40	50	100	,,
Factor	.	.	13	7·25	5·55	7·3	3·62	2·79	1·65	,,

According to Schulz,[1] those who do not possess an Engler apparatus can make approximate viscosity determinations, for technical purposes, by means of the following simple arrangement.   A 5-mm. glass tube 18–20 cm. long, drawn out at one end to a point about 1 mm. diameter, is provided with a temporary millimetre scale (gummed on) and carefully calibrated by charging it, up to a certain point, with oil of known viscosity (e. g. 5° E.) and at 20° C.   This oil is allowed to escape freely through the fine orifice at the point, and as soon as the flow breaks up into separate drops, the top of the tube is closed with the index finger, and the lower meniscus—the lower level of the concave surface—of the oil is read off on the scale.

According to the results of this preliminary test, the discharge orifice is restricted, by slight fusion, or enlarged, by rubbing on glass paper, so that the scale mark for the viscosity 5° E. is about 20 mm. from the orifice, this being ascertained by repeating the test.   In such case, the scale intervals for 1° E. will correspond to 3–5 mm.

Readings are taken, in the same manner, with 4–5 oils of different viscosities; and, on the basis of these results, a true viscosity scale can be plotted, this scale being mounted on the tube in place of the temporary scale.   With a tube equipped in this manner, the viscosity of oils between 5 and 30° E. (at 20° C.) can be measured to within 1° E. For those above 30° E. the apparatus is less suitable.

Of the numerous other types of viscosimeter that have been proposed, the most important are those of Redwood, Lamansky–Nobel, and Sayboldt.

The Redwood viscosimeter, which is used in England, is, in general, similar to the Engler apparatus, and gives readings for a discharge of 50 c.c. of oil.

The Lamansky–Nobel viscosimeter is chiefly employed in Russia.   Like the Engler apparatus, the readings express the time taken for the outflow of a definite volume of oil, but with the difference that means are provided for maintaining a constant pressure on the oil, which is an important advantage.

The quantity of oil used is 400 c.c., and the readings express the outflow of 100 c.c. of oil at 50° C. in comparison with that of the same volume of water at the same temperature.   Since the oil is under constant pressure, the value

[1] F. Schulz, *Chemiker Zeitung*, 1908, p. 891; A. Speedy, *loc. cit.*, 1917; *Chem.-Techn. Uebersicht*, p. 205.

for 100 c.c. of oil can be ascertained direct from the reading for any smaller quantity.

The relation between the Engler and Lamansky–Nobel viscosities is approximately the same, so that either can be calculated in terms of the other.

For thin oils the relation is : $\dfrac{\text{L--N}^\circ}{\text{E}^\circ} = 1\cdot13\text{--}1\cdot18$ and for thick oils $1\cdot20\text{--}1\cdot26$.

The Sayboldt viscosimeter is mainly used in the United States, and differs considerably from the Engler apparatus in construction. It consists principally of a brass tube, 3 cm. wide and 8 cm. long, having a capacity of about 66 c.c., the tapered lower end being closed by a pin. The tube is mounted in a water bath ; and the readings represent the time occupied for the outflow of 60 c.c. of oil.

The apparatus used in France is the Barbey ixometer, which, however, is employed to determine, not the viscosity, but the number of c.c. of oil flowing through the apparatus in ten minutes.

As already mentioned, the Engler apparatus does not reveal either the absolute internal friction [1] or the specific viscosity. Nevertheless, these characteristics can be calculated by the Ubellohde formula or determined in special apparatus, as described by Holde.

The Ubellohde formula [2] for the approximate calculation of the specific viscosity is : $Z = s\,(4\cdot072\,E - \dfrac{3\cdot514}{E})$, in which Z is the specific viscosity at any temperature referred to water as unity at zero C. ; s the sp. gr. of the oil at the temperature of the experiment ; E the Engler value of the oil referred to water at 20° C. as unity.

When the Engler value is greater than 10, the simplified formula : $Z = s \times 4\cdot072\,E$ can be used.

Since it is the practice, in preparing mineral oils, to mix different kinds in order to obtain a given viscosity, e. g. to suit the requirements of the consumer, it is desirable to be able to calculate the viscosity of such mixtures without

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[1] This property is expressed by the force μ required to displace a stratum of liquid with an area of 1 sq. cm. for a distance of 1 cm. over a layer of the same area at a velocity of 1 cm. per second. For water at 20° C., $\mu = 7\cdot010164$; but usually the water value is taken as unity and employed as the basis of comparison for other liquids, the result being the specific viscosity.

[2] *Chemiker Zeitung*, 1907, p. 38. Ubellohde has also compiled tables enabling the specific viscosity to be easily calculated.

having to make a fresh determination. This cannot, however, be done simply in accordance with the rule of mixtures, inasmuch as the experimental values always come out lower than the calculated values, and therefore a special formula must be employed.

Such formulæ have been drawn up by Pyhälä and Schulz; but, according to Molin, that of the former is not quite accurate, whilst that of Schulz is complicated and entails protracted calculations. Molin [1] has therefore compiled, from graphical data, a table which enables the viscosity of a mixture of two mineral oils of known viscosity in known proportions to be easily ascertained.

Table for Calculating the Viscosity of Oil Mixtures at 20° C.

1 Viscos ° E.	2 Vol. %	3 Diff. per 0·01° E.	1 Viscos. ° E.	2 Vol. %	3 Diff. per 0·01° E.	1 Viscos. ° E.	2 Vol. %	3 Diff. per 0·01° E.
2·50	0·00	0·250	5·20	33·50	0·070	25·00	79·07	0·009
2·60	2·50	0·230	5·30	34·20	0·068	26·00	79·99	0·009
2·70	4·80	0·200	5·40	34·88	0·067	27·80	80·86	0·008
2·80	6·80	0·187	5·50	35·53	0·066	28·00	81·70	0·008
2·90	8·67	0·167	5·60	36·19	0·062	29·00	82·51	0·008
3·00	10·33	0·166	5·70	36·81	0·060	30·00	83·29	0·008
3·10	12·00	0·143	5·80	37·41	0·059	31·00	84·04	0·008
3·20	13·43	0·143	5·90	38·00	0·059	32·00	84·77	0·007
3·30	14·86	0·139	6·00	38·59	0·051	33·00	85·47	0·007
3·40	16·25	0·125	7·00	43·68	0·043	34·00	86·16	0·007
3·50	17·50	0·125	8·00	47·96	0·037	35·00	86·82	0·007
3·60	18·75	0·125	9·00	51·62	0·032	36·00	87·46	0·001
3·70	20·00	0·111	10·00	52·82	0·029	37·00	88·09	0·006
3·80	21·11	0·111	11·00	57·69	0·025	38·00	88·70	0·006
3·90	22·22	0·108	12·00	60·24	0·023	39·00	89·29	0·006
4·00	23·30	0·100	13·00	62·52	0·021	40·00	89·87	0·006
4·10	24·30	0·100	14·00	64·58	0·019	41·00	90·42	0·006
4·20	25·30	0·097	15·00	66·44	0·017	42·00	90·92	0·005
4·30	26·27	0·091	16·00	68·13	0·016	43·00	91·42	0·005
4·40	27·18	0·090	17·00	69·68	0·015	44·00	91·90	0·005
4·50	28·08	0·084	18·00	71·14	0·013	45·00	92·40	0·005
4·60	28·92	0·083	19·00	72·48	0·013	46·00	92·80	0·004
4·70	29·75	0·079	20·00	73·74	0·012	47·00	93·20	0·004
4·80	30·54	0·077	21·00	74·93	0·011	48·00	93·60	0·004
4·90	31·31	0·076	22·00	76·05	0·011	49·00	94·00	0·004
5·00	32·07	0·072	23·00	77·11	0·010	50·00	94·35	0·004
5·10	32·79	0·071	24·00	78·11	0·010			

In order to make use of this Table, the viscosity of the first component of the mixture is found in the first column,

[1] *Chemiker Zeitung*, 1914, p. 857.

the corresponding percentage volume is read off in the second column, and this value is multiplied by P/100, P being the percentage of the component by volume. The result may be set down as x. The same procedure is adopted for the second component, the result being stated as y. The sum $x + y$ is then found in column 2, and the corresponding viscosity, $i.\ e.$ the viscosity of the mixture, will be found opposite to it in column 1.

This calculation, however, is inapplicable to mixtures of mineral oils with fatty oils, because the viscosity of a mixture is lowered to a greater extent by the presence of a mineral oil than by a fatty oil of the same viscosity. If equal parts of a mineral oil and a fatty oil be mixed, and, on the other hand, equal parts of the same mineral oil and another mineral oil having the same viscosity as the fatty oil, the second mixture will have a considerably lower viscosity than the first.

EVAPORATION VALUE

Mineral lubricating oils volatilise only at high temperatures; but as they are mixtures of hydrocarbons of different boiling points, the lighter constituents evaporate at temperatures below the boiling point of the oil, the evaporation being the greater the higher the temperature to which the oil is exposed.

The greater the evaporation, the greater the consumption of oil; and it is therefore occasionally advisable to determine the evaporation value of the oil, especially where it is found to have a low flash point.

The test is performed in an apparatus described by Holde,[1] by heating a sample of the oil for two hours at 100 or 200° C. (if necessary 300° C.), in a cup similar to the Pensky or Marcusson flash point tester, and placed in a special steam bath, the loss in weight being ascertained on cooling. The liquid for the heating bath may consist of various substances boiling above 100° C., such as brine, toluol, aniline, nitrobenzol, anthracene, etc. Any other suitable heating bath may replace that described by Holde.

The loss in weight sustained by cylinder oils with a flash point of 250–300° C., when heated for two hours at 200° C., averages 0·03–0·1 per cent. and rarely attains 0·13 per cent.; whilst the loss after a similar heating at 300° C. is 0·2–1·2 per cent., rarely exceeding 2·3 per cent. In practice, the

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[1] *Kohlenwasserstoffe und Fette*, p. 170.

evaporation test is only applied to oils intended for lubricating high-pressure steam engines, those driven by superheated steam, steam turbines, or transformers.

FLASH AND BURNING POINTS

The flash point is the temperature at which the gases and vapours liberated by heating the oil will ignite on the approach of a flame, without the oil itself igniting on the surface and continuing to burn. The burning point is the temperature at which the heated oil ignites on contact with a flame, and continues to burn.

There is no uniformity in the methods for determining the flash point and burning point, both closed and open apparatus, which give very divergent results, being used.

The closed testers include that of Abel, which, however, is only used for oils flashing below 50° C., and the Pensky–Martens apparatus, which enables the oils to be tested at higher temperatures, but is complicated and therefore expensive.

Whereas the Abel apparatus uses a water bath to heat the oil and operates the test flame

FIG. 10.

by clockwork, an air bath is used in the Pensky–Martens apparatus, and the test flame is moved by hand. In testing the lower flash oils with the Abel apparatus, the barometric pressure is not taken into account as in testing petroleum.

Railway carriage oils are tested with an open-cup apparatus designed by the Prussian railway authorities.

Engine and cylinder oils of specially high flash point are tested in the Brenken apparatus as improved by Marcusson.

This apparatus (Fig. 10) consists of a porcelain crucible, a, measuring 4×4 cm., which is heated in a sand bath, s. The cup is provided, 10 mm. below the rim, with an annular lug by means of which it can be suspended so that the bottom
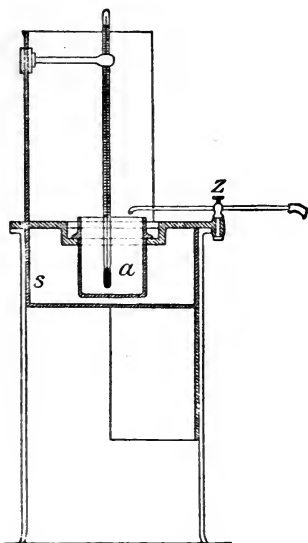
of the cup lies 2 mm. above the bottom of the sand bath. The cup is also secured by means of two small bars, the arrangement enabling the cup to be kept at a constant level in relation to the ignition tube.

The igniter, z, is mounted so that the test flame can be moved horizontally to and fro, on a level with the rim of the cup and across the surface of the oil, once for every degree of rise.

The cup is provided with two marks, at 10 and 15 mm. distance respectively from the rim, the upper mark denoting the charge in the case of engine oils, and the lower the level for cylinder oils (because the latter expand more under the higher temperatures employed and might overflow). The cup is immersed in the sand bath up to the level of the oil surface.

For technical analyses, however, the following simple apparatus will suffice :—

A conical iron basin, 6 cm. high, 10 cm. wide at the top, and 7·5 cm. at the base, is partly filled with sand of medium-fine grain ; and in this basin a 4×4 cm. cup of 1 mm. sheet-iron is embedded to a depth of 3 cm. in the sand, and so that the bottom of the cup is 4 cm. from that of the basin. The iron cup may be replaced by a porcelain crucible of the same dimensions.

The cup is charged with oil to a depth of 3 cm., and a thermometer with a short bulb is suspended in such a way that the bulb is just covered by the oil.

The sand bath is heated quickly to 100° C. and then more gradually so that, above 120° C., the temperature rises only 3° C. (maximum 5° C.) per minute. From time to time, a small test flame is passed, at a distance of about 5 mm., over the oil surface. The flame is obtained by wrapping a short thread of asbestos round a looped nickel wire, the wick being dipped in alcohol and lighted ; or a small gas flame may be used, a tube, drawn out to a point, being fixed on a swing clamp and connected to a gas pipe by means of a rubber tube.

As soon as inflammable vapours are given off by the oil, they will ignite on the approach of the test flame, a bluish flicker being observed over the surface of the oil, whilst the flame is extinguished with a slight pop. The temperature at which this occurs is the open-cup flash point (open test).

The heating of the oil is then continued, with occasional application of the test flame, until the oil finally ignites on

the surface and goes on burning.   This temperature is the burning point (fire test) of the oil.

The flame must be blown out at once, to prevent the bursting of the thermometer; and this must be removed immediately.

The difference between the flash point and burning point of the oil may amount to 20–60° C.

In precise determinations, a correction is made for the length of mercury column projecting above the oil, and also for any error in the thermometer; but, in practice, the former correction is mostly neglected, and the simple thermometer reading is accepted.

The room in which the tests are performed should be free from draughts, and it is advisable to work in a poor light, so that the first flicker of the flash may not be overlooked.   Both the flash and burning tests should be repeated with fresh quantities of oil, and the results should not vary by more than 3° C.

Even small quantities of water in the oil affect the flash point, and oftentimes the test flame is prematurely extinguished by the liberated water vapour.   Water should be tested for prior to making the flash test, and if present must be removed by shaking the oil up with fused, anhydrous calcium chloride and filtering.

The results obtained in closed apparatus (Pensky–Martens) may differ considerably from those in the open cup test, because small quantities of volatile vapours, which dissipate freely in the latter case, will greatly reduce the Pensky–Martens flash point.   For example, a very slight addition of benzine to lubricating oil may lower the flash point by 20°, and even as much as 80° C.   Consequently, the values obtained are only comparable with others from the same apparatus, except that, in the case of low flash oils, the Pensky and Abel values are comparable.   In any event, the flash points obtained in closed apparatus are lower than those in the open cup test.

It is desirable to prescribe the use of a standard apparatus for testing the flash point of lubricating oils, so as to avoid confusion and uncertainty in judging their quality.

COLD TESTS AND MELTING POINT

The solidification point is the temperature at which the oil passes into a non-fluid condition, vegetable and animal

oils being changed by cold into a tallowy mass, mineral oils to a soft ointment.   Pale mineral oils low in paraffin sometimes solidify to a jelly and remain limpid.

The solidification point is determined by means of the following arrangement (Fig. 11).   A small circular sheet-iron pot, *b*, 20 × 10 cm., filled with a 10–20 per cent. brine, is placed, on a washer 1 cm. thick, in a porcelain or iron vessel, *a*, 10 cm. deep and 20 cm. across, this outer vessel being filled with finely crushed ice, or, if temperatures below zero C. are desired, with a mixture of 2 parts ice or snow and 1 part common salt.   The outer vessel is wrapped in a cloth and provided with a cover, to keep out external heat.   A small quantity (3–4 c.c.) of the oil is placed in a 15-mm. test tube, into which a thermometer is fitted, by means of a cork, so that the bulb dips into the oil.   The test tube and contents are placed in the brine and slowly cooled.
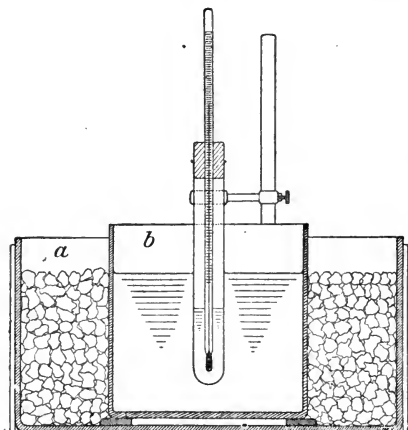
FIG. 11.

The oil takes some time to acquire the external temperature, and the contained paraffin only separates out slowly. For this reason the cooling should be continued for at least an hour.

To prevent super-cooling of the brine in the inner vessel, the frozen portions are scraped off at intervals, and the vessel itself is taken out of the freezing mixture.   The test tube also is lifted out of the brine from time to time, and is slowly tilted without shaking or stirring.   As soon as the oil ceases to flow and has assumed the consistency of ointment, the solidification point (cold test) is read off on the thermometer.   A correction for the mercury above the oil is made by means of the formula : $k = \dfrac{(t - a)(t - t_1)}{6300 - (t - a)}$ in which t is the thermometer reading, t_1 the mean temperature of the external column of mercury (practically the room temperature), a the mark to which the thermometer

dips in the oil, and $(t - a)$ the length (in degrees) of the projecting part of the mercury column.

The oil must not be shaken while cooling, since that would destroy the scaly and reticulated deposits of paraffin or pitch particles and thereby considerably delay congelation.

Any particles of paraffin or pitch in the oil will dissolve in the oil if warmed prior to the cold test, but they do not always separate out again at once, and therefore the oil may show a different solidification point. Such changes, which are more particularly due to the colloidal character of the mineral oil constituents, may also occur when the warmed oil is brought to room temperature and re-cooled. It may therefore happen that oil which has been exposed to changes of temperature during transport or storage will give divergent solidification points when examined at different times. For this reason it is the custom to test the oil in the condition in which the sample arrived for examination. It is first warmed to 50° C. during ten minutes and then cooled to 20° C. for thirty minutes.

If the oil contain water it is first shaken up with anhydrous calcium chloride and filtered, since the presence of water renders it liable to supercooling without congelation.

In the case of a mixture of mineral and fatty oils, one sample is tested without agitation, and another with continuous stirring with a glass rod for a quarter of an hour, since, unless stirred occasionally, the fatty oil—unlike mineral oil—may remain fluid—through supercooling—below its solidification temperature for several hours. The cooling should be continued for at least four hours.

A question that has not infrequently to be answered is whether the oil still remains fluid at a given temperature. In such cases the inner vessel is charged with definite saline solutions freezing at known temperatures.

Thus, the following solutions (in 100 c.c. of water) freeze at the temperatures stated :—

13 grms. of potassium nitrate	.	.	.	— 3° C.
13 ,, ,, and 3·3 grms. sodium chloride				— 5° C.
22 ,, ,, chloride	.	.	.	—10° C.
25 ,, ammonium chloride .	.	.	.	—15° C.
36 ,, sodium chloride	.	.	.	—20° C.

These solutions are gradually cooled with the aforesaid mixture of ice and salt.

In this method, the setting point of the oil is ascertained by a preliminary test, so as to avoid having to make

tentative trials with various saline solutions and enable the suitable one to be selected at first.

If a still lower temperature is required, alcohol is placed in the inner vessel and solid carbon dioxide in the outer one, by which means a temperature of $-25°$ to $-30°$ C. can be obtained.

For the reasons already given, the oil must be slowly cooled for at least an hour without being disturbed in any way.

Other determinations sometimes required for mineral lubricating oils are the turbidity and setting points, the method of which has been already given (p. 86). All three tests can be performed at the same time, in three separate test tubes. Instead of a thermometer, a glass rod is placed on the tube for the setting point test. By lifting this rod at intervals, the point at which the oil still remains in a pulpy condition can be ascertained, the temperature of the saline solution, and therefore that of the oil, being read off on a thermometer.

Another method, the so-called U-tube method, of determining the behaviour of lubricating oils in cooling, is prescribed by the Prussian railway authorities.

It consists in filling the oil into a U-tube, up to the level of the marks on each limb, and then cooling it for an hour in a definite cooling solution, whereupon the longer limb of the tube is connected to a source of pressure and the oil subjected to a pressure of 50 mm. (2 ins.) water gauge for one minute. The tube being taken out of the bath, the height to which the oil has been forced in the shorter limb is read off on the scale, this being indicated by the oil adhering to the glass after the former has returned to its original level. The degree of the ascent is a measure of the behaviour of the oil on cooling.

The method not having yet been employed for motor-car cylinder oils, it will not be described in detail, this having been done in Holde's work already referred to.

The melting point of a solid lubricant is determined by dipping the bulb of a mercury thermometer into the melted material and then withdrawing it slowly, whereupon a thin film of the solidified lubricant will remain adhering to the thermometer on cooling. The thermometer is fixed in a test tube, by means of a cork, so that the bulb is about 1 cm. from the bottom of the tube; and tube and thermometer are laid aside for at least six hours.

At the end of this time the tube is immersed half-way in a one-litre beaker full of water, and clamped in that position, the water being warmed so that the temperature rises about 1° C. per minute. As soon as a liquid drop of the lubricant is observed to form on the bulb, the melting point is read off on the thermometer.

In the case of liquid oils, the melting point and solidification point are determined in the same test. After solidification the test tube is taken out of the cooling vessel, and the temperature at which the oil just begins to flow when the tube is tilted is read off. This point is usually a few degrees higher than the solidification point.

COEFFICIENT OF REFRACTION

It is sometimes advantageous to determine the coefficient of refraction of the oil, chiefly with the object of detecting the presence of rosin oils. This coefficient, in the mineral oils, increases with the boiling point, and is usually higher than in the case of vegetable and animal oils, but lower than in rosin oils.

The coefficient of refraction of pale transparent engine oils is between 1·4950 and 1·5175 at 15° C., that of spindle oil being 1·5028, and of motor-car cylinder oil 1·5175. In the vegetable and animal oils, the coefficient, at the same temperature, is 1·4700–1·4880; for example, rape oil, 1·4780; olive oil, 1·469–1·470; bone oil, 1·4871, etc. The rosin oils of high boiling point have the coefficient 1·530–1·550.

The coefficient of refraction of dark oils cannot be determined, because the line of demarcation between light and shade in the refractometer becomes quite indefinite.

SPECIFIC ROTATORY POWER

In many cases the specific rotatory power of oils is very important, as affording a means of identification or of detecting the presence of certain oils in mineral oils.

Examined in a 200-mm. polarimeter tube, in a half-shadow apparatus, mineral oils give a dextro-rotation of 0° to + 3° (circular degrees). The rotation increases with the boiling point of the oil.

Rosin oils give a much higher reading, 30–44°, and even 50°, also dextro-rotatory; and consequently, the polarimeter

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affords a means of detecting the amount of rosin oil in mineral oils.

Pale mineral oils can be examined direct in the polarimeter, but darker oils must first be decolorised with bone black, or diluted with benzol, and examined in a shorter (100 or 50 mm.) tube. Dark oils, however, cannot be examined in this way, being insufficiently decolorised, and still coming out too dark, even in short tubes, when diluted with benzol.

Of the natural fats and oils, a decided dextro-rotation is exhibited by sesamum oil, $+ 3$ to $+ 9°$, and more particularly castor oil, $+ 7·6$ to $+ 9·7°$ (sometimes as high as $+ 43°$), in a 200-mm. tube. Wool fat, also, strongly rotates the plane of polarisation, in consequence of its content of cholesterin and isocholesterin.

The tests are performed in a Laurent half-shadow apparatus with circular scale; but any other half-shadow apparatus, such as a saccharimeter, can also be used, though in this latter case the reading must be calculated to circular degrees in order to be comparable with the foregoing values.

Neutrality (Acidity, Alkalinity)

Every oil should have a neutral reaction; but if (as, however, rarely happens) it has not been properly refined, it may have either an acid or an alkaline reaction from the sulphuric acid or soda used for refining.

An acid reaction may also be due to the presence of petroleum acids, such as naphthenic acids, or from resinous substances, in the oil. The oil may also have an alkaline reaction caused by the intentional addition of soap.

The qualitative test for neutrality is performed by shaking up 50–100 c.c. of the oil with an equal quantity of warm water in a glass flask for about a quarter of an hour, the water being filtered off after settling, and one portion tested with a drop of a 1 per cent. aqueous solution of ethyl orange, which stains the water red if the oil is acid. If this test gives a negative result, a second portion of the water is treated with 1 drop of a 1 per cent. alcoholic solution of phenolphthalein, which gives a red colour reaction if the oil is alkaline.

In practice, the neutrality of the oil is tested in the following manner : A small circular depression, about 0·5–1 cm. wide and 0·3 mm. deep is made in a piece of

sheet copper 1 mm. thick, oil being dropped in so as to fill the pit to the brim ; and the plate is exposed to a temperature of 100–110° C. for about an hour.   If the oil is acid it will turn green, particularly round the edge of the depression.

The total acidity of an oil is ascertained by quantitative tests which differ according as the oil is dark or light in colour.

(1) *Dark Oils.*—Twenty c.c. of the oil are placed in a 100-c.c. glass measuring cylinder, fitted with a ground glass stopper, and sufficient anhydrous ethyl alcohol (previously neutralised if necessary) is added to bring the volume up to 60 c.c., the mixture being shaken gently for two to three minutes and left to stand.   As soon as the oil has settled out, the volume of the alcohol is read off on the graduated scale on the cylinder, and a portion, *e. g.* 30 c.c., is poured off into a glass beaker.

This solution is treated with sufficient alcoholic solution of alkali blue 6B [1]—as indicator—to give it a decided blue colour, and is then titrated with decinormal (aqueous or alcoholic) caustic potash, from a burette, until the greenish-blue shade turns to a yellowish-red.

The volume of potash consumed is calculated to the total volume of the alcohol, and from this the amount of caustic potash required to neutralise the oil is computed.   As a rule this quantity is expressed in terms of sulphur trioxide (SO_3) or oleic acid, the molecular weight of the acids present in the oil being unknown.

One c.c of decinormal caustic potash corresponds to 4 mgrms. of sulphur trioxide or 28 mgrms. of oleic acid. The acid content is stated in percentages of one or other of these two substances.

If the test indicates more than 0·03 per cent. of SO_3, the test sample of the oil, after being separated from the residual alcohol in the cylinder, is shaken up with another 40 c.c. of alcohol and titrated as before, these operations being repeated if necessary.

Provided a margin of error of + 0·01 per cent. SO_3 can be tolerated, the following empirical table of corrections may be employed, to save repeated testing.   If, for example, the result of the first test was 0·08 per cent. of acid, the

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[1] This indicator is prepared by dissolving 2 grms. of alkali blue 6B (Meister, Lucius, and Brüning) in 100 c.c. of alcohol and carefully adding just enough decinormal caustic potash to turn the colour red.

corresponding correction 0·018 must be added. Corrections for other values than those given in the table are obtained by interpolation.

Corrections for Acidity Determinations in Oils

Per cent. SO₃

			Per cent. SO$_3$			
1. Agitation	.	.	.	0·015–0·025	0·030	0·040	0·047
Correction	.	.	.	0·005	0·008	0·011	0·012
1. Agitation	.	.	.	0·054	0·062	0·069	0·077
Correction	.	.	.	0·013	0·014	0·015	0·017
1. Agitation	.	.	.	0·085	0·093	0·102	0·121
Correction	.	.	.	0·019	0·022	0·026	0·031
1. Agitation	.	.	.	0·139	0·151	0·165	0·179
Correction	.	.	.	0·034	0·042	0·060	0·077

If the acid content is found to exceed 0·2 per cent. SO_3, there is no alternative but to repeat the agitation with alcohol, once if not twice.

The new specification of the German Association for Testing Materials proposes to express the acid content in percentages of oleic acid, or in the form of the acid value (*i. e.* the number of milligrams of caustic potash required to neutralise 1 grm. of oil).

(2) *Pale Oils.*—Ten to twenty grms. of the oil are weighed into a 200-c.c. Erlenmeyer flask, thoroughly mixed with about 50–75 c.c. of a perfectly neutral mixture of 1 part alcohol and 2 parts benzol, and the whole titrated direct with decinormal caustic potash in presence of alkali blue solution.

ASPHALTUM AND ROSIN CONTENT

A distinction is drawn between hard asphaltums of high boiling point, which can be extracted with benzine, and soft asphaltic substances, melting below 100° C. and insoluble in ether-alcohol or amyl-alcohol. Both varieties are substantially composed of carbon, hydrogen, and oxygen, sulphur being sometimes present. The soft asphaltic substances form a transition stage on the way to the heavy hydrocarbons, and therefore contain little oxygen and little sulphur.

QUALITATIVE TESTS FOR ASPHALTIC SUBSTANCES

The qualitative tests are performed in two ways :—

(1) *Hard Asphaltum.*—One c.c. of oil is shaken up in a flask with 40 c.c. of standard benzine and left to stand for

twelve hours. Pure oil dissolves completely, but any asphaltum present subsides quickly, or at most within twenty-four hours, as blackish-brown flakes which are dissolved in benzol after the benzine has been poured off. The evaporation of the benzol leaves a residue of hard asphaltum which does not melt when heated on the water bath.

(2) *Soft Asphaltic Substances.*—Two c.c of the oil are dissolved in 25 c.c. of sulphuric ether in a flask, and treated with 12·5 c.c of alcohol. If asphaltum and asphaltic substances are present, they deposit on the sides of the flask as brown or black flakes which are soluble in benzol and usually melt when heated on the water bath.

QUANTITATIVE DETERMINATION OF ASPHALTIC SUBSTANCES

Hard Asphaltum.—In the quantitative examination, 5 grms. of the oil (or 10–20 grms. if the asphaltum content is considered likely to be small) are placed in a 500-c.c. glass flask with ground stopper, shaken up well with a 40-fold quantity of standard benzine (220 c.c., assuming the sp. gr. of the oil to be 0·91–0·92), and left to stand twenty-four hours in the dark at a temperature not exceeding 20° C. and not below 15° C.

The liquid is then filtered through a folded filter of close texture, that has been previously washed with standard benzine, the flask being rinsed out with standard benzine and the residue washed until the runnings no longer leave any oily residue behind on evaporation.

Such of the deposit as remains in the flask is dissolved, without delay, in hot pure benzol and passed through the same filter into a flask, the filter being then washed out with benzol. The greater part of the benzol in the flask is distilled off, the residue being transferred to a tared basin and completely evaporated over a moderately warmed water bath, being stirred the while with a glass rod (also weighed). The residue is finally dried for a quarter of an hour at 105° C. and weighed.

A benzine of definite composition must be used in this determination, it having been found that the asphaltic substances in different benzines differ in composition. Hence, in order to obtain uniform and comparable results, it is necessary to use a standard benzine of sp. gr. 0·695–

0·705 at 16° C., boiling between 65° and 96° C. and free from aromatic and unsaturated hydrocarbons.[1]

In place of standard benzine, Schwarz recommends butanone (methylethylketone) on the assumption that, being a single substance, it will give more concordant results. It may be pointed out that the results furnished by butanone are higher than those obtained with benzine.

It has also been proposed to use amyl alcohol, ethyl acetate, and propyl acetate in the determination of these asphaltic substances.

Soft Asphaltic Substances.—Holde gives the following method : 5 grms. of the oil are placed in a glass flask with ground stopper and dissolved in a 25-fold quantity of anhydrous ether (137·5 c.c. assuming the sp. gr. of the oil to be 0·91–0·92). Into this solution, a 12½-fold quantity (68·5 c.c.) of 96 per cent. (weight) alcohol is gradually run from a burette, with continuous stirring, and the mixture is left to stand for five hours at 15° C.

