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THE PRINCIPLES OF MOTOR FUEL PREPARATION AND APPLICATION

VOLUME I

THE PRINCIPLES OF MOTOR FUEL PREPARATION AND APPLICATION

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" Should be of great value as a work of reference, both to the oil industry and also to those interested in the development and uses of the petrol engine."—*The Engineer.*

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THE PRINCIPLES OF MOTOR FUEL PREPARATION & APPLICATION

BY

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VOLUME II



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FOREWORD

I HAVE special pleasure in writing this foreword because I have long known the Authors and have taken a great interest in their publications on petroleum subjects.

It is rather remarkable, in view of the great importance of the subject with which they deal, that so few authoritative text-books have been devoted to it, and indeed this applies broadly to the subject of petroleum technology as a whole. It is very true that the state of flux within the Industry, the astonishing development of new technique and the demand for new and improved products involving the rapid obsolescence of so many processes, make it difficult to get anything but a fleeting glimpse of the march of progress. The authors have presented a work on the subject of motor fuels that contains not only very complete descriptions of present day technique but includes also discussions of problems that will undoubtedly arise in the future.

The basic attitude of the book is directed to the modern high speed, high efficiency, internal combustion engine which has revolutionized demands for motor fuel. Partly due to the incidence of taxation, partly due to its inherent efficiency, this type of engine has undoubtedly come to stay, and the fuelling of it has set a variety of problems that are by no means solved to-day. Along with this has come a new and improved technique of engine testing, and at the moment of writing it appears that practical unanimity throughout the world has been arrived at in developing a universal engine testing procedure, which is due to the devoted efforts of special committees set up by the Society of Automotive Engineers, the American Petroleum Institute, the American Society for Testing Materials and the Institution of Petroleum Technologists. This achievement is really of the first importance, and it is probably the first time that there has been a world wide acceptance of a testing method.

The Authors naturally and reasonably give very considerable attention to the compression ignition engine, a type of prime mover that is passing from infancy into a very healthy childhood. The general refining of motor fuels is treated in a thoroughly exhaustive way, and all the ancillary operations are discussed with a degree of completeness that has not hitherto been accorded them.

There is not the slightest doubt but that this work will be invaluable not only to the refiner and the oil industry generally, but to the consumer, and to-day everyone of us comes into one or the other category.

A. E. DUNSTAN,
Chief Chemist,
Anglo-Persian Oil Co., Ltd.

Britannic House, E.C.2.
January, 1934.

PREFACE

THERE are probably few branches of technology which can show so much progress in the past few years as that covering the production of fuels for internal combustion engines. Looking back on old laboratory certificates of tests for petrols it will be seen that the tests determined were : density, distillation characteristics, colour, odour, water content, suspended matter and colour of distillation residue. Such details were considered sufficient for the evaluation of a petrol years ago, but at the present time when automotive engines operate at high efficiencies and high compression ratios such tests are inadequate. Such properties as anti-knock value and gumming tendencies are now of prime importance, while colour and odour have now lost some of their original significance.

The production of Crude Oil in the various parts of the world favoured by Nature with this valuable raw material has a fascination to technologist and layman alike. The team work of geologist, petroleum engineer, refinery chemist, business man and sometimes mathematician, to discover, produce, refine and distribute petroleum and its products may indeed be classed among the great industrial achievements.

This book, because of its length, has been divided into two volumes. Volume 1 deals with the production of motor fuels by methods of distillation, cracking, extraction from natural gas and hydrogenation. It also contains chapters concerning the production of Benzole, various Synthetic Fuels, including Alcohols, and general Storage and Distribution. Volume 2 deals with the properties of motor fuels and covers such subjects as Analysis, Sulphur Contents, Gumming Properties, Volatility Requirements and Knock Ratings as well as Motor Fuel and Aviation Spirit Specifications and a chapter on Automotive Diesel engines and Diesel fuels.

The chapters on the distillation of petroleum to produce motor spirit, the refining of this to market demands and the development of the cracking and hydrogenation processes, whereby the crude oil is made to yield even more spirit than it originally contains, by conversion of the heavier oils, will serve no small purpose if they only bring home to the layman the vast work and capital expenditure involved in maintaining at each wayside petrol pump a constant, standard and reliable supply of motor fuel.

The chapters describing the analysis of motor spirit will show clearly the modern trend in this subject. Previously, much painstaking research has been carried out in attempts to provide schemes for the analysis of petrols into the constituent groups of hydrocarbon series such as paraffins, naphthenes, aromatics and olefines. With the recent work on the determination of the anti-knock value of many pure hydrocarbons, it has been found that similar anti-knock value is not a common property to hydrocarbons of one main series, as this property varies with such fundamental properties of hydrocarbon individuals as length of saturated carbon chain and compactness of the molecule. It might then be asked if much of the previous work on the chemical analysis of petrols was not in vain now that the more practical tests, of anti-knock value, volatility and gumming tendency, tell nearly all that is required to be known.

The collection together of motor fuel specifications should prove of considerable value to many, as such information is usually very scattered.

The information on knock-rating and the descriptions of the development and present day features of test engines should prove a useful portion of this book.

The special requirements of aviation fuels are given the consideration they merit and again much of this information has been collected from widely divergent sources. The position and significance of benzole is not treated at any great length as this subject has been amply treated before.

Alcohol fuels, which derive importance in many countries where intensive nationalism is the order of the day, and synthetic motor fuels, are dealt with somewhat more fully; and the Authors' researches in this latter field have enabled them to include their own conclusions.

As automotive diesel engines are becoming competitors of petrol engines in heavy lorries and buses, no survey of motor fuels would be complete without an account of diesel engines, their fuel oils and fuel oil evaluation.

In writing this book numerous reference books and other contributions have been used freely, and to the Authors of these we desire to express our indebtedness. We also wish to record our thanks to those who have provided us with hitherto unpublished information and those who have loaned us blocks and illustrations.

The Authors are particularly indebted to Mr. L. V. Woodhouse Clark for his assistance in the chapters on petroleum storage and on diesel engines, to Mr. T. G. Hunter for calculations on the subject of plant design especially relating to distillation and counter-current refining methods, and to Mr. Reza Fallah for his assistance in the chapters which include heat transfer and adsorption. The Authors are

also especially indebted to Dr. A. R. Bowen for his help on the subject of possible auxiliary motor fuels, for his valuable criticism of the various chapters, and for much valuable assistance in the preparation of the book for publication.

In conclusion, we would point out that, while we have made every endeavour to eliminate errors, it is difficult to avoid them entirely in a book of this size covering such a variety of subjects. We shall be very grateful if errors are pointed out to us, and also for any helpful criticisms of the subject matter of the book that will enable us to make the book of greater use to those for whom it is intended.

A. W. Nash,

D. A. Howes,

Oil Engineering and Refining Department,
University of Birmingham,
July, 1934.

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Chapter XI.

THE ANALYSIS AND EXAMINATION OF MOTOR FUELS.

513. Introduction.—The analysis and testing of motor fuels is an extremely important subject, especially when it is concerned with the testing of finished products, but it is fraught with many difficulties, chiefly because motor fuels are complex, composite substances and not chemical entities. Many of the tests in use are empirical, while much confusion exists because of the multiplicity of testing methods which have been proposed.

The tests and methods of analysis dealt with in this chapter are those which are normally used in the motor fuel industries, little used methods are not discussed.

The reader is referred to the following publications for more complete details.

1. Standard Methods of Testing Petroleum and its Products. The Institution of Petroleum Technologists, 2nd Edition, London, 1929.
2. Book of A.S.T.M. Standards, 1934 Edition. The American Society for Testing Materials, 1315 Spruce Street, Philadelphia.
3. Report of Committee D.2 on Petroleum Products and Lubricants, 1932. American Society for Testing Materials.
4. Standard Methods for Testing Tar and its Products.
5. Standard Specifications for Benzole and Allied Products, 1929.

Sampling

514. The correct sampling of light oils, motor fuels, etc., and indeed all petroleum products, prior to analysis, is just as important as the analysis itself. No matter how well the analysis is conducted, it cannot compensate for imperfect sampling. Unfortunately, it is not possible to lay down hard and fast rules to cover the many varieties of sampling operations that are, from time to time, required and, indeed, no set of directions for sampling, however explicit, can take the place of judgment, skill and previous experience on the part of persons engaged in this most important work. The following directions[1] are, for the above reasons, only intended to be a general guide in the selection of sampling methods. The sampling of light oils such as petrols, benzoles and natural gas gasolines, and of crude oils and cracked products are alone considered here.

The purpose of sampling is to obtain an *average sample*, which may be defined as one so taken as to contain parts from all sections of the container or pipe from which it is taken in proportion to the volume of each part.

The quantity of the sample taken should be sufficient to enable the required tests, together with any check or referee tests, to be carried out and to admit an additional quantity of the sample being retained if desired. In general, the quantity of the sample should be at least three times as great as the amount required for a complete series of tests.

515. Protection and Preservation of Samples.—Sample containers, which should be filled to approximately nine-tenths of their total capacity, should be closed immediately after samples have been taken. Tin cans or clear glass bottles may be used as sample containers, but it is essential that they be thoroughly clean and dry. In the case of light-sensitive samples, such as unrefined petrols, these should be wrapped or otherwise covered, at once, to protect them from the light. Good quality corks may be used but never rubber stoppers, since these are attacked by hydrocarbons. Contact of the cork with the liquid may be prevented by wrapping metal foil round the cork, which should be of good quality and free from holes and loose pieces. Sealing wax or paraffin should never be poured over the corks after filling. Whenever tin cans are used to contain the samples, care should be taken to ensure that they are free from dirt, water, washing compounds, naphtha or other solvents, soldering flux or acids, corrosion, rust or pin holes. Especial care is necessary with volatile samples to protect them from evaporation.

516. Choice of Sampling Methods. Sampling Tanks, Drums, etc. All levels sample.—An " all levels " sample is one obtained by submerging a closed sample container to a point as near as possible to the draw-off level, opening it and raising it at such a rate that it will be nearly but not quite full when withdrawn. An upper sample should be taken at a level of one-tenth of the depth of the liquid from the surface, a middle sample at half the depth of the material and a lower sample at a level of nine-tenths of the total depth. When the contents of the container are not homogeneous, a bottom sample should be taken from the lowest point of the container or from the drain cock.

Particular care should be taken in the sampling of benzole-petrol blends which may not be properly mixed, and in the sampling of alcohol fuels which may have become separated into layers by the adventitious addition of water.

" Thief " Samples.—Samples may conveniently be removed from

tanks, drums, and barrels by the use of a " thief," which is an apparatus specially designed for this purpose. A convenient form of " thief " for sampling 50 gallon drum containers is shown in Figure 126 and is made of tinned steel, $1\frac{1}{4}$ inches diameter, 36 inches overall length, with cone shaped cups over the ends and having openings at the ends $\frac{3}{8}$ inches in diameter. Three legs, equally spaced round the thief at the lower end, long enough to hold the opening $\frac{1}{8}$ inch from the bottom of the container, aid in securing a good representative sample. Two rings soldered on opposite sides of the tube at the upper end are found convenient for holding the thief by slipping two fingers through them, leaving the thumb free to close the opening.

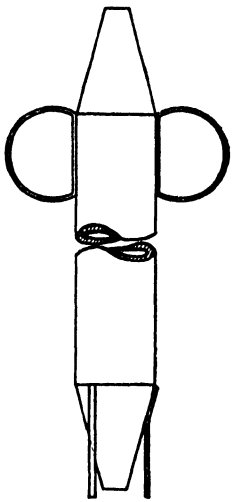


FIG. 126.—THIEF FOR SAMPLING DRUMS. (A.S.T.M. SERIAL DESIGNATION D 270–33.)

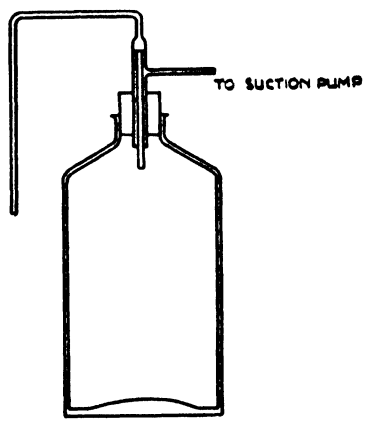


FIG. 127.—SUCTION SAMPLING APPARATUS. *Courtesy of The Institution of Petroleum Technologists.*

The " thief " is used by closing the top hole with the thumb and by lowering it to the required depth in the container. The thumb is then removed and oil is allowed to flow into the apparatus. When full the top hole is again closed, the " thief " withdrawn and the contents allowed to flow into the sample receptacle. When emptying the " thief," the liquid must not be allowed to flow over the hand before it enters the sample receptacle and no excess must be allowed to flow over the drum and back into the drum through the open bung-hole.

Smaller containers, such as 5 gallon cans, may be sampled with a " thief " similar to the drum " thief " but of proportionately smaller dimensions.

When samples larger than the contents of a " thief " are required from drums and barrels, these may conveniently be obtained by means of the apparatus shown in Figure 127. The exhaustion of the container

must never be done by the mouth, and when there is a risk that volatile constituents would be lost by the suction method of sampling, it is preferable to blow over, or siphon, or to use a nearly completely exhausted bottle with a tap on the inlet tube, so that no vapours are pumped away during filling.

Bottle or Beaker Samples.—The bottle or beaker method of sampling is applicable to liquids contained in tanks, tank cars, etc. A clean, weighted bottle or beaker (see Figure 128), provided with a cork

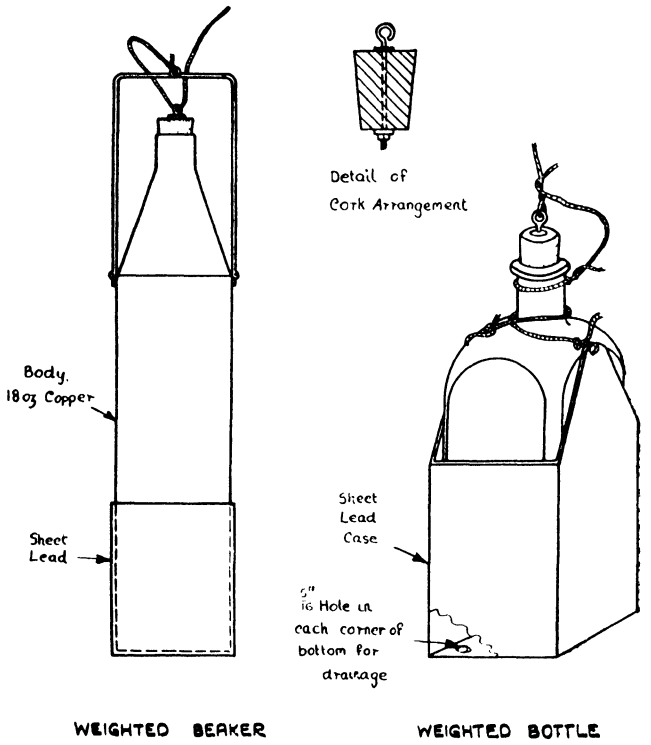


FIG. 128.—STANDARD SAMPLING CONTAINERS FOR BOTTLE OR BEAKER SAMPLING.
(Courtesy of The American Society for Testing Materials)

so arranged that it can be withdrawn when the beaker or bottle is at the desired position in the liquid being sampled, is used. The container is lowered into the tank until it reaches the depth from which a sample is required ; the cork is then withdrawn by a quick jerk, allowing the container to fill completely, as evidenced by cessation of air bubbles. The container is then withdrawn. Particular care is necessary to ensure that this type of apparatus is perfectly clean before use.

Continuous Sampling.—The continuous method of sampling is applicable to the sampling of oils flowing through pipes and lines, and a convenient apparatus to employ for this purpose is that described in detail in A.S.T.M. publications (Designation D.270–33.)

Sampling of Natural Gas Gasolines.—(A.S.T.M. Designation D.216–32.) Samples of very volatile liquids, such as natural gas gasolines, should be collected in previously cooled bottles, preferably by immersing the bottle in the liquid, where possible, and discarding the first sample. Where immersion is not possible, the sample should be drawn off into a previously cooled bottle in such a manner that agitation is kept at a minimum. The bottle should be immediately closed with a tight-fitting stopper and placed in an ice bath or refrigerator capable of bringing the gasoline to a temperature of not less than 0°C. and not more than 4·5°C.

Estimation of the Petrol Contents of Crude Oils and Cracked Products, etc.

517. The quantitative determination of the petrol contents of crude petroleums and of cracked distillates, etc., is a very important analytical procedure, but one which has not, up to the present, received the attention it merits. This is probably due to the fact that the petroleum industry makes use of a very wide variety of large scale fractionating equipment possessing varying efficiencies and, consequently, no single laboratory method of assay can find universal acceptance with the whole industry. We find, therefore, that some laboratory methods of estimating the petrol contents of crude oils make use of a distillation procedure in which practically no fractionation occurs, while others make use of the most efficient fractionating columns operating at high reflux ratios. This unsatisfactory state of affairs has improved somewhat during the past few years with the introduction and rapidly growing use of the pipe still and bubble tower as large scale fractionating equipment, and the simultaneous decrease in the use of shell stills. The bubble tower gives remarkably efficient fractionation and it is possible to estimate the yields of distillate products obtainable from such equipment with moderate accuracy by means of laboratory distillations.

518. Engler Distillations.—The most common method of estimating the petrol present in a crude oil is by means of the standard A.S.T.M. and I.P.T. 100 c.c. side-arm flask distillations which are described in detail in paragraph 527. These distillations are, of course, not primarily intended to be used for such a purpose because they give little or no fractionation, but it has been found that they can be made to give reasonably accurate results in estimating the composition of normal

crude oils. (This method of analysis fails, however, in the case of crude oils containing very small amounts of petrol of very low volatility.) As an example of this we may take the results obtained in a typical bubble tower installation described by Peterkin.[2]

	Per Cent. in Crude	
	Obtained in large scale column	By A.S.T.M. distillation
1. *Central Texas Crude.*		
Naphtha, E. P. 370°F. ..	25·63	24·5
Refined oil, E. P. 540°F. ..	25·78	25·5
Gas oil, E. P. 615°F. ..	8·32	10·0
2. *Pennsylvanian Crude.*		
Naphtha, E. P. 409° F. ..	34·0	34·5
Refined oil, E. P. 576°F. ..	20·0	23·5
Gas oil, E. P. 674°F. ..	11·0	14·0

The figures given by the A.S.T.M. distillation for the gas oil quantities are, in each case, a little high. This is accounted for by the slight overlap between the refined oil and gas oil fractions obtained in the large scale column.

One of the greatest difficulties in using the A.S.T.M. and I.P.T. 100 c.c. Engler distillations for the estimation of petrol in crude oils is the accuracy obtainable. Results generally cannot be checked to within $\pm$ 1% on the crude oil, and, in the case of a crude containing 20% of petrol, this causes an error of $\pm$ 5% in the yield of petrol.