The contents of the flask are then passed through a close, folded filter (previously washed with a mixture of 1 part 96 per cent. alcohol and 2 parts ether), and both filter and flask are washed with this alcohol-ether until 20 c.c. of the filtrate no longer leave any oily residue, but at most traces of asphaltic substances, when evaporated in a dish.

The deposit on the filter and in the flask is dissolved in hot benzol, the further treatment of the solution being the same as for hard asphaltum.

If only minute quantities (a few tenths per cent.) of merely light brown asphaltic substances are found, the residue is extracted—to remove accompanying paraffin— several times, by stirring with 30 c.c. of warm absolute alcohol in a dish, until the cooled alcoholic extract, after energetic shaking, no longer gives any deposit of paraffin. The evaporation residue of the alcoholic extract is dried a quarter of an hour at 105° C. and weighed.

If any considerable amount of deep black asphaltic substances is revealed by the test, simple extraction with alcohol is insufficient for the complete removal of the paraffin contained therein, and the only alternative is to perform the operation in an extraction apparatus.

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[1] This benzine is tested by the German Official Testing Station at Lichterfelde, Berlin, and is obtainable from C. A. F. Kahlbaum, Adlershof, Berlin.

According to the proposals of Holde and Meyerheim, the weighed residue from the evaporation of the benzol is stirred up with 10 c.c. of ether and thoroughly mixed with 2 grms. of bone black (previously well washed with alcohol) and 10–15 grms. of coarse, calcined sand, the ether being carefully evaporated on the water bath. The mass is transferred, as completely as possible, into an extraction shell, the residue in the dish being dissolved in a little ether, mixed with small quantities of bone black and sand and placed in the shell.

The shell is closed with a plug of cotton wool and attached, by means of nickel wire or string, to the lower end of a Gräfe extraction apparatus (Fig. 12) provided with a tight-fitting reflux condenser, the extraction being carried out with absolute alcohol in the usual way, on a water bath. The operation is continued, until finally the alcohol, after renewed extraction for an hour, only leaves behind, on evaporation, less than 1·5 mgrm. of residue.

The united alcoholic extracts are evaporated in a tared dish, the residue being dried for ten minutes and weighed when cold.

The difference between the weight of the impure asphaltic substances and that of the paraffin resulting from the alcoholic extraction gives the pure asphaltic substances.

FIG. 12.

The results obtained by this method are not satisfactory enough, because in the separation of the asphaltic substances with alcohol-ether, larger or smaller quantities of paraffin—according to the character of the oil—are carried off as well, together with a little oil which is difficult to eliminate with alcohol.

However, even the first method of determination of hard asphaltum does not furnish concordant results, in spite of the conditions being maintained unaltered.[1] Moreover, other resinous and asphaltic substances are separated along with the asphaltum, no matter whether benzol, alcohol-ether, or other previously recommended separating agent be employed.
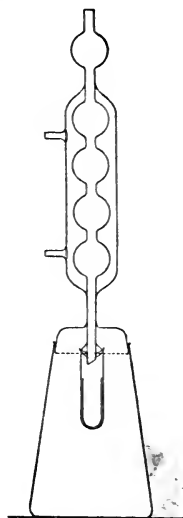
[1] See also H. Kantorowicz, *Chem. Zeit.*, 1913, pp. 1394, 1483, 1565, 1594.

None of these methods gives an accurate criterion of the true amount of the asphaltum originally present in the oil, the asphaltum they furnish being different from the technical goudron asphaltum. Nevertheless, the two methods are specified officially and generally recognised in the industry, and suffice for purposes of comparison.

The first method is employed for the determination of asphaltic substances in cylinder and car-axle oils for railway use, and the second for cylinder oils only.

Rosins and Colophony

The usual method employed for the detection of rosins and colophony consists in shaking up 10 c.c. of oil with 50 c.c. of 70 per cent. alcohol in a glass flask and leaving to settle, the upper clear layer being pipetted off and passed through a double filter paper. The filtrate is treated with a few drops of lead acetate solution, whereupon, if any rosins are present, a milky turbidity is produced and a deposit of yellowish flakes separates out, the action being accelerated by adding a few drops of water.

Rosins soluble in alcohol are determined quantitatively, in an approximately similar manner by shaking up 5 grms. of the oil with 100 c.c. of 70 per cent. alcohol and leaving the mixture to stand for twenty-four hours at room temperature. The clear alcoholic layer is then passed through a filter (moistened with alcohol), and the oily residue is washed with 70 per cent. alcohol. The filtrate is evaporated to dryness in a tared glass dish on the water bath, and the residue weighed on cooling.

The natural rosins obtained from the oil in this manner do not give the Storch–Morawski rosin reaction (see later) with acetic anhydride and sulphuric acid.

Colophony is occasionally added to oil in order to increase the viscosity. Like the oil rosins, it is soluble in 70 per cent. alcohol.

Since colophony consists chiefly of organic acids (abietic and pimaric acid), its presence may be suspected if the acid value of the oil is unusually high. It has the saponification value 167–194 and the iodine value 100–125; and gives the rosin reaction, i. e. a violet coloration with acetic anhydride and sulphuric acid.

Resinification (Gumming) Value, Tar and Tarification Value, Coke Value and Coking Value

The resinification, tar, and coke values are mostly determined only in the case of dark, unrefined or unfiltered oils, axle oils, and steam cylinder oils.

The simplest empirical test for resinification value consists in spreading out a drop of oil on a glass plate (5 × 10 cm.), heating it to 50° (engine and axle oils) or 100° C. (steam cylinder oils) in a drying cupboard and examining the consistency of the layer of oil, at intervals, after cooling.

For the more accurate examination of the oils, Kissling has proposed to make use of the tar and coke values, and the following methods of determining the tarification and coking values.

(1) *Tar Value.*—Fifty grms. of oil are placed in an Erlenmeyer flask—fitted with a stopper and a glass tube about 60 cm. long—and warmed, with 50 c.c. of alcoholic caustic soda (prepared by treating 50 grms. of a $7\frac{1}{2}$ per cent. aqueous solution of caustic soda with 50 grms. of alcohol), to about 80° C. The flask is then closed with a solid stopper and energetically shaken for five minutes, the still warm mixture being transferred to a separating funnel and left to stand, in the warm, until the oil and alkali solution have separated completely.

The alkaline liquor, which has now absorbed the tarry constituents of the oil, is drawn off as completely as possible when cold, and filtered, as large a proportion as possible being measured off into a separating funnel, acidified, and shaken up with 50 c.c. of benzol. The benzol layer is drawn off, and the alkali liquor shaken up with another 50 c.c. of benzol. In this way the tarry substances are extracted from the soda solution.

The united benzol extracts are evaporated, in a tared glass basin, on the water bath, the residue being dried for thirty minutes at 105° C., in a drying cupboard, and weighed when cold. The weight of the residue, calculated to 50 c.c. of caustic soda solution and to 100 grms. of oil, gives the tar value.

(2) *Coke Value.*—When the tarry substances in mineral lubricating oil are accompanied by substances of a coky nature, the oil from the tar determination is mixed with 500 c.c. of petroleum spirit (petroleum " ether," of which at least 90 per cent. distil over between 30° and 80° C.),

the flask, separating funnel and filter used in the tar deter-
mination being also rinsed out with the same spirit.   After
the solution has stood for twelve hours, the coky sediment
is filtered (on a filter dried at 105° C. till of constant weight),
washed, first with petroleum spirit and afterwards thoroughly
with hot water, and is finally dried at 105° C.   The weight
of the residue gives the amount of coky substances, but
includes asphaltic substances as well, hard asphaltum being
precipitated by petroleum spirit.

(2) *Tarification and Coking Value.*—According to Kiss-
ling, these values are determined by heating the oil at
150° C. for fifty hours, and then determining the tarry
and coky substances in the manner just described.   The
difference in the results given by the oil before and after
this heating gives the tarification and coking values
respectively.

Since the point at issue is to determine how the tarry
substances in a given motor-car oil would increase during
continuous lubrication over a given period of time; and
since the temperature in the oil tank and bearings does not
exceed 100° C.; heating the oil to only 100° C. and for a
hundred hours would seem to be more in approximation
to actual conditions.

Paraffin Content

Five to 10 grms. of the oil are treated with absolute
alcohol and ether in equal parts until a clear solution has
been obtained.   This solution is cooled to − 20° C. and
treated with a further quantity of alcohol-ether until all
the oily particles remain in solution at that temperature,
only paraffin flakes being deposited.

If the oil is high in paraffin, it is first dissolved in ether
by moderate heating, and then treated with an equal
volume of alcohol.

The deposited flakes of paraffin are filtered on a filter
which is cooled to − 21° C. by a mixture of salt and ice
(Fig. 13), and they are then washed with a mixture of
alcohol and ether at the same temperature until 5 c.c.
leave merely a paraffin-like residue (free from oily particles)
on evaporation.   The washing should not be continued too
long, since the paraffin is slightly soluble in alcohol-ether.

The filtrate is evaporated on the water bath and dis-
solved in a little alcohol-ether, the solution being cooled

to − 21° C. and any further paraffin obtained being filtered and washed under the same conditions as before.

The two paraffin residues are rinsed with warm benzine or benzol into a weighed dish, and evaporated on the water bath. If the paraffin is found to be hard when cold, it is dried for a quarter of an hour at 105° C. in the drying cupboard and weighed.

If the paraffin is soft, and melts below 45° C., it is dried at 50° C. *in vacuo* before weighing. If the colour is brown, from the presence of resinous substances, the paraffin is repeatedly extracted with hot, anhydrous alcohol and separated from the undissolved resinous substances by filtration.

Should this treatment be insufficient, the paraffin must be refined with a small percentage of concentrated sulphuric acid, or dissolved in benzine and filtered through fuller's earth or bone black.

Since paraffin is slightly soluble in alcohol-ether, a correction (ascertained by practical experiment) must be added, viz. 0·2 per cent. in the case of perfectly fluid oils; 0·4 per cent. for oils that deposit paraffin at 15° C., and 1 per cent. in the case of solid masses (distillates).

FIG. 13.

The method, however, only gives actual values of paraffin content for hard paraffin, soft paraffins which melt below 50° C. failing to separate out completely even at − 21° C. and remaining behind, in fairly considerable quantities, in the alcohol-ether solution. Nevertheless, by repeated evaporation of the alcohol-ether filtrate and re-dissolving in a little alcohol-ether (2 : 1), they may be recovered, for the most part, at − 20° to − 21° C., or at still lower temperatures if necessary.

Schwarz (*Chem. Zeit.*, 1911, p. 1419) proposed to replace alcohol-ether for this purpose by butanone, stating that all the paraffin can thus be recovered by one precipitation and a single filtration at − 15° C.
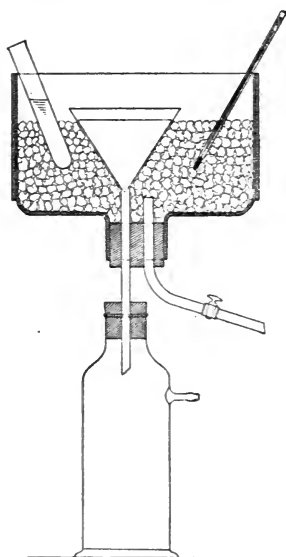
Rubber Content

Mineral oils dissolve unvulcanised rubber (caoutchouc) to some extent, and such solutions are used for certain purposes; but they are only occasionally mixed with lubricants, in order to increase the density and viscosity.

If a little oil be taken between thumb and finger, the oil will draw out in thin filaments, on separating the fingers, if rubber be present. However, soap will produce the same result, and therefore the absence of soap should be ascertained before testing the oil for rubber.

Oils containing rubber are imperfectly soluble in a mixture of 4 parts ether and 3 parts alcohol; and therefore any residue left by this mixture may be rubber.

Soap Content

Mineral oils are mixed with anhydrous soaps in order to improve the consistency and adhesion. The soaps used are either water-soluble potash or soda soaps, or insoluble alumina, magnesia, or lime soaps.

Oils containing soap draw out in threads between thumb and finger, like those containing rubber. This property, however, disappears when the oils are shaken up with dilute hydrochloric acid, the soap being decomposed by the latter. The presence of water-soluble soaps in mineral oils can be detected by shaking up 8–10 grms. of the oil with an equal volume of water in a test tube, and leaving it to stand. If the oil is free from soap, the two liquids will separate immediately; otherwise separation takes about half an hour and the bottom layer will be milky. In such case the aqueous solution will give a red coloration with phenolphthalein, the hydrolytic action of the water splitting up the soap into a weak acid and a strong alkali, so that the liquid has an alkaline reaction. The aqueous extract should then be evaporated to dryness, and the residue lightly calcined and tested for potash and soda.

The soaps insoluble in water are tested for by shaking up 10 grms. of the oil with 10 c.c. of dilute hydrochloric acid (1 vol. concentrated acid and 3 vol. distilled water); and after separation the hydrochloric solution is drawn off and tested for calcium, magnesium, and alumina. In the event of an alkaline soap being present, the solution will also contain potash or soda.

The presence of the above-named metals can also be determined in the ash left by the oil on combustion.

When the oil contains larger amounts of soap, the viscosity will be found to be reduced by treatment with hydrochloric acid.

ASH CONTENT

Ash content only need be determined when a sample of the oil is incompletely soluble in benzine or benzol, or when dilute hydrochloric acid, shaken up with the oil and separated therefrom, leaves a residue on evaporation.

The ash is determined by the combustion of 20–30 grms. of filtered oil in a large porcelain crucible or platinum basin. The crucible is first heated with a small flame, and the oil then ignited. When it has been reduced to carbon the residue is more strongly calcined.

The above method is used for dark oils; but for pale oils, which burn very freely, it is advisable, in order to prevent loss, to allow the quantity weighed out into the crucible or basin to be absorbed by an ash-free filter folded as a wick, the filter being lighted, and calcined after the oil has burned away.

Properly refined engine oils should not leave more than 0·01 per cent. of ash, cylinder oils 0·1 per cent., though sometimes these latter give up to 1 per cent.

DEGREE OF REFINING

Insufficiently refined oils contain naphthenic and sulphonic acids, or their sodium salts. The acids can be eliminated by treatment with caustic soda, and the sodium salts by agitation with water.

The salts may also be determined by incineration. The degree of refining is therefore connected with the acid value, soap content, and ash content of the oil.

To ascertain whether an oil has been adequately refined or not, Lissenko and Stepanoff recommend shaking up 10 c.c. of oil with 5 c.c. of a 2 per cent. solution of caustic soda for about three minutes at about 80° C., the mixture being then left to stand in water at 70° C. until the alkali has separated from the oil. In the event of incomplete refining, a soapy film of sodium petrolate will be found between the two layers, the resulting soap being insoluble in the dilute alkali.

Another test is based on the hydrolysis of soap by water. Thirty c.c. of the oil are continuously shaken for five minutes with 10 c.c. of water, in presence of one drop of phenolphthalein solution, in a closed test tube, then warmed to about 80° C. in the water bath and left to cool. If the separated water layer is tinged with red, an alkali soap is present.

The oil should not, of course, contain any free alkali. To test this, the oil is shaken up with alcohol containing one drop of phenolphthalein, a red coloration of the alcohol then indicating alkali.

The degree of refining can also be determined empirically by shaking up the oil with dilute sulphuric acid (1 : 1), which will acquire a brown colour in inverse ratio to the adequacy of the refining.

Water and Mechanical Impurities

Water in oil renders it turbid and causes it to prime when heated. If the proportion of water is high, heating gives rise to decrepitation. On the oil being gently warmed, minute particles of water will coalesce and sink to the bottom of the vessel, leaving the oil clear on cooling.

Turbidity in oil may, however, also be due to the separation of paraffin at a low temperature, or to the intentional addition of ceresine for the purpose of thickening a thin oil.

If such turbid oil be warmed to 40–50° C. in a test tube, the turbidity will disappear, only to return, however, as the oil re-cools.

If the oil is not too dark, additions of ceresine can be detected by the white deposit formed on treatment with alcohol-ether (3 : 4), which deposit is filtered off, washed with alcohol-ether and tested for its melting point in a capillary tube. Ceresine always melts between 60° and 80° C.

In dark oils the turbidity may also be due to particles of asphaltum in suspension.

Coarse, accidental mechanical impurities can be detected by passing about 250 c.c. of oil through a sieve of 0·3-mm. mesh and rinsing the sieve with benzine and ether. Such impurities comprise : sand, rust, glue detached from carelessly lined barrels, bits of rag, etc., splinters of wood, textile fibres, and so forth ; usually due to negligent handling of the oil.

General Specific Characteristics of Mineral, Fatty, Tar, and Rosin Oils

Almost every kind of oil is soluble in sulphuric ether, petroleum spirit, carbon disulphide, and benzol [1]; but differences are observed in the behaviour of oils towards alcoholic caustic potash or soda.

Mineral oils are unaffected by the action of these alkalis, whereas animal and vegetable oils and fats are " saponified " by caustic potash and soda, with separation of glycerine, and formation of soaps, i. e. potassium or sodium salts of the corresponding fatty acids.

The caustic potash test is performed as follows : Three or four drops of the oil are added to a solution of 0·5 grm of caustic potash (or soda) in 10 c.c. of alcohol, in a test tube, and the mixture is boiled for one to two minutes. The liquid is then cooled and shaken up with about 5 c.c. of water.

In the case of mineral, rosin, or tar oils, a milky turbidity is produced, whereas vegetable and animal oils give a clear solution of soap which froths when shaken. (Exceptions, in the animal oils, are afforded by spermaceti and bottlenose oils, which are regarded, chemically, as waxes, and therefore give, on saponification, alcohols that are insoluble in water.)

If the alkali has not reacted with the oil, another portion of the latter is shaken up with an equal volume of a mixture of 1 part concentrated sulphuric acid and 1 part water. (Note : the sulphuric acid should be poured slowly into the water, not the water into the acid !)   Mineral oils are stained yellow to yellow-brown; tar oils, brown to red-brown; beech tar oils, yellow-brown; rosin oils, ruby red.

When tar oils are mixed with concentrated nitric acid a considerable disengagement of heat occurs, whilst with mineral oils under the same conditions the temperature only rises by about 10° C.

According to Valenta (Chem. Zeit., 1906, p. 266), coal-tar oils can be distinguished from mineral oils by means of dimethyl sulphate, in which the benzol hydrocarbons present in coal tar are readily soluble at room temperature, whereas crude and refined petroleum, benzine, and rosin oils remain undissolved.   The test is performed by shaking

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[1] Ordinary castor oil is insoluble in benzine.

up 4 c.c. of oil with 6–8 c.c. of dimethyl sulphate for one minute in a narrow, graduated glass tube with glass stopper, the increase in the volume of the dimethyl sulphate being read off when the layers have separated. Since dimethyl sulphate is poisonous, it should be used with care.

Gräfe (*Chem. Zeit.*, 1907, p. 112) found that this test gave nearly theoretical results with mixtures of heavy coal tar oils and mineral oils, such as are most frequently met with in practice.

The only appreciable solubility in dimethyl sulphate occurs in the case of petroleum derivatives of very low boiling point ; and with the brown-coal-tar oils there is an approximately equal error of 10 per cent. ; but, provided this be borne in mind, the method is also applicable to these last-named oils. On the other hand, E. Küppers is stated to have found the method unsatisfactory.

Vegetable and Animal Oils and Fats in Mineral Lubricating Oils

Mineral lubricating oils are occasionally mixed with various fatty oils and fats, such as rape oil, olive oil, tallow, etc., the detection of which will now be described.

Testing for Saponifiable Oils and Fats

Three to five grms. of the oil are heated, in a test tube, containing a fragment of sodium as large as a pea, to 230–250° C. for twenty-five to thirty minutes, in a small sheet-iron dish containing fine sand, the oil being stirred by means of a thermometer. If, on cooling, the oil becomes very thick or gelatinous, or a soapy froth forms on the surface, it very probably contains fatty oils.

This test will reveal as little as 0·5 per cent. of fatty oil in pale samples, or 2 per cent. in dark oils.

The presence of resinic or naphthenic acids in an oil may cause gelatinisation, without frothing, in the sodium test, even in the absence of any fatty oil.

When the result of this test indicates the probability of a fatty oil being present, the saponifiable oils and fats may be identified by further chemical tests if desired, for which purpose the Köttstorfer saponification values and the colour reactions of the different oils are mainly determined.

Determination of Fat Content

Saponification Value Test.—The saponification value of an oil expresses the number of milligrams of caustic potash required to saponify 1 grm. of the oil. This value is ascertained in the following manner : A 250-c.c. Jena glass flask, rinsed out with neutral alcohol, is charged with 5–10 grms. of the oil (according to the proportion of fatty oil suspected), 25 c.c. of pure benzol being added, together with exactly 25 c.c. of half-normal alcoholic caustic potash (preferably from a burette). If large quantities of fatty oil are believed to be present in the sample, 20 c.c. of normal caustic potash are taken. The object of the benzol is to facilitate the reaction between fat and alkali.

At the same time a second, similarly treated 250-c.c. flask is charged with 25 c.c. of benzol and 25 c.c. of alkali, but without oil.[1] This check experiment is to establish the standard of the alkali solution, which must be re-determined for each test.

Reflux condensers, previously rinsed out with neutral alcohol, are mounted on both flasks, and the solutions are then boiled for half an hour on the water bath.

When cold, 50 c.c. of anhydrous neutral alcohol are added to each flask, and the liquids are titrated back with half-normal hydrochloric acid, in presence of one drop of 1 per cent. phenolphthalein solution as indicator.

If the oil under examination is dark, or assumes a red-brown colour on the addition of caustic potash (due to the presence of fish oil), phenolphthalein is replaced by alkali blue 6B solution.

The saponification value is found by multiplying the difference in the quantity of acid consumed in the two titrations (oil and blank) by the titre of the acid, expressed in milligrams of caustic potash, and dividing the product by the weight of oil taken.

Example.—Five grms. of oil were weighed out, and 25 c.c. of half-normal caustic potash were consumed both for the saponification and for the check experiment.

Amount of half-normal HCl consumed in check experiment		20·5 c.c.
In saponification experiment		17·3 c.c.
Difference		3 2 c.c.

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[1] If the alkali is measured with a pipette, the latter must be operated in precisely the same way in both experiments.

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The half-normal HCl being equivalent to the half-normal KOH, 1 c.c. of the acid will correspond to 28·05 mgrms. of KOH, and therefore the saponification value will be :—

$$(3·2 \times 29·05) \div 5 = 17·9.$$

The vegetable and animal oils and fats differ in respect of their saponification values, and consequently a mean saponification value of 185 is assumed for the oils now under consideration, that of pure mineral oils being taken as 0. Hence, in the above example, the fat content is : $185 : 100 = 17·9 : x$, so that $x = 9·6$ per cent.

Since 1 c.c. of normal HCl corresponds to 56·10 grms. of KOH, 1 c.c. of this acid will be equivalent to 0·303 grm. of fat (*i. e.* 56·10 ÷ 185). Hence, by multiplying the amount of normal acid (half the quantity of the half-normal acid) consumed in the titration (and corresponding to the caustic potash consumed in the saponification) by 0·303, the approximate amount of the fatty oil present in the mineral lubricating oil will be ascertained, viz. : $(1·6 \times 0·303) \div 5 = 9·6$ per cent. of fat.

Accurate values would be obtained if the nature and saponification of value of the added fat were known. If, for example, the oil has been mixed with wool fat (wool wax), the saponification value of that oil forms the basis of calculation.

In the determination of the fat content, the presence and amount of glycerine should be ascertained, because waxes also have a saponification value.

The following table gives the saponification values of several important oils, fats, and waxes :—

Linseed oil	. .	188–195 (221)	Palm oil . .	196–207
,, thickened	.	190–195	Palm kernel oil .	241–259
Cottonseed oil .	.	191–198	Ground-nut oil .	189–194
,, thickened		214–225	Coconut oil .	246–260 (268)
Sesamum oil .	.	188–195	Bone oil . .	191–203
Rape oil . .	.	170–179	Beef tallow .	193–200
,, thickened	.	195–267	Mutton tallow .	192–196
Black mustard-seed oil		174–175	Whale oil . .	188–193 (224)
White ,, ,,		170–171	Dolphin oil (body)	197–203
Olive oil . .	.	185–196	Spermaceti oil .	125–133
Olive kernel oil	.	182–189	Bottle-nose oil .	123–136
Castor oil .	.	176–186	Wool fat . .	82–130

Gravimetric Analysis.—In the absence of waxes and wool fat, the content of fatty oils can be determined indirectly by

the Spitz and Hönig gravimetric method, by transforming the fatty oil, by saponification, into a soap soluble in alcohol and extracting the unsaponifiable portion of the oil by treatment with benzine.

The method is performed as follows : 10 grms. of oil are saponified with 25 c.c. of two-normal alcoholic caustic potash, in presence of 25 c.c. of benzol, by boiling for an hour under a reflux condenser, followed by adding 25 c.c. of water and raising the whole to boiling.

When cold, the liquid is transferred to a separating funnel, the apparatus being rinsed out with 50 c.c. of 50 per cent. (weight) alcohol and 50 c.c. of petroleum ether (b.p. 30–50° C.), and the whole well shaken up. After settling, the alcoholic soap solution is drawn off, and is shaken up with successive quantities (50 c.c.) of petroleum ether, until the final extract leaves no oily residue.

The united benzine extracts are shaken up three times in succession with 15 c.c. of 50 per cent. alcohol (containing a trace of alkali), and this alcohol, after a single shaking with benzine, is added to the soap solution.

The benzine solutions are distilled, and the residue is evaporated in a tared dish, on the water bath, until all smell of benzine has disappeared. If the oily residue contains a few drops of water, it is stirred up with about 5 c.c. of absolute alcohol, and warmed until the alcohol has evaporated. The residue is then dried for five minutes at 100° C. until constant (to within 1–2 mgrms.) and the resulting mineral oil is weighed. The difference between the original amount of oil taken and the separated mineral oil gives the content of saponifiable fat.

When larger proportions of unsaponifiable fats, or those only saponifiable with difficulty, are present, it is advisable to apply qualitative tests for fatty oil to the unsaponifiable portion, and, if necessary, treat an aliquot part again in the manner described above.

When wool fat or waxes are present, the higher alcohols separated along with the mineral oil must be extracted, as esters, by boiling with acetic anhydride. In such cases the method does not give satisfactory results.

IDENTIFYING THE FAT

If it is desired to ascertain the nature of the fatty oil present in the sample, the alcohol is expelled from the

alcoholic-aqueous soap solution (containing the fatty acids) obtained in the foregoing method, and, after dilution with water, the solution is treated with ether, followed by dilute sulphuric acid to separate the fatty acids, the acid aqueous layer being run off and the ethereal solution of the fatty acids washed with concentrated Glauber salt solution and then with water until the latter no longer gives a colour reaction with ethyl orange. The ethereal solution is dried with calcium chloride and filtered, the ether being distilled off and the residual fatty acid dried for five minutes at 105° C.

In the event of insoluble oxy-acids being present—which indicate castor oil, blown oils, or fish oils—these are deposited on the sides of the separating funnel during the acidification of the soap solution, and can be dissolved in absolute alcohol after the ethereal solution has been poured off.

The determination of the melting-point, molecular weight, and iodine value of the recovered fatty acid will identify the fatty oil present.

Determining the Molecular Weight of Fatty Acids

In order to determine the molecular weight of the fatty acids, 1–2 grms. are boiled for a quarter of an hour with 25 c.c. of alcoholic half-normal caustic potash. The resulting solution is titrated back with half-normal HCl, a check experiment being performed, and the saponification value is ascertained.

The mean molecular weight is given by the equation :—

$$M = \frac{56110}{\text{sap. value}}.$$

Molecular Weights of Important Oils and Fats

Rape oil	.	.	.	.	309	Castor oil	.	.	.	.	297
Linseed oil	.	.	.	.	273	Bone oil	.	.	.	.	273
Olive oil	.	.	.	.	279	Beef tallow	.	.	.	271

Determining the Iodine Value

One of the most important characteristics of fatty oils is the iodine value, which expresses the percentage proportion of iodine capable of combining with an oil or fat. The reaction is based on the fact that, in the presence of mercury chloride, an alcoholic solution of iodine acts on oils, at

the ordinary temperature, the action being one of combination (addition) of iodine with unsaturated fatty acids and their glycerides.

(a) Hübl-Waller Method

The Hübl-Waller method is performed by dissolving a weighed quantity [1] of oil in 20 c.c. of pure chloroform [2] in a 300-c.c. stoppered glass flask, 30–60 c.c. of an alcoholic solution of iodine and corrosive sublimate [3] being added and the whole well shaken. If the mixture is turbid, more chloroform is added until it becomes clear.

After standing for twelve hours in the dark, the solution is treated with 20 c.c. of aqueous 10 per cent. potassium iodide and 100–150 c.c. of distilled water, the unconsumed iodine being titrated by shaking up with a standardised [4] solution of sodium thiosulphate (hyposulphite) until the red-brown aqueous liquid is pale yellow, and then to decoloration in presence of a little freshly-made starch solution as indicator. The recurrence of a blue coloration later is disregarded.

A check experiment is performed simultaneously, without oil, in order to determine the iodine content of the iodine-sublimate reagent. The amount of iodine taken up by the oil is calculated from the difference in the volume of thiosulphate consumed in the two tests, and is expressed as percentages (by weight) of oil.

Example.—0·2 grm. of oil was treated with 40 c.c. of iodine-mercury chloride solution. In the reverse titration the solution containing the oil consumed 36·6 c.c. and the check solution 58·6 c.c. of thiosulphate solution, 1 c.c. of which corresponded to 0·0105 grm. of iodine.

The difference, $58\cdot6 - 36\cdot6 = 22\cdot0$ c.c., multiplied by

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[1] Liquid fats 0·18–0·22 grm.; solid fats 0·5–1 grm.; drying oils (linseed, etc.) 0·15–0·18 grm. Turbid oil must first be filtered.

[2] The chloroform must be free from unsaturated compounds, which can be tested for by mixing 10 c.c. of the chloroform with 10 c.c. of iodine solution and titrating the mixture after standing several hours. Chloroform may be replaced by carbon tetrachloride or thiophene-free benzol.

[3] For non-drying oils 30 c.c. are used, 40 c.c. for semi-drying oils, and 60 c.c. for drying oils. The solution is prepared by dissolving 25 grms. of iodine and 30 grms. of mercury chloride, each in 500 c.c. of 95 per cent. alcohol, the solutions being filtered, united, and treated with 50 c.c. of hydrochloric acid of sp. gr. 1·19.

[4] With titrated iodine solution or pure dry potassium bichromate. This test is repeated at intervals. One grm. of bichromate corresponds to 2·5886 grms. of iodine.

the titre of the thiosulphate solution, *i. e.* 22 × 0·0105 = 0·231, gives the number of grammes of iodine taken up by the oil.   The iodine value is therefore :—

$$\frac{0·231 \times 100}{0·2} = 115·5.$$

(*b*) Wijs' Method

Wijs modified the Hübl-Waller method by using a solution of iodine monochloride in glacial acetic acid for the iodine-value determination.

With this object, 9·4 grms. of iodine trichloride and 7·2 grms. of iodine are dissolved separately in glacial acetic acid by gentle heat on the water bath, air being excluded, the solutions being then united and diluted to 1 litre with pure acetic acid.[1]

The determination is made in the same way as in the Hübl method, except that, instead of chloroform (which not infrequently contains alcohol), use is made of carbon tetrachloride, tested beforehand. (It should not turn green when heated with potassium bichromate and concentrated sulphuric acid.)

The Wijs reagent can be used at once and will keep for two to three months unchanged, so that there is no necessity to standardise it for each test.   A further advantage is that, in the case of non-drying oils and solid fats, the iodine value of which is below 100, the reaction is complete within half an hour, within about an hour with semi-drying oils, and within one to two hours with drying oils.

The iodine values obtained by this method agree with those of Hübl-Waller, except that they are a little higher in the case of oils with high iodine values and of wool fat. Since, with these methods, the higher values are the more correct, the Wijs method may be regarded as the more accurate.

Drying oils (linseed, poppy, Japanese wood oil, etc.) have the iodine values 130–204 ; semi-drying oils (rape, cotton-seed, sesamum, maize oil, etc.), 95–130, and non-drying oils (olive, castor, ground-nut oil, etc.) below 95 ; whilst the values for animal fats are below 80 in the case of land animals and always above 100 in the case of marine animals.

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[1] The acid should not show any green coloration when heated with potassium bichromate and concentrated sulphuric acid.

The lowest iodine values are those of the mineral lubricating oils, which are mostly below 6 and rarely above 14 (gas oil 17, for example), whereas cracked products of mineral oils have values up to about 70. Brown-coal tar oils have a high iodine value, e. g. solar oil 77, gas oil 63.

The following table gives the iodine values of a few important oils, fatty waxes, and fatty acids :—

Oils and Fats

Linseed oil . .	171–204	Rape oil . .	94–105 (108)
,, thickened .	110–170	,, thickened .	47–65
Cottonseed oil . .	102–111 (117)	Olive oil . .	79–90
,, thickened	56–66	Olive kernel oil .	187–88
Sesamum oil . .	103–112 (117)	Castor oil . .	82–88
Black mustard oil .	96–107	Palm oil . .	51–58
White ,, ,,	92–98	Palm kernel oil .	10–18
Ground-nut oil .	85–98 (103)	Whale oil . .	110–136
Coconut oil . .	8–9·5	Dolphin oil . .	99–128
Bone oil . . .	44–75 (82)	Sperm oil . .	81–90
Beef tallow . .	35–46	Bottle-nose oil .	67–82·1
Mutton tallow . .	35–46	Wool fat . .	17·1–28·9
		Rosin oils . .	43–48

Fatty Acids

Linseed oil .	.	.	.	.	179–182	
Cottonseed oil	.	.	.	.	111–116	liquid fatty acids 147–148
Sesamum oil	.	.	.	.	109–112	
Rape oil .	.	.	.	.	99–106	liquid fatty acids, 121–126
Black mustard oil·	.	.	.	.	110	
White ,, ,,	.	.	.	.	95–96	
Olive oil .	.	.	.	.	86–90	
Castor oil .	.	.	.	.	86–93	
Palm oil .	.	.	.	.	53·5	liquid fatty acids, 95–99
Palm kernel oil	.	.	.	.	12–13·6	
Ground-nut oil	.	.	.	.	96–103	
Coconut oil	.	.	.	.	8·3–10	liquid fatty acids, 54
Bone oil (crude) .	.	.	.	.	44–75	
Beef tallow	.	.	.	.	41·3	liquid fatty acids, 92
Mutton ,,	.	.	.	.	34·8	liquid fatty acids, 92·7
Whale oil .	.	.	.	.	130–132	liquid fatty acids, 145

The iodine value of an oil is affected to a considerable degree by the method of manufacture, as, for example, in the case of bone oils, hoof fats, ground-nut oil, etc., the larger the proportion of solid glycerides removed by pressing during the production of these oils, the higher the iodine value.

The olive oils prepared by the extraction process have a lower iodine value than those obtained by pressing : and the process of thickening such oils as rape and cottonseed oils lowers their iodine value. Thus the iodine value of

linseed oil recedes in proportion to the duration and temperature of the heating process and to the degree of oxidation, so that a thickened linseed oil may have an iodine value as low as 70.

Considerable changes in the capacity for taking up iodine may be produced in oils during prolonged storage and consequent exposure to the influence of atmospheric oxygen. In determining the iodine value it is therefore necessary to take this circumstance into consideration, especially with drying oils, to avoid drawing erroneous conclusions from the results.   In such cases the sp. gr. and the content of oxyacids should also be taken into account.

SPECIAL TESTS FOR PARTICULAR OILS, FATS, AND WAXES

In addition to the general methods for the determination of oils and fats, colour reactions are also employed, some of which are now given for the oils, etc., mentioned below.

Rape Oil Test.—Five c.c. of the oil are shaken up in a test-tube with 2 c.c. of an alcoholic solution of silver nitrate (2 grms. in 10 c.c. of distilled water, made up to 100 c.c. with alcohol), and gently heated for half to three-quarters of an hour on the water bath.

If the oil contains rape oil, a brown film of silver sulphide will be observed in the liquid after the alcohol has evaporated, and especially on the plane separating the oil and residual water, the oil also becoming turbid and brown.

The reaction is based on the fact that rape oil contains sulphur compounds, which blacken the silver salt; but the same reaction is also obtained with other oils containing sulphur.

Olive Oil Test (Elaidin Reaction).—Five to 10 c.c. of oil are shaken up for two minutes in a test tube with 5 c.c. of nitric acid (sp. gr. 1·38–1·41), and left until oil and acid have separated.   One grm. of mercury (or copper turnings) is then added, and when dissolved, the mixture is vigorously agitated for four minutes.   The mixture, which has risen in temperature through the heat generated by the reaction and, in the case of pure olive oil, acquired the consistency of ointment, is cooled by dipping the tube in cold water or setting it in a cool place, and is examined to ascertain the time at which turbidity appears.   Olive oil frequently deposits a yellowish-white substance after half an hour, and the oil becomes quite solid in eight to twelve hours, the

chief constituent, triolein, being transformed into solid elaidin by the action of the nitrous acid.

According to the literature, other oils give the same reaction, ground-nut oil, for example, depositing elaidin in cne and a half hours, sheep's foot oil in two hours, and sesamum oil in three hours, under the same conditions.

The separation of elaidin being dependent on several factors, the test is not altogether reliable.   For instance, Gintl reports that an olive oil that had been exposed to the sun for a fortnight, no longer gave the elaidin reaction.

In the elaidin test pure olive oil is pale to dark yellow, whereas if extraneous oils be present, or if the oil is not olive oil, it turns brown.

COTTONSEED OIL TEST

(1) *The Halphen Reaction.*—Equal quantities of the oil under examination, amyl alcohol and carbon disulphide (containing 1 per cent. of flowers of sulphur in solution) are warmed in a flask for about fifteen minutes on the water bath.

In presence of cottonseed oil an orange-red to red coloration will be produced; and if this does not appear in the time specified, the evaporated carbon disulphide should be replaced and heating continued for a further ten minutes.

This test will reveal down to 5 per cent. of cottonseed oil.

(2) *The Becchi Reaction.*—Ten c.c. of oil are treated in a flask with 150 c.c. of an alcohol-ether solution of silver nitrate (1 grm. dissolved in 200 c.c. of alcohol and 40 c.c. of ether, with addition of two drops of nitric acid).   The flask is fitted with a cork traversed by a glass tube about 100 cm. long, and is warmed on the water bath for a quarter of an hour.   A brownish-black deposit of silver is quickly formed by reduction, whereas in the case of other oils the reduction proceeds very much more slowly.   An old or boiled cottonseed oil, however, will not give this reaction.

(3) *The Wellman Reaction.*—A solution of 1 grm. of fat in 5 c.c. of chloroform is treated with 2 c.c. of phosphomolybdic acid solution, and well shaken.   In presence of cottonseed oil the mixture assumes a green colour.   On standing the mixture separates into two layers, the lower being water-white and the upper green, the latter turning blue on addition of ammonia.

(4) *Nitric Acid Reaction.*—About 5 c.c. of oil are shaken

up in a test-tube with an equal quantity of nitric acid (sp. gr. 1·38–1·40) and left to stand for twenty-four hours. If cottonseed oil be present, a brown coloration appears even in the case of oils that have been heated to a considerable temperature.

SESAMUM OIL TEST

(1) *The Baudouin Reaction.*—Five c.c. of oil are mixed with 10 c.c. of hydrochloric acid (sp. gr. about 1·19) and shaken up for about half a minute with 0·2 grm. of finely ground beet sugar. In presence of sesamum oil, the acid layer which separates from the oil will quickly assume a crimson tinge, but otherwise will become brownish-yellow or yellow.

This reaction is based on the presence in sesamum oil of a compound which gives a red colour reaction with the furfurol produced by the action of hydrochloric acid on levulose. The sugar may, accordingly, be replaced by a 1 per cent. solution of furfurol, 0·5 c.c. of which is shaken up with the mixture of oil and acid. This modification is considered to be more reliable, since certain olive oils (African, Portuguese, Bari) give a faint pink coloration when sugar is used.

The Baudouin reaction will reveal as little as 0·5 per cent. of sesamum oil.

FIG. 14.

When fats or oils have been coloured with coal-tar dyes, a red coloration may be produced by hydrochloric acid alone (without addition of sugar), in which event spectroscopical examination is the most reliable.[1]

When suitably diluted with hydrochloric acid, the red solution furnished by the action of hydrochloric acid and

[1] J. Formanek, *Die qualitative Spektralanalyse anorganischer und organischer Körper*, Berlin, 1915, R. Mückenberger; and J. Formanek and E. Grandmougin, *Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege*, Berlin, 1911, J. Springer.
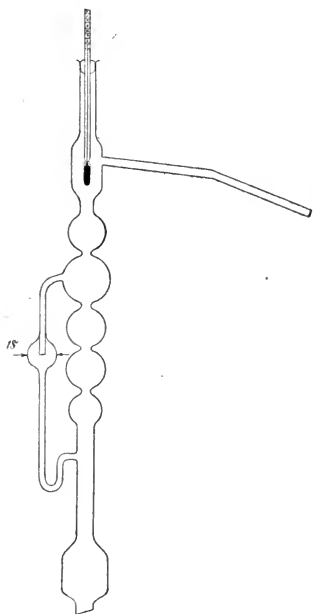
furfurol on sesamum oil gives two absorption bands at approximately λ528·0 and 492·5.

(2) *The Soltsien Reaction.*—Two parts, by volume, of oil are dissolved in four of benzol (b. p. about 70–80° C.) in a test tube, shaken up with three parts of concentrated stannous chloride solution (previously saturated with hydrochloric acid gas) and placed in a water bath at 40° C. After the stannous chloride solution has settled down, the tube is immersed in water at 80° C. up to the surface of the stannous chloride solution, in order to minimise the boiling of the benzol. If sesamum oil be present, the stannous chloride solution will turn red.

According to Soltsien, the oil from which the carrier of this reaction has been extracted with hydrochloric acid, will continue to give the reaction with stannous chloride. The reaction permits the rapid detection of sesamum oil, even in cases where the Baudouin reaction is unreliable, that is to say, in certain olive oils and oils that have been coloured artificially.

Wool-Fat Test

(2) *The Liebermann Reaction.*—If about 0·25 grm. of wool fat be mixed with 3 c.c. of acetic anhydride, filtered and treated with 1 drop of concentrated sulphuric acid, a red coloration is produced, which quickly turns green in contrast with the same reaction on the part of rosin oils. The reaction is due to the cholesterin of the wool fat.

(2) *The Hager-Salkowski Reaction.*—If about 0·25 grm. of wool fat be dissolved in chloroform and shaken up with an equal quantity of concentrated sulphuric acid, the liquid assumes a permanent red colour, with green fluorescence.

Tar and Rosin Oils

Coal-tar oils smell of cresol and will dissolve to water-soluble compounds in concentrated sulphuric acid at a moderate heat. Mixed with concentrated nitric acid, a thermogenic reaction occurs, nitro-compounds being formed. The temperature should not be allowed to rise too high, owing to the risk of explosion.

These oils are completely soluble in absolute alcohol at room temperature. The alcoholic solution has a greenish-blue fluorescence, and gives a transitory blue coloration on addition of a dilute solution of ferric chloride.

Brown-Coal Tar Oils also smell of cresol, but not so strongly as the coal-tar oils. The reaction with concentrated nitric acid is also weaker than that of the coal-tar oils, but considerably more powerful than that of the mineral oils, the rise in temperature in the latter case being only about 10° C.

Mixed with twice their own volume of alcohol, the brown-coal tar oils dissolve to the extent of 22–66 per cent. The solution is not fluorescent, nor does it give any coloration with ferric chloride solution.

The Grafe diazobenzol reaction, which is characteristic for both these classes of tar oils, is performed by boiling 2 grms. of oil for five minutes with 20 c.c. of half-normal aqueous caustic soda, and, after filtration and cooling, treating the liquid with a few drops of freshly prepared benzoldiazonium chloride solution.[1] If either class of tar oils be present, a red coloration or precipitate will be produced by the formation of an azo dyestuff from the phenols present in such oils.

Of the wood tars, beech-tar oil is used as a lubricant. This oil has a peculiar cresolic smell, differing, however, from that of the coal-tar or brown-coal tar oils. It is completely soluble in absolute alcohol, the solution being devoid of fluorescence, but giving a blue coloration with a small quantity of ferric chloride solution, the colour becoming blue if the quantity is larger. This reaction is due to the guaiacol $(OH \cdot C_6H_4 \cdot OCH_3)$ or cresol $(CH_3 \cdot C_6H_3 \cdot \begin{cases} O \cdot CH_3), \\ OH \end{cases}$ present in the oil.

Beech-tar oil also gives the above-described diazobenzol reaction, but in a less decided manner.

Rosin Oils.—These oils are soluble in 2 vols. of absolute alcohol to the extent of 50–100 per cent., the solution sometimes having a faint greenish-blue fluorescence, which is more apparent in ethereal solution. In contrast to mineral oils, they are miscible in all proportions with acetone.

Rosin oils are best detected by the Liebermann–Storch (Storch–Morawski) reaction in the following manner : 2 c.c. of oil are shaken up in a test-tube with 2 c.c. of acetic anhydride and gently warmed. After settling, the two layers of liquid are separated, and one drop of sulphuric

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[1] An ice-cooled, acidified solution of aniline hydrochloride treated with a few drops of sodium nitrite solution

acid (sp. gr. 1·53) [1] is placed on the acetic anhydride.   In presence of rosin oil, the liquid assumes a pink to violet tinge, otherwise becoming greyish-green.   The violet coloration, however, soon turns brown.

The reaction is fairly reliable and enables down to ·2 per cent. of rosin oil to be detected.   Wool fat (q.v.) also gives a red colour reaction with acetic anhydride.

Carles (*Chem. Ztg. Rep.*, 1910, p. 492) recommends the following test for rosin oils : About 5 grms. of oil are heated with a five-fold quantity of 60 per cent. alcohol at about 40–50° C. on the water bath, well shaken for a few minutes and cooled, the separated alcoholic layer being filtered off.   The filtrate is warmed on the water bath until the alcohol has evaporated, and when cold is treated with 2–3 c.c. of dimethyl sulphate, added drop by drop.   If rosin oil be present, the liquid turns red.

Another rosin oil reaction consists in dissolving the oil in carbon disulphide, adding one drop of tin tetrachloride (or tetrabromide) and agitating. Rosin oil give a violet coloration.

The rosin oils rotate the plane of polarised light to a considerably greater extent than mineral oils (see p. 129).

Solid Lubricants (Greases)

The method of testing solid lubricants varies according to the purpose for which they are used. Greases for motor vehicles are usually tested for the dropping point (incipient flow), soap content,

Fig. 15.

water content, free lime, loading ingredients, and graphite or paraffin.

The dropping point of a grease is the temperature at which a test fragment placed on the bulb of a thermometer begins to drop under its own weight.   This test is performed by means of the Ubellohde apparatus (Fig. 15), which consists of a thermometer, *a*, secured to a metal sleeve, *b*, which has a small opening at *c*, and carries on its flexible lower end a glass sleeve, *e*, 10 mm. long and 3 mm. wide at the lower orifice.
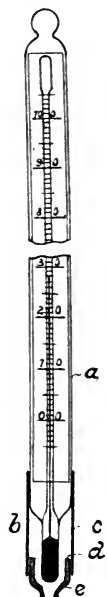
[1] This acid is prepared by slowly pouring concentrated H_2SO_4 into an equal volume of water.

In carrying out the test the glass sleeve, *e*, is filled with the grease, taking care to avoid the production of air bubbles, the surplus at the top being scraped off clean and level, and the sleeve inserted into the apparatus so as to be parallel with the axis thereof. Any surplus grease at the bottom of *e* is also removed. Solids, like paraffin, ceresine, etc., which might cause damage to the glass in filling, are melted and poured into the glass sleeve, which is placed on a sheet of glass; and the thermometer is attached before the grease is quite cold.

The glass sleeve, *e*, must be pushed into the metal sleeve as far as the three studs, *d*, will allow. The apparatus is then secured in a 4 cm. test tube by means of a cork and heated in a water bath—consisting of the 2-litre beaker filled with water and supported on an asbestos-wire gauze—so that the temperature rises at the rate of about 1° C. per minute.

High temperature (Calypsol) greases, which melt above 100° C., and sometimes only at about 200°, are heated in a bath of vaseline oil instead of water.

The temperature at which a decided bulge appears at the nozzle of the apparatus is the (incipient) flow point, whilst that at which the first drop becomes detached is the dropping point.

In consequence of the temperature drop between the external surface of the layer of grease and the bulb of the thermometer, the actual heat of the grease is a little higher than the thermometer reading. Although a correction of about + 0·5° C. should be made to allow for this, it is omitted for practical reasons.

In the absence of such an apparatus, and where absolute accuracy is not essential, a layer, about 1 mm. thick, of the grease (previously melted and stirred if necessary) is applied to the bulb of the thermometer by a brush, and the thermometer is mounted in a 3-cm. test tube, by means of a cork, so that the bulb is about 1 cm. above the bottom of the tube, the whole being left to stand for twelve hours. The tube is then supported half-way in a 2-litre beaker of water, and the operation continued in the manner already described. As soon as a drop begins to form on the bottom of the bulb, the flow point is read off on the thermometer, and the dropping point when the first drop has formed and is ready to fall.

Soap Content.—The soap content is usually determined by the Holde titrimetric method. Ten grms. of grease are

boiled in an Erlenmeyer flask with 50 c.c. of benzine (sp. gr. 0·700) and 10–15 c.c. of dilute hydrochloric acid (1 : 5) under a reflux condenser until clear.   They are then rinsed with benzine into a separating funnel, where the hydrochloric acid layer is removed for ascertaining the nature of the soap by qualitative tests.

If the hydrochloric acid layer is stained red by organic dyes used for colouring the grease, the benzine solution is shaken up with repeated quantities of hydrochloric acid until only a colourless extract is obtained.   Unless the greases have been artificially coloured, this extraction need only be performed twice.   The united hydrochloric extracts are washed twice with benzine (20 c.c. each time), the benzine solutions are united, freed from final traces of the mineral acid by washing with a concentrated solution of Glauber salt, followed by two washings with distilled water, and finally titrated with decinormal alcoholic caustic soda, in presence of 20 c.c. of neutralised absolute alcohol, until the phenolphthalein indicator used turns red.

The amount of acid found corresponds to that combined in the soap.   In order to calculate the soap content it is also necessary to know the molecular weight, M, of the fatty acids combined with the base.

For this purpose the titrated benzine solution of the decomposed fat is mixed with sufficient water to reduce the strength of the contained alcohol to about 50 per cent., the previously added 20 c.c. of absolute alcohol and the 96 per cent. alcohol in the titration reagent being taken into account.   To obviate emulsification, it is advisable to add a few c.c. of strong aqueous caustic potash and an equal amount of absolute alcohol, and after the bottom layer has been drawn off, to shake up the benzine solution several times with 50 per cent. alcohol as described by Spitz and Hönig.

The fatty acids are separated from the alcoholic soap solution, purified with benzine, according to the method already described for the identification of fats.

To estimate the molecular weight, $\frac{1}{2}$–1 grm. is dissolved in neutral absolute alcohol, and titrated with decinormal alkali, the molecular weight being found from the resulting acid value by the formula : $M = \dfrac{56\ 110}{\text{acid value}}.$

The soap content is calculated from the molecular weight of the fatty acids and from the acid value (p. 146).

Example.—If the molecular weight is 280, and the acid value of the fatty acids in the soap is 38, the base of the soap being lime, the amount of the lime soap is found from—

$$2KOH : Ca(m - 1)_2 = \text{acid value} : x$$
(mol. of the lime soap)

$$112 \cdot 22 : 598 \qquad = 38 : x$$

$$x = 20 \cdot 25 \text{ per cent. of lime soap.}$$

For sodium soaps the equation would be—

$$KOH : Na(m - 1) = \text{acid value} : x.$$

$$56 \cdot 11 : 302 \qquad = 38 : x.$$

$$x = 20 \cdot 45 \text{ per cent. of sodium soap.}$$

Water Content.—One hundred grms. of oil or grease (or a correspondingly smaller quantity when much water is present) are placed in a 300-c.c. flask and mixed with 100 c.c. of xylol, previously saturated with water by agitation.   A few lumps of pumice being added to prevent bumping, the liquid is distilled over an oil bath, until 80–90 c.c. of liquid have passed over (a Liebig condenser being used) into a narrow measuring cylinder graduated in c.c.   The volume of water is read off direct after the inside of the condenser tube has been rinsed out with xylol, the drops of water adhering to the sides of the cylinder have been forced down with a thin glass rod, and the cylinder has been warmed and re-cooled to room temperature.

Free Lime.—To determine the amount of free lime, 10 grms. of the grease are placed in an extraction shell and extracted for an hour in a Soxhlet apparatus with 60 c.c. of a neutralised mixture of 90 vol. of benzine (sp. gr. about 0·700) and 10 vol. of absolute alcohol.   In the case of greases of high melting point, the quantity of alcohol is doubled (or even more), because the alkali soaps present in such greases are very sparingly soluble in benzine.   Soaps, mineral oil, and fat pass into solution, leaving free lime and/or extraneous additions, graphite, etc., in the shell.

The free lime is determined, together with the carbonate, in the residue by the usual titrimetric method.

CHAPTER IX

APPEARANCE—COLOUR—SMELL—CONSISTENCE

LUBRICANTS can be judged to some extent by their external characteristics, such as appearance, smell, and consistence.

With this object the oil under examination is poured into a 15 mm. test tube and viewed both by transmitted and reflected light.

Refined distillate and residuum oils will appear perfectly limpid by transmitted light, and more or less transparent. The colour will be a more or less light red, yellow-red to pale yellow, according to the degree of refining, only a few kinds, such as white vaseline oil, being nearly colourless.

Unrefined lubricating oils are always opaque, even in thin strata, and are of a yellow-red, mostly very dark colour, distillate oils being far lighter than residuum oils. A dark colour, however, is no proof that the oil has not been refined, and, in spite of its colour, a dark oil may be purer than a light one.

Consequently, oils which have been prepared solely by distillation and careful filtration, without refining, may occasionally be more valuable than many refined oils. In general, however, well-refined oils are the best.

The colour of an oil is no reliable criterion of the degree of refining, being more dependent on the origin and kind of oil. Oils are also sometimes coloured in order to give them the appearance of definite grades. For example, 0·005–0·01 per cent. of quinoline yellow may be added to an oil to produce a golden yellow shade. Some oils, too, are occasionally coloured for the express purpose of distinguishing them from other oils : compressor oils, for instance, being coloured red.

Viewed by reflected light, all mineral lubricating oils exhibit more or less fluorescence, Galician oils being bluish-green to green, Russian oils blue and American oils grass-

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green. The fluorescence shows up very clearly when a drop of the oil is placed on glazed black paper. The colour of the fluorescence, however, is not a reliable criterion of the origin of an oil, since it can be produced artificially by means of aniline dyes.

The substances causing fluorescence are presumably compounds of the benzol series, such as chrysene, fluorene, and pyrene (see *Petroleum*, 1915, p. 334). The opinion that fluorescence is due to the presence of colloidal particles of paraffin is erroneous.

The natural fluorescence of the mineral oils is sometimes masked artificially in order to give the oils the appearance of (for example) vegetable oils, these latter—except ground-nut oil, which has a bluish sheen at the edges—being devoid of fluorescence. This treatment is known as " de-blooming," and the resulting oils are termed " de-bloomed " oils. The means employed consist of an addition of $\frac{1}{4}-\frac{1}{2}$ per cent. of a-nitronaphthalene $(C_{10}H_7NO_2)$ or aniline dyes soluble in oil; and the treated oils appear black when dropped on to black glazed paper.

This treatment, however, cannot completely destroy the fluorescence, which is still visible when the oil is viewed as a thick layer; and the fluorescence returns when the de-blooming agent has separated out again. Oils de-bloomed with nitronaphthalene darken considerably in colour, though they bleach again on exposure to direct sunlight.

Nitronaphthalene can be detected by boiling about 2 c.c. of the oil for a minute with 2–3 c.c. of a 10 per cent. alcoholic solution of caustic potash, the alcoholic solution turning red to violet through the conversion of the nitronaphthalene into an azo compound. Fish oils give a blood-red, and all other oils a yellow-brown or reddish-brown coloration.

This is a merely preliminary test, and if it gives a positive result, the presumed nitronaphthalene must be identified by heating and shaking up with zinc dust and hydrochloric acid, which reduce it to a-naphthylamine, this in turn being tested by oxidation with ferric chloride or by conversion into azo dyes.[1]

If an oil is turbid, this may be due to intentional or accidental admixtures, such as water, paraffin, ceresine, particles of asphaltum or pitch, graphite, mineral substances, etc.

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[1] D. Holde, *Kohlenwasserstoffe*, p. 222; R. Wischin, *Vademecum des Mineralölchemikers*, p. 119.

Coarse mechanical impurities, originating in careless handling, such as sand, rust, rags, fragments of straw, bungs, or textile fibres, should not be allowed in oils, by reason of the damage they may cause to the machine parts lubricated.

Even a small amount of water makes oil turbid, but is unimportant, though larger quantities, especially in cylinder oils, impair the quality of the oil.

Pure mineral oils are either inodorous, or have a mild, characteristic smell which becomes fainter as the density increases.   Unrefined lubricating oils have for the most part a decided, unpleasant smell, which is generally fainter in oils from residuum than in those from distillates.   The smell of mineral oils is intensified by rubbing a small quantity between the hands, especially if the oil be slightly warmed.

A disagreeable smell gives rise to the suspicion that the oil contains decomposition products, has been imperfectly refined or has been admixed with rancid oils or fats.   A smell of creosote indicates coal tar—or brown-coal tar oils. Rosin oils, beech-tar oils, and raw rape oil can also be sometimes detected by their characteristic smell.

Disagreeable smell in an oil can be ameliorated or masked to some extent by various agents or an addition of nitrobenzol, this latter preventing even a large amount of smelly oil from being detected.

Nitrobenzol is tested for in the same way as nitronaphthalene.

The consistence of oils is generally judged by the eye, the following gradations being differentiated :—

Thin (like petroleum).
Slightly viscous (like spindle oil).
Moderately viscous (corresponding to light engine oils).
Viscous   (,,   heavy   ,,   ).
Very thick   (,,   cylinder oils).
Thin ointment.
Lardy.
Buttery.
Tallowy.

For the purpose of judging the consistence on a uniform basis, the oils are filled, to a depth of 3 c.c. in a 15-mm. test-tube, heated for ten minutes in boiling water, and left perfectly quiet in water at 20° C. for an hour.   The consistence is then examined by tilting the test tube.   Oils containing soaps and rubber have a peculiar, ropy consistence.

VISCOSITY

Lubricating oils should have the greatest possible lubricating value, with minimum consumption, and therefore the viscosity is the most important criterion for classifying and judging them. What has already been mentioned with regard to this property in the chapter on Mineral Oils will serve as a guide.

Although the viscosity can be artificially heightened by various additions, such as rosin oils, asphaltum, and other agents, the real lubricating value is by no means increased thereby.

An addition of soap (especially alumina soap) or rubber (1–2 per cent.) temporarily increases the viscosity, which, however, recedes again on the oil being warmed.

If two oils, one of high and the other of low viscosity, be mixed, the viscosity of the mixture is below the theoretical mean.

As already mentioned, the viscosity of an oil also depends on the temperature ; and with rising temperature the viscosity of mineral oils diminishes more rapidly than is the case with vegetable oils (see pp. 112 and 174).

At 50° C. the viscosity of engine oils is only about one-fifth to one-sixth that at 20° C. ; and at 200–300° C. is only about 1–1·5° E. The higher the initial viscosity of an oil, the greater the relative diminution with rising temperature. Consequently the determination of viscosities at high temperatures does not possess the importance that has been ascribed to it, though it nevertheless affords, in practice, a useful basis for judging an oil.

In the case of motor oil, the viscosity is liable to continuous alteration, in certain circumstances, while in use. The author has examined oils of this kind before and after prolonged use in circulation lubricators, and has found that the viscosity of some imperfectly or unrefined oils, such as are now met with owing to the scarcity (in some countries) of sulphuric acid for refining, is liable to considerable diminution during use. Thus, one unrefined oil, which originally had the viscosity 26·2° E. at 20° C., declined to 13·0° E. after six days' running, and to 11·0° E. (at 20° C.) at the end of a twenty-days' run. Another oil with the initial viscosity 6·3° E. at 50° C. fell to 4.3° E. after a run of 100 kiloms., and to 4·3° E. after double that distance, but suffered no further change after running 500 kiloms.

Well-refined motor-car oils showed little change in viscosity while in use, one with the initial viscosity 8·9° E. at 50° C. still giving the value 7·6° E. after a run of 1000 kiloms. Another refined oil, of initial viscosity 7·6° E (at 50° C.), gave 6·5° E. after running 600 kiloms., and suffered no further reduction even at the end of 1100 kiloms.   Another well-refined oil, of viscosity 5·6° E. at 50° C., gave 5·5° E. after a run of 1200 kiloms., so that the alteration in viscosity of motor oils during use is evidently dependent on the degree of refining.   The higher, unstable viscosity is therefore due to the presence of unsaturated hydrocarbons or to the decomposition products formed during distillation.   The viscosity will be the more stable in proportion as these constituents are eliminated in refining.

It is therefore advisable, in addition to analysing the oil, to subject it to a practical test in order to see to what extent the viscosity suffers alteration in use.

On the other hand, in the case of good gear oils, which are used cold, the viscosity may remain unaltered, or even increase.   Thus, for example, an oil of this kind, with the initial viscosity 16·3° E., gave the value 17·7° E. at 50° C., after running 580 hours.   This increase may be ascribed to the volatilisation of the lighter constituents of the oil.

It is worthy of note that prolonged exposure to the sun's rays may increase the viscosity of an oil.   Thus the author has found that a gas oil (initial viscosity 1·9° E. at 20° C.) increased in viscosity to 4·0° E. after standing for a long time in the sun (see also Refining, p. 22).

It must also be remembered that the lubricating value of different oils of equal viscosity is not necessarily identical, experience having shown that, occasionally, a cheap oil of low viscosity lubricates just as well as an expensive one of higher viscosity.   The explanation is, however, to be found in factors that bear no relation to the lubricant, such, for instance, as the construction of the bearings, distribution of pressure, system of lubrication, temperature, etc.

Oils high in paraffin have generally a lower viscosity and flow more readily than those low in that constituent.

An important point is the condition—depending on the method of preparation—in which the paraffin is present in the oil; whether crystalline, colloidal or vaselinic structure, and the purpose for which the oil is designed.

It has been urged that paraffin is an undesirable constituent, but no direct proof of this has yet been adduced.

On the contrary, an oil high in paraffin may be well adapted for certain special purposes, it having been demonstrated that paraffin opposes considerable resistance to being pressed out of bearings, etc.   Thus American cylinder oils, high in paraffin, are superior to Russian cylinder oils which are low in that substance.

Galician crude oils furnish good, viscous engine oils, but cylinder oils of only medium quality; whilst Russian crude oils yield good viscous oils, and American crude, good engine oils and particularly good cylinder oils.

Flash Point, Burning Point, and Volatility

In the case of engine oils for lubricating bearings at ordinary temperature, the flash point has more of an indicational value and is almost always above 160° C., a temperature of rare occurrence in bearings.   On the other hand, it is of importance in the case of oils for lubricating gas engines, whether stationary or for vehicular use, and also those used for the cylinders of portable agricultural engines.

The flash point of lubricating oils for stationary and vehicular motors should not be excessively high, because the high fractions in oils of high flash point burn only with difficulty in the cylinder and leave greasy, charred residues which form a crust in the cylinder and under the valves. Moreover, the incompletely burned oil gives off a deal of smoke, and the air is contaminated by malodorous exhaust gases.

The larger the proportion of high viscous fractions, the more imperfect is the combustion of the oil, and therefore the greater the contamination of the motors.