During the past two or three years, the fractionating efficiencies of large size bubble tower installations have been noticeably improved and the yield of the lighter fractions from crude oils, particularly that of the petrol fractions, has been increased. Consequently, it has been found that higher yields of petrol are obtained from a crude in this way than would be expected from the A.S.T.M. 100 c.c. distillation. The reason for this is not difficult to find. As already mentioned, little or no fractionation occurs in the A.S.T.M. distillation, consequently, if a "cut" is made at any given point, only a very rough separation is made. The lower fraction will contain a certain amount of material boiling above the "cutting" temperature, and the higher fraction will contain material boiling below this temperature. In the case of a modern and efficient bubble column, however, the state of affairs does not prevail and such "overlaps" are not observed, i.e., the bubble column gives much more efficient fractionation than the A.S.T.M. distillation and, consequently, gives a larger yield of petrol. The discrepancy, however,

is not great, and, in the majority of cases, only amounts to 2—5% by volume. In certain abnormal cases, however, the discrepancy may amount to as much as 20%, but this is only true for those crude oils or cracked products which contain only a small amount of petrol (up to 10%) of low volatility (5—10% at 100°C.). Because of these considerations, fractional distillation methods have been adopted for estimating the petrol contents of crude oils, and a case of particular interest in this connection is the A.S.T.M. Test (A.S.T.M. Designation : D.285—33), which only defines apparatus and procedure and leaves selection of cutting points and interpretation to be agreed upon by interested parties. The A.S.T.M. state, in the description of this test, that it cannot be expected to duplicate the results of commercial refining operations, having in mind, no doubt, the fact that such operations are carried out in a number of ways and with varying degrees of fractionation efficiency. Details of this test are as follows :—

519. Method of Test for Distillation of Crude Petroleum.—A.S.T.M. Designation : D.285-33.

Apparatus.—The distillation flask used is a 300-ml. Hempel flask of the general shape shown in Figure 129, the fractionating column of which is accommodated in the neck as shown .

This consists of a piece of No. 18 iron jack chain long enough to pack under its own weight into a column 2·54 cms. (1 inch) in diameter and 6½ inches in length. The device for supporting this column of chain is preferably made of nickel-chromium No. 18 gauge wire, one end of which is wound in a spiral a little less than 1 inch in diameter and the remainder bent at right angles and cut off at a length of about 9½ inches. A small loop is bent into the end away from the spiral and put through a hole drilled in a strip of spring steel. When allowed to expand this spring clip holds firmly inside the neck of the flask and provides a secure support for the column of chain.

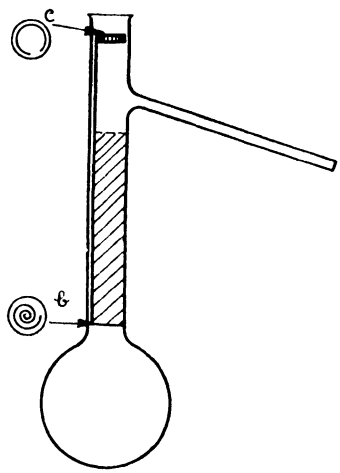


FIG. 129.—FRACTIONATING COLUMN AND SUPPORTING DEVICE IN A HEMPEL FLASK.
(*Courtesy of The American Society for Testing Materials*)

Condenser.—As described in A.S.T.M. Test, Designation : D.86-30, and I.P.T. Test G.3. (See paragraph 527).

Shield Support and Gas Burner.—The shield is of any convenient type. The support takes the form of a hard asbestos board, ¼ in. thick,

having a $3\frac{1}{2}$ in. hole in the centre and of 6 in. minimum overall length. The gas burner is so adjusted that the flame does not spread over a circle of greater diameter than 5 in. on the under side of the asbestos board.

Procedure.—300-ml. of the oil to be examined is measured into the flask, the supporting device for the fractionating column is put in place and the iron chain dropped in carefully so that it fills the space uniformly. After fitting the thermometer and filling the condenser bath with cracked ice, the gas burner is placed under the flask and heat is applied. For the first 5–10 ml. distilled, the rate should be from 2–3 ml. per minute, thereafter the rate of distillation is increased to from 4 to 5 ml. per minute. When the thermometer reaches the required cutting temperature (190°C. is a convenient cutting point for 200°C. end point petrol) the distillation is discontinued and the percentage of petrol in the crude oil is calculated.

A somewhat similar method is that described by the Institution of Petroleum Technologists (Method of Test : C.P.3a.).

520. The Standard I.P.T. Method of Estimating the Petrol Contents of Crude Oils, etc.—I.P.T. Serial Designation : C.P.3a. Considerable latitude is allowed in the details of design of the apparatus used in this test, which consists, essentially, of a still fabricated in resistance glass, silica or, preferably, metal, of more than 1 litre distilling capacity, surmounted by an efficient fractionating column containing suitable packing material. The design of the column must be such as to allow the collection of fractions up to and including a boiling temperature of 275°C., without it being necessary to raise the temperature of the oil in the still above a maximum of 320°C. The column must, therefore, be efficiently lagged. Subsequent to removal of the light fractions (i.e., up to 275°C.), at atmospheric pressure, the fractionation may be proceeded with under high vacuum conditions or by the use of steam to take off the heavier fractions of the oil. Suitable fractions of the light oil are taken and these are blended and examined by the more usual distillation methods for the purpose of determining how much of the oil can be utilized as petrol, etc.

521. The Use of True Boiling Point Columns in the Estimation of Petrol in Crude Oils, etc.—The essential difference between "true boiling point" distillations and 100 c.c. Engler distillations is that in the former type of distillation, the various oil components leave the distilling apparatus at, approximately, their correct boiling points and that the effects of "carry over" by light ends and "hold back" by heavier fractions, observed in the Engler distillations, are not present.

Various fractionating columns of this type have been described, but all make use of a high reflux ratio and efficient column packing material to give the high degree of fractionation required. The columns are fairly long (2 ft. to 6 ft.) and are made as nearly adiabatic as possible, so as to prevent either loss or gain of heat from the column walls and in order to provide as much of the reflux as possible from the top of the column. Descriptions of such columns have been given in the literature by Peters and Baker,[3] Marshall[4] and many others, while Figure 130 is an illustration of a true boiling point column used by Beiswenger and Child[5] in the evaluation of crude oils.

The flask A, attached to the column, is of 2 litres capacity and is normally charged to the extent of 1600 mls. The glass column B C is 48 ins. long from flask to vapour outlet, 1 in. outside diameter at B, and $\frac{3}{4}$ in. diameter at C. The tower is packed with No. 16 brass jack chain for the lower third, No. 18 for the centre third and No. 20 for the upper third. At three points along the column (bottom, centre and top), the magnesia covering is cut away and a glass window is inserted in order that the operation of the tower can be observed. When operating at the lower temperatures, reflux is produced by means of air jets introduced at the bottom and centre of the column. As the distilling temperatures gradually rise, the air is gradually decreased and, finally, heat is applied by means of the resistance wire L L. The amount of this cooling or heating is adjusted so that the tower is kept just below the flooding point at all times.

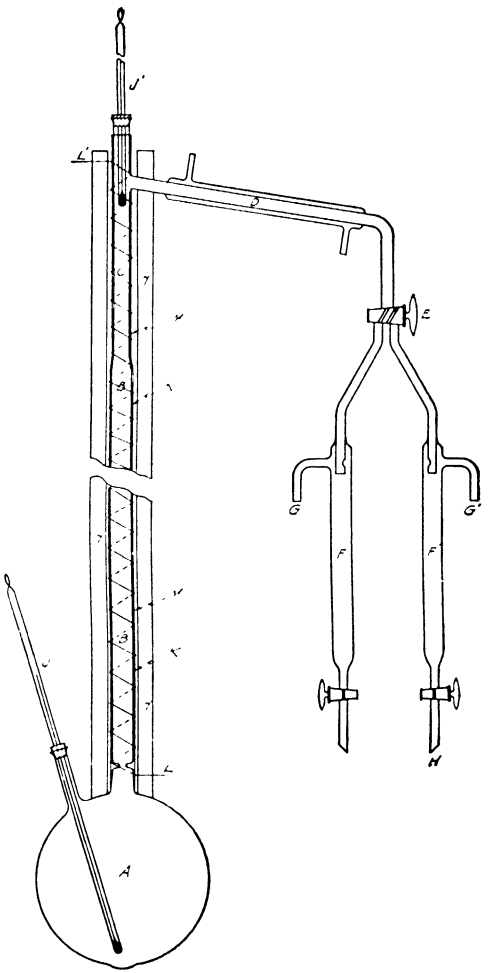


FIG. 130.—TRUE BOILING POINT COLUMN. (BEISWENGER AND CHILD.)

The fractionation obtained in this true boiling point column is very

good, and if, for example, a petrol fraction is taken from a crude up to a vapour temperature of 200°C., that fraction will, on subsequent distillation in the A.S.T.M. or I.P.T. 100 c.c. Engler distillation apparatus, have a final boiling point of 200°C. ± 2°C.

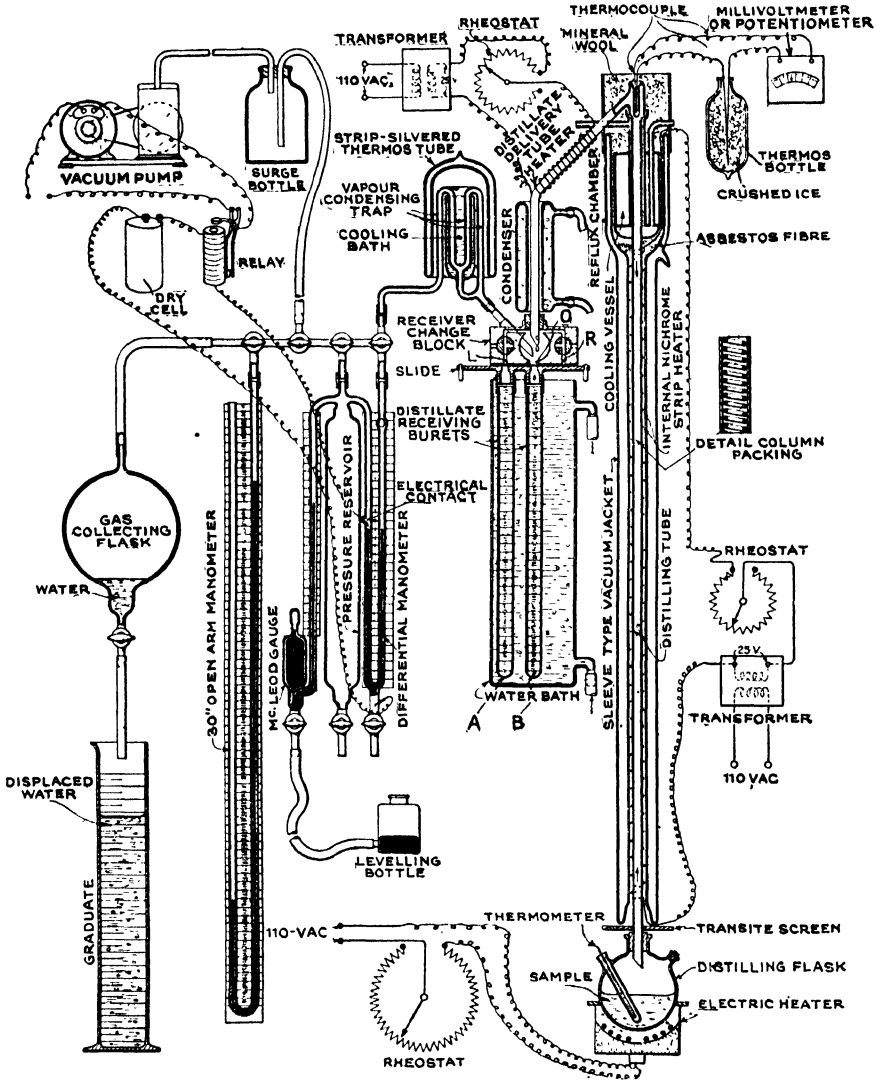


FIG. 132.—DIAGRAM MODEL-B PODBIELNIAK HIGH-TEMPERATURE FRACTIONAL DISTILLATION ANALYSIS APPARATUS.

522. The Podbielniak Precision Fractionating Column. — Podbielniak[6] has recently developed a fractional distillation apparatus suitable for the examination of oils boiling up to 500°C., at atmospheric

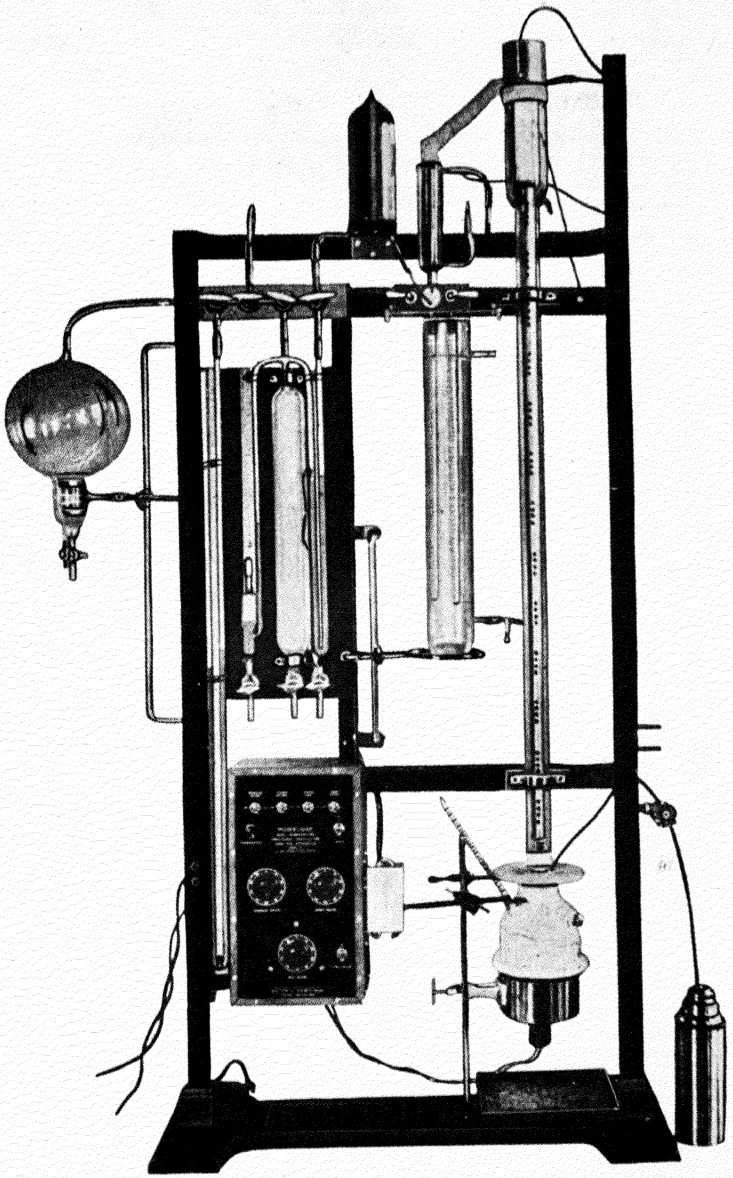


FIG. 131.—MODEL B PODBIELNIAK HIGH TEMPERATURE FRACTIONAL DISTILLATION ANALYSIS APPARATUS.

[*Facing p.* 10

pressure, which is capable of extreme accuracy and achieves much better separation between fractions than the most efficient bubble tower installations.

This apparatus, which is known as the Podbielniak High Temperature Fractional Distillation Apparatus to avoid confusion with the well known Podbielniak Low Temperature Apparatus, used to estimate the gasoline contents of natural gases, etc., is shown in Figures 131 and 132. It consists, essentially, of a long and narrow fractionating column packed with wire coil packing and thermally insulated with a vacuum jacket which is said to be ten times more efficient than either a plain air jacket or a mineral wool packed jacket. This high degree of thermal

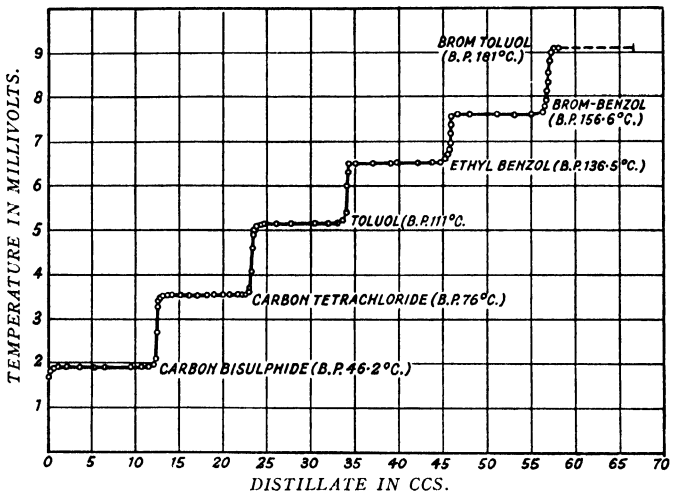


FIG. 133.—DISTILLATION CURVE OF A SYNTHETIC MIXTURE ON THE PODBIELNIAK COLUMN.

insulation is obtained by means of a novel highly polished double metal reflector with perforations for visibility. Whatever small amount of radiant heat escapes from the column through the perforations is compensated for by a miniature fine resistance wire electric heater wrapped around the fractionating tube, but this heater is not required until a temperature of 250°C. is reached, and its maximum power consumption at a vapour temperature of 300°C. is only 10 watts. This illustrates the thermal efficiency of the column.

Reflux is provided by means of a cooling vessel accommodated in the enlarged portion of the vacuum jacket at the top of the column. For all oils boiling above room temperatures, compressed air is used as the cooling agent, but if solid carbon dioxide is used, a mixture of ethane and propane may be refluxed and separated into its components.

The vapour temperature at the top of the column is measured by a

thermocouple and millivoltmeter as thermometers have a high heat capacity and are unsuitable. The distillate delivery line, prior to the condenser, is furnished with a small electric heater, so that when waxy oils are being distilled no solidification occurs. Long graduated burettes are used for the collection and the measurement of the distillate and these are maintained at constant temperature in a water cooling bath. Change over from one receiver to another is made possible by a slide arrangement which is suitable for use in vacuum distillations.

The apparatus is also provided with a vacuum regulating device, a McLeod gauge for pressure measurement, and a flask for collecting any evolved gas.

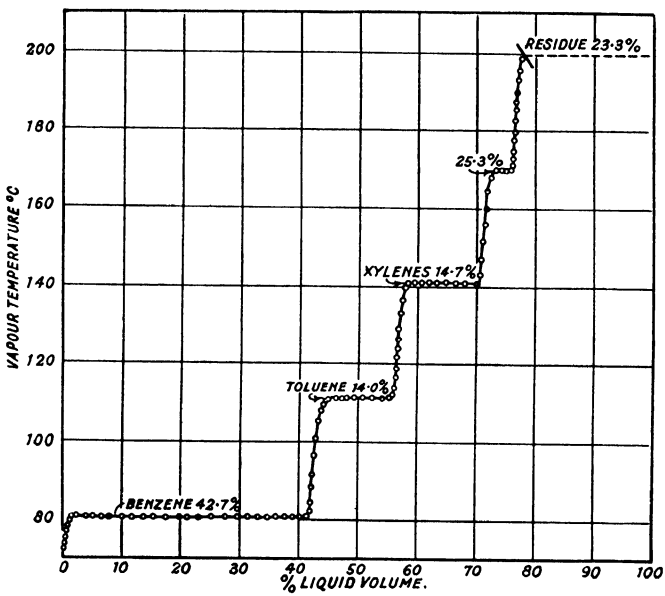


FIG. 134.—PODBIELNIAK DISTILLATION CURVE OF AN AROMATIC CONDENSATE.

The fractionating efficiency of the Podbielniak High-Temperature fractionating apparatus is shown to the full in the fractionation of synthetic mixtures, an example of which is shown in Figure 133. The distillation curve of an aromatic condensate from cracked gas is shown in Figure 134.

THE DETERMINATION OF THE GASOLINE CONTENT OF NATURAL GAS, CRACKED GASES, ETC.

523. The determination of the gasoline contents of natural and other gases is best carried out by means of an efficient fractionating apparatus working at low temperatures, such as that developed by Podbielniak. For further details the literature on the subject should be consulted.

General Tests in the Examination of Motor Fuels

524. Specific Gravity.—The specific gravity of a substance may be defined as the ratio of the mass of any given volume of the substance to the mass of an equal volume of water measured at the same temperature. In the petroleum and allied industries, the temperature 60°F. (15·55°C.) is usually employed as the standard temperature for specific gravity determinations and the results are expressed in terms of $S\ \frac{60°F.}{60°F.}$, signifying that the specific gravity in question is the ratio of the mass of any given volume of the substance to the mass of a quantity of water which, at 60°F., occupies a volume equal to that of the substance at 60°F.