For internal combustion (explosion) engines, the oil should have a flash point of 180–235° C.

The oil used for lubricating the cylinders of portable agricultural steam engines should have a flash point of 250–300° C., in order that the condensate used as feed water may not be contaminated by burnt oil.

Since every oil is composed of fractions of different boiling points, the lighter of these constituents volatilise to a relatively greater extent, even below the boiling point of the oil; and the larger the proportion of these light fractions, the greater will be the quantity volatilising at a given temperature.   Consequently, the flash point will give an approximate idea of the volatility of an oil; though, in some

cases, oils of identical flash point differ in respect of volatility. On the other hand, the flash point bears no definite and direct relation to the lubricating value of the oil.

The burning point is of subordinate importance, being always higher than the flash point and differing only slightly therefrom.

SOLIDIFICATION POINT

In all oils for motor vehicles and stationary internal combustion engines, and which are exposed to low temperatures in cold weather, winter especially, the solidification point plays an important part. Such oils should never congeal, even when cooled below zero C.

American oils and also certain Galician oils (from crude oil high in paraffin) solidify, for the most part, in the neighbourhood of 0° C. Other Galician oils (from crude high in naphthenes) are distinguished by a very low solidification point, — 10° to — 25° C. However, it has latterly been found practicable to produce lubricating oils with very low solidification point from crude oils high in paraffin : for instance, motor-car oil solidifying at — 14° to — 18° C., from Boryslaw-Tustanowice crude. Russian oils congeal at — 10°, some at as low as — 25° C.

The solidification point of mineral oils depends on their composition. Paraffin and the saturated hydrocarbons cause the oil to solidify at about zero C., and consequently, as a general rule, the solidification point is the lower as the original crude oil was the poorer in paraffin and the more completely the paraffin has been separated, as an intermediate product, in the course of manufacture.

Although American crude oils contain relatively little paraffin, the latter is more difficult to eliminate ; and since they contain practically nothing but saturated hydrocarbons, the resulting oils congeal already at about 0° C.

Russian oils, mostly prepared from crude oils free from or low in paraffin, contain larger proportions of unsaturated hydrocarbons, and therefore congeal with difficulty—often not above — 25° C.

As already mentioned in the chapter on the Treatment of Petroleum, Galician crude oils vary in composition, some of them containing large proportions of unsaturated hydrocarbons, and furnishing oils which do not solidify until — 10° to — 25° C.

That the presence of unsaturated hydrocarbons lowers

the tendency to solidification, is shown by the fact that the solidification point of unrefined oils rises after intensive refining (see also p. 179). Thus, oils which originally congealed at 1° C., solidified at 4–7° C. when refined.

The congelation of the oils by cold sets up a high frictional resistance in the lubricating appliances or bearings in starting the engine ; and the lubricating ducts, in particular, are liable to become choked, a condition which may lead to serious working troubles.

The employment of a motor oil high in paraffin has been known to cause trouble from piston and journal friction in the motor, owing to the oil having become semi-solid at 6° C. and depositing paraffin, which choked the sieve in the lubricating circulation so that no oil could reach the bearings and cylinder.

It should therefore be specified that oil for this purpose must remain limpid down to about zero C., and that winter oil must not solidify at − 10° C.

No relation exists between the viscosity and solidification point of an oil ; and in oils of the same viscosity the solidification point may be high in one case and low in another.

To lower a high solidification point, the oil is mixed with another that solidifies at a lower temperature. That every oil, however, is not suitable for this purpose can be gathered from the following example, taken from practical experience. In order to lower the solidification point of a motor-car oil, of viscosity 10° E. at 50° C. and setting at 4° C., it was mixed, in equal proportions, with a compressor oil of viscosity 2° E. at 50° C. and setting at − 22° C. The mixture had the solidification point − 9° C., but its viscosity fell to 2·7° E. at 50° C., which was too low for the lubrication of an internal-combustion engine.

On changing the proportions of the mixture to 2 parts motor oil and 1 part compressor oil, the viscosity increased to about 3·8° E. at 50° C., but the oil congealed at about − 1° C., and therefore this mixture did not meet the requirements of the case.

Consequently, it is not feasible to obtain all the desired properties by simply mixing two indiscriminately selected oils, but oils suitable for the purpose in view must be chosen, and the mixture examined afresh. When no choice is available, the oils at disposal must be mixed only in such proportions that the desired improvement in one property

does not result in the others being adversely affected to any appreciable extent.

Finally, it should be noted that, in order to obtain a perfectly homogeneous mixture, thick oils should be heated to about 50° C. for mixing.

Classifying Oils according to Viscosity, Flash Point, and Solidification Point

Good oils for small internal-combustion and motor-vehicle engines should have the viscosity 4·5–13° E. at 50° C., and a flash point of 180–235° C.

Oils suitable for large internal combustion-engines, of 100 h.p. and upwards, should have the viscosity 8–15° E. at 50° C., and a flash point of about 210° C.

A distinction is drawn in the trade between summer and winter oils.

Summer oils are thicker, contain more paraffin, and solidify at about 1° C. Winter oils are thinner, lower in paraffin, and solidify only below zero C.

Summer oils for motor vehicles have the viscosity 7–11° E. at 50° C., and a solidification point of 4° to − 1° C.

Winter oils for the same purpose have the viscosity 4–7° E. at 50° C., and usually a solidification point of − 2° to − 12° C. or even lower.

For motor-car oils a high viscosity, not below 8° E. at 50° C., is advisable, since it cannot be known beforehand whether the viscosity will remain constant when the oil is in use (see p. 164).

Neutrality

Well-refined oils should not attack the metal surfaces of the machine parts lubricated, and they must therefore be perfectly neutral.

In general, the acid content of engine oils is 0·01–0·03 per cent., expressed as sulphuric anhydride. In dark lubricating oils the amount should not exceed 0·1 per cent.

It should be noted that unduly prolonged storage and the resulting resinification of an oil will lead to an increase in the content of oxygenated substances liable to corrode metal.

If a mineral oil containing vegetable or animal oils or fats, such as tallow, is used for lubricating the cylinders

of high-pressure steam engines, the hot steam may decompose such oil or fat into glycerine and fatty acids, which latter corrode the cylinders extensively in the course of time, vegetable and animal oils being decomposed at as low as 250–300° C. by steam under high pressure.

Rosins and Asphaltic Substances

Well-refined oils are free from resinic substances, but through the influence of light and atmospheric oxygen (autoxidation), and possibly by polymerisation of the terpenes present, oxygenated, resinous substances are formed in all mineral oils, especially in the warm (*e. g.* in motor-car use), and finally a black insoluble mass is deposited. For example, a motor oil, originally free from rosins, was found to contain 0·6 per cent. after running 1100 kiloms., and 0·95 per cent. after 1200 kiloms.

Russian oils resinify more rapidly than those of Galician or American origin.

For the above reasons it is therefore advisable to store oils in tightly closed, opaque receptacles in a cool place, where direct sunlight cannot gain access and the storage vessels cannot become warm.

Pale, transparent oils contain not more than 0·6 per cent. of resinous substances, and dark oils not over 1 per cent., only badly refined oils containing as much as 3–3·5 per cent.

Carefully refined oils should be free from asphaltic bodies, since the presence of these causes the oil to adhere to the metal surfaces and increases bearing friction to an unfavourable extent.

In cheap oils, up to 0·2 per cent. of hard asphaltum, insoluble in benzine, may be permitted. Soft asphaltic substances, insoluble in alcohol-ether, do no harm so long as they are not present in more than small quantities.

Dark cylinder oils contain up to about 1·5 per cent. (rarely 2–3 per cent.) of soft asphaltic bodies.

In lubricating internal-combustion engines on the circulation system, in which the oil is forced by a small pump from the tank through the bearing ducts, and runs back into the tank, asphaltic substances are gradually formed in the oil by the influence of the hot engine, especially when some of these substances were originally present in the oil. The author has found 0·26 per cent. of asphaltic bodies, after a run of twenty days, in oil that was originally

quite free therefrom.   Another oil, containing 0·06 per cent.
of asphaltic substances, was found to contain 0·34 per cent.
after a run of 500 kiloms.; whilst another oil, devoid of
these constituents, contained 1·6 per cent. after 1200
kiloms.

The presence of large quantities of asphaltums may lead
to resinification and clogging of the bearings and bearing
ducts, and also to the formation of injurious residues in
the cylinders.

It is therefore inadvisable to allow the oil, in circulation
systems, to remain too long in use, even when the wastage
is replaced by fresh oil.   It is far better to replace the whole
with fresh oil as soon as it has gone dark in colour and
nearly opaque, and has a strong burnt smell.

The old oil can always be used for some other purpose
—for instance, mixed with solid fat for greasing the
differential.

More important than the determination of the original
asphaltum content, is to ascertain the extent to which the
percentage of asphaltum increases during a given length
of service, this depending on the kind and origin of the
oil, and varying therewith.

Susceptibility to Resinification, Tar Value, Tarification Value

Distilled and well-refined mineral lubricating oils do not
resinify, even when heated to 100° C.   Under similar
treatment, dark, unrefined, and also unfiltered oils thicken,
gradually become sticky, and finally resinify, this condition
being the more completely attained in proportion to the
degree of impurity of the oil, or the greater its content of
pitch-forming or asphaltogenic substances.

With regard to the tar value and tarification value, no
definite limits can be set in the absence of any precise
specification, the results being influenced by various factors,
such as the superficial area of the heated oil.   In general,
however, it may be said that the higher these values the
more liable is the oil to undergo alteration in use.

The following table gives the tar and tarification values
of various refined and unrefined motor-car cylinder oils of
Galician origin, which may serve for guidance.   For the
sake of comparison, two sets of tarification values are given,
being those obtained after heating the oil at 100° C. for

a hundred hours, and after fifty hours at 150° C. respectively. The superficial area of the oil was 16 sq. cm. for 50 c.c. in a 75-c.c. glass beaker.

Oil	Viscosity Engler @ 50 deg. C.	Tar value	Tarification Value	
			@ 100° C.	@ 50° C.
Auto oil V, refined . . .	5·6	0·27	0·37	0·48
,, S, refined . . .	6·1	0·24	0·28	—
,, K, refined . . .	7·3	0·36	0·52	0·56
,, K, refined . . .	7·8	0·40	0·43	0·46
,, R, refined . . .	9·7	0·44	0·52	—
Heavy engine oil, refined .	6·6	0·36	0·47	0·52
,, P, lightly refined .	10·8	0·36	0·50	—
,, P, well refined .	11·3	0·25	0·35	—
,, K, unrefined . .	4·5	0·83	0·92	0·99
,, ,, ,, .	5·5	0·80	1·00	1·21
,, ,, ,, .	6·5	0·85	0·98	1·03
,, H, unrefined . .	7·1	0·89	—	—
,, I, unrefined . .	8·6	0·95	—	—
,, Z, unrefined . .	9·6	0·97	1·45	—
,, P, unrefined . .	11·7	1·39	1·50	—
,, R, unrefined . .	12·4	0·84	0·96	—
,, AB, unrefined . .	13·0	1·17	1·40	—
Steam cylinder oil . . .	14·4	0·59	0·75	—

Soap and Rubber Content

Oils for lubricating the cylinders of internal-combustion engines should not contain either soap or rubber. Such additions increase the viscosity, but, as already mentioned, this decreases again when the oil is heated. These substances also lead to the formation of incrustations and injurious residues in the cylinders, and must therefore be regarded as adulterants in motor oils.

Vegetable and Animal Oils and Fats in Mineral Lubricating Oils

In addition to individual mineral oil fractions and mixtures of such fractions, mixtures of mineral oils with vegetable and animal oils and fats, such as compound oils and fats, are met with in commerce, but only, as a rule, for lubricating cold-running bearings. Even for this purpose, however, no drying oil, liable to become tacky after a short period of service, should be used.

The oils chiefly employed are raw and refined rape oil,

olive oil (cold- and hot-pressed), cottonseed oil, castor oil and palm oil, tallow, bone oil, and, finally, wool fat. The only non-drying vegetable oils or animal fats that should be used for lubricating internal-combustion engines are such as will not form any injurious residues in the cylinders, chief among these being olive oils, tallow and castor oil (see also Brake Tests). Rotary engines on aircraft are lubricated with rape oil exclusively.

The effect of the addition of fatty oils to mineral oils for lubricating machine parts should not be underestimated, since it enables certain properties, such as viscosity, flash point, solidification point, etc., to be regulated, and exerts a beneficial influence on the lubrication, increasing the power of withstanding the forces which tend to press the oil out of the space between shaft and bearing.

Many fatty oils are distinguished by high viscosity, high flash point, and low solidification point, and these oils generally possess good adhesion. Provided such mixtures be used cold, there is no risk of the formation of acids from the fatty oils present.

In order to ascertain the behaviour of an addition of rape oil to mineral oil for engine use, a brake test was performed with a four-cylinder engine, 110-mm. bore and 180-mm. stroke, the output of the motor being measured when lubricated with pure mineral oil and then with the same mineral oil containing 25 per cent. of rape oil. The motor was run for ten consecutive hours, and the oil was then examined, with the following results.

The engine output at 800 revs. per minute was 35·5 h.p. with pure mineral oil, and, under the same conditions, but lubricated with a mixture (4 : 1) of mineral oil and rape oil, 36·85 h.p., an increase of 1·35 h.p. This increased output was also maintained under full load during the ten hours of the test.

The small amount of friction noticed in the piston rings when using the pure mineral oil, disappeared when the mixed oil was used. No injurious changes were sustained by the mixed oil during the test ; and the acid content only increased by 0·01 per cent.

Practical trial runs with a motor-car using the mixture of mineral and rape oils also gave highly satisfactory results, and consequently the use of rape or other suitable vegetable oil can be recommended, especially when vegetable oils are cheap.

The viscosity of the fatty oils does not sink so rapidly with rising temperature as that of mineral oils, and usually undergoes very little change, whereas mineral oils exhibit all degrees of consistence between narrow limits of temperature.

Mineral oils evaporate with difficulty at high temperatures, but always more readily than fatty oils; but, on the other hand, they are far less prone to spontaneous ignition than vegetable or animal oils and fats, and, on this account, are mixed with the latter for certain purposes.

Mixtures of mineral and fatty oils should not be regarded as adulterations provided they are expressly stated to be mixtures, or when the addition of fatty oil is beneficial to the lubricant. Of all the fatty oils, castor oil is the only one that is difficult to incorporate with mineral oils; and in making a mixture of this kind the castor oil must first be stirred up with at least 10 per cent. of a fatty oil that mixes easily with mineral oil, the latter not being added until that has been done.

When castor oil is heated quickly to about 300° C., a viscous mass consisting of triundecylenic anhydride is obtained, which is sold as " Floricine." In contrast to the original castor oil, this product is miscible in all proportions with mineral lubricating oils, and accordingly will take up any desired amounts of ceresine and vaseline, on which account it is particularly suitable for the preparation of viscous lubricating oils. It is also capable of absorbing considerable quantities of water, even in presence of mineral oil. It is, however, not miscible with 90 per cent. alcohol, though castor oil is soluble in that agent at 25° C.

When rape oil or cottonseed oil is heated to 70–120° C., and air or oxygen is simultaneously blown in until the density is approximately the same as castor oil (0·97), the so-called blown oils are obtained. Oil treated in this way is also sold as soluble castor oil (blown or thickened oil), and is readily soluble in benzine and mineral oil. Mixtures of mineral oils with this oil are sold as " marine oil " for lubricating marine engines.

Blown rape and cottonseed oils show increased viscosity, reduced flash point, higher saponification value, and lower iodine value.

Mixtures of mineral oils with olive oil (hot-pressed), raw rape, cottonseed or castor oil, and thickened oils, are most frequently used for marine and railway purposes.

The following table gives the viscosity, flash point, and solidification point of some of the oils under consideration :—

	Viscosity (Engler)		Flash point °C.	Solidification point °C.
	At 20° C.	At 50° C.		
Rape oil . . .	13	4–5	298–320	0 to −16
Oxidised rape oil .	—	12	210	
Olive oil (hot-pressed)	11–13	3·8	205	0 to −10
White mustard oil .	—	3·9	280	—18
Cottonseed oil . .	9–10	4·2	286	0 to −7
Castor oil . .	140	16·5	275–290	−8 to −18
Sesamum oil . .	10	—	245	−3 to −18
Bone oil . . .	12	—	153	−5

Tar Oils and Rosin Oils

Coal-tar oils and brown-coal-tar oils are only added to cheap oils, and can be detected by their smell of creosote. The dark heavy oils (anthracene oil, green oil) obtained by pressing anthracene are used for this purpose. Unless acid, they do not corrode the bearings, but they are only of low viscosity.

Coal-tar oils have a density exceeding 1, and a viscosity of 2·3–4·6° E. at 20° C.

Brown-coal-tar oils have a density of 0·890–0·970, and a viscosity of 1·5–3·0° E. at 20° C. The flash point is about 120° C.

Beech-tar oils also are sometimes mixed with low-grade lubricating oils. They have a characteristic, penetrating and easily recognisable smell of creosote.

Rosin oils are comparatively dear, and are therefore seldom mixed with mineral oils. Moreover, their great tendency to resinify unfits them for this purpose.

Unrefined rosin oils are employed in making greases for lubricating wagon axles.

Addition of Graphite

To lessen the dry friction which is liable to occur, in addition to the liquid friction, when journals and bearings rub together, especially under heavy load or at low speed, it is customary to mix solid graphite with the lubricating oil, this substance having the property of smoothing the

rugidities of metallic surfaces by coating them with a soft layer.

Crude granite cannot be used for lubricating, because, in that condition, it is unable to penetrate into all the parts to be lubricated. The material used, preferably flaked graphite, must be perfectly pure and as far as possible free from other mineral substances, especially from sharp-edged particles of quartz. For this purpose, the graphite is purified by treatment with concentrated sulphuric acid and hydrofluoric acid.

Various graphitic preparations are on the market, such as " Aquadag," an extremely fine emulsion of pure (Acheson)[1] graphite in water, and " Oildag," a similar, 10–15 per cent., emulsion of graphite in oil. The graphite is maintained in the colloidal condition by the addition of an aqueous solution of tannin and small quantities of ammonia.

Both lubricants, Aquadag and Oildag, are sold as " Kollag " (*Chem. Ztg.*, 1916, p. 358).

Such specially prepared graphite does not settle down immediately to the bottom of the water or oil, but remains in suspension, in a finely divided state, for a long time.

It is stated that an addition of 1–2 per cent. of one of these graphite preparations saves up to 50 per cent. of oil. The extent to which Oildag is suitable for lubricating internal-combustion engines is a matter still to be ascertained by accurate experiment ; and since graphite does not burn away in the cylinder, a gradual deposition on the cylinder walls, piston rings, and valves seems not improbable. In the experiments made in Germany on lubricating Fiat engines with graphite and oil, good results were only obtained by the application of a filter to catch the deposited graphite.

Graphite has been found highly useful as an admixture to solid greases, for which purpose an ordinary, but pure, variety, free from quartz particles, can be employed.

Solid Greases

From motives of economy and cleanliness, solid greases (see p. 25) are used, in addition to mineral oils, for lubri-

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[1] Acheson graphite is manufactured, along with carborundum, from anthracite and sand in an electric furnace, and is then transformed into the colloidal state.

cating the journals, ball bearings, and less accessible cold running parts of motor-cars. Solid greases, mixed with oil, are employed for greasing change-gear pinions, differential gear, steering pinions, etc., on account of the difficulty in supervising the lubrication of these parts. Such solid greases must have a uniform consistence like ointment, and not contain any granular particles of soap or free lime.

Their colour is either yellow, yellow-brown, or brown, according to the materials used in the preparation. Sometimes they are intentionally stained. They must be free from any disagreeable smell, such as tar, etc.

These solid greases must not be liable to any injurious alteration during storage. For example, they must not resinify, or deposit oil or soap during storage or use. On this account, ceresine and mineral wax form suitable additions to solid greases, ceresine in particular having the property of not separating out when mixed with mineral oils.

The dropping point should not be lower than 70° C., and is generally 75–90° C. (120–150° C. in the case of Calypsol greases). The dropping and flow points are affected by various factors, such as the kind and quantity of the contained soap, the nature of the materials from which the soap is made, and the water content and viscosity of the oil. The flow point is usually about 5° C. above the dropping point.

The soap content should be 20–25 per cent., though in some cases 15 per cent. will suffice.

The water content is usually 4 per cent., though some solid greases contain up to 7 per cent.

The free lime should not exceed 0·3 per cent.

Loading agents, such as talc, gypsum, barytes, etc., cannot be permitted, but a certain amount of pure graphite is beneficial.

Economics of Lubrication

A lubricating oil should always be true to grade. In addition to analytical examination, practical tests are of great importance for ascertaining the properties of an oil after prolonged use for the purpose for which it is intended.

Apart from the composition and properties of an oil, the economic aspect, *i. e.* the cost of lubrication, should also be considered.

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It not infrequently happens that a practical test shows an advantage, as regards running costs, in replacing a cheap oil by one of higher price, on account of the lower consumption, reduced wear and tear, and diminished loss of power with the dearer oil.   On the other hand, the unfortunate experience is only too common that money has been wasted on oils that have been boomed under all kinds of fantastic names, and therefore sold at specially high prices, when equal results could have been obtained by a proper selection of a cheaper oil.   (See also the section on " Viscosity," for the changes sustained by oil in use.)

Sometimes a practical test will reveal that the running costs can be reduced, whilst obtaining the same effect in other respects, by using a different oil or mixture, because this is more economical in use.   Consequently, all circumstances should be taken into consideration before deciding on any particular kind of oil.

From the economic standpoint it is also important to be able to use spent oil over again, even if for some other purpose, after suitable treatment if necessary.

The engine oils that have been used for lubricating the cold running parts of the machinery mostly contain water and mechanical impurities.   Such oils may be successfully used over again after being warmed along with fused neutral calcium chloride, or shaken up with strongly dried (partially fused) common salt, or filtered hot through sawdust, pure wood wool and granulated bone black, or fuller's earth (bleaching earth), and finally freed from the last traces of water by heating to 105° C.

Oils purified in this manner are generally darkened in colour, and their density and viscosity may be higher than those of the original oil, through the volatilisation of the lighter constituents during service ; but as a rule their lubricating value is not increased.   (See " Viscosity " section.)

If the oils contain fatty oils, the acidity of the spent oil should certainly be tested before using it again.

Spent oils from the lubrication of the hot running parts of internal-combustion engines are contaminated by decomposition products, resinous and asphaltic bodies, but may be used for greasing the pinions of the speed gear, differential gear, etc., after being carefully filtered, warm, through linen cloth (with or without the assistance of bone black, fuller's earth, or other decolorising agents), and mixed with solid greases.

Moreover, motor-car oils can be purified, after prolonged use, so as to refit them for cylinder lubrication. The two following examples show how this can be accomplished by intensive refining with sulphuric acid and alkali, or decoloration with fuller's earth and hot filtering (as mentioned above).

Oil after Running 1200 Kiloms

	Before refining: nearly black, opaque, smell of burnt oil.	After refining: brownish-yellow, transparent, inodorous.
Viscosity	5·5	5·3
Asphaltic bodies . .	1·63	—
Rosins	0·95	—
Flash point . . .	88° C.	178° C.
Burning point . . .	132° C.	225° C.
Acid content . . .	0·017	0·01
Solidification point . .	7·5° C.	4·0° C.

Oil after Running 1700 Kiloms

	Before refining: nearly black, opaque, smell of burnt oil.	After refining: brownish-yellow, transparent, inodorous.
Viscosity	6·6 E.	6·3 E.
Asphaltic bodies . .	0·8	—
Rosins	0·6	—
Flash point : . .	140° C.	235° C.
Burning point . . .	245° C.	278° C.
Acid content . . .	0·018	0·04
Solidification point . .	7° C.	5° C.

Prior to use, this second oil had the viscosity 7·6, flash point 238°, burning point 268°, acid content 0·014, and setting point 7·0°.

It is noteworthy that the refining raised both the flash point and burning point.

Both the purified oils behaved perfectly when used again for lubricating the engine. It is therefore evident that spent oils should not be thrown away unconditionally, especially at a period when oil is not only scarce, but also very dear. Of course, the decisive factor is the cost of the refining.

TECHNICAL SECTION

CHAPTER X

PROPERTIES AND USES OF FUELS

THE following fuels are in general use in internal-combustion engines :—

(1) Aliphatic hydrocarbons : refined or crude petroleum benzine, crude or refined petroleum, solar oil, gas oil, and, finally, acetylene.

(2) Aromatic hydrocarbons : coal-tar products, such as benzol, toluol, and xylol (light and heavy benzol, solvent naphtha, etc.), and naphthalene.

(3) Mixtures of aliphatic and aromatic hydrocarbons, such as benzine from brown-coal tar and the tar from bituminous shale, light solar oil from brown-coal tar, cracked products, liquefied oil gas, etc.

(4) Ethyl- and methyl alcohol.

Motor lorries and vans are usually driven by benzine, benzol, or alcohol, either alone or mixed; in some cases with additions of petroleum, acetone, ether, carbon disulphide, etc. Each of the fuels mentioned has its special advantages, and also certain drawbacks, it being possible, however, to remedy the latter, to a greater or smaller extent, by the admixture of suitable substances.

From the technical standpoint it is essentia that the fuels used for internal-combustion engines, especially those for lorries, should be as uniform as possible in composition, gasify easily and uniformly without the aid of external heat, be readily inflammable and burn without leaving any appreciable residue or giving off a disagreeable smell, have a minimum fire risk, and finally a maximum heating value and consequent efficiency.

It is, however, impossible for any single fuel to fulfil the whole of these requirements, more especially since the cost also plays a very important part, cheapness being essential to ensure low running costs.

This last circumstance is of particular importance because the useful effect of a fuel in the internal-combustion engine is, as is well known, only 20–25 per cent. of the heating value. Special consideration will now be given to these questions in connection with individual fuels and their application in the internal-combustion engine.

Benzine

Of all the fuels employed or suggested for motors, the best in respect of properties and efficiency is the benzine obtained by distilling, refining, and rectifying petroleum.

The term benzine is also applied to certain fractions from brown-coal tar, bituminous shale, and, as will be seen later, petroleum residues. Formerly the term was applied to coal-tar benzene (benzol) and all the liquids specified.

Both light and medium petroleum benzine vaporise readily and form a comparatively homogeneous mixture with air in the engine cylinder—a point of importance in relation to complete combustion in the engine. Both kinds burn with scarcely any smell, so that no difficulty is encountered in cranking up and starting the engine.

Heavy benzine vaporises less readily that either of the above at ordinary temperature, being chiefly composed of constituents of higher boiling point. Since these heavier constituents, which are not vaporised under ordinary conditions in the carburettor, are carried by the air current into the engine, a particularly heavy benzine may furnish a mixture that explodes irregularly ; and as such a benzine will contain a comparatively small proportion of readily volatile constituents, it may give rise to some difficulty in starting the engine, especially from the cold state.

Such starting difficulties can, however, be overcome by first injecting a light benzine into the cylinder, or adding to the starting charge a certain quantity of benzol or light benzine. Uniform gasification can be obtained by suitably warming the carburettor or by introducing warm air into the latter. As soon as the engine has warmed up after a short run, it will begin to work regularly ; so that the use of heavy benzine is not attended with any special difficulty.

Apart from acetylene, benzine has the greatest heating value of all the above-mentioned fuels. The heating value, whilst enabling a conclusion to be formed as to the work a given quantity of fuel is capable of doing, is no guide as

to the output of the engine.   If, on the one hand, a large quantity of fuel of low heating value be rapidly burned in an engine, and, on the other hand, a small quantity of fuel of greater heating value be burned slowly therein, the engine output, expressed as horse-power, may be the same per second in both cases.

Since alcohol (an oxygen compound), for example, requires a good deal less air for its combustion than benzine or benzol (which contain no oxygen), the charge in the engine cylinder can develop almost the same amount of energy whether composed of benzine, benzol, or alcohol, mixed in the most favourable conditions with air.   Therefore, by charging the cylinder with a larger quantity of alcohol, approximately the same output can be obtained as with benzine or benzol, though, of course, the running cost will be considerably higher.

The following table shows the heating values of some of the fuels used in motors or capable of forming adjuncts to motor fuel.

Heat Units (Calories) Liberated by the Combustion of 1 *Kilo*

Acetylene	12,200
Hexane (present in benzine)	11,500
Heptane (,, ,,)	11,370
Benzine	11,160–11,225
Xylol	10,220
Petroleum (according to kind) . . .	9,960–11,160
Crude oil, approximately	9,900
Benzol	9,500–10,038
Naphthalene	9,700
Sulphuric ether	8,920
Acetone	6,720
Ethyl alcohol (95 per cent.) . . .	5,875–5,940
Methyl alcohol	5,300
Carbon disulphide	3,300

The benzine (light solar oil or photogene) from brown-coal tar contains both saturated and unsaturated aliphatic hydrocarbons, together with aromatic hydrocarbons (heptane, octane, nonane, olefines, naphthenes, benzol). It has the density 0·780–0·810, begins to boil at 100° C., but only furnishes 20 per cent. of constituents boiling up to 150° C., and has a final boiling point of 250° C.   For this reason it is only used for stationary engines, for example, Daimler engines.

Benzine is a readily inflammable substance with a high fire risk.   In the liquid condition it is neither explosive

nor liable to spontaneous ignition, and if lighted in an open vessel will burn quietly with a smoky flame. When, however, its vapour is mixed with air in certain proportions, it explodes on ignition by a flame or electric spark. This explosion, or explosive combustion, is propagated spontaneously through the whole mixture with great velocity. This velocity of ignition or propagation—termed by Berthelot the explosion wave—is independent of the pressure and is a constant for each explosive mixture.

The violence, i. e. the disruptive force, of the explosion depends on the heat disengaged by the reaction and on the alteration in volume, and is considerably greater in the case of solids and liquids than with gases.

On the explosion of a mixture of combustible gases or vapours and air, the heat generated causes the products of combustion to expand and exert on the walls of the vessel a more or less intensive pressure or shock according to the composition of the mixture and the nature of the exploding gases. This pressure is utilised in gas engines as useful work.

The velocity of ignition of mixtures of benzine vapour and air averages 2·5 metres (8 feet) per second, but varies according to the proportion of combustible vapour in the mixture.

Many hitherto unexplained fires caused by the spontaneous ignition of benzine are ascribed to the peculiar circumstance that the friction of benzine against metallic surfaces (for instance, when benzine is forced through narrow metal tubes) generates electricity of fairly high tension, which, springing across in the form of electric sparks, ignites the benzine.

In order to reduce or entirely prevent the ignition of benzine by electrical excitation in dry-cleaning works, various substances are added to the benzine, such as soluble soaps containing 0·01–0·1 per cent. of magnesium oleate (antibenzinepyrine, Richterol).[1] Attempts are made to obviate the high fire risk by " earthing " the metal storage vessel by means of a conductor.

When approached by a flame, benzine ignites very readily,

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[1] Holde investigated the electric excitation of liquid insulators, and found Richter's proposals suitable. He also found that an addition of as little as 4 per cent. (vol.) of 96·5 per cent. alcohol, or 0·1 per cent. of acetic acid, considerably increases the specific conductivity of benzine, so that dangerous electrical excitation occurs only at very high pressures or greatly increased friction. Acetic acid, however, cannot very well be used in metallic vessels (*Chem. Ztg.*, 1915, p. 819).

even at low temperatures, its inflammability being in direct
proportion to the volatility of its constituent fractions.

Flash and Burning Point of Benzines

	50–60	60–78	80–115	100–150 deg. C.
Flash point . . .	− 58	− 39	− 21	+ 10 ,,
Burning point . .		− 34	− 19	+ 16 ,,

Fractions boiling at

The burning point of benzol is about − 8° C., and that of
94 per cent. alcohol, 18° C.

The terms inflammability and explosibility are not
infrequently confounded. All petroleum and tar products
are inflammable, but benzine vapours are explosive only
when mixed in a definite proportion with oxygen or air,
mixtures containing above or below a certain range of air-
or oxygen content failing to explode on ignition.