The specific gravities of oils, determined by weighing methods (bottle, pyknometer, etc.), are not *true* specific gravities, but are the ratios between the weights *in air* of equal volumes of the oils and water, and it is necessary, in accurate determinations, to apply corrections for the buoyancy effect of the air. Usually, however, this correction is neglected.

When a specific gravity bottle or pyknometer is used, if W_w be the observed weight in air of the water content at 15·5°C. (60°F.), and W_s the observed weight in air of the sample contained in the bottle or pyknometer at 15·5°C. (60°F.), then the *approximate* specific gravity $S'\ \frac{60°F.}{60°F.}$ is given by the equation

$$S'\ \frac{60°F.}{60°F.} = \frac{W_s}{W_w} \quad \ldots\ldots\ldots\ldots (1)$$

The value given by the above formula may be corrected for the buoyancy effect of the air by means of the following equation

$$S\ \frac{60°F.}{60°F.} = S'\ \frac{60°F.}{60°F.} - 0{\cdot}0012\left[S'\ \frac{60°F.}{60°F.} - 1\right].$$

where $S'\ \frac{60°F.}{60°F.}$ is the value obtained from Equation (1) and $S\ \frac{60°F.}{60°F.}$ is the corrected specific gravity. Table 113 gives the values of $-\left[0{\cdot}0012\left(S'\ \frac{60°F.}{60°F.} - 1\right)\right]$ expressed as units in the fourth decimal place, to be added to (when the sign is positive) or subtracted from (when negative) the approximate specific gravity $S'\ \frac{60°F.}{60°F.}$, to give the corrected specific gravity $S\ \frac{60°F.}{60°F.}$

TABLE 113.—Buoyancy Corrections. Values of $-\left[0{\cdot}0012\left(S'\frac{60°F.}{60°F.}-1\right)\right]$ as units in the fourth decimal place.

$S'\frac{60°F.}{60°F.}$	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·60	+5	+5	+5	+4	+4	+4	+4	+4	+4	+4
0·70	+4	+3	+3	+3	+3	+3	+3	+3	+3	+3
0·80	+2	+2	+2	+2	+2	+2	+2	+2	+1	+1
0·90	+1	+1	+1	+1	+1	+1	0	0	0	0
1·00	0	0	0	0	−1	−1	−1	−1	−1	−1
1·10	−1	−1	−1	−2	−2	−2	−2	−2	−2	−2
1·20	−2	−3	−3	−3	−3	−3	−3	−3	−3	−3
1·30	−4	—	—	—	—	—	—	—	—	—

Temperature Corrections.—The specific gravity of a substance naturally varies with changes in temperature, due to the different rates of thermal expansion of the substance and of water, and in order to determine the specific gravity of a substance at a temperature other than that at which the specific gravity is known, resource is made to tables, which are sufficiently accurate for most purposes. The actual correction to be applied will vary with the product being tested and with the temperature at which the determination is carried out, and, it is clear, therefore, that any correction factors that are given will only be average figures. The following table gives the correction to add to, for temperatures above, or to subtract from, for temperatures below, 15·5°C., i.e., 60°F., for various substances.

TABLE 114.—CORRECTIONS OF SPECIFIC GRAVITY FOR TEMPERATURE.

	Correction per Centigrade Degree
Aviation petrol (*a*)	0·000855
No. 1 Petrol (*a*)	0·000830
No. 3 Petrol (*a*)	0·000820
Tractor Vaporising oil (*a*) ..	0·000745
Benzole (*b*)	0·0009
Crude Benzole (*b*)	0·00085
Toluole (*b*)	0·0009
White Spirit	0·00076
Kerosene	0·00072

(*a*). Spiers, "Technical Data on Fuel." London, 1930, p. 176.
(*b*). Hoffert and Claxton, "Motor Benzole." London, 1931, p. 546.

The change in density of a petroleum oil with temperature is represented with sufficient accuracy by the equation

$$D_t = D_T = \alpha\,(t - T) + \beta\,(t - T)^2$$

where D_t is the density at any temperature t, D_T is the density at the standard temperature T, and α and β constants for each kind of oil.

The most elaborate study of the change of density of oils with temperature yet made is that by Bearce and Peffer,[7] which is taken as the basis of "United States Standard Tables" for petroleum oils.[8]

525. Methods of Determining Specific Gravities.—The specific gravity of light oils and motor fuels may be determined by means of any of the following instruments which are given in order of their accuracy.

(a) The pyknometer.
(b) The specific gravity bottle.
(c) The specific gravity balance (Westphal Balance).
(d) The hydrometer.

(a) *The pyknometer method.*—This method is the only one that can be carried out with an accuracy of 1 in the fourth place of decimals. The apparatus, the most suitable type of which is shown in Figure 135, is first thoroughly cleaned and dried and then accurately weighed. The instrument is then filled with previously boiled distilled water and is then placed in a thermostat for such a period of time that both the vessel and its contents are at the required temperature. This usually takes about half an hour. The distilled water in the vessel is then adjusted completely to fill the instrument from A to the mark B, by removing the water from A with a piece of filter paper. The caps are then replaced and the instrument is weighed, after due precautions have been taken to see that the outside is clean and dry. Exactly the same operation is then carried out with the motor fuel or other oil to be examined. The ratio of the weights of oil and of water contained in the instrument gives the apparent specific gravity, which may be corrected for buoyancy to give the true specific gravity.

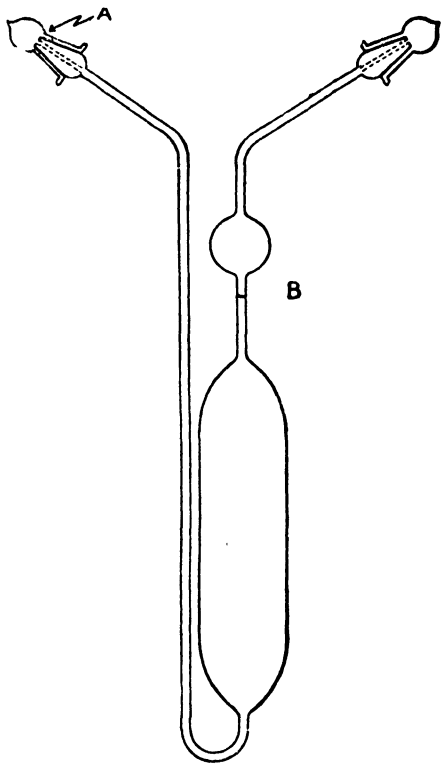


FIG. 135.—PYKNOMETER.

When but very small samples are available, a convenient type of

pyknometer to use is that devised by Drushel.[9] The instrument is a capillary pipette with a bulb of capacity between 1 and 2 mls. The oil to be examined is first of all brought to the desired temperature and then the pyknometer is filled to the mark by suction, a piece of rubber tubing being used as the mouthpiece. The rubber tubing is then removed, the outside of the pyknometer wiped dry and its weight determined in the usual way. The use of the Drushel pyknometer depends upon the fact that the capillary tip prevents flow of the oil in either direction, provided it is kept approximately horizontal. The bore of the tip should be made to vary somewhat according to whether the pyknometer is to be used for light, medium or viscous oils. When distillates of the motor fuel range are to be tested, an instrument should be selected that has a long fine capillary tip.

(b) *The specific gravity bottle method.*—This is a simple method but it is not quite so accurate as that using the pyknometer. For volatile oils, such as motor fuels, etc., it is advisable to use a bottle fitted with a cap, to reduce the risk of evaporation losses. The apparatus is used in exactly the same way as the pyknometer but particular care should be exercised to see that (a) no bubbles are trapped below the drilled stopper and (b) that no liquid is left on or around the stopper.

(c) *The specific gravity (Westphal) balance method.*—This instrument, illustrated in Figure 136, is a convenient direct reading means of determining the specific gravity of non-viscous oils, when an accuracy not greater than $\pm$ 0·001 is required.

The liquid to be tested is poured into the cylinder shown and the plummet is immersed and attached to the hook. The plummet should be immersed so that, on the upward swing, it does not come above the surface. By means of the rider weights placed in the notches of the beam, the beam is brought to equilibrium with the pointer opposite the zero mark. Thus, the specific gravity of the liquid is shown directly. Wherever possible, the specific gravity determination should be done at the temperature required to obviate the need for correction tables. A convenient thermostat capable of being maintained at 15·5°C. (60°F.), for the purpose of doing specific gravity tests by means of the Westphal Balance, is described by Dean, Hill, Smith and Jacobs.[10]

(d) *The hydrometer method.*—A.S.T.M. Designation: D.287-33, I.P.T. Serial Designation: G.I.

The hydrometer is less accurate than either the pyknometer, the specific gravity bottle or the Westphal balance, but because it is the simplest and most rapid instrument in use, it finds wide application. For convenience, in hydrometer specific gravity determinations, measurements are nearly always made at room temperatures and suitable corrections employed to calculate the specific gravity at 15·5°C. (60°F.). Buoyancy corrections are sometimes used.

The correct procedure adopted in specific gravity determinations with the aid of this instrument is as follows :—

The oil to be examined is poured into a cylinder and the hydrometer inserted, together with a thermometer, the former being allowed to float, while the latter is suspended in the oil half way down the cylinder. After sufficient time has elapsed for the hydrometer to become steady, readings of the hydrometer and thermometer are recorded simultaneously. The hydrometer reading should be made directly on the meniscus for clear oils, but when dark oils are being examined which do not permit reading the intersection of the level liquid surface and the stem, allowance must be made for the height of the meniscus round the stem, and the reading corresponding to the position of the level liquid surface and the stem must be estimated.

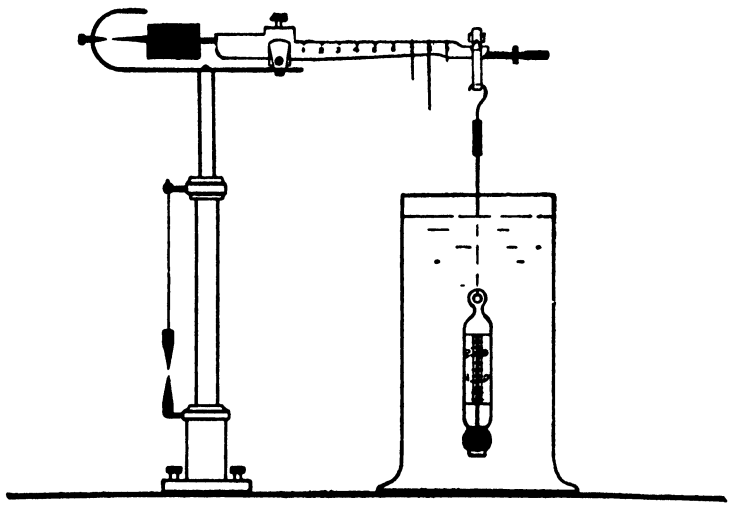


FIG. 136.—WESTPHAL BALANCE.

Precise details regarding the construction of hydrometers used especially for the testing of oils, according to the standardized procedures of the Institution of Petroleum Technologists, The American Society of Testing Materials and The National Benzole Association of Great Britain, may be found in the handbooks of testing methods issued by these bodies.

526. The Baumé and A.P.I. Scales of Specific Gravities.—In the United States of America two specific gravity scales are used, both of which are subdivided into arbitrary degrees. The U.S. Petroleum Association in 1864 adopted a set of hydrometers graduated in accordance with the relationship

$$\text{Baumé degrees} = \frac{141{\cdot}5}{\text{Sp. gr.}\ \frac{60°\text{F.}}{60°\text{F.}}} - 131{\cdot}5$$

and ever since this formula has been widely used in the petroleum industry. However, in other industries another formula, used by the U.S. Bureau of Standards since 1904, has been applied, namely,

$$\text{Baumé degrees} = \frac{140}{\text{Sp. gr.}\ \frac{60°\text{F.}}{60°\text{F.}}} - 130$$

Naturally much confusion arose as a result of these two scales. On January 23rd, 1922, the American Petroleum Institute sent a questionnaire to the industry asking whether the modulus 141·5 was approved for use in the oil industry and whether it was agreed that such a scale be known as the American Petroleum Institute Scale (A.P.I. scale). The replies to this enquiry were unanimously affirmative and it was later agreed that the modulus 141·5 be adopted for general use in the oil industry and that the scale be named the *A.P.I. scale* to avoid confusion with the *Baumé scale* of 140 modulus.

For liquids heavier than water, *Baumé* degrees and specific gravity are related by the equation

$$\text{Bé}_{\text{H}} = 145 - \frac{145}{\text{Sp. gr.}\ \frac{60°\text{F.}}{60°\text{F.}}}$$

A valuable paper on the Baumé scale was published by Taber in 1920,[11] in which some of the frequently misunderstood features of the Baumé scale are pointed out. The divisions representing Baumé degrees are spaced equal distances apart on the stem of a hydrometer. This is the result of the fact that Baumé degree numbers are the reciprocals of a harmonic series of specific gravities, modified only by being multiplied by a constant and added to another constant. They thus form an arithmetic progression and, consequently, on the stem of a hydrometer the divisions indicate equal increments of immersion, so that the corresponding specific gravity numbers form the harmonic series just referred to. It will thus be seen that the Baumé scale is neither inaccurate nor unscientific; in fact, because of its equally spaced divisions, it offers many advantages and it is easy to make accurate interpolations when readings are being made.

The disadvantage of the Baumé readings is that, for many purposes, they must be converted to specific gravities before they can be used. Thus, for example, a blend of equal volumes of liquids of 10°Bé and 70°Bé has a Baumé gravity of 39·4°B′ and not 40° Bé. On the other

hand, if *weights* are used instead of *volumes*, blending calculations can be made directly in terms of degrees Baumé.

Tables showing the relationship between A.P.I. degrees, Baumé degrees for liquids heavier than water and specific gravities are given in the Appendix.

Distillation Methods

527. The standard distillation test for motor fuels adopted by the Institution of Petroleum Technologists and the American Society of Testing Materials.

I.P.T. Serial Designation : G.3.

A.S.T.M. Serial Designation : D.86-30.

This test is intended for use in the routine examination of motor fuels and, in order to minimize the risk of error and to ensure the duplication of results in different laboratories (often in different countries), the test has been rigidly standardized, even in the case of the smallest details. The apparatus employed is essentially simple.

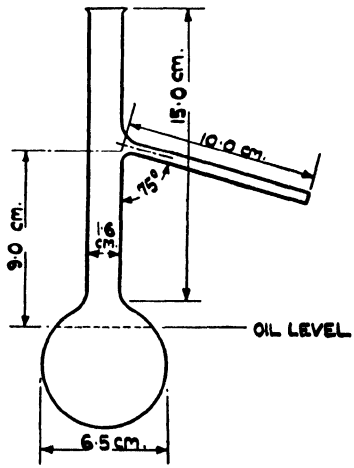


Fig. 137.—Standard Engler 100 ml. Distillation Flask (I.P.T. & A.S.T.M.)

Apparatus.—*Flask.* The standard 100 ml. Engler flask is shown in Fig. 137, the dimensions and allowable tolerances being as follows :

	Cms.	Tolerance in cms.
Diameter of bulb, outside	6·5	0·2
Diameter of neck, inside	1·6	0·1
Length of neck	15·0	0·4
Length of vapour tube	10·0	0·3
Diameter of vapour tube, outside ..	0·6	0·05
Diameter of vapour tube, inside ..	0·4	0·05
Thickness of vapour tube wall ..	0·1	0·05

The position of the vapour tube is 9 cms. ±0·3 cms. above the surface of the liquid when the flask contains its charge of 100 ml. The tube is approximately in the middle of the neck and set at an angle of 75 degrees (tolerance ±3 degrees) with the vertical.

Condenser. The condenser (Fig. 138) is a No. 18 I.W.G. seamless brass tube $\frac{9}{16}$ in. outside diameter and 22 in. long. It is set at an angle of 75 degrees from the perpendicular and is surrounded with a cooling bath, 15 in. long, approximately 4 in. wide by 6 in. high. The lower end of the condenser is cut off at an acute angle and curved downwards for a length of 3 in. and slightly backward, so as to ensure contact with the graduated receiver at a point 1 to $1\frac{1}{4}$ in. below the top of the receiver when it is in a position to receive the distillate.

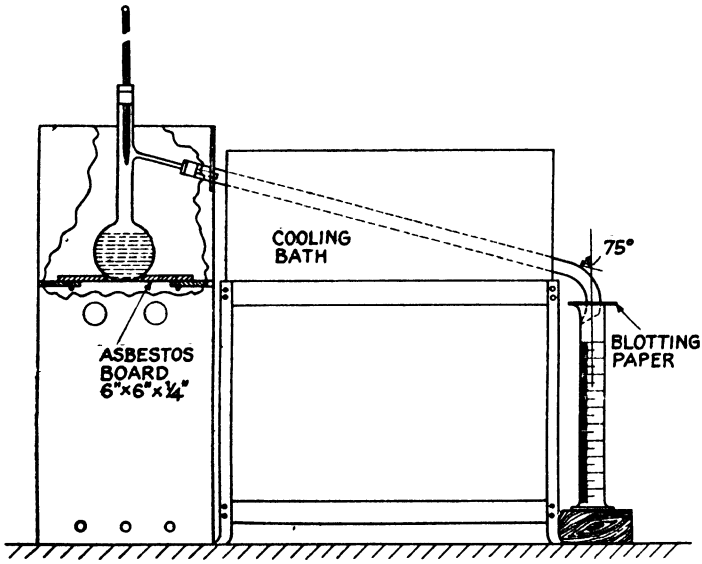


FIG. 138.—STANDARD 100 ML. DISTILLATION APPARATUS (I.P.T. & A.S.T.M.)

Shield. The shield (Fig. 138) is made of approximately 22 gauge sheet metal and is 19 in. high, 11 in. long and 8 in. wide, with a door on one narrow side, with two openings 1 in. in diameter, equally spaced, in each of the two narrow sides, and with a slot cut in one side for the vapour tube. The centres of these four openings are $8\frac{1}{2}$ in. below the top of the shield. There are also three $\frac{1}{2}$ in. holes in each of the four sides with their centres 1 in. above the base of the shield.

Two mica windows may be inserted to facilitate adjustment of the heater.

Ring support and hard asbestos boards. The ring support is of the ordinary laboratory type, 4 in. or larger in diameter, and is supported on a stand inside the shield. There are two hard asbestos boards: one 6 in. by 6 in. by $\frac{1}{4}$ in. with a central circular hole $1\frac{1}{4}$ ins. in diameter cut at right angles to the surface; the other, an asbestos board to fit tightly inside the shield, with an opening 4 in. in diameter concentric with the ring support. These are arranged as follows: the second asbestos board is placed on the ring and the first or smaller asbestos board on top so that it may be moved in accordance with the directions for placing the distilling flask. Direct heat is applied to the flask only through the $1\frac{1}{4}$ in. opening in the first asbestos board.

Gas burner or electric heater. The gas burner is so constructed that sufficient heat can be applied to distil the product at the uniform rate specified below. The flame should never be so large that it spreads over a circle of diameter greater than $3\frac{1}{2}$ in. on the under surface of the asbestos board. A sensitive regulating valve is necessary.

The electric heater, which may be used in place of the gas flame, must be capable of bringing over the first drop within the time specified below, when started cold, and of continuing the distillation at the uniform rate. The electric heater must be fitted with an asbestos board top $\frac{1}{8}$ to $\frac{1}{4}$ in. thick, having a central hole $1\frac{1}{4}$ in. in diameter. When the electric heater is employed, the portion of the shield above the asbestos board shall be the same as with the gas burner, but the part below the board may be omitted.