For this reason a distinction is drawn between the upper
and lower explosive limit of mixtures of benzine and air,
the former being attained as the result of an excess of benzine
and a deficit of air, and the latter through an excess of air
and a deficit of benzine, both of which causes prevent the
mixture from exploding.

The lower limit implies the maximum percentage volume
of benzine vapour present in a mixture which fails to explode
when ignited ; and the upper limit expresses the minimum
percentage of benzine at which the mixture ceases to be
explosive on ignition.

The limits of explosibility of such mixtures were deter-
mined by Bunte, with the following results :—

	No explosion.	Explosion.	No explosion.
Percentage of benzine :	2·3	2·5–4·8	5·0

This range of explosibility varies, however, with the
dimensions of the space, the kind of ignition, the room
temperature and pressure, and finally with the origin of
the benzine vapours, from light or heavy benzines. Whilst
the range is actually very small, the danger of explosion
is quite great enough, in view of the fact that even a small
proportion of benzine vapour in air is sufficient to render
the latter explosive.

For the sake of comparison the range of explosibility
of mixtures of coal gas and air is appended, viz. : lower

limit (no explosion) 7·8 ; explosive range 8·0–19·0 ; upper limit (no explosion) 19·2 per cent. of gas.

In the case of gases the range is expressed in percentages by volume of the combustible gas ; but in the case of benzine vapours, which consist of fractions with different boiling points, and accordingly differ in respect of vapour tension, this would not be a suitable method. It is therefore preferable to express the lower limit of explosibility by the temperature at which the vapour tension of the benzine is sufficiently high to cause the supernatant air to detonate slightly on ignition, whilst the upper limit is expressed by the temperature at which the mixture of benzine and air just ceases to be explosive on ignition and merely burns quietly.

For internal-combustion engines it is always essential to keep the mixture down to the lower limit of explosibility, in order to get the highest possible output from the engine with a minimum consumption of vapour.

In storage, the best means of lessening the risk of explosion is by ample ventilation of the storage space, bearing in mind the fact that benzine vapours, being two and a half times heavier than air, tend to sink to the ground. Storage rooms must also be lighted by means of specially constructed safety (Davey) lamps or hermetically sealed electric lamps, preferably mounted outside the chamber. Further particulars will be given in the section on the safe storage of benzine and benzol.

Given a sufficient supply of air, benzine furnishes mainly carbon dioxide and water on combustion, according to the equation (for hexane) :—

$$\underset{\text{Hexane.}}{C_6H_{14}} + \underset{\text{Oxygen.}}{19O} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{6CO_2} + \underset{\text{Water.}}{7H_2O}$$
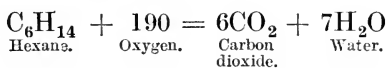
Under the influence of the pressure and high temperature prevailing in the engine cylinder, the water is partially decomposed, liberating hydrogen, which combines with the carbon dioxide to form carbon monoxide :—

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Hydrogen.}}{H_2} \rightleftarrows \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO} + \underset{\text{Water.}}{H_2O}$$
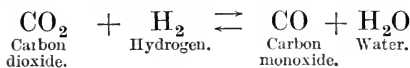
methane also being probably formed :—

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Hydrogen.}}{4H_2} \rightleftarrows \underset{\text{Methane.}}{CH_4} + \underset{\text{Water.}}{2H_2O}$$
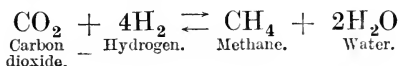
The probability of this reaction is confirmed by the detection of methane in the exhaust gases.

When combustion is incomplete, the very poisonous carbon monoxide is also produced, though it may be formed, by reduction, from the dioxide. Moreover, the high temperature and pressure in the cylinder render the process of combustion very complicated.

In addition to the gases mentioned above, the exhaust gases contain water vapour, oxygen, and nitrogen from the air, and small quantities of unconsumed gases and vapours which have escaped combustion through irregular mixing of the charge or in consequence of the engine misfiring. If the fuel contains sulphur compounds, sulphur dioxide will also be present in the exhaust. Soot is formed in the event of incomplete combustion, or through the decomposition of certain hydrocarbons (oils), and is deposited on the sides of the cylinder and on the valves.

Theoretically 1 kg. of benzine requires 11·8 cb. metres of air for its complete combustion; but, in reality, the quantity needed is at least 20 per cent. more.[1]

Benzine vapours are stupefactive, and cause headache, mainly on account of the pentane present in light benzine.

Benzol

Benzol is an aromatic hydrocarbon obtained from coal tar or coal gas.

The commercial grades of benzol, such as solvent and motor benzols, are not pure, but, as already mentioned, consist chiefly of mixtures of benzol, toluol, and xylol. They also contain about 0·5 per cent. of thiophene, and, when imperfectly refined, about 4–6 per cent. of carbon disulphide.

The benzol used as a motor fuel consists of about 70–90 per cent. of benzol, 8·25 per cent. of toluol, and 2–5 per cent. of xylol.

Crude benzol is unsuitable for use in motor-car engines, because it forms resinous constituents chiefly by the polymerisation of the cyclopentanes present, the amount increasing, during storage, to about double the original quantity in a month. These substances separate out in

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[1] For this computation the formula of benzine is assumed to be C_6H_{14}, and the oxygen content of the air 23·15 per cent.

the carburettor, clog the fine passages of the nozzle, and are also deposited in the cylinder itself—in so far as they escape combustion—and encrust it.[1]

Benzol has the undesirable property of solidifying in the vicinity of zero C. (pure benzol sets at 5·5° C.), and not re-melting below 7–8° C. This tendency can be counteracted by an addition of toluol, xylol, benzine, or alcohol, as described more fully under Fuel Mixtures. The setting point can also be improved by adding naphthalene, a solution of 30 grms., for instance, of naphthalene in 100 grms. of benzol being still free from any deposit of solid benzol at – 3° C. This use of naphthalene, however, is restricted by the fact that it crystallises out when the benzol issues from the nozzles of the carburettor, and chokes them.

When benzol is cooled very slowly and then left completely at rest, the temperature can be reduced considerably below zero C. without congelation ; but the slightest agitation produces immediate solidification, the heat of crystallisation raising the temperature at once to zero C. The melting point being, however, above that temperature, the benzol has to be warmed for a long time before again becoming liquid. This behaviour must be taken into consideration in storing benzol, either in the store or in the motor-car tank.

In the trade a distinction is drawn between summer and winter motor benzol, the former containing up to 90 per cent. of benzol and solidifying in the vicinity of zero C., whereas the winter grade is mixed with toluol or xylol, and consequently does not freeze until the temperature is considerably lower (see pp. 62 and 110).

Like benzine, benzol furnishes carbon dioxide and water on combustion. Theoretically 1 kg. of benzol requires 10·27 cb. metres of air for combustion, but the actual amount needed is about 20 per cent. more.[2]

Benzol gives far more smoke when ignited than benzine, and if the supply of air to the carburettor is inadequate, the valves and sparking plugs of the engine are sooted to a considerable degree, whilst incrustation is set up in the exhaust pipe. With an ample supply of air, however, there is no fear of this drawback.

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[1] A. Spilker, *Chem. Ztg.*, 1910, p. 478.

[2] For this computation the composition of benzol is assumed as represented by C_6H_6, and the oxygen content of the air to be 23·15 per cent.

The author has examined car engines after numerous trial trips and has found that no more soot was deposited on the valves and sparking plugs from benzol than from petrol.

When benzol is used in place of petrol, there is no need to make any alteration in the nozzle aperture or in the float of the carburettor, even if the latter has been adjusted for benzine of only 0·700–0·760 density. Whilst, owing to the higher specific gravity of benzol (0·885, as compared with 0·680–0·760), the float cuts off the flow of benzol to the nozzle sooner, a sufficient amount of the fuel is drawn into the carburettor by the partial vacuum produced by the rapid suction of air by the engine.

Benzol will give nearly the same engine output as heavy benzine, provided sufficient vapour is supplied, but for a given engine output and given main and auxiliary nozzles in the carburettor, the consumption of benzol is higher than that of benzine, 1 kg. of medium benzine corresponding to a consumption of 1·05–1·15 kg. of benzol (see pp. 207 et seq.).

Although benzol is of greater density than benzine, and therefore weighs heavier, volume for volume, a greater mileage can be covered, for a given tank capacity, with benzol than with petrol. As will be shown, however, in the section dealing with Trial Car Runs, this property is not peculiar to benzol, since the same applies to medium benzine in comparison with a light petrol.

It is frequently stated in the literature that one litre of benzol furnishes 8480 calories, and therefore more than the same volume of benzine (for example, 7550 calories from a benzine of density 0·720). This is easily understood, since one litre of benzol weighs 885 grms., whilst the benzine mentioned weighs only 720 grms.

Whereas benzol is more uniform in composition than benzine, the major portion of its constituents boiling at about 81° C., it is nevertheless more difficult to gasify, at a given temperature, than benzine (light or medium); but this notwithstanding, no difficulty arises in cranking up the engine, especially in warm weather.

When considerable proportions of carbon disulphide are present in benzol, sulphur dioxide is produced on combustion; and the prolonged use of such a fuel may result in gradual corrosion of the valve seats and heads, causing leakage and also corrosion of the sparking plugs; so that it

is desirable that the benzol should be as free as possibl from that substance.[1]

It has been asserted that the combustion products of sulphur, viz. sulphur dioxide and sulphur trioxide, cannot act injuriously on the engine because corrosion of the metal can only take place in presence of water, whereas the latter is present solely in the form of steam and is unable to dissolve the sulphur oxides. Nevertheless, experience has shown that sulphur dioxide, in presence of hot steam, is capable of attacking valves and valve seats when the exposure is prolonged.

Small quantities of thiophene in benzol are not appreciably injurious. Since thiophene boils at 84° C., and benzol at 80·5° C., the two cannot be separated by distillation, but the thiophene can be extracted by repeated treatment with fuming sulphuric acid.

Benzine vapours ignite spontaneously under a pressure of 3–5 atmospheres and at a temperature of 380° C., whereas, under the same pressure, benzol vapours require a temperature of 470° C. for spontaneous ignition. If benzine vapours are subjected to still higher pressure, premature ignition takes place at a higher temperature, but benzol vapour can stand the pressure being doubled, without igniting.

This behaviour is probably connected with the relative stability of the two materials, aliphatic hydrocarbons being more readily decomposable, whereas the carbon atoms in benzol and other aromatic hydrocarbons are firmly linked in a ring.

Benzol is also superior to benzine in being suitable for engines constructed for higher compression than is usual for petrol engines, so that a greater engine output can be obtained. If the compression space of an engine intended for petrol be suitably reduced (e. g. by mounting a piece on the inner end of the piston, or by lengthening the piston rod), the output can be increased by using benzol, though only up to a certain point, i. e. the power of the engine to stand this pressure.[2]

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[1] Apart from fractional distillation, carbon disulphide may be eliminated by repeated partial solidification at 4° C. and aspirating the liquid portion. A more convenient way is by treatment with 2–3 per cent. of a 20 per cent. solution of caustic potash in anhydrous alcohol, the disulphide being converted into potassium xanthate, which can be washed out with water.

[2] Kolacek and Deinlein, *Automobilversuche mit Spiritusantrieb* (" Experiments with Alcohol as Motor-car Fuel "), p. 7.

It is, however, uneconomical to use benzol (or alcohol) in a petrol engine with low compression, because benzol does not burn so readily unless compressed to the degree necessary to obtain complete combustion.

With regard to the combustion and explosibility of benzol, the same general conditions apply as already described for benzine. In the liquid state, benzol is neither explosive nor liable to spontaneous ignition. On the other hand, though volatilising less rapidly than benzine, it has a higher fire risk, because of the wider range of explosibility of its mixtures with air.[1]

Bunte gives the following figures for the explosive range, expressed in percentage volumes :—

No explosion.	Explosive range.	No explosion.
2·6	2·7–6·5	6·7

The velocity of ignition is lower than that of benzine, and therefore the spark can be advanced more than for the latter. Moreover, the explosions are less violent than with benzine.

According to Holde, electrical excitation, in the case of 90 per cent. benzol saturated with moisture, occurs only with a high velocity of flow or high friction in very narrow tubes, such benzol having a relatively high specific conductivity.

Benzol vapours are stupefactive, so that this fuel must be used with care. Owing to its solvent action on rosins, it should not be allowed to come into contact with varnished parts of the engine, nor should it be used for cleaning them.

ALCOHOL

Ethyl alcohol, or spirits of wine, can be used alone as a fuel for engines and motor-cars.[2]

At the present time, alcohol is produced in various ways. In the oldest method it is prepared by fermenting saccharine materials (beet juice, molasses) and subsequent distillation. Other natural products (potatoes, maize, etc.) which contain starch or carbohydrates are converted into alcohol by saccharification and fermentation; and nowadays, waste products, such as spent sulphite liquor from wood-

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[1] Martini and Hüneke, *Chem. Ztg.*, 1916, p. 948.
[2] Hempel, *Zeits. angewandte Chemie*, 1914, I, 8, p. 521; Mohr, *ibid.* 1914, p. 559.

pulp works, and sawdust, are utilised. These sulphite
liquors contain the grape sugar formed in the production
of cellulose, which sugar can be fermented to alcohol.   Saw-
dust is treated with dilute sulphuric acid under pressure,
which transforms part of the cellulose into grape sugar,
which can then be worked up into alcohol.

According to the newest process, alcohol is produced
synthetically from acetylene, in a very pure condition and
at low cost.   The alcohol used as motor fuel, however,
is not rectified, excisable spirit, but the waste product from
rectification, *i. e.* the first and last distillates obtained in
the rectifying process.

The waste spirit from the distillation of grain, potatoes,
and molasses contains varying proportions of water (5–10
per cent.), 5–10 per cent. of acetaldehyde, up to 5 per cent.
of amyl alcohol (fusel oil), and small quantities of butyl-
and propyl alcohol, ethyl- and amyl acetate, and other
esters.

Although alcohol has a relatively low boiling point (pure
ethyl alcohol 78° C., pure methyl alcohol as low as 66° C.),
it is nevertheless difficult to vaporise at ordinary temperature,
the heat of evaporation of 1 kg. of 95 per cent. spirit being
270 calories, as compared with 115 calories and 128 calories
for benzine and benzol respectively.   For this reason it is
necessary to warm the intake air by the exhaust gases
from the engine by means of a special, but simple arrange-
ment.

Since the engine cannot be started from cold, benzine
from a small special tank is supplied to the carburettor,
and as soon as the engine has run sufficiently for the exhaust
gases to heat up the intake air for the carburettor, the
benzine is shut off and the engine run on spirit only.

For alcohol fuel the sectional area of the nozzle should
be 60 per cent. greater than for benzine, or else the air
nozzle must be narrowed.

Whereas mixtures of benzine vapour and air will still
ignite explosively even when the relative proportions are
not quite correct, the ratio between vapour and air must be
strictly maintained when alcohol is used, because ignition
becomes difficult when there is an excess of air, whilst,
under the converse conditions, acetaldehyde and acetic
acid are produced as the result of incomplete combustion.

Defective gasification of the alcohol is revealed by the
engine running irregularly to a much greater extent than

with petrol, especially when the piston rings and valves are not perfectly tight.

Ethyl alcohol, the chief constituent of motor alcohol, furnishes carbon dioxide and water (like benzine) when burned with a sufficient supply of air; but as motor alcohol is not pure and the combustion is not always complete, various other products result.

The presence of 5–10 per cent. of water in motor alcohol adds to the amount of water vapour in the products of combustion; and on this account it is advisable not to use alcohol containing more than 5 per cent. of water. Small quantities of water are said to be no disadvantage, and it is stated that the steam improves the propagation of combustion.

Since, from its chemical composition (C_2H_5OH), alcohol also contains oxygen, 1 kg. of 95 per cent. spirit requires (theoretically) only 6·61 cb. metres of air for complete combustion (anhydrous alcohol 7·0 cb. metres). Pure alcohol burns without smell, but since industrial spirit is frequently denatured with pyridine bases, which are only incompletely consumed, the products of combustion have a very disagreeable smell. Spirits for motor use should therefore be denatured with benzol or methyl alcohol instead of pyridine.

An explosive mixture of alcohol vapour and air is formed when the proportion of the former amounts to at least 5·2 per cent. by volume. The explosion risk of alcohol is far smaller than that of benzine.

The alcohol used for motors does not solidify above −110 to −118° C., according to the amount of water present; so that there is no danger of the fuel freezing in winter.

It has been alleged that the use of alcohol fuel rusts the engine cylinders; but others claim that this is impossible because the cylinders are continually oiled while running, and that the film of oil prevents rusting which can only take place if the engine is left unused for some considerable time.

The allegation that the water of condensation from the combustion of the alcohol finds its way into the crank shaft and into the engine bearings, is hardly imaginable in the present state of motor engineering. Moreover, this trouble could be prevented by supplying the engine with benzine shortly before the end of a run, in the same manner as is usual at starting.

A recommendation has been made that 1 per cent. by volume of engine oil should be added to motor alcohol (whether alone or mixed with other fuels) in order to protect the engine parts from rusting; but the author considers this unsuitable, since it would dirty the carburettor, encrust the valves and sparking plugs, and impart an unpleasant smell to the exhaust gases.

Owing to the lower heating value of alcohol (5900 calories), the engine output is about 10–15 per cent. less than is obtained with heavy benzine. On the basis of heating value, the consumption of alcohol for a given engine output is theoretically double that of benzine; but Kolacek and Deinlein found it to be only about 60 per cent. greater, an engine of 32 h.p. and running at 1150 revolutions per minute under full load, consuming 485 grms. of 95 per cent. alcohol per h.p.-hour, as compared with 270 grms. and 295 grms. respectively for benzine and benzol. On this basis the relative cost of running with these three fuels can be calculated from their current prices.

Wood spirit (methyl alcohol) may replace ordinary alcohol if, in view of the difference in chemical composition (CH_4O instead of C_2H_6O) and boiling point (66° C. as compared with 78° C.), the price works out favourably.

The treatise by Kolacek and Deinlein, to which reference has already been made, deals exhaustively with the relative engine output furnished by benzine, alcohol, benzol, and benzol-alcohol mixtures, as ascertained by experiments carried on in a large motor-car works (Erste Böhmisch-Mährische Maschinenfabrik) in Prague. It is, however, regrettable that the fractional constitution of the benzol and benzine used was not ascertained at the same time, an omission which impairs the value of the experiments.

Trial runs with a car made at the above works gave fairly satisfactory results; and it was found that, with a suitable carburettor, alcohol can be used alone, in place of petrol, as motor fuel.

Since, in order to obtain approximately the same engine output, the consumption of alcohol per h.p.-hour is considerably larger than that of heavy benzine, so that in normal times the cost of running will be higher; and furthermore because alcohol can only be used with a special carburettor; it is advisable, when alcohol has to be used, that it should be mixed with benzol in such proportions as will render alteration of the carburettor unnecessary.

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Petroleum

The question whether petroleum can be used as a motor-car fuel has not yet been solved satisfactorily. Inasmuch as petroleum does not boil below 170–250° C., and is therefore difficult to vaporise, it requires to be preheated either by a special burner or by hot exhaust gases, atomised and converted into vapour. On this account its use is restricted to stationary engines, e. g. Diesel engines.

Nevertheless, when other materials are not available, petroleum may be used as a makeshift for driving motor-cars, if mixed with benzine or benzol, since it has about the same heating value as benzine. However, only the fractions 150–275° C. should be used for this purpose.

When burned in the engine, petroleum gives rise to malodorous gases which pollute the air, and therefore make this fuel unsuitable for use in towns. Moreover, the valves and plugs are liable to incrustation by the unconsumed residues.

A mixture of petroleum vapour and air will only stand slight compression, igniting spontaneously below 380° C. under a pressure of 4 atmospheres.

Naphthalene [1]

Naphthalene is a solid hydrocarbon which is recovered in large quantities from coal tar, and also from coal gas (in which it remains in consequence of its vapour tension), by washing with heavy tar fractions. Coal tar contains 5–10 per cent. of naphthalene, as compared with only 1–1·5 per cent. of crude benzol; and, by reason of its high volatility, naphthalene is present in nearly all coal-tar fractions.

It forms colourless, rhombic, and lustrous scales of sp. gr. 1·15 at 15° C. (0·977 at 80° C.). At 79·6° C. it melts to a colourless liquid, with considerable increase in volume, and boils at 218° C. under standard pressure. The latent heat of fusion is only 36 heat units. Theoretically 1 kg. of naphthalene requires 10·11 cb. metres of air for combustion. The flash point in the Pensky–Marcuson apparatus is 80° C., the burning point, 98° C. The minimum calorific value is 9700 calories.

Naphthalene is insoluble in water, but soluble in alcohol, petroleum ether, and particularly in benzol, 100 parts of which dissolve 40 of naphthalene at 10° C.

[1] K. Bruhn, *Jl. Gasbeleuchtung*, 1915, p. 579.

Industrially, it finds wide application, for example, in colour manufacture, the production of explosives, and as a preservative and impregnating agent, etc. It would also form a very suitable motor-car fuel, having a high calorific value (9700 calories) and high vapour tension (18·5—expressed in mm. of mercury—at 100° C.), which is very favourable for its combustion in the engine; and, furthermore, a higher compression can be employed for naphthalene vapours than for those of benzine.

Although naphthalene contains a higher percentage of carbon than either benzol or benzine, it will burn without smoke if an adequate supply of air is provided. It is easily stored and transported; neither inflammable nor explosive in the solid state; and its low price constitutes an advantage.

Nevertheless, its general application as a motor-car fuel is opposed by certain difficulties arising from its high melting and boiling points, which necessitate special means for transforming it into vapour, the consequence being that it is not in condition for immediate use.

The attempts made by Chenier and Lion, in 1904, to run engines on naphthalene fuel, did not lead to satisfactory results. The first practicable naphthalene engine was put on the market by the Gasmotorenfabrik Deutz in 1907; and this was followed, a few years later, by the Benz works. At present stationary naphthalene engines of 4–20 h.p. are manufactured.

To get naphthalene into condition for use, it must first be warmed in a special vessel, either by the hot exhaust gases (which, however, are liable to cause overheating), or melted by the heat of the cooling water and then atomised into the engine.

It is therefore not directly feasible to start the engine on naphthalene, since the initial heat for melting the naphthalene and warming up the engine has to be supplied from another source, for example by starting the engine on benzol and changing over to naphthalene as soon as the requisite heat has been provided.

According to the results of experiment, the consumption of naphthalene in an 8 h.p. engine (load 6·7 h.p.) amounts to 282 grms. per h.p.-hour, as compared with 276 grms. in the case of benzol. Since naphthalene is only one-third the cost of benzol, it forms a very much cheaper fuel.

The melted naphthalene is atomised by causing the air drawn in by the piston stroke to flow at very high velocity

past the end of a specially constructed nozzle, so as to transport, in a very fine state of division, the liquid issuing from the small orifices, the mixture of fuel and air being led into the engine.

In spite of its advantages, naphthalene was practically restricted to stationary engines until 1912, when, as the result of exhaustive experiments carried out in the laboratory of the French Automobile Club and by several French motor-car firms, both motor-cars and wagons run on naphthalene were introduced, and are stated to have been satisfactory. The naphthalene engines for motor-cars are designed on the same lines as the stationary engines mentioned above, are fitted with Noel naphthalene carburettor, and can be shut off for a quarter of an hour at a time without the naphthalene solidifying. In this case, also, the engines are started on benzol.

This system of employing benzol for starting naphthalene engines, however, entails the use of special appliances which are not of a very simple character and were only introduced on the basis of exhaustive experiments.

It would be simpler to liquefy the naphthalene and keep it in that condition; but, except by melting, the only way in which this could be done would be by absorbing the naphthalene in a combustible solvent, for which purpose benzol is the most suitable. This is only feasible to a certain extent, inasmuch as the naphthalene separates out again from the saturated solution in benzol as soon as the temperature is slightly lowered.

A process patented by the Rütgerswerke, Berlin, attempts to overcome this difficulty by causing a vessel filled with naphthalene to dip into a benzol tank as required, and to be withdrawn before the engine is shut off, so that the engine continues to run on benzol alone and there is no risk of choking the pipes.

Another way of getting over the difficulty would be by using a weaker solution of naphthalene in benzol; but this would entail altering the carburettor in such a way that it could not choke up so rapidly.

As already mentioned in an earlier section (Products from Petroleum, etc.), many solid hydrocarbons can be rendered liquid by hydrogenation; and during the war Professor Schrötter of Berlin succeeded in devising a process of manufacturing liquid tetra- and deca-hydro-naphthalene, which was used as motor fuel on German submarines. At present

these products are extensively used as turpentine substitutes, under the names " Tetralin " (tetrahydronaphthalenes) and " Tetralin extra " (decahydronaphthalene).

Coal Gas and Acetylene Gas

The idea of using coal gas as a fuel for motor vehicles in place of petrol is not new, but its employment for motor-lorries and vans was first taken up on a large scale in England in 1915. The gas was, at first, carried on the vehicles in receptacles made of canvas and rubber; but as these could not stand more than a light pressure, and consequently held comparatively little gas, they had to be very bulky and took up too much room.

On this account they were afterwards replaced by steel cylinders charged with gas compressed to 120 atmospheres. The disadvantages of these cylinders, however, are their great weight and that, in view of the high internal pressure, they have to be kept constantly under supervision, whilst the continuous vibration fatigues the metal. Moreover, the cylinders must be provided with rather delicate automatic regulators for reducing the pressure in the cylinder to working pressure; and, at the same time, the high pressure lowers the heating value of the gas by about 10 per cent.

Attention has latterly been directed also to acetylene as a fuel for motor vehicles, an application that is of particular interest in countries like Switzerland, where carbide is manufactured in large quantities. The high heating value (12,000 calories) of acetylene would make it peculiarly suitable for this purpose, were it not for the existence of numerous difficulties. For example, it must not be too strongly compressed, or even liquefied, like coal gas, because, in that condition, it is very liable to explode spontaneously. Some years ago it was proposed to use acetylene dissolved in acetone under slight pressure as a motor fuel, but the experiments did not succeed, chiefly on account of the excessively high explosive power of the acetylene.

It is only recently that experiments made in Switzerland by Professor C. F. Keel have shown that, given a suitable arrangement of the engine, acetylene gas can be employed as fuel.

Since, under heavy pressure, the mixture of acetylene and air ignites spontaneously between 380° and 400° C., the compression in the engine must not exceed 2–3 atmo-

spheres.   In order to moderate the violence of the explosion and increase the utilisation of the energy, a fine spray of water is injected into the engine along with the acetylene, 1 cb. metre of acetylene requiring 70 grms. of water in order to reduce the pressure from 4 atmospheres to 3.

The endothermic heat of acetylene being very high (2200 units), the heat of combustion is partly consumed, in this system, in the production and superheating of steam.   The resulting high pressure, superheated steam then expands along with the products of combustion and performs mechanical work.

The acetylene engine, with water injection, thus operates partly as a steam engine, the steam being generated in the engine itself.   Practical tests have shown that the proportion of acetylene in the mixture may be varied between 1·5 and 8 per cent., so that the volume of air can be modified between the limits of 12 and 50-fold.   Further particulars on the subject are given in Professor Keel's paper in the *Mitteilungen des schweizerischen Acetylenvereines*.

MIXED FUELS

In the endeavour to utilise other cheap materials as fuel for internal-combustion engines and motor vehicles, various more or less suitable mixtures have been prepared and put on the market.[1]   They are chiefly composed of benzine, benzol, toluol, alcohol, and petroleum, with additions of sulphuric ether, acetone, or carbon disulphide to render them more inflammable.

Transformin, a mixture of alcohol and picric acid (to increase the engine output) has proved unsuitable, owing to the danger of explosive metallic picrates being formed through the action of the water present in the alcohol.

The addition of nitrobenzol, ammonium nitrate, ethyl nitrate, and similar substances is open to the objection that the nitrous fumes disengaged therefrom during combustion corrode the engine cylinders, valves, and sparking plugs. Naphthalene, too, cannot be successfully added to alcohol or benzol, owing to its tendency to crystallise out at low temperatures and, being non-volatile at ordinary temperature, choke the carburettor nozzles.

Moreover, as has already been shown, the substances

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[1] Recipes for this purpose have been given by K. Dieterich, *Zeits. angew. Chemie*, 1914, p. 543.

employed in mixed fuels possess certain properties which militate against their suitability for unconditional employment by themselves. Thus, benzol solidifies at a temperature approaching zero C.; alcohol and petroleum (in particular) will not gasify unless preheated; whilst alcohol requires the nozzle orifices in the carburettor to be of larger area than is needed for benzine.

Consequently, the object of a mixture of different fuels is not only to provide a usable substitute for petrol, but also to remedy the defects which prevent one or other of the substitutes from being really suitable when used alone with the ordinary engine arrangements. If the use of such mixtures becomes necessary, their preparation must not entail any alteration to the car or carburettor.

For example, if alcohol be mixed with a sufficient proportion of benzol, the engine will run perfectly without requiring the intake air to be preheated, or any alteration in the nozzle aperture.

Sometimes, on a journey, it is necessary to supplement the stock of benzine carried, so as not to be stranded for lack of fuel; and it may happen that, whilst no benzine is available, benzol, alcohol, or petroleum can be obtained. In such circumstances one should be able to know what substances can be mixed together without spoiling the existing small stock of benzine.

If the use of mixed fuels is contemplated or obligatory, it is advisable for the motorist to prepare these himself; firstly, because this can be done more cheaply than they can be bought ready made, and secondly, because one knows the composition of the mixture.

For all these reasons it is very important that the motorist should know both the properties of the individual fuels and those of their mixtures. On this account, the preparation and properties of mixed fuels will now be described, in so far as they have not already been dealt with earlier.

Benzine–Benzol Mixtures

Benzine and benzol are miscible in all proportions, without becoming turbid, even if the benzol used contains water.

Benzine has the advantage of solidifying only at low temperatures, whereas benzol becomes solid near zero C. Hence the addition of benzine to benzol will retard the freezing of the mixture.

A mixture of 80–70 parts by volume of benzol with 20–30 of benzine becomes turbid when cooled below zero C.; at − 10° C. a thin crystalline pulp is formed by the deposition of benzol; and at − 20° C. the whole sets to a thick pulp.

Benzol–benzine mixtures between 50 : 50 and 20 : 80, still remain liquid at − 20° C.; a mixture of 50 per cent. benzol (containing toluol and xylol) with benzine in proportions between 25 : 75 and 75 : 25 does not set even at − 25° C., and there is no deposition of benzol crystals.[1] Consequently, if it is desired to prevent 90 per cent. benzol from freezing in the winter, it must be mixed with at least 40 per cent. of benzine.

The author recommends the addition of about 20–30 per cent. of benzol in all cases, experiments having shown that the unpleasant knocking which occurs during overloads when the engine is being run on benzine is mostly prevented by the addition of benzol to the fuel. (See Section on "Trial Runs with the Car ").

Benzine–Benzol–Alcohol Mixtures

Benzol and alcohol are miscible in all proportions without turbidity; but if benzine be mixed with alcohol, or with alcohol and benzol, turbidity may occur from the deposition of the water present in the alcohol and benzol. Such a mixture cannot be used until the separated water has settled down to the bottom of the vessel, which may take as long as a week.

When the ratio of benzine to alcohol is unfavourable, e. g. when benzine predominates, a gradual separation of alcohol occurs, because alcohol that contains water is insoluble in benzine, though anhydrous alcohol is miscible in all proportions.

A uniform mixture is only obtained when the alcohol is 5–6 parts to 1 part of benzine; but this is not employed in practice.

For these reasons it is advisable to mix benzine with alcohol and benzol together, and not with the former alone.

The author has ascertained by experiment that not more than 70 parts (vol.) of benzine can be mixed with 15 of benzol and 15 of alcohol without turbidity being produced. If, however, 80–100 parts of benzine be mixed with 10 of

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[1] See also K. Dieterich, *Allgemeine Automobil-Zeitung*, 1917, No. 8.

benzol and 10 of alcohol, the separation of water from the alcohol causes turbidity, and, if such a mixture be kept for some time, the alcohol will separate out as well. Consequently, the most favourable ratios for such mixtures are 20–25 parts of benzine, 50–25 of benzol, and 25–50 of alcohol.