Thermometer. The thermometer used in this test must conform to the rigid specifications of the I.P.T. and A.S.T.M. These two specifications are not exactly the same and further details may be obtained from (*a*) Standard Methods of Testing Petroleum and its Products, I.P.T., 2nd Edition, 1929, and (*b*) A.S.T.M. Standard Method of Test Designation D.86-30.

Graduated receiver. This consists of a cylinder of approximately uniform diameter for its whole length, or a cylinder with conical lower portion to facilitate accurate reading of the first small quantities of distillate.

Method of Conducting the Test.—The condenser bath is first filled with cracked ice and water or any other cooling medium capable of being maintained between 0° and 4·45°C. (i.e., 32 and 40°F.). The

condenser tube is then swabbed by means of a small piece of soft cloth on a cord or copper wire to remove any liquid remaining from the previous test. One hundred millilitres of the sample are then measured in the 100 ml. graduated receiver, at a temperature of 12-18°C. (55-65°F.), and transferred directly to the Engler flask. None of the liquid is, of course, allowed to flow into the vapour tube. The thermometer, provided with a cork, is then fitted into the flask so that it is in the middle of the neck and so that the lower end of the mercury capillary tube is on a level with the inside of the bottom of the vapour outlet tube, at its junction with the neck of the flask. The thermometer must be approximately at room temperature when placed in the flask.

The charged flask is then placed in the opening in the smaller asbestos board, completely closing the hole, with its vapour outlet tube inserted into the condenser tube. A tight connection is made here with a cork. The vapour tube is arranged to extend into the condenser tube not less than 1 in. and not more than 2 in. The graduated receiver used in measuring the charge is placed, without drying, at the outlet of the condenser tube in such a position that the condenser tube shall extend into the receiver at least 1 in., but not below the 100 ml. mark. Unless the temperature is between 18 and 12°C., the receiver is immersed up to the 100 ml. mark in a transparent bath maintained between these temperatures. The top of the receiver is covered closely during the distillation with a piece of moistened filter paper so as to fit the condenser tube tightly.

When everything is in readiness, heat is applied at a uniform rate, so regulated that the first drop of condensate falls from the condenser in not less than five nor more than ten minutes. The distillation thermometer is read two minutes after heat is applied and the indication recorded as the "*correction temperature.*" This figure is of significance only in the cases where there is a question as to the accuracy of the initial boiling point * as subsequently determined.

* If the correction temperature is below 21°C. or above 27°C., the initial boiling point may be in error if it falls below 60°C., and may be considered incorrect by an amount not less than one third the difference between the "*correction temperature*" and 24°C. In cases of dispute, a corrected initial boiling point is calculated as follows.

$$\text{Revised I.B.P. (°C.)} = \text{Observed I.B.P. (°C.)} - \left\{\frac{\text{Correction Temp. (°C.)} - 24}{3}\right\}$$

or in degrees Fahrenheit

$$\text{Revised I.B.P. (°F.)} = \text{Observed I.B.P. (°F.)} - \left\{\frac{\text{Correction Temp. (°F.)} - 75}{3}\right\}$$

The need for this correction arises from the fact that initial boiling points are still found in some specifications and such determinations are sometimes difficult to check when repeat tests are done at different room temperatures.

When the first drop falls from the end of the condenser the reading of the distillation thermometer is recorded as the *Initial Boiling Point.*

The receiving cylinder is then moved so that the end of the condenser tube touches the side of the cylinder, and heat is then so regulated that the distillation proceeds at a uniform rate of not less than and not more than 5 ml. per minute.

The volume of distillate collected in the cylinder is observed to the nearest 0·5 ml., when the mercury of the thermometer reaches each point that is a multiple of 10°C. (A.S.T.M. specification), or 25°C. (I.P.T. specification). If preferred, the reading of the thermometer is observed and recorded when the level of the distillate reaches each 10 ml. mark on the receiver.

No adjustment of the heat is made after the liquid residue in the flask is approximately 5 ml., unless the time required to bring over the last 5 ml. of distillate exceeds 5 minutes. The heating is continued until the thermometer gives its highest reading and starts to fall consistently. The *End Point* is the maximum temperature observed on the thermometer and is usually reached after the bottom of the flask has become dry.

The total volume of the distillate collected in the receiver is recorded as the *Recovery*, and the volume of residue left in the flask, measured in a cylinder graduated in 0·1 ml. after cooling, is recorded as the *Residue.* The difference between 100 ml. and the sum of the *Recovery* and the *Residue* is calculated and recorded as the *Distillation Loss.*

Accuracy of the Method.—With due care, duplicate results for Initial Boiling Point and End Point should not differ by more than 3°C., and the volume of distillate collected at any given temperature should not vary by more than 2 mls.

Correction for Barometric Pressure.—No correction is normally applied for barometric pressure, but this is recorded so that a correction may be applied in the case of a dispute. In this case, corrections are made according to the equation

$$C = 0{\cdot}00012\ (760 - P)\ (273 + t)$$

in which C = correction to be added to the observed temperature t°C.

P = actual barometric pressure.

In the case of the Fahrenheit scale, the equation is

$$C_f = 0{\cdot}00012\ (760 - P)\ (460 + t_f).$$

Emergent Stem Correction.—The thermometers specified for use in these distillation tests are calibrated for total immersion, and no emergent stem corrections are normally employed.

528. Standard Test for the Distillation of Natural Gas Gasoline.—A.S.T.M. Designation : D.216-32.

No I.P.T. equivalent.

Exactly the same apparatus and mode of procedure is used in this test as in the distillation test for gasolines (motor fuels) described above, but greater precautions to prevent evaporation loss are specified. In particular, care must be exercised in sampling. Samples should be collected in a previously cooled bottle, preferably by immersing the bottle in the liquid, where this is possible, and discarding the first sample. The bottle is then immediately closed with a tight fitting stopper and placed in a cool place such that the temperature of the gasoline is brought to 0°—4·45°C. (i.e., 32°F. to 40°F.).

The condenser bath is maintained at a temperature of 0—1·1°C. (i.e., 32—34°F.) and both cooled Engler flasks and graduates (0—1·1°C.) are used.

In other respects, the distillation is carried out in exactly the same way as that for motor fuels, etc., as in I.P.T. Serial Designation : G.3.

529. "Index Numbers."—The "Index Number" of a motor fuel is obtained by adding the temperatures at which 5%, 15%, 25%, etc., distil in the standard I.P.T. and A.S.T.M. distillations and dividing the sum by 10. It is, therefore, a kind of "average boiling point." The evaluation of motor fuels by means of their index numbers has been proposed by Ostwald,[12] but according to Kroch [13] this procedure is misleading.

530. Colour Measurements.—The colours of petroleum products are important because they are still regarded as indices of purity, even though recent developments have shown that colour and quality are not complementary. In the United Kingdom, at any rate, a good colour is still an asset in marketing.

The colours of motor fuels are usually measured by

(*a*) The Lovibond Tintometer, and
(*b*) The Saybolt Chromometer.

The Lovibond Tintometer.—The Lovibond tintometer may be used for measuring the colours of most kinds of petroleum oils, and is

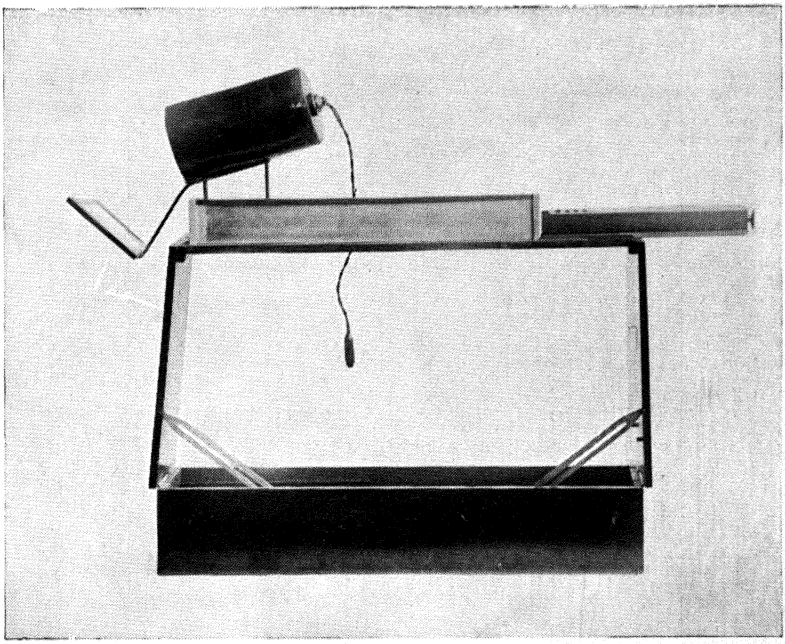


FIG. 139.—THE LOVIBOND TINTOMETER.
(Courtesy of Baird and Tatlock (London), Ltd.)

[*Facing p.* 24

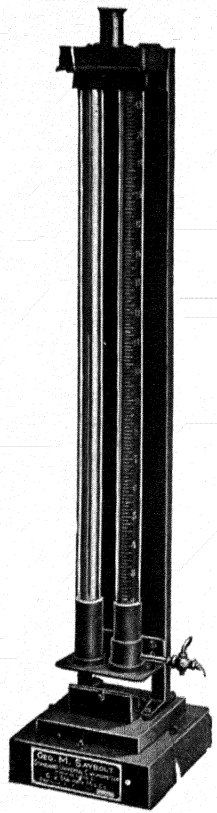


FIG. 140.—THE SAYBOLT CHRONOMETER.
(Courtesy of Baird and Tatlock (London), Ltd.)

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adopted in Standard I.P.T. tests on gasolines (petrols), white spirit, benzole mixtures and kerosene.

This piece of apparatus consists of a long and narrow rectangular metal cell, fitted with glasses at each end, so that a beam of light from a porcelain reflector may pass through it. The cell is fitted with a light-proof cover. The oil whose colour is required is placed in the cell (usually of 18 in. length) and standard colour glasses placed alongside the cell so that lines of vision may be obtained both through the oil in the cell and the standard glasses to enable a colour comparison to be made. Four special standard glasses are used: Water white (1·0), Superfine white (2·0), Prime white (3·0) and Standard white (4·0), while intermediate glasses may be used if necessary.

The apparatus is illustrated in Fig. 139. When daylight is employed, the apparatus may be used facing a good north window which has been covered with a special diffusing tissue. Direct sunlight must be avoided. When artificial light is employed (e.g., electric light), care must be taken to ensure that the lamp is free from discoloration.

If a sample is found to be darker than any of the standard glasses the colour is described by the next standard, and intermediate glasses between used to determine the position of the colour between the two standards. For example, if the colour is mid-way between Superfine white (2·0) and Prime white (3·0), it is expressed as Prime white (2·5).

531. The Saybolt Chromometer.—This apparatus is commonly used in the U.S.A. for the determination of the colours of light distillates. Its use in measuring the colour of refined petrols, etc., is specified in A.S.T.M. Standard Method, Designation D.156-34T.

As shown in Fig. 140, the Saybolt chromometer consists of two similar glass tubes, 20 in. long and about $\frac{5}{8}$ in. internal diameter. One tube is open at both ends, the other (the oil tube) permanently closed at the bottom with a colourless glass disc, and is provided with a drain cock at the bottom. The tubes are supported in a vertical position above a mirror arranged to reflect light upward through the tubes, while above the tubes is an eyepiece, so designed that the field of vision is equally divided between the two tubes. A standard yellow glass disc is placed at the bottom of the open tube.

A colour measurement is carried out as follows: The apparatus is placed at a north window so that only direct light from the sky is reflected upward through the two tubes from the reflector. The oil tube is thoroughly cleaned and then filled with the spirit to be examined. On looking through the eyepiece, the relative colours of the standard colour disc and the column oil may be compared, and if that of the latter is the darker of the two, oil is gradually run out of the stop cock until the two colours are equal. The colour of the oil on

the Saybolt scale is then computed by reference to the following table:

One Disc.

Inches of Oil in Tube	*Colour Shades*	
20	+25	
18	+24	
16	+23	Water White.
14	+22	
12	+21	
$10\frac{3}{4}$	+20	
$9\frac{1}{2}$	+19	
$8\frac{1}{4}$	+18	Prime White.
$7\frac{1}{4}$	+17	
$6\frac{1}{4}$	+16	

Two Discs.

Inches of Oil in Tube	*Colour Shade*		*Inches of Oil in Tube*	*Colour Shade*	
$10\frac{1}{2}$	+15		$5\frac{1}{2}$	+4	
$9\frac{3}{4}$	+14		$5\frac{1}{4}$	+3	Standard
9	+13		5	+2	White.
$8\frac{3}{4}$	+12		$4\frac{3}{4}$	+1	
$8\frac{1}{4}$	+11	Standard	$4\frac{1}{2}$	0	
$7\frac{1}{4}$	+10	White.	$4\frac{1}{4}$	−1	
$6\frac{3}{4}$	+9		4	−2	
$6\frac{1}{2}$	+8		$3\frac{3}{4}$	−3	
$6\frac{1}{4}$	+7		$3\frac{5}{8}$	−4	Lily
6	+6		$3\frac{1}{2}$	−5	White.
$5\frac{3}{4}$	+5		$3\frac{3}{8}$	−6	
			$3\frac{1}{4}$	−7	
			$3\frac{1}{8}$	−8	
			3	−9	

From this table it is evident that no oils are to be compared against one disc unless they are definitely whiter than two discs at $10\frac{1}{2}$ in. depth. A spirit which is whiter than one disc when in a depth of 20 inches is recorded as Saybolt 25+.

532. Colour Measurement by the aid of Standard Solutions.— In cases where a colour measuring instrument is not available, colour measurements may be made by comparison with standard coloured solutions, e.g., acid solutions of potassium bichromate, contained in small colour tubes or small bottles.

The following table [14, 15] shows the relationship between Saybolt colour, the Lovibond scale and the strength of acid bichromate solutions:

TABLE 115.—COMPARISON OF COLOURS OF BICHROMATE SOLUTIONS WITH SAYBOLT AND LOVIBOND SCALES.

Potassium Bichromate mgs. per litre	Saybolt Colour	Lovibond Colour. 18″ cell with W.W. slide
2·6	+25	W.W. +0·5
2·9	+24	W.W.
3·7	+23	W.W. −0·3
4·5	+22	W.W. −0·5
5·5	+21	W.W. −0·8
6·5	+20	W.W. −1·3
7·5	+19	W.W. −1·5
8·5	+18	W.W. −2·0
9·5	+17	W.W. −2·2
11·0	+16	W.W. −2·8
12·5	+15	W.W. −3·8
13·5	+14	W.W. −4·5
15·0	+13	W.W. −5·2
16·5	+12	W.W. −6·0
17·5	+11	W.W. −6·5
18·5	+10	W.W. −6·9
19·5	+9	W.W. −7·4
20·5	+8	W.W. −9·0
21·7	+7	W.W. −9·4
23·0	+6	W.W. −10·0
24·0	+5	W.W. −10·2
25·5	+4	W.W. −11·0
26·5	+3	
27·5	+2	
28·5	+1	
30·0	0	

533. Vapour Pressure Determinations.—The standard method of vapour pressure determination now used extensively in the Petroleum Industry is that known as the Reid Method and standardized by the A.S.T.M. (Serial Designation No. D.323-32T). This cannot be considered in any way as a precision method but it is simple in operation and gives results accurate to within 0·5 pounds per square inch, an accuracy sufficient for most refinery purposes.

The apparatus consists of a cylindrical vessel 2 in. diameter and 10 in. long fitted at one end with a pressure gauge and at the other end with a small chamber 2 in. diameter which serves as a gasoline chamber. The upper part is called the air chamber and has a volume 3·8 to 4·2 times the volume of the lower chamber.

A test is conducted by filling the gasoline chamber completely with the fuel to be tested, and connecting it to the air chamber. The whole vessel is then placed in a constant temperature bath and the vapour pressure as shown by the reading on the pressure gauge recorded.

For complete details of this test reference should be made to the publications of the American Society for Testing Materials.

534. The Determination of the Acidities of Petrols and Light Oils.—Acidity in petrols and other refined light hydrocarbon oils is usually the result of inefficient refining, e.g., inefficient alkali washing, etc. No standard test for acidity in gasolines is found in the " Standard Methods " of the Institution of Petroleum Technologists, but similar tests for White Spirits and Benzole Mixtures are included. Details of these are as follows :

I.P.T. Standard Tests for the Acidity of White Spirits and Benzole Mixtures.

I.P.T. Serial Designation : L.0.5.

Total Acidity.—Ten grammes of the oil to be examined is weighed into a flask and 50 mls. of 95 per cent. alcohol is added. The mixture is then warmed on the water bath to ensure solution of the acids in the alcohol. Shaking is generally necessary. Phenol phthalein indicator is then added and the mixture titrated with N /10 potassium hydroxide. The result is expressed as the number of milligrams of potassium hydroxide necessary to neutralize the acidity of 100 g. of the oil.

Inorganic Acidity.—The oil to be examined is shaken vigorously with an equal volume of warm water, the water separated and titrated with N /10 potassium hydroxide, using methyl orange as indicator. The result is expressed in the same terms as the total acidity.

Organic Acidity.—This is obtained by subtracting the inorganic acidity from the total acidity. Generally, it is the inorganic acidity which is of the greatest importance in connection with petrols and light oils, and if a test reveals any inorganic acidity in such a refined oil, the inference can at once be drawn that the acidic materials used in refining or resulting from refining have not been completely removed. Acidity in a refined petrol nearly always indicates the presence of sulphuric acid and, hence, of sulphur, in a highly corrosive form.

U.S. Government Method 510·2.[16]—In this test, the cooled distillation residue from the standard A.S.T.M. 100 c.c. Engler distillation (see paragraph 527) is placed in a test tube with three volumes of distilled water and shaken thoroughly. The mixture is allowed to separate, the aqueous layer removed and one drop of a one per cent. solution of methyl orange added. The development of a pink or red colour indicates acidity.

This test is of value in determining whether the sulphur compounds present in petrols, etc., decompose on heating to give acidic products. The presence of acidity indicates inefficient refining.

The Determination of Sulphur and Sulphur Compounds in Motor Fuels

535. The significance of sulphur in motor fuels is fully discussed in Chapter XII, where it is shown that a certain content of some sulphur compounds can be permitted, but that other sulphur compounds are very objectionable in very small amounts and must be entirely removed. It is, therefore, necessary to know the relative amounts of the various sulphur compounds appearing in motor fuels as well as the total sulphur content. Besides such purely chemical analyses, there are used, in the examination of motor fuels, various other qualitative tests by which the objectionable properties of sulphur compounds are exhibited, e.g., corrosion tests.

536. Methods for the Estimation of the Total Sulphur Contents of Motor Fuels.—The total sulphur contents of motor fuels are usually determined by burning small samples in a current of air. The sulphur is oxidized to sulphur dioxide, and the combustion products are passed either through a solution of hydrogen peroxide, which oxidises the sulphur dioxide to trioxide and hence to sulphuric acid, or else into a solution of sodium carbonate, in which the sulphur dioxide is absorbed and in which it may be estimated by the usual volumetric or gravimetric analytical methods.

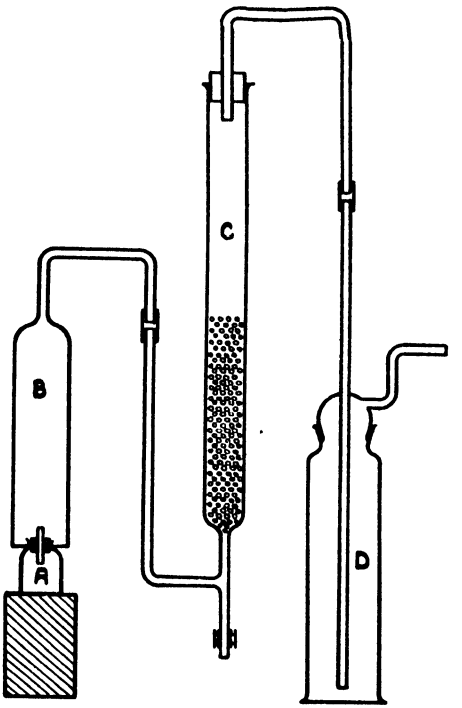


Fig. 141.—The I.P.T. Total Sulphur Apparatus.
(*Courtesy of The Institution of Petroleum Technologists.*)

"Lamp" Methods.—(1) I.P.T. Serial Designation G.4.—The apparatus used in this procedure is shown in Fig. 141, and consists of a fuel reservoir in the form of a small glass bottle A, which is fitted with a cork carrying a transparent silica tube which acts as a support for the wick—a length of lead-free glass wool; a glass chimney B through which the products of combustion are drawn into the glass absorbing vessel C, and a Dreschel wash bottle D, which acts as a trap for any spray carried over from C. Air is drawn through the apparatus by means of a pump.

The test is carried out as follows :
Five millilitres of the sample, the specific gravity of which is known, is pipetted into the lamp, 20 mls. of 10 per cent. sodium carbonate solution is placed in the vessel C and 20 mls. of water and 1 ml. of 10 per cent. sodium carbonate are placed in D. The lamp is lighted, placed under the chimney and steady suction is applied to the apparatus so that a flame $\frac{1}{2}$ in. to $\frac{3}{4}$ in. in height and just free from smoke, is obtained. When burned to dryness the lamp is rinsed out twice with 2 ml. of amyl acetate, and burned to dryness after each addition. The lamp and wick is thereby freed from all traces of the oil. The contents of C and D and all connections are then washed into a beaker, keeping the bulk of liquid less than 200 mls. About 0·5 g. of sodium peroxide is added and the liquid heated to boiling, made slightly acid with hydrochloric acid and 5 mls. of a boiling solution of barium chloride added. Barium sulphate is then precipitated and dried and weighed in the usual manner.

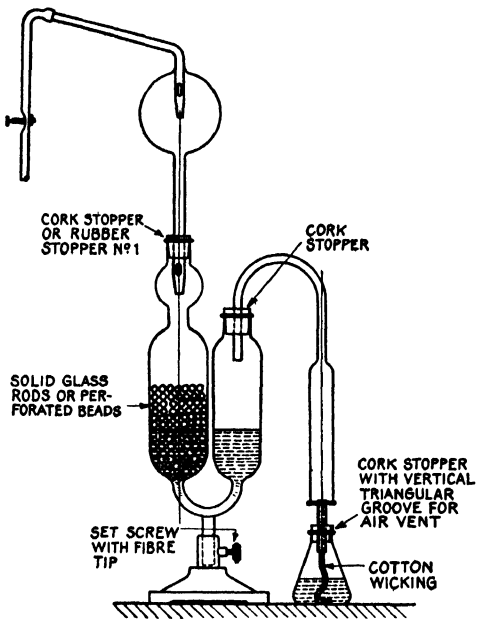


FIG. 142.—THE A.S.T.M. TOTAL SULPHUR APPARATUS.
(A.S.T.M. SERIAL DESIGNATION D.90–34 T.)

537. (2) I.P.T. Serial Designation : G.4a.—This method makes use of the well-known Richardson lamp, which is available in three separate forms, especially suitable for use with petroleum spirits, benzole mixtures and kerosines, respectively. For further details reference should be made to the I.P.T. Handbook of Standard Methods.

538. (3) A.S.T.M. Serial Designation D.90-34 T.—The apparatus used in this method of analysis is shown in Fig. 142, and its operation is similar to that of the above I.P.T. method.

The wick consists of two strands of new cotton wicking, 10-12 cms. long (not twisted together), and is held in position in a small glass wick tube, 6-7 mm. outside diameter and 3 mm. inside diameter. The amount of oil sample burnt is determined by weighing the lamp before and after the experiment ; this usually amounts to about 15 ccs. Exactly 10 ccs. of standard sodium carbonate solution is placed in the

absorber. At the end of the experiment the absorber liquid is carefully washed into another container and titrated against standard hydrochloric acid, using methyl orange as indicator. A blank experiment burning sulphur-free alcohol is also run at the same time.

Edgar and Calingaert [17] have recently described various modifications whereby the operation of this analytical method may be simplified, and have given details concerning the construction and operation of laboratory devices whereby the height of the flame may be altered without interrupting the test. They have also described new volumetric lamps and a modified absorber.

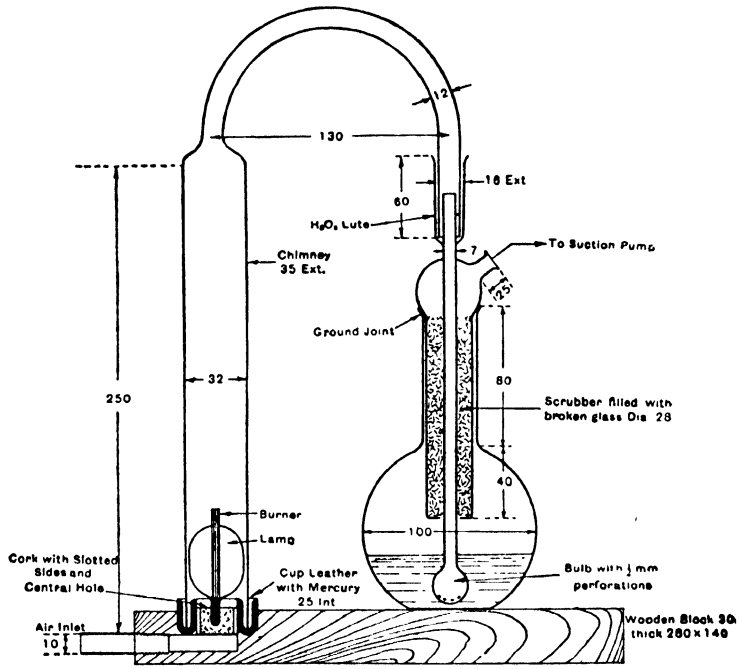


FIG. 143.—APPARATUS FOR THE DETERMINATION OF THE TOTAL SULPHUR CONTENTS OF BENZOLES.
(Courtesy of The Standardisation of Tar Products Tests Committee, London.)

539. (4) Methods for Determining the Total Sulphur Contents of Benzoles.—*Serial No. L.B.* 11. (*"Standard Methods of Testing Tar and its Products," page* 90.) This standard method used in the examination of benzole is exactly similar in principles to those described above. The apparatus used is shown in Fig. 143.

The absorber flask contains carefully neutralized hydrogen peroxide and a small quantity of the same reagent is placed in the tube between the chimney and the absorber. After the benzole in the lamp has been burned, the hydrogen peroxide solution is titrated against N/10 sodium carbonate solution, using methyl orange as indicator. The

quantity of fuel burnt is measured by volume and is diluted with ethyl alcohol.

This apparatus has been critically examined in a recent paper by Claxton, Hancock and Hoffert,[18] who have pointed out various improvements and modifications which may be made in order to obtain more accurate results, of which a new device for measuring the volume of the sample and a means for supplying it to the lamp is of particular interest. The apparatus devised by Claxton, Hancock and Hoffert is shown in Fig. 144.

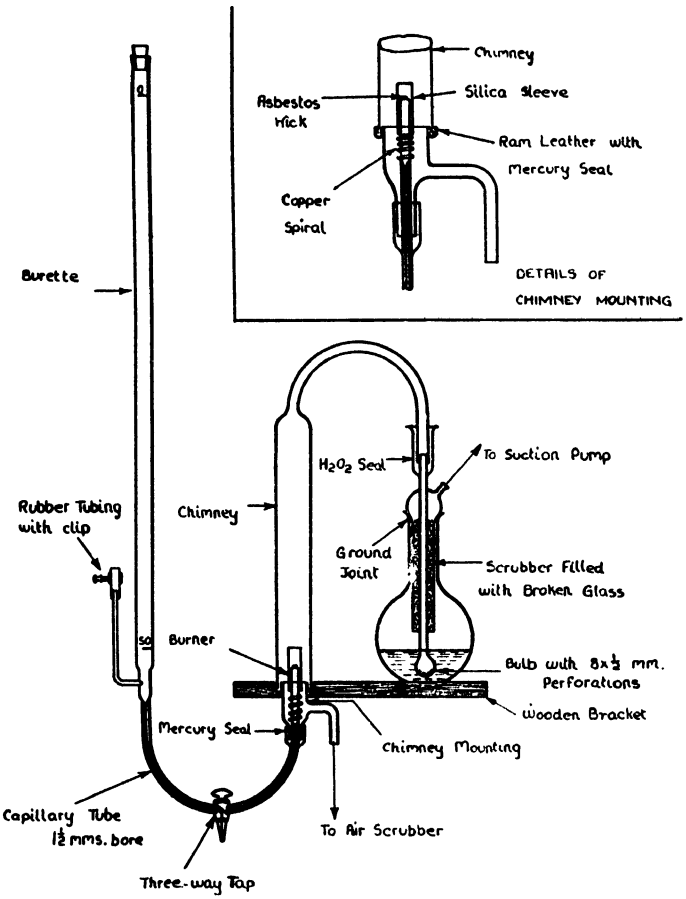


FIG. 144.—APPARATUS OF CLAXTON, HANCOCK AND HOFFERT FOR DETERMINATION OF TOTAL SULPHUR.

540. Limitations of the "Lamp" Method for Determining the Total Sulphur Contents of Motor Fuels.—The principles involved in the above "lamp" methods are fundamentally sound and any errors that are obtained are generally due to the inefficiencies of the apparatus

employed. Often such methods fail to give accurate results in the case of fuels containing appreciable quantities of volatile sulphur compounds, such as carbon disulphide, because the lamp becomes warm after the test has been in progress a short time and part of the sulphur content is lost by evaporation. These vapours pass up the space between the wick and the wick tube and escape combustion; consequently, low results are obtained. Errors due to this effect are minimized by using a method in which the lamp is totally enclosed. Furthermore, in the case of light fractions and natural gas gasolines, which are very volatile, difficulties are incurred in weighing such materials accurately. In such cases, volumetric methods of measuring the liquids are to be preferred, and it is advisable to use a cooling medium to keep the liquid in the lamp at a temperature low enough to keep evaporation at a minimum (c.f., Wood and Mattox[19]). A method whereby the errors due to evaporation may be reduced has been described by Kennedy,[20] in which the fuel is contained and measured in a reservoir from which it flows through a regulator and drops on to glass wool, over which heated air is passed. The resulting vapour air mixture is passed to a burner.

According to Waterman[21] the lamp methods give low results for oils containing mercaptans due to the formation of asphaltic bodies which remain on the wick, but Fischer and Hess[22] state that the error involved is negligible for oils containing up to 0·05% sulphur.

541. The Oxygen Bomb Method for the Estimation of Total Sulphur. This method, which involves the combustion of a weighed sample of material in a compressed atmosphere of oxygen in a small bomb, is only generally used in the case of oils heavier than kerosenes and need not be considered here.

542. The Estimation of "Free" or "Elemental" Sulphur. —As free sulphur is a very active corrosive agent when present in petrols, its estimation is a matter of importance. The following methods may be used.

(a) *I.P.T. Standard Method. Serial Designation G.*4b.—According to this procedure, one hundred grams of the spirit is shaken for one hour with 2 ml. of clean mercury and a few mls. of dilute hydrochloric acid (1 : 100) added to coagulate the mercury sulphide produced. The mixture is then filtered through a Gooch crucible and the precipitate washed with dilute hydrochloric acid. The crucible is then transferred to a beaker and digested with 30 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid till all mercury, sulphur and mercury sulphide are dissolved. The resulting liquid is then approximately neutralized with sulphur-free ammonia, 1 ml. of concentrated

hydrochloric acid is then added and the sulphate precipitated by barium chloride and estimated by the usual gravimetric procedure.

543. (b) *The Standard Method of the National Benzole Association.* (*Standard Methods for Testing Tar and its Products, Serial No. L.B.* 12, p. 94; *Standard Specifications for Benzole and Allied Products,* p. 77.)—The apparatus used in this test is shown in Figure 145. The sample to be examined (100 ml.), which must, of course, be free of H_2S, is placed in the flask A, together with one or two ml. of clean mercury and shaken vigorously. The sample is then decanted through a filter paper which is drained and replaced in the flask A. 50 ml. of boiling water is placed in B, 50 ml. of ammoniacal cadmium acetate in C and about 25 ml. of the same reagent in D. Hydrogen gas is then used to remove the air from the apparatus and 50 ml. of concentrated hydrochloric acid (chlorine free) is admitted to A, the contents of which are then heated cautiously with a small flame and finally boiled for fifteen minutes. In this way, the mercury sulphide is decomposed with the formation of H_2S. which then passes into the wash bottle C, where it precipitates cadmium sulphide from the cadmium acetate solution. The cadmium sulphide is estimated by treatment with iodine followed by titration against sodium thiosulphate solution in the usual manner.

Although elemental sulphur is the substance usually responsible for the corrosive properties of motor fuels, other compounds such as polysulphides may also have a similar effect. It is, therefore, often preferable to conduct actual corrosion tests than to do elemental sulphur determinations.

544. The Estimation of Mercaptans in Motor Fuels.—The estimation of mercaptans in motor fuels is of especial importance because of the highly corrosive properties of these compounds and also because of their foul odour even when in very dilute solution. The complete absence of mercaptans from refined motor fuels is invariably demanded for these reasons.

Methods for the Qualitative Estimation of Mercaptans.—By far the most common method for detecting the presence of mercaptans in motor fuels is the well known "Doctor" test, the chemistry of which has been studied by Wendt and Diggs.[23] This test involves treatment of the fuel with an alkaline plumbite solution (i.e., a solution of litharge in caustic soda) and a small amount of elemental sulphur. If mercaptans are present, the following reaction occurs

$$2\,RSH + Pb(ONa)_2 \rightarrow (RS)_2Pb + 2\,NaOH$$

Mercaptan → Lead Mercaptide

The lead mercaptides are either yellow precipitates (low molecular

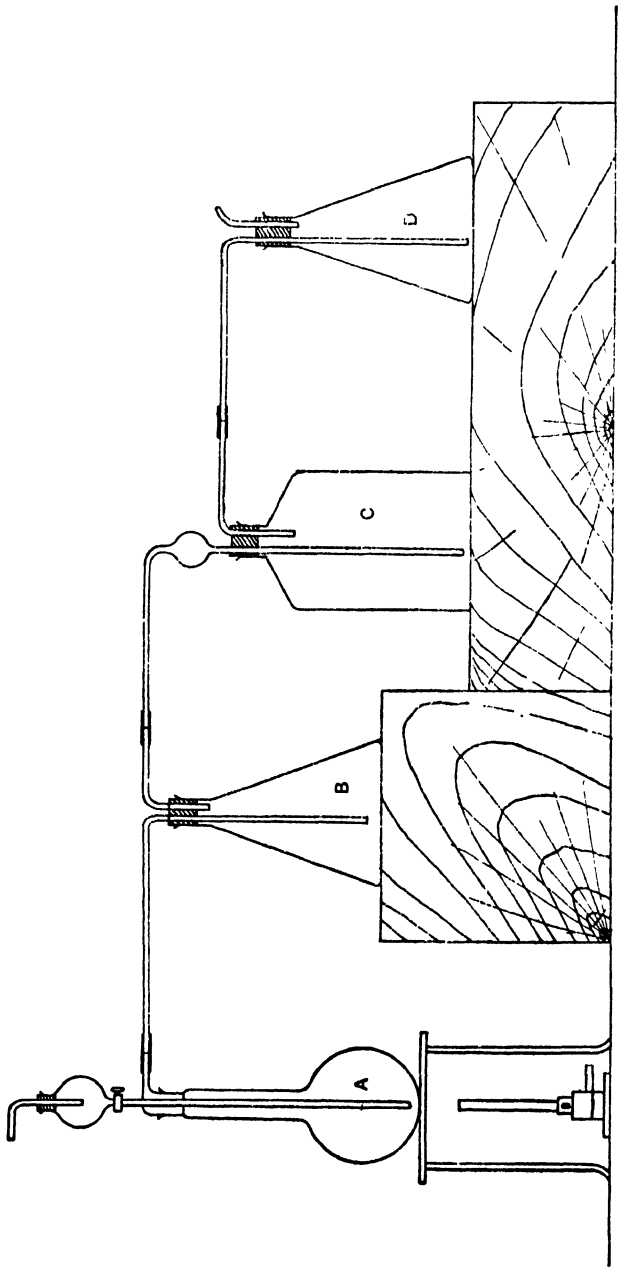


FIG. 145.—STANDARD APPARATUS OF THE NATIONAL BENZOLE ASSOCIATION FOR THE DETERMINATION OF FREE SULPHUR IN BENZOLES.
(*Courtesy of The National Benzole Association.*)

weight) or compounds soluble in the fuel with a brown coloration (higher derivatives). When elemental sulphur is now added, the

mercaptides react with the formation of a black precipitate of lead sulphide and the simultaneous liberation of organic disulphides, thus :—

$$\left.\begin{matrix}RS\\RS\end{matrix}\right\rangle Pb + S \rightarrow PbS + RS - SR.$$

It will be observed that if sulphuretted hydrogen (H_2S) is present, this will react with the plumbite to give lead sulphide, as follows :—

$$Pb(ONa)_2 + H_2S \rightarrow PbS + 2\,NaOH.$$

Consequently, if a black precipitate is formed prior to the addition of elemental sulphur, the presence of H_2S is indicated, or, alternatively, the presence of both mercaptans and elemental sulphur in the fuel. It is, therefore, essential to remove H_2S from the fuel before testing for mercaptans in this way. This is usually accomplished by exhaustive treatment with cadmium chloride solution. The presence or absence of elemental sulphur in the fuel under test is indicated by the nature of the colour that results on the addition of the plumbite solution. If the colour remains a clear yellow or light brown before the addition of sulphur, the absence of elemental sulphur in the fuel under test may be assumed, but if the colour changes to black, the opposite is the case.

545. The Doctor Test has recently been standardized by the Natural Gasoline Association of America,[24] as follows :—

Reagents employed—

1. Sodium plumbite solution containing 125*g.* caustic soda and 25*g.* litharge per litre.
2. Pure dry flowers of sulphur ground and screened to 100—200 mesh.

The test is carried out in standard cylindrical 4 oz. sample bottles fitted with clean cork stoppers. 10 ml. of the sample are added to 5 ml. of plumbite solution in the bottle, which is tightly stoppered and shaken vigorously for 15 seconds. Just sufficient sulphur (25—30 mgs.) to cover the interface between the sample and the plumbite solution is added, the bottle is again shaken vigorously for a further 15 seconds, and the contents then allowed to settle. The sample is reported as " sweet " or " negative " if there is no discoloration of the sulphur film, and " sour " or " positive " if the film immediately becomes discoloured or flecked with brown or black.

The " Doctor " test has also been standardized by the Institution of Petroleum Technologists, Serial Designation G. 33.

546. The Quantitative Estimation of Mercaptans in Motor

Fuels.—Mercaptans may be quantitatively estimated in either of two ways; by direct analytical methods, or by the determination of total sulphur before and after their removal from the solution to be examined. The former procedure has been adopted by Wendt and Diggs,[23] who have described a method based upon the formation of lead sulphide in the presence of sulphur and the conversion of this to lead sulphate, which is weighed; while Borgstrom and Reid[25] have made use of the reaction between mercaptans and silver nitrate. According to this latter method, the mercaptans may be determined by shaking the sample with excess of silver nitrate, when the reaction occurs readily. A few mls. of iron alum solution are then added, followed by ammonium thiocyanate to an excess, as indicated by a deep red colour, and the mixture again shaken. The excess of thiocyanate is then removed by silver nitrate and the mixture titrated to a permanent pink colour. The percentage of mercaptan sulphur is then calculated as follows:—

$$\% \text{ mercaptan sulphur} = \frac{\text{ccs. } AgNO_3 \times \text{normality} \times 3{\cdot}206}{\text{weight of sample}}$$

It is doubtful, however, if this method of Borgstrom and Reid is applicable to all motor fuels, since the silver nitrate may be found to react with other sulphur compounds, such as organic sulphides, while the method has not yet been applied to the higher mercaptans.