In preparing these mixtures the benzol is first poured into and stirred with the alcohol, the benzine being then added by degrees and stirred at the same time.

Mixtures of benzol and alcohol are used in a variety of proportions. In warm weather the motor-car engine will run well on a mixture of 60 parts of alcohol and 40 of benzol, but not with a mixture of 75 parts of alcohol and 25 of benzol unless the intake air is pre-heated. Mixtures of equal parts of benzol and alcohol are used for motor omnibuses.

Such benzol–alcohol mixtures naturally give a higher engine output than alcohol alone; and the addition of benzol has the further advantage of facilitating the combustion of the alcohol.

From the point of view of the process of combustion of benzol–alcohol mixtures, it is best to employ two parts (weight or volume) of benzol to one of alcohol. In mixing, the benzol should always be poured into the alcohol, and not inversely, since otherwise the mixture would become turbid through the separation of water from the alcohol, and such water takes a long time to redissolve.

Another advantage of the benzol–alcohol mixture is that the alcohol retards the freezing of benzol at low temperatures.

In preparing mixtures the possibility of the separation of certain constituents at low temperatures must also be borne in mind. For example, at $-10°$ C., benzol will separate out, as a solid crystalline mass, from a mixture of 70 parts benzol and 30 alcohol; whereas it is essential that a fuel should still be perfectly liquid at $-10°$ to $-20°$ C. in winter.

The separation of individual components from a mixture will be the more difficult, and the setting point of the mixture the lower, in proportion as the individual components are in a more dilute state of solution, and as the number of such components increases.

For this reason the behaviour of a benzol–alcohol mixture will improve with the amount of alcohol present. It is also advantageous to add benzine to the mixture, since it lowers

the solidification point and retards the separation of benzol
. For example, if 40 parts of benzine be added to a mixture
of 80 parts benzol and 20 parts alcohol, the mixture will
congeal at $-15°$ C.   If 50 parts of alcohol and 20 of benzine
be added to 50 of benzol, the mixture will not freeze above
$-18°$ C.

Probably the most favourable mixture would be one of
benzol, alcohol, benzine, and petroleum ; but since such
mixtures do not burn uniformly, they can only be used
when compounded in certain definite proportions which
have stood the test of practice.

Setting-point tests of benzol–alcohol mixtures gave the
following results : A mixture of 80–50 parts (vol.) of benzol
with 20–50 parts of alcohol, became turbid when cooled
below zero C., turning to a thick pulpy mass at $-10°$ C.,
and solidifying completely at $-20°$ C.

A mixture of 20–25 parts benzol with 80–75 parts alcohol,
on the other hand, was still fluid at $-20°$ C. ; and a mixture
of 25–75 parts of 50 per cent. benzol with 25 parts of alcohol
did not solidify even at $-25°$ C.

If benzine be replaced by a benzol–alcohol mixture con-
taining at least 50 per cent. of benzol, no alteration will
be needed in respect of the area of either the fuel- or air-
nozzle of the carburettor. Since benzol requires more air
for combustion, and alcohol less, than benzine, this mixture
can be used with success in place of benzine, even in
sensitive carburettors.

No water separates out from a mixture of benzol and
alcohol. If, nevertheless, any water should find its way
into the fuel or into the float chamber of the car,[1] it would
be absorbed—if only in small amount—by a benzol–alcohol
mixture, though benzine cannot absorb water.

Benzine–Benzol–Petroleum–Alcohol Mixtures

Benzine, benzol, and mixtures of the two can be
mixed with petroleum in any proportions. From mixtures
of alcohol and petroleum, however, the former gradually
separates. It also separates out, either at once or after

[1] Water may be gradually deposited in the petrol tank, *e. g.* from
compressed air, especially in damp or foggy weather, or from the gases
which force the fuel into the carburettor, and may find its way from
the tank into the float chamber, where, in consequence of its greater
density, it checks the flow of fuel in the nozzle and thus causes irregular
running of the engine.

prolonged standing, from mixtures of benzine, petroleum, and alcohol, if much alcohol and much petroleum be added simultaneously to the benzine.   In this case the separation of the alcohol can be prevented by an addition of sulphuric ether, benzol, acetone, or ethyl acetate.

A good mixture consists of 25 parts (vol.) of petroleum and 25 of benzol well mixed, 25 parts of alcohol being then added and well stirred in.   To prevent separation of the alcohol, 0·5–1 part of sulphuric ether is added to 10 parts of the mixture.   Such a mixture, however, cannot be used in cold weather without pre-heating.

Mixtures of benzine or benzol with petroleum will be only incompletely consumed in an engine designed for petrol, and therefore the exhaust gases will have an unpleasant smell.

Other Mixtures

In the motor works at Prague already referred to, when petrol was scarce, a mixture of equal parts of alcohol, benzine, and benzol was used, this being superseded by one of 50 parts alcohol, 25 benzol, and 25 benzine.   In warm weather both these mixtures could be used without any alteration to the carburettor, but in cold weather the intake air required considerable pre-heating.

Only one disadvantage, and that of a subordinate character, was found in connection with these mixtures, namely, that the brass nozzles became choked with verdigris if the motor vehicle was left unused for some time, e. g. a fortnight, the carburettor then having to be cleaned every time before use.

When petrol was scarce or dear, another motor-car works (Laurin & Klement, Jungbunzlau) employed a mixture of heavy benzine and benzol in equal proportions—the carburettor being equipped with an air pre-heater—and finally a mixture of 1 part heavy benzine (sp. gr. 0·750–0·760) and 1 of petroleum, an air pre-heater being employed and the nozzle apertures of the carburettor widened by 0·1–0·2 mm.

The consumption of this mixed fuel was somewhat larger than with pure benzine, but no trouble was experienced with the engine, except that benzine had to be injected into the cylinder to facilitate starting.

A mixture of benzine and alcohol was only subjected to the brake test ; and the pipe leading the mixture into the

carburettor had to be led round the exhaust pipe in order to get the largest possible pre-heating effect. The nozzle apertures had to be enlarged, thus increasing the fuel consumption. In view of the high-running costs this mixture was not put into service.

For pure benzol, the carburettor nozzle was reduced.

At the motor-car works of Walter & Co., Jinonic, near Prague, the following mixtures have been successfully used. Benzol and alcohol in equal parts; alcohol 70 parts, petroleum 29, petroleum ether 1. The carburettor nozzle had to be enlarged by 10 per cent. in comparison with the size used for petrol of 0·720 density.

The following substitutes for petrol have also been placed on the market in Prague : Benzinersatz (petrol substitute), Etol, Motorit, Benzolin, and Benzolit.

Benzinersatz had the sp. gr. 0·880 and contained 58 per cent. of benzol, 32 per cent. of toluol, and 8 per cent. of xylol, being therefore identical with technical benzol.

Etol had the density 0·787 and consisted of 25 per cent. of petroleum, 50 per cent. of alcohol, and 25 per cent. of sulphuric ether. Owing to the high content of ether, the mixture was readily inflammable, notwithstanding which it was wasteful in consumption, and, in addition, soon made the cylinders very hot, whereupon the engine output diminished.

Motorit contained 25 per cent. of petroleum, 25 per cent. of benzol, and 50 per cent. of alcohol.

Benzolin was a mixture of benzol, alcohol, and carbon disulphide, which latter was injurious for the engine.

Various mixtures of benzol, toluol, alcohol, acetone, and petroleum are used in Germany, under different names, such as : Autin, ergin, autonaphtha, motonaphtha, motorkraft, etc.

Technical acetone is also used in mixed fuels, chiefly, however, for the sole purpose of facilitating ignition. Acetone has the density 0·810 and the boiling-point 56° C. It is easily gasified, but is dear in comparison with other fuel materials. Mixtures are made of 50 parts of 90 per cent. alcohol with 20 of acetone, 30 parts of benzol being added; or of alcohol 50, acetone 20, and benzine 30 parts.

Alcohol also is mixed with acetone in the proportions 50 : 50 to 70 : 30, 1 per cent. of motor oil being added to the mixture with the idea of preventing rust in the engine. Mixtures of alcohol and acetone require the fuel nozzle

to be enlarged and the intake air to the carburettor pre-heated.

Experiments on the Vaporisation of Various Grades of Benzine and Benzol in the Carburettor

In the Analytical Section the behaviour of individual fractions of benzine and different grades of benzine during spontaneous and accelerated evaporation (aspiration by air) was described. Similar vaporising tests have also been performed in the carburettor, in order to ascertain how the operation proceeds under such conditions.

The tests were performed in a Zenith carburettor under the following conditions : The petrol feed-pipe to the carburettor was connected, by a rubber tube, to a glass flask acting as petrol tank. The flask was mounted at such a height above the carburettor that the petrol could flow into the float chamber under a moderate pressure, in the same manner as in a motor-car.

At the opening where the fuel mixture from the carburettor enters the engine, a pipe, 50 cm. (20 ins.) long, having the same internal diameter as the orifice of the carburettor, was secured, this pipe being connected to a vacuum-pump drawing 500 litres of air, at 20° C. per minute.

Although the engine of a motor vehicle does not draw air in continuously like an air-pump, the intervals are so very small that there was no need to employ means to obtain an exact imitation of working conditions, the arrangement described being sufficient for comparing the relative behaviour of individual fractions in the carburettor.

The progress of vaporisation was observed in the glass tube and also at the lower orifices through which the air was drawn into the carburettor.

It was found that benzine fractions which did not vaporise in the carburettor were carried away from the mouth of the nozzle, in the form of minute drops, by the powerful current of air. Some of these drops remained suspended in the air and gradually vaporised, but for the most part they impinged against the sides of the air nozzle of the carburettor and were forced upward by the air along the sides of the glass tube (being partially vaporised the while), to a height increasing with the boiling point of the fraction in question.

The fractions boiling up to 100° C. were completely

vaporised in the carburettor, those between 100° and 120° C. less readily, so that portions travelled up the glass tube, where vaporisation also proceeded. The fractions 120–140° C. vaporised to only a small extent, the bulk ascending further up the tube (where vaporisation also continued), whilst the fractions 140–160° C. were mostly forced out of the carburettor nozzle as small drops which travelled half-way up the tube. Finally, the fractions 160–200° C. ascended the whole length of the tube and were carried as far as the catcher provided between the carburettor and the suction pump.

Pure benzol vaporised almost completely in the carburettor, and only ascended a little way up the glass tube. Toluol was partly carried off in drops by the air, and partly ascended the tube further than benzol, whilst xylol travelled in a thin film up to and over the top end of the tube.

Of the grades of benzine given in Table I, the light benzine No. 1 (sp. gr. 0·696) vaporised almost completely in the carburettor; the medium benzine No. 8 (sp. gr. 0·740) also vaporised well and only travelled a short distance up the tube; and the heavy benzine No. 14 (sp. gr. 0·760) was only partially vaporised, the bulk rising, as a thin film, right to the top of the glass tube.

The pipe connecting the carburettor and motor-car engine is only a short one, and it may therefore be assumed, from the above particulars, that heavy benzine will find its way into the engine, partly along the sides of the pipe and partly in the form of small drops, and only then will be vaporised by the high temperature prevailing there.

Since the connecting pipe receives heat from the engine, the vaporisation of the benzine ascending the pipe and in suspension will be assisted (and more particularly) by the heat of that pipe, as well as by the warm air.

CHAPTER XI

THE CONSUMPTION AND EFFICIENCY OF VARIOUS FUELS IN INTERNAL-COMBUSTION ENGINES

THE motorist who has closely examined the question of the consumption of different kinds of motor fuel, noting the relative quantities consumed for a given mileage on the same road and under approximately the same conditions, and calculating therefrom the number of miles traversed per unit quantity, will have found considerable differences in the results obtained.

Notes taken by the author in this way led him to make accurate experiments in order to ascertain whether and to what extent the composition of a fuel affects the consumption and the engine output.

These experiments were performed with various engines, the brake test being applied in some cases and actual road work in others, the fuels tested consisting of separate benzine fractions, various commercial grades of benzine, benzol, and benzol–alcohol mixtures, the composition of which was determined by fractional distillation.

BRAKE TESTS

The brake tests were conducted at the " Praga " motor-car works, Prague, use being made of the electric brake of the Française Electrique Co. (Paris), which consists, in principle, of a dynamo the armature of which is coupled to the main shaft of the engine under examination, whilst the fixed casing (stator) containing the electromagnets is rotatably mounted on the armature shaft and is balanced, by weight and counterweight, so as to keep the pointer at the zero mark when the apparatus is at rest.

When the armature of the brake generator is rotated by the engine, the resulting induction current tends to carry the movable casing round at the same time.   The windings of the rotor driven by the engine intersect the curves of

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force of the magnetic field of the dynamo and set up an electromagnetic moment. In an ordinary dynamo, this moment is absorbed by the bolts holding down the stator, but with the brake apparatus described, the moment can be counterbalanced and measured by a weight adapted to slide on an arm attached to the dynamo casing.

If the movement of the lever on the arm l (expressed in metres) corresponds to a force P (expressed in kilos.), the engine is loaded with the moment of rotation $M = P \cdot l$ mkg., which, at a speed of n revs. of the shaft per minute, corresponds to the engine output :—

$$Ne = \frac{M \cdot n}{716} = \frac{P \cdot l \cdot n}{716} \text{ brake h.p.}$$

in which 716 is a constant.

In order to facilitate rapid calculation of the engine output, the arm is graduated in kilos., thus giving a direct reading of the peripheral force on the constant arm.

If l_1 expresses the distance of the sliding weight (at any given position) from the axis of the dynamo ; l the leverage to which the weight of the sliding weight g is reduced ; and P the resulting reduced weight ; the equation

$$P \cdot l = g \cdot l_1$$

is obtained. From this equation the reduced weights P for different values of l_1 can be calculated, and the various positions of the weight marked accordingly.

The value $\dfrac{1}{176}$ is the same for all tests, and therefore forms a constant, C. Since, in the present instance, $l = 1 \cdot 35$ metres, the value of C is $\dfrac{1 \cdot 35}{716} = 0 \cdot 001885$. Consequently, $Ne = 0 \cdot 001885 \cdot P \cdot n$, the value of P being read off on the lever arm, and n on the speed counter.

The " Praga " petrol engine used for the first set of tests was a 39-h.p. engine with four cylinders, 105 mm. bore and 160 mm. stroke. The Zenith carburettor (No. ABC42) had a 26-mm. air nozzle, 1·10-mm. main injector (central) nozzle, and 1·31-mm. compensating nozzle.

The tests were made with the benzine fractions : 60–80° C., 80–100°, 100–120°, and 120–140° C. ; a light, medium, and heavy benzine ; and, finally, 90 per cent. motor benzol.

The composition of the fractions, for intervals of 20°, is given in Table V.[1]

TABLE V

Fuel Fractions	Benzol					Benzine		
	60–80°	80–100°	100–120°	120–140°		Light	Medium	Heavy
Sp. gr.	0·6990	0·7370	0·7500	0·7598	0·8833	0·693	0·736	0·7619
Up to 40°	—	—	—	—·	—	2·7	0·4	—
40–60°	5·0	—	—	—	—	31·5	3·0	0·2
60–80°	91·0	4·0	—	—	56·2	34·5	15·6	0·4
80–100°	4·0	92·9	5·0	—	43·8	17·3	38·7	5·2
100–120°	—	3·1	93·5	4·0	—	9·8	25·0	27·0
120–140°	—	—	1·5	92·7	—		13·7	32·0
140–160°	—	—	—	3·2	—	3·9		24·5
160–175°	—	—	—	—	—		3·3	7·7
Residue	—	—	—	—	—			3·0
	100·0	100·0	100·0	99·9	100·0	99·7	99·7	100·0

The grades of benzine were chosen so that in the light benzine the fraction 40–80°, in the medium the fraction 80–120°, and in the heavy the fraction 100–160°, predominated.

Prior to the main experiments the accuracy of the method was tested with a heavy benzine (density 0·750), the engine output and fuel consumption being determined twice in succession. In the first test the benzine consumption was 312 grms. per h.p.-hour, and in the second 310 grms., a difference of about 0·6 per cent. The brake test is therefore accurate to within one two-hundredth.

The same main injection nozzle and compensating nozzle of the carburettor were used throughout; and the engine was run at a constant speed of 1000 revs., and the cooling water kept at 60° C.

The results are given in Tables VI and VII, in which the figures in the third column express the mean weight P required to balance the electromagnetic moment set up by the engine, whilst the fourth column represents the engine output in horse-power; the fifth the average time (minutes and decimals) taken for the consumption of 1 litre of the fuel, and the remaining columns the fuel consumption, in

[1] The composition of the benzol fractions is given at intervals of 20°. According to the usual method of fractional distillation, this benzol contains 96·0 per cent. of constituents boiling up to 85° C., and 4·0 per cent. boiling between 85° and 100° C.

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litres or kilogrammes, per minute, and per horse-power-hour respectively.

Table VI shows that, as a rule, the engine output and consumption of fuel—in point of volume—diminish, whereas the weight of fuel consumed increases, as the boiling point of the benzine fractions increases.

TABLE VI

FUEL CONSUMPTION IN BRAKE TESTS

Benzine fractions	Sp. gr.	Brake weight, kg. at 1000 revs.	Engine output, h.p.	Rate of Fuel con-sump-tion, min. per litre	Fuel consumption				Nozzle dia-meter, mm.	
					litres per mm.	kg. per mm.	litres per h.p.-hour	kg. per h.p.-hour	Cen-tral	Com-pensg.
60–80° C.	0·6990	21·0	39·6	3·77	0·265	0·185	0·402	0·280	1·1	1·31
80–100°	0·7370	20·8	39·2	3·89	0·257	0·189	0·393	0·290	1·1	1·31
100–120°	0·7500	20·7	39·0	3·85	0·260	0·195	0·399	0·299	1·1	1·31
120–140°	0·7598	19·6	37·0	4·11	0·244	0·185	0·395	0·300	1·1	1·31

TABLE VII

FUEL CONSUMPTION IN BRAKE TESTS

Benzine fractions	Sp. gr.	Brake weight, kg. at 1000 revs.	Engine output, h.p.	Rate of Fuel con-sump-tion, min. per litre	Fuel consumption				Nozzle dia-meter. mm.	
					litres per mm.	kg. per mm.	litres per h.p.-hour	kg. per h.p.-hour	Cen-tral	Com-pensg.
Light Benzine	0·6930	3·67	20·9	3·94	0·272	0·188	0·414	0·288	1·1	1·31
Medium ,,	0·7360	3·69	21·0	3·96	0·271	0·199	0·410	0·302	1·1	1·31
Heavy ,,	0·7619	3·76	20·7	3·90	0·266	0·202	0·409	0·311	1·1	1·31
Benzol . .	0·8833	4·15	21·0	3·96	0·241	0·212	0·365	0·322	1·1	1·31

Table VII shows that the highest engine output is obtained from medium benzine and benzol, the smallest fuel consumption with light benzine, and the highest (in point of weight) with benzol.

However, since the densities of the fuels are unequal, and it is usual to measure, and not weigh, the fuel consumed from the tank, the weights should be calculated to volume, which done, benzol is found to give the smallest consumption and light benzine the largest.

In the second series of tests, a Praga " Grand " four-cylinder engine, 90-mm. bore and 160-mm. stroke, was used.

Three central nozzles, of 0·89, 0·93, and 0·97 mm. aperture respectively, were employed, the compensating nozzle having the same diameter (1·19 mm.) throughout. The engine was run at 1200 revs. per minute; the cooling water temperature ranged between 65° and 68° C., whilst the air temperature was 26° C. and that of the fuel 24° C.

The tests were performed with benzine fractions; 40–60°, 60–80°, 80–100°, 100–120°, and 120–140°; benzol free from toluol, pure toluol, and finally, a mixture of equal parts of benzol and 96 per cent. alcohol. The composition of the benzine fractions, at intervals of 20° C., is given in Table VIII. The benzol, distilled under the usual conditions, passed over in toto below 100° C.

TABLE   VIII

COMPOSITION   OF   FUELS

Benzine fractions	°C 40 60	°C 60 80	°C 80 100	°C 100 1 20	°C 120 140	Light	Medium	Heavy L.	Heavy II.	Benzine Fractions
Sp. gr.	0·6590	0·7037	0·7353	0·7510	0·7617	0·6872	0·7286	0·7682	0·7646	Sp. gr.
Up to 40° C.	2·0	—	—	—	—	5·2	—	—	—	Up to 40°C.
40–60°	94·0	1·0	—	—	—	38·4	1·6	—	2·2	40–60°
60–80°	4·0	95·0	1·0	—	—	40·8	16·4	1·6	3·4	60–80°
80–100°	—	3·6	98·0	4·0	—	9·8	65·0	3·2	8·0	80–100°
100–120°	—	—	1·0	93·0	3·8	3·6	16·2	20·8	32·8	100–120°
120–140°	—	—	—	3·0	92·0	—	—	50·0	28·0	120–140°
140–160°	—	—	—	—	4·0	2·0	0·8	16·0	17·6	140–160°
160–180°	—	—	—	—	—	—	—	6·4	8·0	160–180°
Residue	—	—	—	—	—	—	—	2·0	—	Residue
	100·0	99·6	100·0	100·0	99·8	99·8	100·0	100·0	100·0	

The results of the tests are shown in Table IX.

Comparison of the data furnished by the benzine fractions shows that, with a 0·93-mm. central nozzle, the fraction 80–100° C. gives the smallest consumption of fuel, by volume, per h.p.-hour, and the highest engine output.

If the fuel consumption be compared on the basis of weight, it is found that, as in the first series, the consumption increases with the boiling-point of the fractions, and that the engine output diminishes.

Benzol and toluol show a much smaller consumption, as regards volume, than benzine fractions, but higher in point of weight. The explanation of the fact that, for a given nozzle, the benzol consumption is the lowest in volume, is that, being of greater density (0·884), benzol issues from the nozzle, under a given pressure, more slowly than the

TABLE IX. FUEL CONSUMPTION IN BRAKE TESTS

Fuel Benzine Fraction	Sp. gr.	Engine output at 1200 revs. Brakeweight kg.	h.p.	Rate of consumption, min per litre	Fuel consumption l. pr. min.	kg. pr. min.	l. pr. h.p.-hr.	kg. pr. h.p.-hr.	Cooling water temp. °C.	Nozzle diameter mm. Central.	Compen.
40–60° C.	0·6590	14·0	31·6	4·20	0·238	0·157	0·452	0·298	67°	0·89	1·19
		13·9	31·4	3·93	0·254	0·168	0·486	0·320		0·93	
		13·7	31·0	3·83	0·261	0·172	0·505	0·333		0·97	
60–80°	0·7037	13·9	31·4	4·46	0·224	0·158	0·429	0·302	66°	0·89	1·19
		13·8	31·2	4·07	0·246	0·173	0·473	0·332	67°	0·93	
		13·8	31·2	3·90	0·256	0·180	0·493	0·347	65°	0·97	
80–100°	0·7353	13·9	31·4	4·56	0·219	0·161	0·479	0·308	67°	0·89	1·19
		14·2	32·0	4·15	0·241	0·177	0·452	0·332	66°	0·93	
		14·1	31·8	3·83	0·261	0·192	0·493	0·362	66°	0·97	
100–120°	0·7510	13·8	31·2	4·52	0·221	0·166	0·426	0·320	66°	0·89	1·19
		14·0	31·6	4·13	0·242	0·182	0·460	0·345	64°	0·93	
		14·0	31·6	3·92	0·255	0·192	0·484	0·364	65°	0·97	
120–140°	0·7617	13·4	30·3	4·73	0·211	0·161	0·419	0·319	64°	0·89	1·19
		13·6	30·7	4·28	0·234	0·178	0·457	0·348	68°	0·93	
		13·4	30·3	3·99	0·251	0·191	0·496	0·378	66°	0·97	
Benzol	0·8845	14·1	31·8	5·05	0·198	0·175	0·374	0·330	67°	0·89	1·19
		13·6	30·7	4·81	0·208	0·184	0·406	0·359	68°	0·93	
		13·9	31·4	4·35	0·230	0·203	0·439	0·388	66°	0·97	
Toluol	0·8711	14·1	31·8	4·97	0·201	0·175	0·380	0·331	66°	0·89	1·19
		13·7	31·0	4·47	0·224	0·195	0·433	0·377	67°	0·93	
		13·8	31·2	4·21	0·237	0·207	0·457	0·398	65°	0·97	
Benzol–Alcohol (96%) 1 : 1	0·8471	12·1	27·2	5·12	0·195	0·165	0·431	0·365	65°	0·89	1·19
		12·6	28·7	4·51	0·222	0·188	0·463	0·392		0·93	
		12·9	29·5	4·24	0·236	0·200	0·480	0·406		0·97	

specifically lighter benzine fractions, which latter also set up less friction than benzol. This is also manifest from a comparison of the rates of flow per unit volume of the fuels through one and the same nozzle.

In using benzol with the 0·93-mm. nozzle, the engine output was smaller than with benzine fractions; but when this nozzle was replaced by the smaller one (0·89 mm.), the engine output increased considerably with a lessened consumption of benzol.

A point worthy of note is that, in the case of the lighter benzine fractions (especially 40–60°) and benzol, increasing the nozzle orifice, and consequently the fuel feed, reduced the engine output, whereas the best output from a mixture of benzol and alcohol was obtained with a larger nozzle. The reason for this is that the supply was too large in the case of benzol, and too small in the case of the benzol–alcohol mixture, the ratio between fuel vapour and air being therefore unsatisfactory.

Hence it follows that the most suitable nozzle orifice to give the maximum engine output for minimum fuel consumption must be determined experimentally for each fuel, in order to run a car economically.

The consumption of benzol–alcohol mixture, with a 0·93-mm. nozzle, was considerably larger than that of benzol, and the engine output smaller ; but on using a larger nozzle (*i. e.* 0·97 mm.), the increased fuel supply gave a better output, though still inferior to that obtained from the benzine fraction 40–60° or 120–140°. This is due to the lower heating value of the alcohol in comparison with benzine or benzol.

Another series of experiments was devoted to ascertain the fuel consumption at different engine speeds.

This series was performed with a " Raba G " engine (made at Györ, Hungary) of 90-mm. bore and 150-mm. stroke, equipped with a Zenith carburettor (DEF36), having a 22-mm. air nozzle, a 0·94-mm. central nozzle, and a 1·19 mm. compensating nozzle.

The benzine employed had the composition :—

Sp. gr.			0·7390				
Fraction	.	.	40–60° C.	.	.	0	per cent
,,	.	.	60–80°	.	.	16·5	,,
,,	.	.	80–100°	.	.	49·5	,,
,,	.	.	100–120°	.	.	27·8	,,
,,	.	.	120–140°	.	.	4·9	,,
			Residue	.	.	1·0	,,
						99·7	,,

The measurements were made with the carburettor wide open, and the speed was increased, by stages, from 400 to 2000 revs. by the interposition of different resistances traversed by the current generated in the brake. The results of these tests are given in Table X.

TABLE X

Speed revs.	Engine output		Rate of consumption min. per litre	Fuel consumption			
	Brake weight kg.	H.p.		l. per min.	kg. per min.	l. per h.p.-hr.	kg. pr. h.p.-hr.
400	13·3	10·0	10·13	0·099	0·073	0·592	0·438
800	13·9	21·0	5·95	0·168	0·124	0·480	0·355
1200	13·8	31·2	4·48	0·223	0·165	0·429	0·317
1600	12·7	38·3	3·50	0·286	0·211	0·448	0·331
2000	10·6	40·0	3·22	0·311	0·229	0·466	0·344

Carburettor fully open.   Temperature of cooling water, 50–60° C.

From these tests it appears that the fuel consumption (expressed as volume or weight) per h.p.-hour, decreases up to a speed of 1200 revs., above which it increases again. Hence, a given engine has only one optimum speed.

The total fuel consumption (volume or weight) per minute increases with the speed, but in diminishing proportion, though, on the other hand, it increases almost *pari passu* with the engine output.

Of course, similar experiments can be carried out with the carburettor opened to any desired extent.

Another test was made by first bringing the engine (with fully opened carburettor) to 2000 revs., and then reducing the speed, by gradually throttling the carburettor, down to 1600, 1200, 800, and 400 revs., without altering the resistance interposed at 2000 revs.   The results are given in Table XI.

The fuel consumption (volume or weight) per h.p.-hour falls as the speed rises, *i. e.* with increased supply of gas, up to a certain point—in the present instance 1600 revs.— and then increases, after the carburettor has been fully opened, on attaining 2000 revs.   In order to economise fuel it is accordingly advisable to throttle down the carburettor a little.

The total fuel consumption (volume or weight) per minute rises quickly with the increase in speed.   On the other hand, taken in relation to the engine output, it increases slightly

at first, but considerably quicker at speeds between 1600 and
2000 revs.

TABLE XI

Speed revs.	Engine output		Rate of consumption min. per litre	Fuel consumption			
	Brake weight kg.	H.p.		l. per min.	kg. per min.	l. per h.p.-hr.	kg. per h.p.-hr.
400*	2·5	1·9	30·42	0·033	0·024	1·038	0·767
800*	4·8	7·2	11·75	0·085	0·063	0·709	0·524
1200*	6·6	14·9	7·75	0·129	0·095	0·520	0·384
1600*	8·6	25·9	5·37	0·186	0·138	0·432	0·319
2000†	10·5	40·0	3·22	0·311	0·229	0·466	0·344

Temperature of cooling water, 50–50° C.

* Carburettor partly open.   † Carburettor fully open.

Finally, a test was made with the " Raba G " engine to
ascertain the effect on the engine output of an addition of
vegetable oil or animal fat to the mineral oil.   With this
object 15 per cent. of rape oil was added to the mineral oil
used in the engine, in one case, and 20 per cent. of rape oil
and 8 per cent. of castor oil in another.   The benzine used
had the density 0·741 and the following fractional composi-
tion :—

Fraction.			
0–40° C.	0·8	per cent.	by volume
40–60°	4·8	,,	,,
60–80°	12·0	,,	,,
80–100°	28·0	,	,,
100–120°	24·0	,,	,,
120–140°	21·7	,,	,,
140–160°	6·3	,,	,,
above 160°	4·1	,,	,,
	99·7		

The results are given in

TABLE   XII

Speed revs.	Engine output		Rate of consumption min. per litre	Fuel consumption			
	. in kg.	in h.p.		l. per min.	kg. per min.	l. per h.p.-hr.	kg. gr. h.p.-hr.
1200*	13·8	31·2	4·37	0·229	0·170	0·440	0·326
1200†	13·9	31·5	4·38	0·228	0·169	0·435	0·322
200‡	14·0	31·7	4·36	0·229	0·170	0·434	0·322

* Mineral oil.   † Mineral oil + rape oil.   ‡ Mineral oil + rape and castor oil.

From this Table it can be seen that the addition of vegetable oil slightly improved the engine output, whilst the oil mixture reduced the fuel consumption (volume and weight) per h.p.-hour.

The mineral oil had the viscosity 7·9° E. at 50° C., and an acid content of 0·05 per cent. expressed as SO_3.

The mixture of mineral oil and rape oil after being in use a short time had the viscosity 5·4° E. at 50° C., and the acidity 0·082 per cent. SO_3.

Examined after a short period of service, the mixture of mineral, rape, and castor oil gave the viscosity 6·0° E. at 50° C., and the acid content 0·10 per cent. SO_3.

The viscosity of pure rape oil was 4·0° E. at 50° C., and the acid content 0·19 per cent. SO_3, the corresponding values for pure castor oil being 16·6° E. and 0·10 per cent. SO_3.

After being in use a short time, the mixture of mineral, rape, and castor oil was found to have an unpleasant, penetrating smell, indicating decomposition of the castor oil.

These experiments with oils must only be regarded as preliminary, and will be followed up with other oils and fats.

Road Trials

Practical road trials were carried out with various motor-cars and motor vans.

(a) Car Trials

The car, an 8/20 h.p. Praga " Mignon," had four cylinders of 70-mm. bore and 120-mm. stroke, and was equipped with No. 26 Zenith carburettor, having a 0·90-mm. main petrol nozzle.