Mercaptans have also been estimated by an iodometric method involving the oxidation of mercaptans to disulphides by the action of iodine, as described by Kimball, Kramer and Reid.[26] Sampey and Reid[27] have pointed out, however, that this oxidation takes a long time to reach completion and that, normally, 24 hours should be allowed in order that the long chain secondary mercaptans may react quantitatively. This method suffers from the disadvantage that it cannot be used in the case of fuels containing unsaturated compounds which react with iodine and, therefore, cannot be used with most motor fuels. A modification by Sampey and Reid,[27] however, involving the titration of the hydriodic acid formed during the oxidation of the mercaptans, is free from this objection.

A further method for the determination of mercaptans has also been described by Sampey and Reid. This involves the determination of the hydrochloric acid liberated by the action of mercuric chloride on mercaptans, thus:—

$$RSH + HgCl_2 = RSHgCl + HCl$$

one molecule of HCl being liberated for each molecule of mercaptan. This method is also of limited application because, as first discovered by Hofmann and Sand,[28] many olefine hydrocarbons react with mercuric chloride in a similar way, with the formation of hydrochloric acid.

A method free from such objections is that of Faragher, Morrell and Monroe,[29] in which the sample is first examined for total sulphur content by a lamp method and the mercaptans then completely removed by exhaustive treatment with alcoholic plumbite solution. A further total sulphur determination on the sample, after such treatment, gives the amount of mercaptan sulphur removed.

547. The Quantitative Determination of Disulphides.—The organic disulphides may be reduced by zinc and acetic acid or by acetic acid solutions of stannous chloride to mercaptans, thus :—

$$\begin{matrix} RS \\ | \\ RS \end{matrix} + H_2 \rightarrow 2\,RSH.$$

Consequently they may be estimated as mercaptans by the above methods after such treatment. Faragher, Morrell and Monroe (loc. cit.) have used zinc and acetic acid as the reducing agent and have carried out the reduction by refluxing for three hours, while Sampey and Reid[27] have used a 10 hours' treatment on a water bath with an acetic acid and hydrochloric acid solution of stannous chloride. The latter procedure is stated to be suitable for the lower disulphides only. Borgstrom and Reid[25] have pointed out that the reduction of disulphides by glacial acetic acid and zinc to the corresponding mercaptans is accompanied by reactions that decompose the mercaptans formed. For this reason, the amount of mercaptans formed is lower than would be expected and consequently the disulphides can only be estimated by a total sulphur method after reduction, and not by a method specific for mercaptans alone.

548. The Quantitative Estimation of Sulphides.—In light oils from which H_2S, elemental sulphur, mercaptans and disulphides have been removed by the foregoing methods, sulphides may be determined by a total sulphur estimation before and after treatment with a solution of normal mercurous nitrate ($HgNO_3 \cdot H_2O$,) with which the sulphides form addition compounds, probably of the type $R_2S \cdot HgNO_3$. This is the basis of the method proposed by Faragher, Morrell and Monroe.[29]

Sampey, Slagle and Reid[30] have recently observed that this method is not applicable to the estimation of alkyl sulphides dissolved in benzene because the compounds formed are too soluble in this solvent to give quantitative separation. These investigators have, therefore, made use of the reaction noticed by Patein,[31] in which the bromine addition compound of methyl sulphide is hydrolyzed to completion by water, thus :—

$$(CH_3)_2S \cdot Br_2 + H_2O \rightarrow (CH_3)_2SO + 2\,HBr.$$

Sampey, Slagle and Reid have estimated sulphides by measuring the amount of HBr formed in this reaction, but their procedure is limited to oils not containing unsaturated hydrocarbons.

549. The Estimation of Thiophene in Motor Fuels.—Thiophene is usually detected and estimated in motor fuels by the well known Denigés reagent,[32] mercuric sulphate. This reacts with thiophene to form an addition compound having the probable formula

$$2(HgO{\cdot}HgSO_4)C_4H_4S.$$

A standard test for the determination of thiophene in benzole free from unsaturated hydrocarbons is described in "Standard Methods of Testing Tar and its Products," Serial No. L.O.7, page 113. This test is conducted as follows:—

The Denigés reagent is prepared by treating five grams of mercuric oxide with 100 ml. of distilled water and 20 ml. of concentrated sulphuric acid. The solution is stirred vigorously and filtered. 20 mls. of the reagent are placed in a test tube and 2 mls. of the sample to be tested added. A glass stopper is then inserted in the tube and the whole placed in a shaking machine designed to give violent agitation. After three hours' shaking, the precipitate is washed into a specially prepared Gooch crucible by means of hot water and it is then washed until free of any residual acidity. It is finally dried at 110—115°C. in an air oven and weighed.

$$\%\ \text{Thiophene by weight} = \frac{0{\cdot}0757 \times 100\,A}{2S}$$

where A = weight of precipitate in grams and S = Sp. gr. of sample at 15·5/15·5°C.

This method is useless in the presence of unsaturated hydrocarbons as these also form addition compounds with the reagent used.

550. The Estimation of Carbon Disulphide in Motor Fuels.—Carbon disulphide readily reacts with an alcoholic solution of caustic potash to form potassium xanthate, and this reaction forms the basis of the methods of estimation now in use; e.g., the Standard Test Method of the National Benzole Association given in "Standard Methods of Testing Tar and its Products," Serial No. L.B.9, page 88. According to this method the sample to be examined is heated with alcoholic caustic potash and the aqueous layer diluted, neutralized with acetic acid, and titrated with copper sulphate, using potassium ferrocyanide as indicator.

551. Corrosion Tests.—A variety of tests are used by the petroleum

and allied industries to determine the corrosive action of motor fuels. In general, elemental sulphur is the substance chiefly responsible for this corrosion, but, as pointed out elsewhere, mercaptans, sulphoxides and polysulphides may also have an appreciable effect. Copper is the metal usually chosen to detect the corrosive effect.

In 1922, the American Society of Testing Materials adopted a test in which a freshly cleaned strip of copper is immersed in the petrol to be examined maintained at a temperature of 122°F. (50°C.). In the most recent modification of this test,[33] it is allowed to continue for three hours, after which the copper strip is examined. The petrol is reported as not passing the test if the strip shows more than extremely slight discoloration as compared with a freshly cleaned copper strip. This test is sometimes also carried out at the higher temperature of 212°F. (100°C.).

An equally well known test for corrosive sulphur is the mercury test, in which the petrol to be examined is shaken with a small quantity of clean mercury. If elemental sulphur is present, a black precipitate is formed. This test is extremely delicate and, according to Trusty,[34] if a casinghead gasoline gives a negative result to this test, it will also give a negative result in the above A.S.T.M. test. This does not apply, however, to cracked gasolines, refinery absorption gasolines or other comparatively high sulphur content fuels. A similar test has been described by Rue.[35]

The copper dish test, in which the petrol to be examined for corrosive sulphur is evaporated in a hemispherical dish of spun copper about 3 in. in diameter, is also widely used. This test was first developed during the late war by the United States Bureau of Mines[16] for controlling the purchases of fuel by the U.S. government. A copper dish test was adopted by the Institution of Petroleum Technologists in its 1924 Edition of Standard Methods, but this was replaced in 1929 by a method for the determination of free sulphur and no corrosion test was then included.[36, 37]

The methods of testing coal and its by-products of the U.S. Steel Corporation[38] includes a method for detecting the corrosive action of benzoles, depending on refluxing with a copper strip, while as long ago as 1909, Lomax used a somewhat similar test in which the sample to be tested is distilled from an Engler flask containing a 2 × 1 cm. piece of copper foil cleaned with potassium cyanide.

A very reliable and accurate corrosion test has recently been devised by Garner and Evans,[39] in which the fuel to be examined is refluxed in the presence of copper bronze powder. The refluxing is continued for 1 to 1½ hours. When the mixture has cooled down a little and settled, the fuel is decanted through a filter paper. The bronze is then washed with light spirit and dried in a steam oven for a few minutes. Distilled water is then added and excess of bromine until all the bronze and

sulphide is dissolved. A little hydrochloric acid is added, the excess bromine boiled off, the solution filtered, and boiled, and sulphate precipitated by barium chloride and estimated by the usual gravimetric procedure. The results obtained by this method appear to be reproducible to about 0·1 mgs./100 mls.

THE DETECTION AND ESTIMATION OF TETRA-ETHYL LEAD IN FUELS, ETC.

552. The Detection of Tetra-Ethyl Lead in Motor Fuels.—The detection of tetra-ethyl lead in petrols is easily accomplished. A yellow precipitate of lead bromine is easily thrown down by the addition of a 30 per cent. solution of bromine in carbon tetrachloride. This precipitate should be washed with a little petroleum ether and dissolved in warm 10 per cent. nitric acid. The solution is now neutralized with ammonium hydroxide and acidified with acetic acid. From this solution may now be precipitated

(a) yellow lead chromate by the addition of a solution of potassium bichromate.
(b) lead molybdate by the addition of a solution of ammonium molybdate.

These qualitative tests serve as a complete confirmation of the presence of lead.

553. The Quantitative Determination of Tetra-Ethyl Lead.—(1) In Concentrated Preparations. (E.g., Ethyl-fluid). The more common methods used for the determination of tetra-ethyl lead in dilute solutions in motor fuels are hardly applicable to the analysis of concentrated solutions, and for such determinations the following methods of Edgar and Calingaert[40] are recommended.

Method (a).—Gravimetric.

Caution.—Concentrated preparations of organic compounds of lead are highly poisonous and should be handled with extreme care under a well ventilated hood.

This method involves the decomposition of tetra-ethyl lead by bromine with the formation of lead bromide, which is then converted to lead chromate and weighed as such.

$$\text{Thus} \quad Pb(Et)_4 \rightarrow Pb(Br)_2 \rightarrow PbCrO_4$$

To about 25 ml. of carbon tetrachloride in a 500 c.c. Erlenmeyer flask add about 1 ml. of tetra-ethyl lead or its concentrated solution, weighed in a Lunge pipette. Keep the flask cold and add with constant shaking a slight excess (5 to 10 ml.) of a 30 per cent. solution of bromine in carbon

tetrachloride. Lead bromide is precipitated. Evaporate off the carbon tetrachloride on a water bath, and to the dry lead bromide add a mixture of 30 ml. of concentrated ammonia (sp. gr. 0·90) and 50 ml. of 50% acetic acid. Boil until the precipitate is completely dissolved and until any remaining carbon tetrachloride is removed. Filter the solution from insoluble matter and then dilute the filtrate and washings to 450 ml. and heat to boiling. While still boiling, add slowly and with constant stirring, 40 ml. of a 5 per cent. solution of potassium dichromate and maintain at boiling point for a further five minutes. The solution should then be set aside in a warm place for an hour and filtered, collecting the precipitate on a weighed and ignited Gooch crucible and washing well with water. The crucible is then dried in an oven at 105°C., and the precipitate is weighed as $PbCrO_4$.

$$1 \text{ gram } PbCrO_4 = 0{\cdot}6410\,g.\ Pb = 1{\cdot}000\,g\ Pb(Et)_4$$

Method (*b*). *Volumetric.*—The ammonium acetate solution of lead is prepared as in method (*a*) above and then boiled down to 150 ml. The solution is then titrated hot with standard ammonium molybdate solution until a yellow coloration is obtained with tannic acid used as an external indicator. The molybdate solution may be standardized against a known weight of lead or lead chloride, according to the method described in Treadwell and Hall's "Analytical Chemistry," Vol. II, p. 618 (John Wiley and Sons, New York, 1928), while the indicator is preferably used in the form of a freshly prepared 0·5% solution of tannic acid. A blank is run on the same amount of water and ammonium acetate and the amount of molybdate solution used to give a distinct coloration (about 0·3 ml.) is subtracted from the result of the titration.

Method (*c*). *Volumetric.*—Weigh accurately 0·5 mls. of the concentrated tetra-ethyl lead preparation and add to it 50 mls. benzene in a 250 c.c. glass stoppered flask. Add at once 0·1 N iodine solution in slight excess, shake vigorously for a few minutes and titrate the excess iodine with 0·1 N sodium thiosulphate, using starch as indicator in the usual manner. If a yellow precipitate of lead iodide appears, the analysis should be rejected.

$$\text{Ccs. of 0·1 N Iodine used} \times 0{\cdot}01617 = \text{weight of } Pb(Et)_4$$

The above methods are capable of giving results accurate to 0·3 to 0·1% when the requisite skill and care are applied.

554. (2) In Dilute Solutions in Petrols and Other Motor Fuels.—Numerous methods for the quantitative determination of the tetra-ethyl lead contents of motor fuels have been described in the literature.

Birch [41] treats the fuel with concentrated sulphuric acid in a Kjeldahl flask, slowly distils off the petrol and then heats for half an hour with more sulphuric acid. Potassium nitrate is then added, the heating continued until no more brown fumes are evolved and the solution diluted with water. The solution is then heated to coagulate the precipitated lead sulphate and filtered through a Gooch filter. The lead sulphate is weighed as such after drying. Tetra-ethyl lead may also be decomposed with acetyl chloride [42, 43] when white flakes separate. These are washed with petroleum ether, dissolved in nitric acid and estimated as sulphate.

Methods based upon the decomposition of tetra-ethyl lead by sulphur dioxide have been used by Botte [44] and Toms and Money,[45] while Baldeschwieler [46] has used nitric acid for the same purpose. Catlin and Starrett [47] have used the method described as method (*b*) above.

Recommended method.—The recommended method for the estimation of tetra-ethyl lead in dilute solutions is that described by Edgar and Calingaert.[40] According to this method the following procedure is adopted :

(*d*) *Gravimetric.*—To 100 ml. of gasoline is slowly added a 30% solution of bromine in carbon tetrachloride, until a permanent brown-red colour is obtained. The solution is then filtered through asbestos in a dry Gooch crucible and the precipitate is washed with petroleum ether. A solution of 10% nitric acid is then poured into the crucible, brought to boiling and evaporated down to a volume of 3 mls. The solution is diluted and filtered through a soft filter paper and the precipitate washed with warm water. The filtrate is neutralized with ammonium hydroxide and acetic acid is added (5 mls.). The analysis is then continued as in method (*a*).

It will be found that gasolines containing a high percentage of unsaturated compounds absorb bromine vigorously. In such cases, it is advisable to dilute with petroleum ether, to add the bromine slowly and to cool in ice.

(*e*) *Volumetric.*—Prepare the ammonium acetate solution as in method (*d*), boil down to 150 mls. and titrate hot with a standard molybdate solution as in method (*b*).

Methods for the analysis of mixtures of tetra-ethyl lead and other alkyl-lead compounds are described by Edgar and Calingaert,[40] and by Calingaert.[48] General information on the analytical examination of alkyl-lead compounds is given by Krause [49] and by Gilman,[50] while the use of X-rays and ultra violet spectroscopy in the quantitative estimation of tetra-ethyl lead in motor fuels has been described by Aborn and Brown [51] and by Clark and Smith,[52] respectively.

The Quantitative Estimation of the Water Contents of Motor Fuels

555. Water is soluble in petrols to a very small extent at ordinary room temperatures, but the amount of water which comes out of solution on a decrease in temperature and which collects in traps and carburettors on automobiles is of importance. If this water is allowed to accumulate in the fuel feed systems of automobiles, it may prevent the flow of fuel to the engine; the flow may also be prevented or interrupted by the accumulation of partially hydrated aluminium oxide formed with prolonged contact of water with aluminium fittings. In winter weather, moreover, the water in the fuel feed system may freeze and so cause considerable inconvenience, if not actual damage. The solubility of water in benzole is about ten times greater than in petrol at ordinary temperature, and if petrol is added to benzole saturated with water, water is thrown out of solution.

Methods for the Estimation of Dissolved Water in Petrols and Benzole.—Because of the very limited solubility of water in petrols and benzoles, physical methods based upon density and refractive index measurements are of very limited application and, in general, are quite incapable of giving accurate results.

Clifford [53] has described a method in which air dried by calcium chloride is bubbled through the petrol to be analysed and then led through weighed calcium chloride tubes. In this way, the water in the gasoline is carried by the air into the calcium chloride tube where it is absorbed. Petrol vapours are then removed from the weighed calcium chloride tube by passing dry air through it for several hours. The increase in weight of the calcium chloride tube represents the amount of water originally present in the petrol sample. Using this method, Clifford has obtained values for the solubility of water in benzene, petrols, carbon disulphide and other liquids, but the method has been criticized by Aldrich,[54] on the grounds that the vapour pressure of water vapour above calcium chloride is approximately 0·2 mms. of mercury, and that some water vapour is lost as a consequence. Aldrich obtained checks by this method in samples containing known amounts of water, but, it is possible, in these tests, that the loss of water vapour was compensated for by the incomplete removal of gasoline vapours from the calcium chloride tube. However, the generality of this compensation for gasolines containing different amounts of water was held by Aldrich to be doubtful. The method of Clifford has been used by the U.S. Army Air Corps [55] in the determination of the solubility of water in a sample of U.S. domestic grade aviation gasoline, and also by Uspenskii [56] in the determination of water in various petrol samples.

Graefe [57] has proposed treating gasolines containing water with

metallic sodium and estimating the water content by means of the quantity of hydrogen evolved, but no results using this method appear to have been recorded. Aldrich,[54] however, has used sodium-potassium alloy in a similar method, the advantage of such an alloy over either sodium or potassium used alone being that, if it is composed of approximately equal parts of the two metals, it is fluid at ordinary temperatures and, therefore, more easy to introduce into the petrol. The use of such an alloy is also preferable because the liquid alloy maintains a fresh active surface. Care must, however, be taken to ensure that the alloy is free from oxide, because this reacts with water without the evolution of hydrogen. The method of Aldrich, which appears to be as accurate as any yet devised, involves the following steps :

(*a*) Transfer of a known weight of the petrol sample to a suitable container filled with dry air.
(*b*) The removal from the gasoline of those constituents which exert more than a very small vapour pressure at the temperature of liquid air.
(*c*) The introduction of the sodium potassium alloy with the resultant evolution of hydrogen.
(*d*) The separation of the hydrogen from the gasoline.

The method is capable of giving accurate results, but it is complicated and time consuming. The removal of all dissolved gases before the hydrogen is evolved requires special equipment and technique.

A method based upon the evolution of ammonia by the interaction of water and magnesium nitride has been proposed by Dietrich and Conrad.[58] The ammonia evolved is absorbed in sulphuric acid and is estimated in the usual manner. This reaction may also be employed in the determination of the water contents of fuels containing ethyl alcohol because magnesium nitride and ethyl alcohol do not react, but cannot be used in the case of fuels containing a high percentage of methanol (methyl alcohol) because of the reaction

$$Mg_3N_2 + 6CH_3OH = 3\ Mg\begin{matrix}OH\\OCH_3\end{matrix} + NH_3 + N(CH_3)_3.$$

Dietrich and Conrad found, however, that, provided the methanol content was not greater than 60 per cent., this reaction did not occur and that this method could be used satisfactorily.

Special Tests for Use in the Examination of Benzoles

556. General Tests.—(*a*) *Crystallising-Point.*

"Standard Methods for Testing Tar and its Products," Serial No. L.B.8, page 79.

"Standard Specifications for Benzole and Allied Products," 1929, page 85.

This test is of importance because pure benzene has a melting point of +5·4°C.

A boiling tube about 6 in. long and 1 in. diameter is placed inside a slightly longer and wider tube which acts as an air jacket. The wider tube is weighted with lead shot or similar material and the inner tube is closed by means of a cork which carries a stirrer and a thermometer. The whole assembly is mounted in a vertical position.

A representative sample of benzole (about 40 *g.*) is introduced into the inner tube and the whole apparatus immersed in a freezing mixture, the temperature of which should not be more than 10°C. below the anticipated freezing point. The temperature of the benzole is read at intervals of half a minute with continuous stirring, the readings being continued for five minutes after the rise of temperature following crystallisation. The crystallising point corresponds with the last five consecutive readings, during which the temperature remains constant within 0·05°C. If super cooling takes place, the constant temperature is observed immediately after super cooling ceases. If a constant temperature is not obtained over five readings after the super cooling period has passed, the readings before the rise and those after the rise should be plotted against the time intervals, and the portion of the curve after the temperature rise is extended backwards until it intersects the portion of the curve before the temperature rise. This point of intersection is taken as the correct crystallising point.

(*b*) *Neutrality.*

"Standard Methods of Testing Tar and its Products," No. L.B.4, page 81.

"Standard Specifications for Benzole and Allied Products," 1929, page 83.

"Fifty millilitres of the sample shall be shaken in a clean stoppered vessel with a little distilled water and a drop of methyl orange solution as an indicator. The colour of the aqueous layer shall be noted; for neutrality this colour will be neither a distinct red nor a distinct yellow."

557. Examination of Crude Benzoles.—(*a*) *Benzene, Toluene, Carbon Disulphide and Saturated Hydrocarbons.*—For this analysis, the method developed by Spielmann and Jones [59] and described in Standard Methods of Testing Tar and its Products (Serial No. L.O.5. p. 103) is used. This method is based upon a combination of fractional distillation and specific gravity measurements. For further details, reference should be made to "Motor Benzole," published by The National Benzole Association, London, 1931, p. 567.

(*b*) *Tar Acids* (*Phenols, etc.*).—An approximate but rapid method for the estimation of tar acids in benzoles consists in measuring the volume loss on shaking with 10% caustic soda solution, but for accurate work, the following method is to be preferred ("Standard Methods for Testing Tar and its Products," Serial No. L.B.14, p. 98).

One hundred millilitres of the sample are shaken vigorously for five minutes with about 25 mls. of 25 per cent. aqueous caustic soda solution and the treatment is repeated until all the tar acids have been removed. The soda washings are then combined and boiled for ten minutes, after which they are cooled and sufficient concentrated hydrochloric acid added to make the solution acid to methyl orange. The aqueous layer is then saturated with sodium chloride and the volume of the liberated tar acids is measured.*

(*c*) *Tar Bases* (*Amines, etc.*).

"Standard Methods of Testing Tar and its Products," Serial No. L.B.15, page 94.

"Standard Specifications for Benzole and Allied Products," 1929, page 103.

According to this procedure, tar acids are first removed as in the former method, and the sample is then treated with 30 per cent. by volume of 25 per cent. sulphuric acid. After agitation the acid layer is drawn off. The residual oil is then washed with water and the aqueous solution added to the acid layer, into which an excess of 16 per cent. caustic soda is next introduced, care having been taken to keep the mixture cool. The resulting solution is then steam distilled into 0·5N sulphuric or hydrochloric acid which is afterwards titrated. The limits of accuracy of this test are ± 10 per cent. of the true value.

Examination of Refined Benzoles

558. Acid Washing or Rectification Test.—If benzole has been refined in such a way that practically all of the unsaturateds have been removed, the degree of refining may be estimated by the "acid-washing" test, which measures the colour imparted to 95% sulphuric acid when the benzole and the acid are agitated together. This test is described in detail in

(*a*) Standard Methods. Serial No. L.B.6, p. 85.
(*b*) Standard Specifications, p. 163.
(*c*) "Motor Benzole," National Benzole Association, London, 1931, p. 581.

and is carried out as follows:

The sample is filtered through a No. 1 Whatman filter paper and the

* Hydrocarbons are appreciably soluble in tar acids. As a result of this, the volume of liberated tar acids may be high.

first ten millilitres of filtrate is rejected. 95 mls. of the filtrate is placed in a separating funnel, 5 mls. of 95 per cent. sulphuric acid is added, and the contents of the funnel well shaken for *exactly* two minutes, after which the funnel is allowed to stand undisturbed for *exactly* ten minutes. The lower acid layer is then withdrawn and its colour compared with that of standard glasses in a Lovibond Tintometer.

Total Sulphur, Elemental Sulphur, etc.—Analytical methods for the determination of sulphur and sulphur compounds in benzole are described in paragraphs 535-542.

Special Tests for Use in the Examination of Alcohol Fuels

559. Alcohol fuels are now becoming increasingly important, particularly in Europe, while their use in high duty racing engines in automobiles, motor cycles, aeroplanes and motor boats is becoming increasingly popular, due to their peculiar advantages in this particular field over straight hydrocarbon fuels or hydrocarbon fuels doped with anti-knock compounds. The analysis of alcohol fuels is, therefore, a matter of importance.

Estimation of the Total Alcohol Contents of Motor Fuels.—The total alcohol contents of motor fuels containing ethyl alcohol and /or methanol can be easily determined by agitation with a considerable excess of water or calcium chloride solution and measurement of the resulting loss in volume. The loss in volume can be read more easily if the water used is coloured with a dye soluble in alcohol and water but insoluble in hydrocarbons, for instance, Fuchsin or Aniline Blue 2B.

The loss in volume obtained in this way represents the alcohol plus water content of the fuel, and if it is definitely known that the fuel contains either ethyl alcohol or methanol, but not both, the alcohol content may be determined by taking the calcium chloride solution containing the alcohol, distilling it, making up the distillate to a known volume with distilled water and measuring its specific gravity extremely carefully to four significant figures. The methanol or ethyl alcohol concentration can then be calculated by reference to standard tables of the specific gravities of mixtures of these alcohols with water. The water contents of alcoholic motor fuels containing less than 60 per cent. of methanol may be determined by the magnesium nitride method of Dietrich and Conrad.[58] (See paragraph 555.)

The quantitative determination of both ethyl alcohol and methanol, when present together in a motor fuel, may be carried out by separating the alcohols from the remainder of the fuel by water solution, concentrating by distillation, and applying the well known organic analytical

methods.[60] Ethyl alcohol may be *detected* by the formation of ethyl benzoate, of characteristic smell, while methanol may be *detected* by oxidation and the application of a modified Schiff's reagent.[61]

560. The Detection and Estimation of Ether (Diethyl Ether).—Quite a number of motor fuels contain ether, which is added to give better starting and vaporization properties. This compound may be detected (preferably in the fraction boiling below 40°C.) by its characteristic reaction with perchromic acid, in which a blue colour is formed.

561. The Detection and Estimation of Acetone.—Acetone may be detected in alcohol fuels by means of the well known sodium bisulphite test. It may be estimated quantitatively in the presence of alcohols by the method of Rakshit.[60]

562. Cloud Points of Alcohol Fuels.—As shown in Chapter IX (Volume 2), one of the most important tests for motor fuels containing alcohol is the determination of "cloud point" or "separation temperature," i.e., the temperature at which separation into two layers just occurs.

For normal purposes, the apparatus used for determining the crystallizing point of benzoles, described above,* may be used for this test, but a different procedure is necessary. The tube containing the alcohol fuel must be closed by a cork to prevent contamination with atmospheric moisture when cloud points below 0°C. are being measured, otherwise the determined cloud points will be too high, and even with this precaution, it is advisable, if the test takes a long time to do, to make a rough determination first of all and to follow this with an accurate measurement. The rate of cooling must be slow, and not greater than 1°C. per minute in the immediate region of the cloud point. The first appearance of persistent cloud is taken as the cloud point, but both the appearance of cloud on cooling and the disappearance of cloud on subsequent warming are noted. If these differ by more than 0·5°C. the test is regarded as unsatisfactory and repeated. In the case of alcohol fuels containing but a small amount of alcohol, the cloud point is often indefinite and difficult to record with accuracy.

Measurement of the Crank Case Dilution of Lubricating Oils

563. No standard test for the measurement of the crank case dilution of lubricating oils is given in the I.P.T. Handbook of Standard Methods, but the following standardized procedure is the subject of

* See paragraph 556.

A.S.T.M. Designation D. 322-33. The method makes use of a steam distillation to carry over the light oils present as diluents into a reflux trap where they can be measured.

25 ml. of the crank case oil is placed in a short neck flask of 1 litre capacity and approximately 500 ml. of water is added. The special trap is connected to the flask and is fitted with a reflux condenser. The trap is illustrated in Figure 146. Heat is applied to the flask and " success depends upon heating at such a rate that boiling is continuous and vigorous enough to prevent the oil from forming, even momentarily, a continuous film on top of the water." Bumping may be prevented by the addition of broken glass, steel wool or about 5 ml. of concentrated hydrochloric acid. Readings of the amount of diluent are made 5 minutes, 15 minutes and each subsequent 15 minutes after refluxing

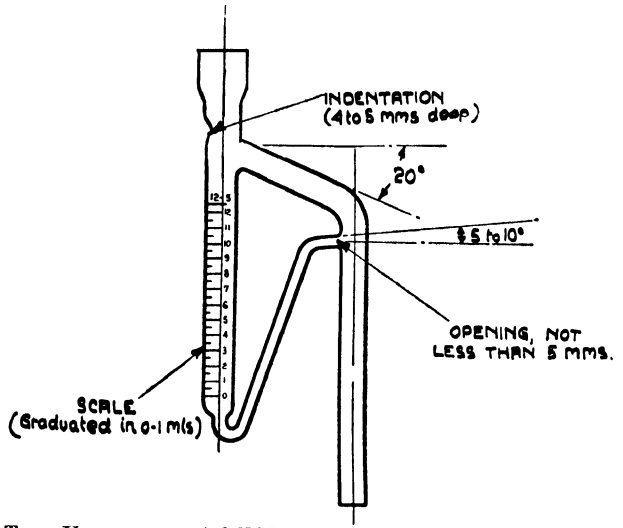


FIG. 146.—TRAP USED IN THE A.S.T.M. STANDARD TEST FOR THE DETERMINATION OF LUBRICATING OIL DILUTION. (A.S.T.M. SERIAL DESIGNATION D322-33.)

begins, and completion of the test is indicated when the volume of diluent increases by not more than 0·1 ml. in any 15 minute period, or when the apparent volume of the diluent collected is equal to, or less than, the following amounts.

Time from Start of Refluxing.	*Mls. Diluent.*
5 minutes	0·1 ml.
30 ,,	2·0 ml.
60 ,,	4·0 ml.
90 ,,	5·0 ml.

After standing at least 15 minutes, to allow the distillate to settle clear

and to cool to approximately room temperature, the volume of diluent is read and recorded as a percentage of the original charge. Determinations by independent operators should agree within 20 per cent. for dilutions under 5 per cent., and within 10 per cent. for dilutions over 5 per cent.

Simple vacuum and steam distillations have been advocated by A. R. Stark [61A] and A. T. Wilford [61B] respectively as means of estimating dilution of diesel engine lubricating oil. Stark has described a method in which the diluted oil is fractionated in a high vacuum distillation unit fitted with an efficient fractionating column. The actual interpretation of results is simple, it being observed that the distillation curves of the diluted and undiluted oils are parallel in the neighbourhood of the initial boiling point of the latter. Hence the dilution percentage is read directly from the distance between the curves parallel to the percentage distillate axes.

The Hydrocarbon Analysis of Motor Fuels

564. Ever since the beginning of the petroleum industry much attention has been devoted to the determination of the chemical nature of mineral oil products, but, although much valuable work has been done on this important subject, little progress has been made in the development of reliable analytical methods whereby the chemical nature of these products may be determined with any degree of accuracy. The difficulties encountered in work of this kind are, of course, very great, and are due to the very complex chemical and physical natures of all petroleum oils, even those of the most narrow boiling ranges. Thus, a common straight-run petrol of B.P. 30°—200°C. may contain up to two or three hundred different hydrocarbons, by far the greater number of which may only be present in concentrations of less than 1% by weight. A further reason for the present unsatisfactory state of hydrocarbon analysis is the fact that the chemistry of pure hydrocarbons is a neglected chapter in organic chemistry; very few hydrocarbons (except those of the aromatic series) have been examined in detail, and what little work has been done has been conducted on substances of doubtful purity, with the result that much contradictory information has been published. The lack of information on the behaviour of pure hydrocarbons, and the very small number of hydrocarbons available in the pure state in any measurable quantity for making test mixtures of known composition, constitute fundamental difficulties in any investigation of methods of analysis of complex hydrocarbon mixtures.

To determine the chemical nature of motor fuels and light hydrocarbon oils, it is sufficient, for most purposes, to determine the relative

proportions of unsaturated, aromatic, naphthenic and paraffinic hydrocarbons, and it is usual to classify these hydrocarbons as follows :

(*a*) *Unsaturated hydrocarbons.*—Those containing olefinic double bonds, i.e., mono- and di-olefines, acetylenes, di- and tetra-hydro-benzene and their homologues and aromatic and naphthenic hydrocarbons containing olefinic double bonds in their side chains.

(*b*) *Aromatic hydrocarbons.*—Benzene, naphthalene, anthracene and and their homologues, having the general formula $C_n H_{2n-6}$.

(*c*) *Naphthenic hydrocarbons.*—Saturated cyclic hydrocarbons or poly-methylenes and their homologues. General formula $C_n H_{2n}$.

(*d*) *Paraffinic hydrocarbons.*—Saturated straight or branched chain hydrocarbons of the general formula $C_n H_{2n+2}$.

The estimation of these four main classes of hydrocarbons is usually carried out by, first of all, removing and estimating the most reactive class, i.e., the olefines. The residue is then examined for aromatics and after both unsaturateds and aromatics have been removed, paraffins and naphthenes are estimated in the residual mixture. Alternatively, the aromatics and unsaturateds may be estimated as one combined class and the unsaturateds estimated separately. Aromatics are then determined by difference. On the other hand, olefines may be determined by difference if the aromatics are estimated separately.

565. The Estimation of Unsaturated Hydrocarbons. — From time to time various methods have been proposed for the estimation of unsaturated hydrocarbons in light oils, and, of these, the following are of the most importance.

(*a*) Solution in sulphuric acid.
(*b*) Halogen absorption.
(*c*) Reactions with mercury salts.
(*d*) Reaction with ozone.
(*e*) Oxidation with perbenzoic acid.
(*f*) Reaction with thiocyanogen.
(*g*) Treatment with sulphur monochloride.

Certain other methods are described later.

566. (*a*) *Estimation by means of Sulphuric Acid.* It has already been shown in Chapter V, Volume I, that the unsaturated (i.e., olefinic) hydrocarbons are attacked by sulphuric acid of lower concentration than is necessary for reaction with aromatic and saturated hydrocarbons. This fact has long been used to effect a very rapid and convenient, if

not accurate, analytical method for the estimation of unsaturated hydrocarbons. It has also been pointed out that the chemical reactions involved are complex, in that the products of the reaction under different conditions are alcohols, mono- and di-alkyl esters and that the action of sulphuric acid upon unsaturated hydrocarbons depends, to a large extent, upon the molecular weight and molecular composition of the latter and upon the strength of the acid employed.

Sulphuric acid cannot be used satisfactorily for the determination of unsaturated hydrocarbons in the presence of other hydrocarbons for a variety of reasons, the most important of which are (*a*) the formation of polymerized products, and (*b*) the fact that sulphuric acid of strength sufficient to react completely with unsaturated hydrocarbons also reacts with hydrocarbons of other types, e.g., the aromatics. Numerous attempts have been made, however, to surmount these difficulties.

The chemistry of olefine polymerization by sulphuric acid has received attention by Morrell,[62] Brooks and Humphrey[63] and Joubert and Norris.[64] Brooks and Humphrey found that the polymers were more stable to sulphuric acid than the parent olefines, although they contained a double bond. Therefore the strength of sulphuric acid used for the estimation of unsaturated hydrocarbons must be capable of dissolving these polymers formed by its own action, but be without action on other hydrocarbons. Realising the errors due to polymerization, Egloff and Morrell [65] have described a method in which a suitable correction is applied. The light oil to be examined is treated with twice its volume of 80% sulphuric acid, agitated, allowed to settle and the acid layer drawn off. The loss in volume of the oil is then measured, and represents the amount of unsaturated hydrocarbons originally present in the oil which has reacted with the acid to form acid-soluble reaction products, such as alcohols and mono-alkyl esters. The acid treated oil is then neutralized with alkali and redistilled through a column, where the amount of high boiling polymers formed by the acid and boiling above the end-point of the original oil, is measured. This quantity, when added to the loss sustained on agitation with acid in the first step, is taken as the quantity of unsaturateds originally present. This correction, however, is only approximate, for some unsaturateds are polymerized to hydrocarbons boiling at temperatures below the end-point of the spirit and are, therefore, not measured by distillation. For example, tri-methyl-ethylene, B.P. 38°C., polymerizes to a mixture of diamylenes boiling between 150 and 160°C., whereas the end-points of the petrols sold in English markets are in the immediate neighbourhood of 190—200°C. The dipolymers of the isomeric hexenes boil between 190 and 200°C., whereas the dipolymer of iso α-heptene has a boiling point of 220°C.—224°C., and a mixture

of octene—1 and octene—2 gives a mixture of dipolymers boiling between 275°C. and 285°C.

The Egloff and Morrell method may, therefore, be improved by treating the oil to be examined in fractions of narrow boiling range. Each fraction may be separately treated with sulphuric acid and both the volume loss and extent of polymerization of each fraction determined. In this way, a much higher figure for polymerization loss is obtained and the error due to this cause is much reduced. In the case of a cracked spirit, Houghton and Bowman[66] found that sulphuric acid of 91% strength produced the maximum amount of polymerization.

567. Besides such phenomena, there is another complication attending the use of sulphuric acid for the quantitative estimation of unsaturated hydrocarbons. It was observed by Kramer and Spilker[67] that, in the presence of strong sulphuric acid, styrene and the xylenes condensed to form styro-xylenes. Later, Brochet[68] found that aliphatic unsaturated hydrocarbons condensed with benzene homologues in the same fashion, e.g., benzene and hexene gave hexyl-benzene. Toluene and xylene behave in the same way and other unsaturateds probably react like hexene. Brame[69] conducted experiments to determine whether similar condensations took place when petrols and synthetic mixtures were shaken with various strengths of sulphuric acid. He found that when 85% acid was used, 30% of the aromatics originally present in a petrol were removed, while when 88% acid was employed, over 50% was removed. The results of his experiments are, however, not conclusive, for Brame did not ascertain whether acid of either 85% or 88% had any action on aromatics alone, although they do indicate that condensations of the type described by Brochet probably take place. More conclusive evidence on this point is given in the recent work of Towne,[70] who found that on treating a synthetic mixture containing 15% of olefines and 10% aromatics with three volumes of cold 93% acid, more than half of the aromatic content was condensed to substances boiling over the original end-point.

568. Much controversy exists regarding the most suitable strength of sulphuric acid to employ for the estimation of unsaturated hydrocarbons, but it is more or less agreed that acid stronger than 80% is required. Ormandy and Craven[71] treated petrols of various strengths and found that the density and refractive index of the residual spirit after acid treatment rose until the acid strength reached 88%. This they ascribed to polymerization and removal of unsaturateds. At higher strengths of acid extraction of aromatics occurred and the density and refractive index fell to lower values. Ormandy and Craven thus confirm the work of Moore and Hobson,[72] who found that an acid

strength of 88—90% is essential for the removal of unsaturateds. Similarly, Lomax and Pemberton[73] treated a cracked distillate with 80% sulphuric acid, distilled it to the original end-point, treated it again with 98% acid and finally redistilled it to its original end-point. After the last distillation, a considerable residue remained, indicating that the treatment with 80% acid did not remove all the olefines. The same conclusions have been arrived at in later work by Nametkin and Robinzon[74] and Tarassov and Popova.[75] Riesenfeld and Bandte[76] have recommended the use of 85% sulphuric acid followed by redistillation for the estimation of unsaturateds in cracked spirits and 92% and 94% acids for the examination of straight run spirits. This recommendation has been supported by Winkler,[77] who makes the important observation, first pointed out by Norris and Joubert,[64] that, under the action of heat, e.g., in distillation, the polymerized products of olefines partly depolymerize. The di-polymers, in this case, remain in the distillate and are likely to be determined as aromatics. Winkler suggests that the distillate resulting from the distillation of acid treated spirit, in such an estimation of unsaturated hydrocarbons, should be treated with a further quantity of sulphuric acid (92·5%) and the percentage loss added to the figure for unsaturateds previously obtained.