The trials were conducted on both level and good hilly roads, and at a time when the air temperature was fairly constant, or under a cloudy sky and in dry weather.

Prior to each run the engine was carefully tested, the compression and sparking plugs examined; all the working parts were well lubricated, and the tyres uniformly inflated; everything, in fact, being taken into consideration that could affect the fuel consumption. The petrol was carefully filtered, to prevent obstruction in the carburettor nozzles, and uniform pressure was maintained in the petrol tank throughout the run. In addition, the air drawn into the

carburettor by the engine was filtered through a device designed by the author (see p. 229).

In all cases the same size nozzles (main and auxiliary) of the carburettor were used, although the densities of the light and heavy benzine, and especially of the benzol, differed considerably.

The fuel in the tank was carefully gauged, and the quantity consumed was ascertained directly after each run.

Table XIII gives the results from a number of benzines and benzols arranged in serial order with increasing density, their percentage composition in fractions of different boiling points being also given. Below are the distances (kiloms.) traversed per litre and kilos. of fuel, the figures being the mean of a series of tests.

TABLE XIII

Fraction ° C.	Benzine					
	1	2	3	4	5	6
	D = 0·700	D = 0·700	D = 0·705	D = 0·720	D = 0·720	D = 0·740
25–60	23·0	14·2	25·0	1·6	1·1	—
60–80	43·0	63·8	38·5	34·5	31·0	4·7
80–100	18·3	12·5	23·5	34·8	39·2	41·7
100–130	11·6	6·0	7·5		23·2	44·4
130–150 over 150 and Residue	3·4	2·5	5·0	28·7	4·5	9·2
	99·3	99·0	99·5	99·6	99·0	100·0
Distance covered per 1 l.	7·0 km.		7–7·7 km.	8·6–10 km.	8·8 km.	9·6 km.
Distance covered per 1 kg.	10 km.		9·9–10·9 km.	11·9–13·9 km.	12·2 km.	12·9 km.
Consumption per 10 km.	1·43 kg.		1·43–1·3 kg.	1·16–1·0 kg.	1·13 kg.	1·04 kg.
	Motor and radiator hot, mean air temperature 10° C.					

The chief features revealed by this Table are that the light benzines Nos. 1 and 2, containing 66–78 per cent. of

fractions between 25° and 80° C. gave a shorter mileage than the medium grades Nos. 4 and 5, which contained only 32–36 per cent. of fractions 25–80° C., but 56–64 per cent. of the fractions 80–130° C.

From these results and the behaviour of the several fractions in the carburettor, the author assumed that the benzine constituents boiling between 80° and 120° C. are the most economical in use; that is to say, give the lowest consumption for a given mileage.

In order to test this hypothesis, the necessary quantities (approximately 1 : 1) of the fractions 80–100° C. and 100–120° C., obtained by fractional distillation, were mixed together. A trial run was made with this mixture (No. 6 on Table XIII), and gave, for a consumption of 1·04 litre, a mileage of 9·6 kiloms., thus corresponding, on the whole, to the medium benzines Nos. 4 and 5.

In the runs with the light benzines Nos. 1 and 2 it was observed that, notwithstanding the comparatively low air temperature (10° C.), the engine became much hotter than with benzines Nos. 4–6, i. e. heavy benzine.

The relatively higher consumption of the light benzines corresponds with the results of the brake tests, and may be attributed to the high volatility of the lower fractions, especially under the effect of the strongly heated engine.

The cooler running of the engine on medium or heavy benzine—the radiator conditions being equal—may be explained as follows : The readily volatile fractions of the light benzine enter the engine in a heated state as vapour, whereas the less volatile, higher fractions arrive rather in small drops, and are first vaporised and then burned in the engine. The extra heat needed to vaporise the heavy benzines is derived from the engine, which therefore runs cooler.

In runs made on heavy benzine in cold weather, one-fourth of the lower surface of the radiator should be covered up (see p. 228), in order to protect the engine from excessive cooling. When the radiator is unprovided with a cover in cold weather, the benzine is incompletely vaporised, and the engine runs very irregularly.

In one case the trial run was made in wet weather on a softened road, benzine No. 5 being used. The average run per litre was 7 kiloms. : a comparatively favourable result.

If the results of the road trials be compared with those of the brake tests, a satisfactory concordance is found to exist between the fuel consumption in both.

Further trial runs were made with a 9/25 h.p. Praga " Mignon " car, with four 75 × 130 mm. cylinders and fitted with a Zenith ABC carburettor (No. 26). The main fuel nozzle was 0·85 mm. and the auxiliary nozzle 1·10 mm. in diameter, the diameter of the air nozzle (atomiser) being 30 mm. These sizes were used throughout, irrespective of the fuel, which consisted of the different benzines shown in Table XIV, and also pure benzol and equal parts of pure benzol and 95 per cent. alcohol.

TABLE XIV

COMPOSITION OF THE BENZINES OF TABLE XV

Benzine Sp. gr.	1 0·721	2 0·721	3 0·746
Fractions ° C.	Fractions per cent.	Fractions per cent.	Fractions per cent.
40–60	12·0	2·6	1·0
60–80	27·0	14·0	8·5
80–100	38·3	51·0	27·0
100–120	18·5	25·6	32·2
120–140	2·6	4·6	13·3
140–160		1·3	16·1
160–180	1·5	0·7	1·6
above 180			
	99·9	99·8	99·7

A small auxiliary tank, directly connected with the carburettor by a short pipe, was filled with a quantity of fuel ascertained by preliminary trials, and the car was run, with all the necessary precautionary measures, at uniform speed until all the fuel was consumed and the motor came to a standstill. The distance travelled was measured, and from this the distance per litre and kg. of fuel was calculated.

The runs were made, on the one hand, out and back on the level, and on the other on a selected constant rise with a gradient of 9–12 per cent. Other runs again were made partly on the level and partly through hilly country.

In all cases the car was run with nearly full admission and direct drive, the hills being climbed with full admission and on direct and third speeds. The speed was measured with

a tachometer and kept at uniform level, and the car carried four. Other runs were made on paved streets in the town. The results of all these trials are given in Table XV.

TABLE XV

ROAD TRIALS WITH 9/25 H.P. PRAGA "MIGNON" CAR

Fuel	Sp.gr.	On the level			Uphill			In town			Over hilly country		
		Mileage		Average speed, km. per hr.	Mileage		Average speed, km. per hr.	Mileage		Average speed, km. per hr.	Mileage		Avera spee km. per h
		per litre.	per kg.		per litre.	per kg.		per litre.	per kg.		per litre.	per kg.	
		kilom.			kilom.			kilom.			kilom.		
Benzine I .	0·723	—	—	—	4·45	6·17	39·5	—	—	—	—	—	—
„ II .	0·736	—	—	—	4·52	6·14	40·5	4·72	6·41	28·5	5·60	7·61	42·
„ III .	0·746	6·18	8·29	60	4·59	6·16	40·5	—	—	—	—	—	—
Benzine-benzol I : 1	0·811	7·02	8·66	60	4·64	5·73	42·5	—	—	—	—	—	—
Benzol .	0·882	7·37	8·35	60	5·02	5·69	42·0	5·63	6·38	29·0	6·79	7·70	43·
Benzol-alcohol 1 : 1	0·847	6·68	7·89	60	4·55	5·37	40·0	—	—	—	—	—	—

In the third series of road trials, a Lancia car was used, the conditions being the same as before. The four-cylinder engine had a 110-mm. bore and 130-mm. stroke, and developed 35 h.p. at 1200 revs. under the brake test.

The first runs were made with a Lancia carburettor, but owing to the higher fuel consumption and difficulty of adjustment (due to the complicated arrangement of the carburettor), the horizontal Zenith carburettor was substituted. The Lancia carburettor had a 10-mm. main fuel nozzle, 1·27-mm. auxiliary nozzle, and 24-mm. air nozzle.

The results of these runs are given in Table XVI.

TABLE XVI

ROAD TRIALS WITH LANCIA CAR

	On the level						Uphill					
	Carburettor :						Carburettor :					
	Lancia			Zenith			Lancia			Zenith		
	Mileage (km.)		Average speed, km. per hr.	Mileage (km.)		Average speed, km. per hr.	Mileage (km.)		Average speed, km. per hr.	Mileage (km.)		Average speed, km. per hr.
	per l.	per kg.		per l.	per kg.		per l.	per kg.		per l.	per kg.	
Benzine 0·733	3·9	5·3	50	5·91	8·06	60	2·58	3·52	46	4·46	6·08	50
Benzol 0·882	4·5	5·1	50	6·7	7·6	60	3·21	3·64	49	5·3	6·01	51
Benzine-benzol 1 : 1 (0·811)	—	—	—	—	—	—	2·90	3·58	48	4·9	6·04	52

It will be evident from all the Tables that, when the volume of fuel is taken as the basis, benzine gives the shortest mileage and benzol the longest, owing to the greater density of the latter. The engine was also found to run better on benzol than on benzine, especially uphill.

The trials with the Lancia car show that the choice of a good and properly adjusted carburettor has an important influence on the fuel consumption for a given engine output. In these trials the oil consumption was also measured, and found to be 2 per cent. by weight of the fuel consumption, the quantity used in the gear-box not being taken into consideration.

(b) Motor-van Trials

A number of vans, of 1½–5 tons capacity, were tried on the road, precautions based on the experience gained in the car trials being taken to obtain unimpugnable results.

The first van, a 3-ton Praga, No. 5, with solid rubber tyres, was equipped with a four-cylinder engine, bore 110-mm. and 180-mm. stroke, and a Cudell carburettor having a 1·34-mm. nozzle.

The engine was provided with a governor preventing the attainment of more than a moderate engine speed, and thus ensuring a regular road speed in all circumstances.

The runs were made on a good, level stretch of road, 7 kiloms. in length, in quiet weather and always under similar conditions, the road being kept free and care taken that any carts that might come on the scene would not impede the van. The van was run light, with only three men on board, on fourth (direct) speed, with carburettor valve wide open, and the trip out and home made without stopping.

The fuels used in the trials were: individual benzine fractions, different benzines, pure benzol, and a mixture of benzol and 96 per cent. alcohol, the composition of which is given in Table XVII. The engine was started with petrol from the main tank, and as soon as it ran evenly and everything was ready for starting, the main tank was shut off and the carburettor connected to an auxiliary tank containing an accurately measured volume of the fuel for the run. The carburettor valve was kept fully open and the van run on fourth speed until the whole of the fuel had been consumed and the engine came to a standstill, the distance travelled being carefully measured, and another run made from the original starting-point.

TABLE XVII

COMPOSITION OF BENZINES IN TABLE XVIII

Fractions	40–60 °C.	60–80 °C.	80–100 °C.	100–120 °C.	120–140 °C.	Light	Medium	Heavy I.	Heavy II.
Sp. gr.	0·6590	0·7037	0·7353	0·7510	0·7167	0·6872	0·7286	0·7682	0·7646
Up to 40° C.	2·0	—	—	—	—	5·2	—	—	—
40–60°	94·0	1·0	—	—	—	38·4	1·6	—	2·2
60–80°	4·0	95·0	1·0	—	—	40·8	16·4	1·6	3·4
80–100°	—	3·6	98·0	4·0	—	9·8	65·0	3·2	8·0
100–120°	—	—	1·0	93·0	3·8	3·6	16·2	20·8	32·8
120–140°	—	—	—	3·0	92·0			50·0	28·0
140–160°	—	—	—	—		2·0	0·8	16·0	17·6
160–180°	—	—	—	—	4·0			6·4	8·0
Residue	—	—	—	—				2·0	—
	100·0	99·6	100·0	100·0	99·8	99·8	100·0	100·0	100·0

TABLE XVIII

MILEAGE WITH DIFFERENT FUELS : 3-TON PRAGA "V" VAN

Fuel	Sp. gr.	Kiloms. pr. litre.	Kiloms. pr. kg.	Average speed, kiloms. pr. hr.	Temp of cooling water	Air Temp.	Remarks
Benzine Fractions { 40–60° C.	0·6590	2·15	3·26	22	55° C.	11° C.	
60–80°	0·7037	2·27	3·23	22	70°	17°	
80–100°	0·7353	2·38	3·23	22	70°	17°	
100–120°	0·7510	2·33	3·10	22	70°	17°	
120–140°	0·7617	2·40	3·15	21·8	70°	17°	
Light Benzine .	0·6872	2·06	2·99	22	45°	11°	
Medium ,, .	0·7286	2·17	2·98	22	50°	11°	
Heavy ,, I .	0·7682	2·27	2·96	21·9	55°	11°	
Benzol . .	0·8845	2·56	2·90	21·8	70°	17°	
Benzol-Alcohol (1:1)	0·8471	2·45	2·88	21·7	58°	11°	
Heavy Benzine II { 1·1	0·7646	1·1	1·44	15·0	54°	0·6°	Radiator uncovered.
{ 1·9		1·9	2·48	21·5	69°	−0·5°	Lower part of radiator covered.

The results of these trial runs are given in Table XVIII. The longest runs on benzine fractions were obtained with the fractions 80–100° C. and 120–140°, the shortest on the fraction 40–60° C. Similar results were given by light, medium, and heavy benzines. Benzol gave the longest

mileage of any fuel, and satisfactory results were also given by the benzol-alcohol mixture. Nevertheless, as can be gathered from the table, the engine output is lower on heavy benzine and benzol-alcohol mixture.

Another trial was made on heavy benzine II up a gradient of 9–12 per cent. on a cold day (about zero C.), the radiator being left exposed during one run, whilst in the other the lower half was covered with a millboard screen (see the section dealing with Engine Cooling).

The difference was remarkable, for whilst in the first run the speed could not be increased above 15 kiloms. per hour, with valve fully open, and the temperature of the cooling water fell from 70° to 54° C., the speed in the second run was practically equal to that on the level, and the mileage greater for the same volume of fuel. After the first run the carburettor was cold, but warm after the second, and in the latter the cooling-water temperature remained at 65° C.

A comparison of the results of all these experiments leads to the conclusion that the benzines in which the middle fractions 80–100° C. predominate give the highest engine output, and a considerably longer mileage than an equal volume of light benzine ; and since they are also cheaper than the light grades, they can be recommended as the most economical to use.

As can be seen from Tables I, II, and III, such benzines are obtainable in commerce or could be prepared and supplied without difficulty (see p. 4).

In summer time it is best to use a heavy medium benzine of about sp. gr. 0·720–0·740 ; and in winter a light medium grade of sp. gr. 0·700–0·720.

The experiments with benzol show that, under otherwise equal conditions, a given volume of this fuel will give a longer mileage than benzine, but a somewhat smaller engine output. This, however, is not a feature that is peculiar to benzol, Table XVIII showing that a longer mileage is obtained on heavy benzine than on light ; that is to say, the distance travelled per unit volume of fuel depends on the density of the liquid, inasmuch as the heavier one contains a greater weight of fuel material than the lighter (e. g. 884 grms. in 1 litre of benzol of sp. gr. 0·8845, as compared with 687 grms. in the case of benzine of sp. gr. 0·6872).

With a properly selected nozzle, benzol will give almost the same engine output as medium benzine (Table IX), and in this way it can be raised to a par with benzine, apart

from the disadvantage attending its higher solidification point (about zero C.), etc.

The author would recommend the addition of 25–30 per cent. of benzol to medium benzine, especially because benzol prevents the engine knocks occurring with many benzines in case of overload, or when the spark is advanced too far.

Additional road trials were made with the following motor vans :—

(1) Praga R : capacity $1\frac{1}{2}$ tons; solid rubber tyres; engine, 90-mm. bore, 150-mm. stroke, developing 20·8 h.p. at 800 revs.   Zenith carburettor ; main fuel nozzle 0·87-mm., auxiliary nozzle 1·19-mm. diameter.

(2) Praga V : capacity 3 tons; solid rubber tyres ; engine, 110-mm. bore, 180-mm. stroke, developing 37 h.p. at 800 revs.   Cudell carburettor with 1·29-mm. fuel nozzle.

(3) Praga N : capacity 5 tons; solid rubber tyres ; engine, 115-mm. bore, 180-mm. stroke, developing $50\frac{1}{2}$ h.p. at 1000 revs.   Praga carburettor with 1·09-mm. central main fuel nozzle and 1·17-mm. outer nozzle.

(4) Raba V : iron tyres ; engine, 110-mm. bore, 180-mm. stroke.   Cudell carburettor with 1·40-mm. main fuel nozzle.

All the engines were equipped with governors.

The fuels employed were : benzine, sp. gr. 0·746; benzol, sp. gr. 0·882; benzine and benzol in equal volumes, sp. gr. 0·911; benzol and alcohol, sp. gr. 0·847; and for the town trials, benzine sp. gr. 0·729.

The 0·746 benzine had the following fractional composition :

	Fractions	
° C.		per cent.
40–60	. . . . . .	1·0
60–80	. . . . . .	8·5
80–100	. . . . . .	27·0
100–120	. . . . . .	32·2
120–140	. . . . . .	13·3
140–160	. . . . . .	16·1
Residue	. . . . . .	1·6
		99·7

The runs were made with empty and loaded vans on the same level and uphill roads, and all carried out under the conditions already described, the nozzles, too, being left unaltered.   In all cases the engine was run under full admission, so that the results set out in Table XIX correspond to the maximum consumption of fuel.

As a rule, the fuel consumption in town streets and on

TABLE XIX. ROAD TRIALS WITH MOTOR VANS

Mileage (kilometres) per 1 litre and 1 kilo of fuel

ON THE LEVEL

Van.	Benzine Empty 1 l.	Benzine Empty 1 kg.	Benzine Loaded 1 l.	Benzine Loaded 1 kg.	Benzine Mean speed, km. per hr.	Benzine-Benzol 1:1 Empty 1 l.	Benzine-Benzol 1:1 Empty 1 kg.	Benzine-Benzol 1:1 Loaded 1 l.	Benzine-Benzol 1:1 Loaded 1 kg.	Benzine-Benzol 1:1 Mean speed	Benzol Empty 1 l.	Benzol Empty 1 kg.	Benzol Loaded 1 l.	Benzol Loaded 1 kg.	Benzol Mean speed	Benzol-Alcohol 1:1 Empty 1 l.	Benzol-Alcohol 1:1 Empty 1 kg.	Benzol-Alcohol 1:1 Loaded 1 l.	Benzol-Alcohol 1:1 Loaded 1 kg.	Benzol-Alcohol 1:1 Mean speed
Praga R. (a)	3·87	5·20	3·85	5·16	22·2	4·16	5·13	4·15	5·12	22·2	4·52	5·12	4·50	5·10	22·2	4·10	4·84	4·06	4·79	22·2
(b)		2·9	3·89										3·6	4·08						
Praga V. (a)	2·22	2·98	2·11	1·83	18·0	2·40	2·96	2·30	2·83	18·0	2·58	2·93	2·50	2·83	18·0	2·28	2·69	2·18	2·57	18·0
(b)			1·56	2·09				2·10	2·59				2·40*	2·72						
Praga N. (a)	1·50	2·01	1·36*	1·82	17·0	1·63	2·01	1·48*	1·82	17·0	1·80	2·04	1·62	1·83	17·0	1·48	1·79	1·34	1·58	17·0
(b)			0·86*	1·18				1·07*	1·21				1·1	1·3						
Raba P. (a)	1·35	1·81	1·20	1·61	15·2	1·40	1·72	1·24	1·53	15·2	1·48	1·68	1·29	1·46	15·2	—	—	—	—	—
(b)			1·12	1·50																

UPHILL

Van.	Benzine Empty 1 l.	Benzine Empty 1 kg.	Benzine Loaded 1 l.	Benzine Loaded 1 kg.	Benzine Mean speed, km. per hr.	Benzine-Benzol 1:1 Empty 1 l.	Benzine-Benzol 1:1 Empty 1 kg.	Benzine-Benzol 1:1 Loaded 1 l.	Benzine-Benzol 1:1 Loaded 1 kg.	Benzine-Benzol 1:1 Mean speed	Benzol Empty 1 l.	Benzol Empty 1 kg.	Benzol Loaded 1 l.	Benzol Loaded 1 kg.	Benzol Mean speed	Benzol-Alcohol 1:1 Empty 1 l.	Benzol-Alcohol 1:1 Empty 1 kg.	Benzol-Alcohol 1:1 Loaded 1 l.	Benzol-Alcohol 1:1 Loaded 1 kg.	Benzol-Alcohol 1:1 Mean speed
Praga R. (a)	3·54	4·76	3·0	4·03	Empty 21·6, Loaded 21·4	3·90	4·81	3·30	4·07	Empty 21·6, Loaded 21·4	4·20	4·77	3·54	4·02	Empty 21·6, Loaded 21·4	3·08	3·64	2·60	3·07	Empty 21·6, Loaded 21·4
Praga V. (a)	1·62	2·17	1·30	1·75	Empty 17·2, Loaded 15·5	1·75	2·16	1·50	1·85	Empty 17·2, Loaded 15·5	1·91	2·16	1·73	1·96	Empty 17·2, Loaded 15·5	—	—	—	—	—
Praga N. (a)	1·10	1·47	0·98	1·31	Empty 16·8, Loaded 15·0	1·19	1·47	1·08	1·33	Empty 16·8, Loaded 15·0	1·30	1·47	1·20	1·36	Empty 16·8, Loaded 15·0	—	—	—	—	—
Raba P. (a)	1·11	1·49	0·8	1·07	Empty 15·0, Loaded 12·0	1·20	1·48	0·88	1·09	Empty 15·0, Loaded 12·0	1·27	1·44	0·96	1·09	Empty 15·0, Loaded 12·0	—	—	—	—	—

(a) = On the road.   (b) = In town.   * = Road partly uphill.

bad roads or in very wet weather is 10 per cent. more than on a good road; and, owing to the hindrances arising, may amount to as much as 30 per cent. more.

The figures given in the Table apply to ordinary spring, summer, and autumn temperatures. In very hot weather the fuel consumption is somewhat higher. These figures, however, only apply when the governor is acting properly— that is to say, when the normal speeds stated are not exceeded. If the governor is disconnected, and the speed of the van is considerably increased in consequence, more fuel will be consumed.

CHAPTER XII

PROTECTING THE CARBURETTOR FROM COOLING

IN order to obtain uniform gasification it is necessary, *inter alia*, to protect both the carburettor and the pipe leading therefrom to the engine against external cooling, and increase the vaporisation of the benzine ascending in the pipe or in suspension therein. The vaporisation can be facilitated, on the one hand, by admitting warm air into the carburettor, and, on the other, by warming the pipe leading to the engine.

The lighter the fuel the greater the cooling of the carburettor during vaporisation, and consequently the larger the proportion of fuel carried onward, in the form of drops, to the engine (especially the higher fractions).[1] The radiation of heat from the carburettor can be considerably lessened by nickel plating or tinning, pure nickel and, more particularly, pure tin being fairly good insulating agents.

In summer the warm air from the warm radiator enters the carburettor, but a portion of the supply can also be admitted, in known manner, through a special pipe connecting the carburettor with the body of the engine.

The flanges of the pipe through which the fuel mixture is drawn from the carburettor into the engine should be packed with lead, which facilitates the conduction of heat from the engine to the carburettor and the warming of the pipe itself. Asbestos packing is generally used, but, owing to the low heat conductivity of asbestos, this retards the supply of heat to the carburettor.

In cold weather, particularly in winter, this connecting

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[1] Some makers have tried to obtain a more uniform mixture of fuel and air by providing a small fan, driven by the air current, in the suction pipe. But this device, intended to atomise the fuel, is complicated and has not proved satisfactory, the flow of air being checked. Moreover, the valve above the carburettor contributes to the atomisation of the fuel injected through the nozzle.

pipe is strongly cooled by the cold air from the fan, with the result that benzine vapours are partly recondensed on the one hand, and the vaporisation of the benzine ascending the pipe is lessened on the other.

Cooling the Engine

The fundamental principles of cooling have not been sufficiently taken into consideration in designing the devices for cooling motor-car engines. The radiator is painted with a bronze paint, and the entire engine casing, together with the pipes leading to the radiator, is either enamelled black or coated with bronze paint, which is a bad conductor and retards radiation. On this account no part of a motor-car that serves as a cooling device should be painted, but polished; and the engine casing should be copper-plated on the outside, copper being the best heat conductor. In this way the cooling of the engine will be facilitated.

In winter it is usual to cover up the upper part of the radiator, to prevent the water from excessive cooling and keep the engine warm. This method is not quite correct, mainly because the colder water that sinks to the bottom is cooled still further by the air flowing through the radiator, and the engine is consequently super-cooled.

If heavy benzine be used as fuel, the engine may run irregularly owing to the irregular vaporisation of the benzine. Moreover, the carburettor is strongly cooled by the cold air passing through the lower part of the radiator, with the result that the benzine vaporises badly in the carburettor and the engine does not run evenly.

For these reasons the author covers up part of the lower portion of the radiator, according to the atmospheric temperature, with three thin strips of aluminium or varnished millboard, 12, 16, and 20 cm. (5, 6½ and 8 ins.) wide respectively, slipped in front of the radiator. This will keep the carburettor and engine warm, as required, and improves the running, as shown at the bottom of Table XIV.

The usual type of cooling fan provided on motor-cars also does not always produce the desired effect properly, as is found by experience on hot summer days, especially in hilly country.

A six-vane fan of the Mælger type (E. Mælger, Berlin) used for room ventilation might, if the vanes were reversed, prove more satisfactory for motor-cars than the existing patterns.

The author used a fan of this kind on a Walter tri-car with air-cooled engine for two years, summers included, with excellent results. Owing to the impossibility of obtaining a fan with reversed blades during the war, the experiment could not be tried on an ordinary car.

FILTERING THE INTAKE AIR

On the road and in the open country, the engine—piston rings especially—is very liable to trouble due to dust and sand carried by the intake air from the fan into the carburettor and thence into the engine, where it settles on the valves, clogs the sparking plugs and forms, with the engine oil, a greasy mass, which grinds the piston rings like emery and gradually causes a loss of compression.

FIG. 16.

Dust and sand mixed with oil also settle on the sides of the cylinders and may give rise to injurious incrustation.

To prevent these inconveniences, the author employs two specially arranged filters, in the shape of a shallow funnel (Fig. 16), the wider opening of which has an area at least twenty times that of the air aperture of the carburettor. On these filters (*a* and *b*) a piece of woollen fabric *c*, of medium texture, is held taut by means of two packing rings, and the resulting filter is pushed over the air intake of the carburettor. The larger filter *a*, which is next the carburettor, is also covered with a fine-mesh sieve, *s*, which acts as a preliminary filter for catching the coarse dust and sand.

The laterally attached filter *b*, is a little smaller and can, when necessary, be closed by a flap in order, for example, to reduce the air supply in cranking-up the engine, and thus facilitate starting.

This attachment keeps the carburettor and engine clean. The upper part of the float chamber is also made perfectly dust-proof by means of a special cover. The filter cloth is cleaned at intervals with a brush, or rinsed with benzine. Another advantage of the filter is that starting of the engine
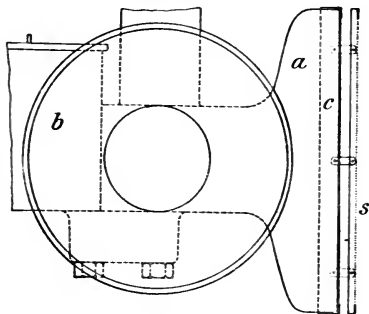
from cold can be greatly facilitated by spraying benzine on the filter cloth.   The ordinary method of injecting benzine through the compression cocks into the cylinder at starting is wrong, because this benzine dissolves the oil adhering to the piston rings, which oil then burns and leaves the engine running without lubricating oil for the time being.

The author has used the above air filter successfully for five years.

CHAPTER XIII

SAFE STORAGE OF BENZINE AND BENZOL

Causes of Fire

THE fire risk of benzine and benzol has already been described in dealing with these fuels ; and we can now proceed to treat of the causes and prevention of fires in stores, etc.

A benzine or benzol fire may originate in ignition and explosion of mixtures of gas and air, and also by ignition of the fuel in the storage barrels, etc.

A fire may be started by various causes, such as naked lights, the dropping of glowing matches, the striking of sparks from nailed boots on stone floors, etc., because the heavy vapours of benzine and benzol mostly accumulate near the ground. Fire may also be transmitted from adjacent burning objects, either directly or through flying sparks, lightning, or finally spontaneous ignition.

In dry-cleaning establishments the washing of the fabrics in benzine generates frictional electricity, woollen or silk fabrics accumulating a positive electric charge and the benzine a negative charge. The discharge, and consequent ignition of the benzine, is effected by the positive charge on the fabric attracting the negative electricity of the earth, the human hand or body generally acting as the conductor. Sparking, however, does not occur until after prolonged washing and strong friction. Owing to the high ignition temperature of the benzine used, white sparks (which are rare) alone are capable of producing ignition, whilst red sparks are not dangerous.

Electricity is also generated when benzine is forced from one tank into another through iron pipes, the metal vessel receiving a positive, and the benzine a negative charge.

In experiments carried out to ascertain whether electricity is generated by the friction of the petrol against the sides of the tank when a motor-car is running, negative results were obtained even with an electroscope.

Storing Inflammable Liquids

The precautions to be taken against accidents in the use of benzine and benzol include fire-proof storage in suitable chambers and receptacles, and fire-proof transport, together with the provision of appliances for the rapid extinction of possible outbreaks of fire.

The storage arrangements differ according as large or small quantities of benzine and benzol are concerned. As examples of the one kind we have the systems employed in petroleum refineries, stores of liquid fuel for bunkering ships, and powder works; and of the other, those in small stores, motor-car works, dry-cleaning establishments, garages, etc. In principle, however, they are all the same.

The great extension of motoring and dry-cleaning have necessitated the storage of benzine and benzol in comparatively large quantities, often in inhabited premises; and in these cases greater care is accordingly needed.

Storage Arrangements

The first condition for safe storage is to select a location in which the temperature cannot fall very low, even in winter, but rather remains constant, for the following reasons :—

The upper flash point of various benzines is between about $-5°$ and $+10°$ C., and the explosion risk of a benzine stored in a receptacle increases with the upper flash point, which can, however, be readily attained if the temperature of the outer air be lowered. In some continental countries the winter temperature is often as low as $-10°$ C., and therefore the explosion risk of a number of grades of benzine is high.

In the case of benzines with a range of explosibility (temperatures between the lower and upper flash points) coinciding with the storage temperature, the explosion risk is greater than in those whose upper flash point is below the lowest storage temperature (e. g. zero C.), the risk being nil in the case of very light benzines, because the high vapour tension prevents the accumulation of sufficient oxygen in the space above the stored liquid. With the heavy benzines, on the other hand, the storage temperature lies within the range of explosibility between the upper and lower flash points, and consequently these benzines have a higher explosion risk in storage than the light grades.

Conversely, outside the storage vessels, the air being

always in excess, naturally makes the explosion risk of the lighter kinds greater than that of the heavier grades.

The simplest and best method, therefore, of minimising the risk of explosion is to keep the storage receptacles at least 2 metres (6½ ft.) below the level of the ground, it having been found that, at that depth, the temperature never falls below 4° C. Consequently, a benzine with an upper flash point of less than 4° C. can always be safely stored under these conditions, though, of course, the benzine is nevertheless still inflammable.

The storage chamber should be provided with the necessary ventilation openings, doors and windows, which can be quickly closed so as to be airtight. Fire-proof doors of the Schwarze-Brackwede type are better than iron doors.

In petrol stores at garages a short ventilation channel should be arranged below the entrance door so as to discharge into the open air, in order to allow the escape of the heavy vapours from spilled benzine or benzol.

The storage chamber must be lighted either from the outside or by means of electric glow lamps protected by glass screens; and all connections, switches, and conductors must be situated outside (see also p. 185).

The floor of the chamber should be of wood blocks, and free from gutters or drains in which explosive mixtures could accumulate.

No electromotor or other machine liable to spark should be set up in the storage chamber. The driving belts (e. g. in dry-cleaning works) must only be lubricated with glycerine, and resinous adhesives must be avoided on account of the risk of generating frictional electricity.

Large Stores

In large works, such as petroleum refineries, the benzine tanks are seldom housed indoors, but are mostly in the open, and walled round to keep off the direct heat of the sun. In some instances the benzine tanks are provided with roofs arranged to contain water.

The covers of the tanks are provided, at regular intervals, with ventilating pipes extending down to a certain depth outside the tank, and fine-mesh copper gauze is inserted at every flanged joint to prevent the backward passage of flame.

Protection against fire from flying sparks is afforded by the construction of the manholes, which must be kept closed,

and are preferably provided with a sand or water seal. Lightning rods are arranged as a protection against danger from that source.

No part of a tank should ever be used for the attachment of supports for electrical conductors.

In establishments other than petroleum refineries a great variety of arrangements are employed for the safe storage and conveyance of inflammable liquids, these being generally divided into two main systems and several sub-groups :—

(1) Protective Gas System, comprising arrangements in which the vacant space above the storage receptacles is filled with an inert gas preventing the formation of explosive mixtures of gas and air in such space.   This system is divided into :

(a) The Simple Pressure System, in which the stored liquid is covered with protective gas under a pressure of about 0·5–2 atmospheres, this pressure being utilised to discharge the liquid.   Examples of this type of storage are the Martini and Hüneke, Hoffmann, Grümmer and Grünberg, and other systems.

(b) The Combined Pressure and Pump System, in which the pressure of the gas in the tank is lower than in the above case, and the discharge of the liquid is chiefly effected by pumping.   The liquid can also be handled by means of a piston motor operated by compressed air, or by the same gas (e. g. carbon dioxide) as is used for protection (Breddin system).

(c) The Combined Atmospheric Pressure and Pump System, in which the protective gas is employed at atmospheric pressure.   To this category belongs the negative-pressure system of the Dampfapparatebaugesellschaft, Vienna.

(d) The Simple Atmospheric Pressure System, in which, although the pressure of the protective gas is employed to discharge the liquid, the gas in the tank is merely at atmospheric pressure.   This class includes the automatic system of the same firm.

(2) Displacement System, comprising methods in which no vacant space is left above the liquid in the tanks, and having the following sub-groups :

(a) Systems, such as the Lange-Ruppel, Deyn-Kraft, Braun, etc., in which the inflammable liquid is displaced in the tank by an inert liquid.

(b) Systems, such as the Volume Method of the Dampf-apparatebauges., in which the cubical content of the receptacle varies with the amount of liquid stored.

In the systems of the first group, the inert gas consists of carbon dioxide or nitrogen.

Whilst a mixture of benzine vapour and carbon dioxide will burn in the air, it will not explode, since it does not contain oxygen. The presence of 25 per cent. of carbon dioxide is sufficient to render a mixture of air and benzine vapour non-explosive.

When the gas is employed under pressure, nitrogen is preferable, since under these conditions carbon dioxide is absorbed in large proportions by benzine.

According to experiments carried out in the author's laboratory, 1 litre of benzine at 6° C., and a pressure of 0·3 atmosphere absorbs about 600–1170 c.c. of carbon dioxide, 2350–2950 c.c. at 1 atmosphere, and 3450–4500 c.c at 1·5 atmosphere. Under corresponding conditions the absorption by benzol is about 750 c.c., 3600 c.c., and 4700 c.c. respectively.

In imitation of actual storage conditions, the experiments were performed by charging a small copper vessel half full of benzine or benzol and gradually introducing carbon dioxide until the gauge attached to the apparatus indicated a constant pressure (0·3, 1·0, and 1·5 atmosphere respectively) which remained unaltered even after a considerable time. The gas was then driven out of the benzine in a suitable manner—certain precautions being observed—and the amount of CO_2 determined by chemical analysis.

The results showed that the absorption of carbon dioxide depends, not only on the temperature, but also on the kind of benzine, light benzines (which usually contain methane, ethane, propane, butane, etc., in solution) being less absorbent than medium benzines, which also absorb more than heavy benzines.

According to the literature, 1 litre of benzine absorbs only 150 c.c. of nitrogen at 0·5 atmosphere pressure and 15° C. ; but according to experiments conducted in the above manner, 1 litre of medium benzine (sp. gr. 0·735) absorbs about 400 c.c. of nitrogen at 6° C. and 0·5 atmosphere pressure ; 600 c.c. at 1 atmosphere pressure, and 800 c.c. at a pressure of 1·5 atmosphere.

Fabrics cleaned with benzine containing carbon dioxide have a yellow tinge, and therefore nitrogen is the only gas
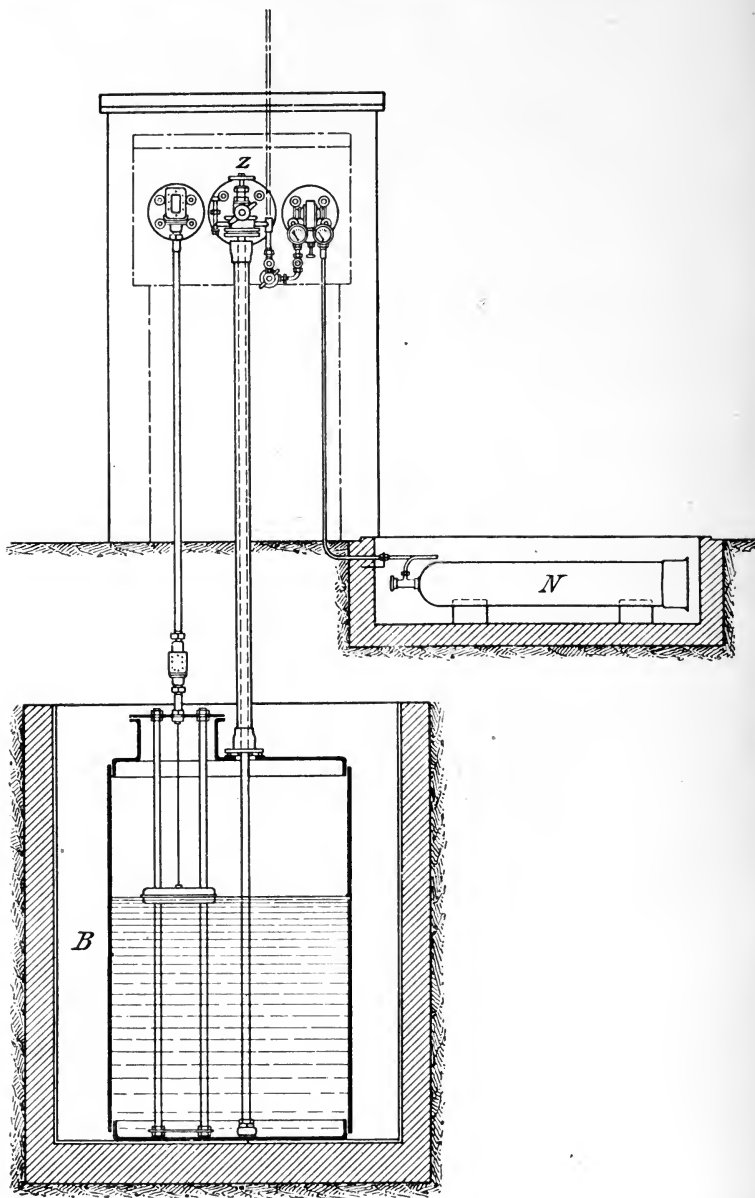
Fig. 17.

suitable for protecting benzine that is to be used in dry-cleaning.

When pressure systems are used, care must be taken to see that the protective gas actually remains in the receptacle all the time, that is to say, cannot escape, and that no air can enter the receptacles in the course of any of the operations.

Air saturated with benzine vapours is also used as the protective gas, instead of carbon dioxide or nitrogen, being non-explosive although inflammable. This principle is adopted in the Saturation Method of the Dampfapparatebauges., Vienna.

Some of the storage systems will now be briefly described.

Martini and Hüneke System. The inflammable liquid is discharged by the pressure of the protective gas. The liquid is stored in an underground tank B (Fig. 17), under a protective atmosphere of carbon dioxide or nitrogen, which prevents the formation of an explosive mixture. This gas, which is supplied from a steel cylinder N, is under a pressure corresponding to the height of the discharge valve, and expels the liquid into z through double (unbreakable) pipes, the jacket space of which is filled with gas communicating with that in the tank and under the same pressure as the latter. Should the pipe be destroyed or damaged by breakage or fire—either the inner or outer pipe, or both together—the protective gas escapes at the seat of the damage and completely relieves the pressure in the tank, so that the inflammable liquid present in the pipe, being no longer under pressure, runs back into the tank. Any flame striking through the pipe is necessarily extinguished for lack of oxygen.

The discharge valves are also jacketed in the same way, so that the same effect will be produced in the event of damage or fracture.

This system is suitable for garages, aircraft sheds, drug stores, motor-car works, and also for larger installations. It has been considerably improved by the H. Hoffmann Apparatenbau Ges., Frankfurt, by the application of a special pressure-reducing valve (universal triple-chamber regulator), which can be fitted to any safe-storage apparatus, and shuts off the supply of protective gas to the store directly any leakage occurs in the outer or inner delivery pipe, or in any of the flange or collar joints, and thus puts the plant out of operation.

To lessen, in pressure systems, the loss of protective gas through absorption by the liquid stored, a no-pressure
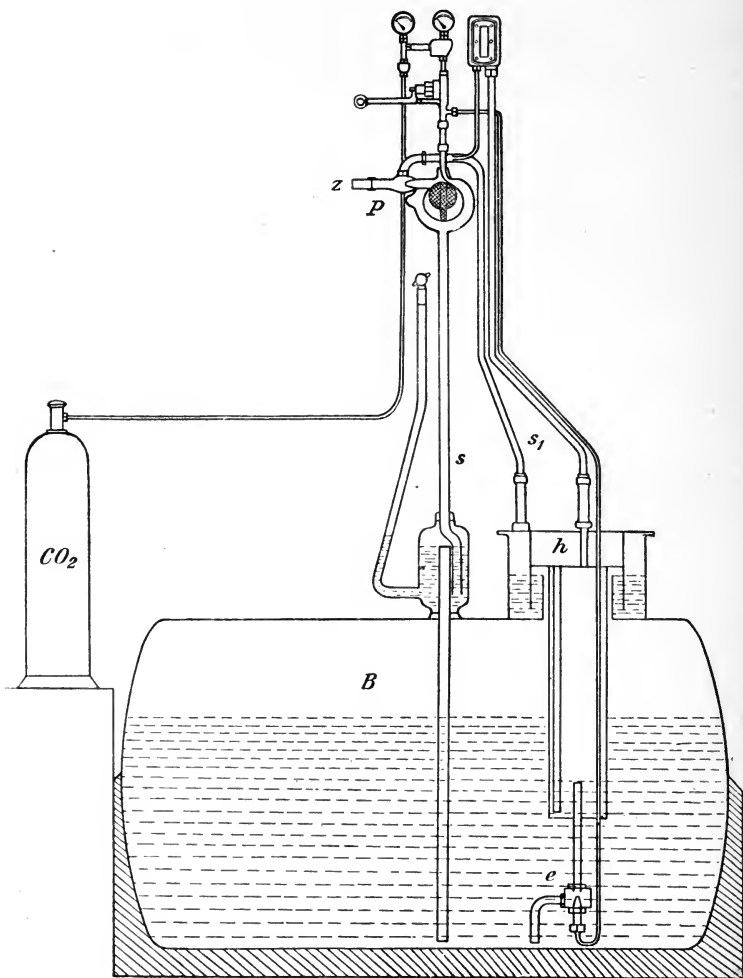
FIG. 18.

system with discharge pump has been introduced, *inter alia*, by the Dampfapparatebaugesellschaft.

This firm has two protective-gas systems, the one a negative-pressure system with pumps, for dealing with

large quantities of liquid (about 1000 litres—220 galls.—per minute), and the other an automatic system for quantities up to 50 litres (11 galls.) per minute.   Both are based on the principle of filling the vacant space of the storage receptacle with a protective gas exerting no pressure.

Negative-Pressure and Pump System (System Ic, Fig. 18). The carbon dioxide [1] issues from an ejector e and forces a portion of the inflammable liquid into a small auxiliary receptacle h, which it keeps constantly full.

After overcoming the liquid seal in this auxiliary vessel, the gas passes into the gas space of the storage tank B.   At the same time that the gas is admitted, a pump P, connected with the tank by a suction pipe s, is set going and raises the liquid to the discharge cock z.   The liquid, however, can only be drawn out of the storage tank when the ejector is operated by carbon dioxide, and the withdrawn liquid is replaced by protective gas.   To produce this effect the pump is provided with an auxiliary suction pipe s_1, which is connected to the auxiliary tank h, and prevents the pump from drawing until the liquid seal is established in h by the lifting action of the inflowing carbon dioxide.

When the pump has stopped working, all the pipes situated above-ground empty themselves automatically, and no excess pressure exists in the tank.

The automatic system (Id) employs the energy of compressed gas (carbon dioxide or nitrogen) contained in steel cylinders for raising the liquid from the tank, whilst the protective gas in the tank itself does not exert any pressure. With this object the gas is introduced, at a pressure of 0·3–0·4 atmosphere, into an auxiliary tank arranged in the main tank.

During the discharge of the liquid the auxiliary tank alone is under pressure, and the plant cannot be operated without a supply of high-pressure gas.   At other times no pressure is exerted by the gas either in the filled auxiliary

[1] Carbon dioxide is used to prevent the nitrogen generally employed being accidentally replaced by oxygen, which is liable to occur—and has resulted in very serious explosions—because nitrogen is obtained as a by-product in the manufacture of oxygen.   To distinguish between them, a glowing splinter of wood is introduced into the flow of gas issuing from the gas cylinder when the regulating valve is opened a little way. In oxygen, the splinter ignites and burns with a bright flame, but is extinguished by nitrogen.   As a precautionary measure it is advisable to paint the cylinders with distinctive colours : for instance, oxygen cylinders red; nitrogen, green; carbon dioxide, white; and hydrogen, blue.

tank or in the main tank, and all the pipes are quite empty
of liquid.
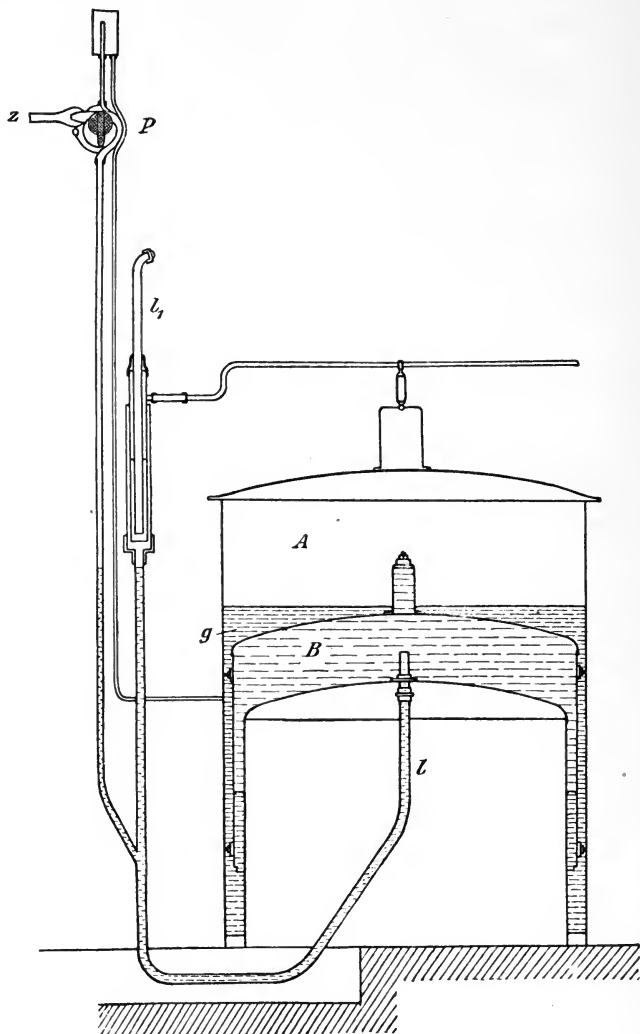
Fig. 19.

No protective gas is employed in either the saturation or
the volume systems, the former of which can be employed

for quantities up to 1000 kg., and the latter for any amount of liquid.

The Saturation System, which is only suitable for light benzine, is based on the principle that benzine can only be taken from the tank provided it is replaced by an equal volume of a non-explosive mixture of benzine vapour and air. This is effected by causing the air that is drawn in during the pumping of the liquid to pass through an apparatus in which it is saturated with benzine vapours. To draw the air through the saturator a partial vacuum is produced, which facilitates the evaporation of the benzine so as to produce a non-explosive mixture.

The suction pipe of the pump is connected with a membrane valve, which keeps the pipe in constant communication with the free space in the tank, and thus prevents the pump from drawing so long as the negative pressure set up by the saturator does not close the valve and shut off the suction pipe.

In the event of air entering the storage tank in any other way than via the saturator—e. g. through leaks in the pipes or the tank itself—the plant cannot be operated.

After benzine has been drawn off, normal atmospheric pressure is restored in the tank, and all the pipes above-ground empty of themselves. To increase the safety of the plant, a flame retarder is provided which prevents the (possibly explosive) mixture of air and vapour from being ignited from outside in any circumstances.

In the Volume System, on the other hand, the formation of vacant spaces and the filling of the same with gases or other liquids is entirely avoided by using a storage vessel, the capacity of which varies automatically according to the amount of liquid it contains for the time being, so that there is never any empty space.

The construction of the plant (Fig. 19) is based on the same principles as the bell gas-holders or gasometers used for storing coal gas.

An outer shell A, encloses a bell B, open at the lower end and dipping into a liquid seal g, of glycerine, which is not miscible with benzine or benzol. A pipe l, which serves both to fill and empty the storage tank, B, passes through the bottom of the tank and is connected to a discharge pump P. The tank is filled through a pipe l_1.

Lange-Ruppel System. In this apparatus (which is no longer manufactured) the benzine is stored in such a way

that no gas space can be formed in the tank while benzine is being withdrawn.   This is effected by floating the benzine on water, a further quantity of which flows in automatically from below in proportion as the benzine is drawn out of the tank.

Generating Protective Gas

In large benzine plants the protective gas is manufactured on the premises, on account of the large quantities required.

The gas, carbon dioxide or nitrogen, is generated by burning a hydrocarbon, such as benzine, in air, the carbon and hydrogen of the hydrocarbon combining with the atmospheric oxygen to form carbon dioxide and water vapour respectively, whilst the nitrogen of the air is left in the free state together with a very small proportion (2–3 per cent.) of unconsumed oxygen.   This oxygen content is unavoidable, since the combustion must always be effected in an excess of air ; but even the nitrogen purchased as a waste product from the oxygen manufacturer is generally contaminated with a similar percentage of oxygen.

The apparatus used consists of a machine similar in principle to an internal combustion engine, using benzine as fuel, and a compressor for compressing the products of combustion.   On issuing from the exhaust pipe of the engine, these latter, consisting mainly of carbon dioxide, nitrogen, and water vapour, are freed from the last-named by cooling down to 25–30° C., and after being freed from oil and purified by passing through a filter charged with gravel, and a second one filled with sawdust, are compressed under a pressure of 20 atmospheres.   In this condition they may be stored in a gas-holder, or else further compressed to 120 atmospheres in steel cylinders, and are used as protective gas for the safe storage of benzine or benzol.   Such gas contains about 15 per cent. (vol.) of carbon dioxide and 85 per cent. of nitrogen.

Storage and Transport of Small Quantities

Small quantities of benzine can be stored and transported in iron drums and tanks.   No protective gas is used in the stores, the vessels being provided with safety gauzes, on the principle of the Davy lamp.   This arrangement, however, is not altogether safe, since in the event of an outbreak of fire on the outside, a sufficient gas pressure may be produced to force the flame through the gauze

and thus ignite the mixture of vapour and air inside the storage vessels.

Various methods have been devised to afford greater security, such as those of Henze (Salzkotten, Westphalia); Rosenthal (" Goliath "), Vienna; Dampfapparatebaugesellschaft (" Capillary "); Schön (" Triumph "), Vienna, etc.

The Henze apparatus consists of cylinders of fine metallic wire gauze, inserted in casings of perforated sheet metal which, in the event of fire, are calculated to conduct the heat away quickly and thus prevent the gauze from becoming red-hot.

The " Goliath " apparatus is similarly arranged, consisting of a shell of perforated sheet metal surrounded by wire gauze, thus dispensing with the perforated outer casing.

The storage vessels are also provided with safety valves which open automatically when the internal pressure attains a certain limit. It should be mentioned that the vapours of benzine and benzol remain in empty vessels for a considerable time, so that great care is necessary when repairs are being carried out. In such cases, the best plan is to expel the dangerous vapours by prolonged steaming.

When a cylinder of liquid carbon dioxide is available, it may be utilised for discharging benzine from small storage vessels, the cylinder (provided with a pressure-regulating valve) being connected to the vessel by means of a copper pipe (about 5 mm. internal diameter), which is passed through the airtight stopper of the vessel so as to project only a short distance into the interior, whilst the benzine is discharged through a second pipe which passes through the same stopper and reaches nearly to the bottom of the vessel. The gas pressure being under perfect control, the desired quantity of liquid can be discharged in a convenient manner. It is also advisable to fit the vessel with a safety valve.

The CO_2 cylinder must be kept in a cool place, at a temperature not exceeding 30° C. (86° F.), since the critical temperature—that is to say, the temperature above which carbon dioxide can no longer remain in the liquid form—is 31° C. At any higher temperature the carbon dioxide would develop a pressure which would burst the steel cylinder.

PREVENTING RISK OF EXPLOSION FROM FRICTIONAL ELECTRICITY

In order to prevent the formation of an electric charge, Richterol is added to the benzine used in dry-cleaning works.

The quantity employed for this purpose is $1\frac{1}{4}$–$1\frac{1}{2}$ parts, by volume, of dilute Richterol (1 part by weight to $7\frac{1}{2}$ of benzine) per 1000 parts of benzine. This addition must be renewed every time the benzine is used. A similar effect is obtained by means of a larger proportion of benzine soap (alkali oleate).

The electrical excitation is measured by an electroscope with tinfoil leaves which diverge in presence of an electric charge. An automatic signal designed by O. Behm (Karlsruhe) rings a bell when the slightest electrical excitation occurs.

Extinguishing Benzine and Benzol Fires

Burning benzine or benzol cannot be extinguished with water ; and even the application of sand or ashes is generally unsuccessful, unless the entire surface affected can be quickly covered up therewith so as to exclude the air.

According to circumstances, the best methods of extinction are : the use of sheets impregnated with fire-proofing agents (asbestos sheeting is too heavy) ; closing all windows, doors, and ventilation openings ; introducing steam, carbon dioxide, carbon tetrachloride, ammonia (in glass grenades) or effervescent substances (which must not, however, contain much water, since benzine, being lighter than water, floats thereon), and finally, projecting powdered bicarbonate of soda on to the flames.

Provision must, of course, be made for manipulating the extinguishing agents, such as steam, carbon dioxide, ammonia, etc., from the outside, in order to prevent access of air to the fire or to the vapour mixture (which might thereby be rendered explosive), and to put out the fire itself.

Various forms of apparatus, known as extinctors, are used for putting out fires in places where small quantities of benzine or benzol are kept, such as motor-car works, garages, aerodromes, shop cellars, motor vehicles, aircraft, etc. Examples of these are afforded by the Minimax, Minimax-Tetra, Excelsior (M. Rentsch, Dresden), and Theo (F. Rungius, Dessau), the last of which projects a powder which generates large volumes of carbon dioxide on contact with flame.

Effervescents are also used, a thick froth of soap, for example, charged with carbon dioxide or sulphur dioxide, being discharged on to the surface of the burning benzine

or other inflammable liquid. This froth is produced, e. g. by the action of water on a mixture of aluminium sulphate or oxalic acid with bicarbonate of soda, or sodium bisulphite and saponin (Saponaria extract). This froth, being lighter than benzine, floats on the surface of the latter and extinguishes the fire by excluding air. Examples of this class of apparatus are the Stankö (Stankö Ges., Vienna), Perkeo (Salzkotten), Perfect (Perfekt-Ges., Berlin), Standard Oil Co., etc.

The Stankö[1] extinguisher consists of a cylindrical iron vessel, in two parts, containing two sheet-metal cartridges, one of which is filled with oxalic acid and saponin, and the other with bicarbonate of soda. The apparatus is connected up to the water hose, or else set up in a fixed position and connected to the ordinary water pipes.

If water under suitable pressure is admitted into the apparatus, it dissolves oxalic acid and saponin from the smaller cartridge, the acid thereupon acting on the bicarbonate of soda in the second cartridge and thereby generating carbon dioxide. In conjunction with the saponin, this gas forms large quantities of froth which are projected through the discharge nozzle.

The cartridges used are easily exchanged, will keep without alteration and do not freeze up.

Ammonia water, and similar preparations, have proved excellent extinguishers used in glass grenades (e. g. Labbé grenades).

Steam, too, forms a good means for extinguishing benzine or benzol fires. Dry steam, projected in sufficient quantity from the boiler into the storage chamber, etc., effects dilution, and consequent change in volume, of the gases forming the explosive mixture of benzine vapour and air, thus preventing the fire from developing into an explosion, and finally extinguishing the flame. Although steam disperses the vapours of benzol or benzine, it does not destroy them; and when the pressure subsides, the water into which the steam condenses settles down to the bottom, leaving the danger of fire or explosion to recur. What should then be done will be described later.

The steam-pipe is arranged so that, on opening a valve outside the storage chamber, the steam will be discharged near the floor level.

[1] Called after the inventors, Stanzig and König, of the Vienna Fire Brigade.

Sprinklers connected with the steam-pipe may be arranged to turn on the steam automatically at a temperature of 50° C., or any higher temperature desired; and such sprinklers may be easily placed in position above the vessels in which benzine is stored.

In the event of an outbreak of fire, for instance in the washing department of a dry-cleaning works, the employees engaged therein must leave immediately. If their clothing is on fire, they must be wrapped in fire-proof sheets kept at hand for that purpose.

Windows and other openings must be shut at once, and steam blown into the room immediately.

Even after the fire has been put out, the doors of the room must not be opened too soon, since the danger of an explosion will still exist for some time. The room should be left under steam for at least an hour first.

All glowing objects must then be covered up with fire-proof sheets, and removed quickly, the doors being shut as soon as possible. The persons engaged in this removal should stoop as low as possible, to avoid injury from the steam.

The doors, windows, and ventilators must not be re-opened until all glowing matter has been got rid of.

As a means of extinguishing benzine fires, Gantsch proposed to pass cooling agents (such as carbon dioxide, sulphur dioxide, ammonia, etc.), which easily evaporate and therefore readily absorb heat, through a system of circulating coils in the liquid.

According to information supplied to the author, a fire which broke out during the emptying of a Merz benzine extractor was extinguished almost immediately (after other means had been tried in vain) by turning on the water circulation in the coiling coils situated in the lower part of the vessel, and thus absorbing the heat.

In large plants, it is most important to confine the fire and prevent it spreading to adjoining buildings, etc. Reservoirs in the vicinity should be cooled by discharging a continuous supply of cold water over them. Sand is useless for this purpose, and introducing water into the burning benzine only aggravates the danger by rendering the latter liable to overflow the tanks.

A reservoir that has taken fire usually burns out more or less quietly according to the quality of the contents.

If the fittings are accessible, the pump valve should be opened at once and the pump set going so as to begin pump-

ing out the contents while the fire is still burning; or they may be run out, through the existing pipes, into a place that is out of danger, such as an underground receptacle.

The contents of the reservoir will continue to burn only so long as the admission of air permits combustion to take place. In many cases, the fire can be put out by shutting off the access of air by means of steam, frothing agents, etc.

In such plants, extinction with incombustible gases is attended with the drawback that these gases are diverted and driven upwards by the flame before they can reach the surface of the burning liquid. To remove this drawback, the following extinguishing device [1] has been introduced for attachment to benzine tanks.

The storage tank (Fig. 20) is provided with a conical false bottom perforated all round at the sides. The apex of the cone faces a pipe which admits carbon dioxide into the vessel. The gas, issuing under a pressure of about $1\frac{1}{2}$ atmospheres, impinges on the apex of the cone, flows in all directions through the benzine towards the perforations and ascends to the surface of the benzine where it mixes with the air and causes the flame to die out for lack of oxygen.

Fig. 20.

It has been found that 40 per cent. of carbon dioxide in the air is sufficient to extinguish flame, and there is therefore no need for the gas to discharge over the whole area of the liquid—round the edges will be quite effectual.
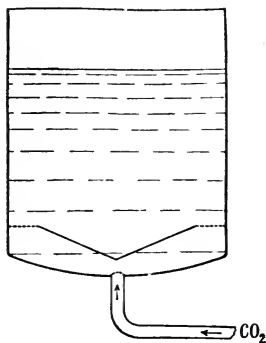
[1] *Petroleum*, 1917, Vol. XVII, p. 89.

CHAPTER XIV

In cases of gassing with benzine and benzol, the first thing is to obtain medical assistance as quickly as possible, whether the sufferer is still breathing or not. In the latter contingency, artificial respiration must be attempted at the earliest possible moment, all articles of clothing likely to impede breathing being removed, and the sufferer taken out into the open so as to get fresh air.

The upper half of the body having been stripped, a pillow or rolled-up coat, etc., is placed under the loins, in order to elevate the lower part of the trunk, leaving the shoulders and the back of the head on the ground. The person rendering first air then kneels astride the body, places both hands on the chest, just below the nipples, and compresses the chest slowly, but with full force, as a first step, after which it is immediately released. This operation is repeated regularly, with the rhythm of natural respiration during sleep, that is to say, twenty times a minute.

The pressure must be strong enough to cause audible expulsion of the air from the lungs, not all at once but gradually.

The lower jaw of the apparent corpse should be drawn forward until the bottom teeth project beyond the top row; the back part of the tongue, which obscures the windpipe, being drawn away and the air allowed free ingress and outlet.

In some cases it is necessary to insert a suitable gag between the teeth in order to obtain a freer passage for the air in and out of the mouth. If this cannot be done because the operator is working single-handed, the head of the sufferer is carefully turned sideways, the tongue being drawn out so as to leave a free passage at least on one side. As soon as the first signs of independent breathing are revealed by the gradual rise of colour in the face and the opposition of a certain resistance to the pressure of the hands by the walls of the chest, the artificial respiration is suspended for a moment, but at once resumed if the face again becomes

pallid and no further signs of breathing are observed. A continuance of artificial respiration will frequently prove successful even when the patient remains apparently lifeless for several hours.

Another method of artificial respiration is to move the two arms backward and forward into normal position, regularly and simultaneously, thus causing the chest to expand (draw in fresh air) and contract (exhale spent air) successively.

Instructions for treatment in cases of gassing should be posted up in all benzine stores, and wherever suitable resuscitation apparatus—such as the Draeger pulmotor—is available, the administration of oxygen is advisable.

The danger to life is smaller when a gassed person, though unconscious, is still able to breathe uninterruptedly. In such cases the sufferer should be removed to a quiet place where there is plenty of fresh air, the only other attention needed being to apply cold water bandages to the head and cold massage to the upper part of the body.

If, however, respiration becomes fainter before medical aid is at hand, the cold suffusions to the head should be supplemented by cold sprays to the chest and neck, and the exhibition of strong aromatics, such as ether, Hoffmann's drops, glacial acetic acid and especially ammonia. If necessary, artificial respiration may also be resorted to.

When consciousness has been restored, the patient is put to bed in a well ventilated room, massaged (under the bedclothes) with hot cloths in an upward direction towards the heart, and carefully looked after for the first few hours.

If respiration should stop during sleep, artificial respiration should again be applied. On consciousness being restored, the sufferer may, on request, be given a few spoonfuls of cordial : grog, warm wine, soup, spirits, tea or coffee, or Hoffmann's drops (equal parts of pure ether and alcohol) on a lump of sugar.

In any event, it is emphatically necessary, in all cases of gassing by benzine, that a doctor should be sent for immediately; and in no circumstances should the sufferer be left alone, since every moment of delay in applying artificial respiration is fraught with danger.

THE END

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