569. Whatever strength of sulphuric acid is employed for the estimation of unsaturated hydrocarbons it should, obviously, be without any action on other hydrocarbons, otherwise the result obtained will be too high. Faragher, Morrell and Levine[78] give results which show that 85% sulphuric acid has an appreciable effect upon benzene and a pronounced effect upon toluene, while Carpenter states[79] that acid of concentration even as low as 80% has a noticeable effect upon a 1 : 3 toluene-xylene mixture. Towne[70] has published the following results on the action of 93% and 98% sulphuric acid on aromatics of various types, in which the importance of the time element is well brought out.

TABLE 116.—SOLUBILITY OF AROMATIC HYDROCARBONS IN SULPHURIC ACID.

	% Soluble in 93% H_2SO_4 in 1 minute	% Soluble in 93% H_2SO_4 in 10 minutes	% Soluble in 98% H_2SO_4 in 10 minutes
Benzene	6·0	27·0	100·0
Toluene	11·0	100·0	100·0
Xylene (mixture)	14·0	98·0	100·0
Ethyl benzene	10·0	78·0	100·0
Diethyl benzene	6·0	44·0	100·0
Mesitylene	23·0	100·0	100·0
Isopropyl benzene	2·0	37·0	100·0
Sec. Butyl benzene	1·0	19·0	100·0
Tert. Butyl benzene	0·0	23·0	100·0
Tert. Amyl benzene	0·0	18·0	100·0
p-Cymene	0·0	73·0	100·0

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These figures show that the action of 93% sulphuric acid upon benzene, toluene, xylene, ethyl benzene and mesitylene is marked, even for such a short contact time as 1 minute.

According to Telichev and Dunski,[80] most aromatic hydrocarbons, with the exception of benzene, para and tetra substituted benzenes, are attacked by sulphuric acid of 91—92% strength, while Nametkin[81] states that 93·6% sulphuric acid has a sulphonating action upon benzene, toluene and xylene.

570. Estimation of Unsaturated Hydrocarbons by means of Halogen Absorption.—Unlike other hydrocarbons, the unsaturateds readily absorb the halogens to form the well known halogen addition compounds, the reaction being a simple addition process. In aqueous solution, however, there is a tendency for part of the halogen to react with the water giving a hypo acid which adds on to the olefine to produce an halogen derivative of an alcohol, thus,

$$R{\cdot}CH = CH_2 + H{\cdot}Br{\cdot}O \rightarrow R{\cdot}CH{\cdot}Br - CH_2OH.$$

When simple and direct addition of two halogen atoms takes place, the relative contents of unsaturated hydrocarbons in two oils may be determined by simple titration. Bromine and iodine "*numbers*" (defined as the number of grams of halogen absorbed per 100 grams of oil) are often used for comparing the "unsaturation" of oils measured in this way. Such an evaluation, however, means but little unless the molecular weight of the unsaturateds is known: otherwise the percentage of unsaturated hydrocarbons cannot be calculated.

The halogenation reaction is complicated by the fact that substitution of hydrogen atoms, indicated by the evolution of hydrogen bromide, often proceeds at the same time as halogen addition, and very likely takes place with greater ease in the case of hydrocarbons of high molecular weight.

Davis[82] has found that, in carbon tetrachloride solution, ethylene brominates at a measurable rate and that, if the solutions are dried and kept away from a bright light, the reaction takes hours, and even days, for completion. Traces of moisture speed up the reaction, whereas added hydrogen bromide does not affect it, while the rate of reaction, in the dark, is gradually increased as the temperature is lowered from 25°C. to 0°C. Davis also observed that temperature has little effect on the bromination of trimethyl ethylene or di-iso butene, and that large amounts of hydrogen bromide are evolved from both these hydrocarbons, showing that substitution occurs.

571. The iodine number methods for the estimation of unsaturation devised by Hubl[83] and Wijs[84] are of great use in the examination of

animal, vegetable and fatty oils, but soon proved themselves not to be so applicable to the examination of mineral oils. The method due to Hubl makes use of a solution of iodine and mercuric chloride in alcohol, but, in practice, is inconvenient and gives discordant results. The method of Wijs utilizes a decinormal solution of iodine monochloride in glacial acetic acid, which has the advantage that it can be stored for some time. Neither of these methods is now much used.

The method of Hanus[85] possesses many advantages over the older methods and has been commented upon favourably by other workers.[86] The reagent employed consists of a solution of equivalent parts of bromine and iodine dissolved in glacial acetic acid.

Faragher, Gruse and Garner[87] have examined the Hanus method when applied to pure unsaturated hydrocarbons with interesting results. They found that, in the case of the mono-olefines, theoretical halogen absorption was obtained but that with di-olefines and also with the acetylene heptine, the maximum absorptions obtained only corresponded to the amount of iodine that would have been required if the hydrocarbons had been mono-olefines. Faragher, Gruse and Garner also found that the Hanus iodine numbers of gasolines were practically unaffected by changes in the relative proportions of spirit and Hanus reagent and that the latter did not cause any appreciable substitution of hydrogen atoms in the molecules of simple paraffins, cycloparaffin or aromatic hydrocarbons, or of straight, branched chain or cyclic olefines, of di-olefines, acetylenes or cracked gasolines. This opinion is not held by Johansen,[88] who states that the iodine absorption obtained by use of the Hanus solution is a combined addition and substitution value, and by employing a modified solution in which the iodine bromide is dissolved in the neutral solvent carbon tetrachloride instead of glacial acetic acid, he was able, by means of a modification of a method due to McIlhiney,[89] to discriminate between these addition and substitution values, and to show that substitution played a very considerable part in the absorption of iodine from Hanus solution by mineral and fatty oils. Morrell and Egloff[90] check all the findings of Johansen within certain limits and show that there is a considerable change in the addition values with change in the relative proportions of the reactants, although this change is not nearly so great as the variation in the substitution values, and they show that, in the cases of certain oils, negative addition values are obtained.

Regarding the time factor in iodine number determinations, Smith and Tuttle[91] found that, in the Hanus method, the maximum absorption was reached within 15 minutes, while Dean and Hill[86] recommend a thirty minute reaction time. The precise effect of the solvent used in the test is obscure, and tests have been described[92] which show that the retarding action of the solvent is something more than a mere diluent effect. Acetic acid, chloroform, carbon tetrachloride and carbon

disulphide were used as solvents and the results varied widely according to which solvent was used.

572. The Bromine Number Method of McIlhiney.—This analytical method was first described in 1899 and is especially suitable for the separate measurement of halogen addition and substitution.[89] It depends upon the fact that for each atom of hydrogen replaced by bromine in a substitution reaction, one molecule of hydrogen bromide is formed. By estimation of this liberated acid, therefore, as well as the total amount of bromine absorbed, it is possible to calculate the extent of both the addition and substitution reactions. The estimation of the hydrobromic acid is accomplished by the addition of potassium iodate to the solution after the excess bromine has been destroyed by potassium iodide and sodium thiosulphate, thus

$$KIO_3 + 5\,KI + 6\,HBr = 6\,KBr + 3\,H_2O + 3\,I_2$$

a reaction which is not brought about by the common organic acids.

This method of bromine number determination is capable of giving accurate results when sufficient attention is given to details and has been used satisfactorily by Waterman, Spijker and Westen,[93] by Waterman and Westen[94] and also by Wilkinson[95] in the determination of the purity of various olefines.

Details for Carrying out the McIlhiney Bromine Number test.—The procedure recommended by McIlhiney was to dissolve 0·25 to 1·0 grams of the oil to be examined in 10 ml. of carbon tetrachloride and to add 20 ml. of 0·3N bromine in the same solvent. The mixture is then allowed to stand for 1—2 minutes and the reaction arrested by the addition of 20—30 ml. of 10% potassium iodide solution and 50 ml. of water, and titrated with thiosulphate. McIlhiney also recommended the use of a special flask fitted with a ground glass stopper to prevent the escape of hydrobromic acid.

Such a procedure is satisfactory in the case of non-volatile oils, but, in the case of motor fuels, Howes[96] found it necessary to modify the procedure somewhat. Difficulty was experienced in the weighing of such materials into conical flasks or bottles. Small glass capsules were tried but these proved unsatisfactory, small amounts of liquid being retained in them even on repeated shaking, and they were often the cause of broken flasks during shaking. Furthermore, it was found that unless a constant weight of oil was used in each experiment (i.e., a constant ratio of oil to bromine), the results obtained varied. Finally, accurately calibrated and graduated pipettes of 1 ml. capacity, cooled in a constant temperature bath, were employed and were found to increase considerably the accuracy and convenience of the method.

Howes also encountered a difficulty in the substitution reaction, which was found to increase with increase of reaction time and with increase of bromine concentration, especially in the presence of moisture. This substitution reaction was found to be particularly evident when high boiling aromatic hydrocarbons were present, e.g., *p*-cymene and *p*-tertiary butyl toluene. The bromine absorbed by direct addition was found to be unaffected by either time, concentration or by the presence of moisture. This difficulty was nearly overcome by the use of only a small excess of bromine. In the case of pure unsaturated hydrocarbons, this excess was usually 30% and when this quantity was used it was generally found that substitution was negligible, except when high boiling aromatic hydrocarbons were present.

573. The Bromine Number Method of Francis.[97]—This method employs a standard solution of potassium bromide and potassium bromate, which in acid solution generates bromine, the rate of generation depending upon the concentration of acid present.

$$KBrO_3 + 5\,KBr + 3\,H_2SO_4 = 3\,K_2SO_4 + 3\,H_2O + 3\,Br_2.$$

By making the solution only slightly acid, the bromine can be generated very slowly and if this is absorbed by substances containing double bonds fast enough to keep it in small concentration, substitution reactions are said to be avoided. The fact that mineral oils and light spirits do not mix with the reagents employed is only a disadvantage in that it necessitates vigorous shaking. As seen from the equation.

$$R\,CH = CH\,R' + Br_2 + H_2O \begin{cases} \nearrow R\,CH{\cdot}Br - CHBr\,R' + H_2O \\ \searrow R\,CH\,Br - CHOH\,R' + HBr. \end{cases}$$

the calculated result is not affected at all whether dibromides or bromohydrins are formed.

Cortese[98] has tested this method with pure unsaturated hydrocarbons of various types and has reached the conclusion that it gives reliable results for aliphatic olefines and di-olefines, whether conjugated or not, but that it only gives approximately correct results for certain ring structures.

A modification of the Francis method has been used by Bacon[99] for determining the bromine numbers of libricating oils.

574. The use of Standard Olefine Mixtures in Bromine Number Determinations.[100]—The errors involved in bromine number determinations, such as substitution and incomplete addition, etc., may be partly overcome when a standard olefine solution is used for purposes of direct comparison. Thus, in the case when the olefine in

the unknown mixture is the same as that in the standard, the olefine content of the former may be calculated as follows :—

$$u = \frac{T_1}{T_2} S.$$

where u = olefine content of the unknown,
S = „ „ „ „ standard,
T_1 = titer of the unknown,
T_2 = „ „ „ standard.

The standard may also contain the same type of olefines as that of the oil under investigation. Thus, Morrell and Levine have shown that the olefines in cracked spirits, produced under similar conditions, are probably of the same type in approximately the same relative proportions, so that a cracked spirit, of which the olefine content is known, may be used as a standard. In the case where the unknown solution contains known olefines different from those in the standard, the olefine content may be calculated by the expression

$$u = \frac{T_1}{T_2} S \frac{(N_S M_1 D_S)}{(N_1 M_S D_1)}$$

where M_1, D_1 and N_1 = actual or average molecular weight, density and number of olefine bonds in the mixture being examined, and
M_S, D_S and N_S = corresponding properties of the standard solution.

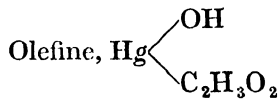
575. The use of Mercuric Salts for the Estimation of Unsaturated Hydrocarbons.—The unsaturated hydrocarbons possess the property of reacting with mercuric salts, either to form complex but loose addition compounds, or else to become oxidized. The tendency of the olefines to react with mercuric salts depends upon a variety of factors : thus, the gaseous olefines [101, 102, 103] readily form addition compounds from which they may be recovered by the action of dilute acids. Unsaturated hydrocarbons of low molecular weight react fairly easily with mercuric salts, but those of high molecular weight, e.g., octylene and diamylene, only react slowly, even on boiling. Olefines in which the double bond carries four alkyl radicles, e.g., tetra-methyl ethylene, do not react with mercuric salts even after prolonged boiling.[104] Thus, the reaction is not applicable to all unsaturated hydrocarbons.

Tausz[105] found that cyclohexene, methyl cyclohexene and the terpenes gave compounds with mercuric acetate, while fully saturated hydrocarbons gave no reaction.

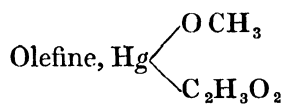
Balbiano and Paolini[106] have made use of mercuric acetate for the

detection of olefines in light petroleum distillates, while Tausz[107] states that, as a rule, the olefines which may be prepared by alcohol dehydration form addition compounds with mercury salts in aqueous solution, while the higher olefines only react in alcoholic solution. Tausz also states that the olefines C_8 to C_{15}, obtained by polymerization of lower olefines, do not react even in alcoholic solution. Sabinene and pinene form addition compounds easily.

In aqueous solution, mercuric acetate gives addition compounds of the type



while in methyl alcohol solution, compounds of the type



are formed.

Mercury salts which do not hydrolyze, e.g., mercury cyanide, do not form addition compounds with olefines. By working in acetic acid solution, Hugel and Hibou[104] have succeeded in making the addition compounds of mercuric acetate and olefines as high as hexadecene. These compounds have the general formula

$$\text{Olefine, Hg}\,(C_2H_3O_2)_2.$$

The decomposition of mercuric acetate-olefine complexes with the regeneration of the original olefine has been discussed by Tausz,[107] Engler[108] and Kutscheroff,[109] each of whom has used acids (HCl) for the decomposition.

576. Various methods for the estimation of unsaturated hydrocarbons in the presence of other hydrocarbons have been proposed, based upon the above characteristic reactions with mercuric salts. Thus, Tausz[107] treated light spirits with 3 volumes of mercuric acetate solution for 5 minutes in the cold and then allowed the reaction to continue for 3 hours under a reflux condenser. The product was then steam distilled and the distillate washed with dilute caustic soda and then with sodium hydrogen sulphite solution to remove acetic acid, aldehydes and ketones respectively. Tausz estimated the unsaturated hydrocarbons by measuring the volume loss sustained on such treatment, and also by measuring the volume of unsaturated hydrocarbons resulting from the decomposition of the mercuric acetate complexes by hydrochloric acid.

Tausz and Wolf[110] use an alcoholic solution of mercuric acetate in the following way :—

To a solution of 30 grams of mercuric acetate in 500 ccs. of water is added 50 mls. of the light oil to be tested and 15 mls. of alcohol. After shaking, the mixture is heated under a reflux condenser for 8 hours on a vigorously boiling water bath. The mixture is then distilled in a current of steam and the distillate washed as above to remove acetic acid, aldehydes and ketones. The washed distillate is the olefine free oil, and the difference between this volume and the original volume taken represents the unsaturated hydrocarbons which have reacted with the mercuric acetate.

An important contribution on the action of mercuric acetate on unsaturated hydrocarbons, etc., has been made by Brame and Hunter[111] who have described their attempts to use the reaction for the identification and separation of the olefines in a cracked spirit. They abandoned the method in favour of a procedure involving bromination because they were unable to obtain good yields of olefine hydrocarbons by the decomposition of the addition compounds, and also because they found that many unsaturated hydrocarbons, instead of forming these complexes, were oxidized and destroyed.

Some of the results of Brame and Hunter were as follows :—

Mixture employed		Amount of Mixture used ml.	Amount of mercuric Solution used ml.	Unsaturateds recovered by	Amylene recovered % on Total	Pentane recovered % on Total
% Amylene	% Pentane					
40	60	20	20	Distilling with HCl	31	80
33·3	66·7	30	50		20	100
33·3	66·7	30	50	Decomposing Hg. compounds with H_2S and distilling.	15	100

Hugel and Hibou[104] have described an analytical method in which the hydrocarbon mixture to be examined is treated with a solution of mercuric acetate in glacial acetic acid, whereupon the unsaturateds present dissolve to form complexes with the mercury salt, and the volume of the unabsorbed hydrocarbons is measured. The saturated hydrocarbons are not, however, completely insoluble in the acetic acid, and their solubility is increased by the solution in the acid of the unsaturated hydrocarbons, but this may be rendered negligible by the careful addition of water, in such quantities that the mercury complexes are not precipitated. The unsaturated hydrocarbons may be recovered from the complexes in the usual way, or the complexes may be pre-

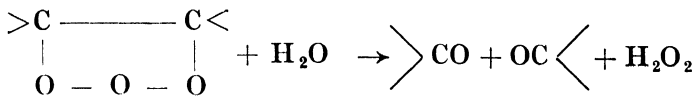
cipitated by the addition of water and the olefines regenerated therefrom by dissolving in ether.

Summarizing the use of mercuric salts for the estimation of unsaturated hydrocarbons, therefore, we may say that such a method is only applicable in certain special cases. The reaction is uncertain, oxidation takes place to a varying degree, depending upon the types of unsaturated hydrocarbons present, and certain hydrocarbons do not react at all. The reaction is not suited to general analytical use.

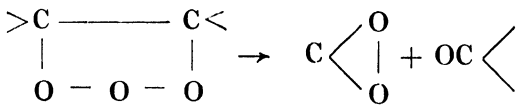
577. The Estimation of Unsaturated Hydrocarbons by means of Ozone. The unsaturated hydrocarbons are readily acted upon by ozone to form ozonides. These compounds are easily decomposed to form water soluble compounds. At first experimental difficulties rendered the production of the ozonides, even of the simple olefines, impossible for a long time (c.f., Schonbein[112] and Hautefeuille[113]), for the gaseous olefines explode at low temperatures in the presence of ozone, while pentene and hexene take fire. After many unsuccessful experiments, Harries and Hafner[114] succeeded in preparing the ozonides of propylene, amylene and hexene by diluting the hydrocarbon with a low boiling inert solvent. Ethylene ozonide was prepared in the same way by Harries and Koetschan.[115]

The true character of the reactions involved was first made clear by Harries, who showed that the initial products, which were viscous explosive substances, contain three atoms of oxygen for each double bond present in the original hydrocarbon. These ozonides can break down in two ways.

(a) By reaction with water to form hydrogen peroxide and ketones and aldehydes, accompanied by complete rupture of the double bond.



(b) By decomposition, on warming or in the presence of solvents such as absolute alcohol or glacial acetic acid, to give a true peroxide and an aldehyde or ketone.



The reaction of substances containing ethylene bonds with ozone is substantially a general reaction as, for instance, the addition of bromine. The ozonides of cyclic olefines are also easily prepared (c.f., cyclohexene-peroxide).[116]

In view of the ease with which unsaturated hydrocarbons react with

ozone, it is not surprising to find that methods for the quantitative estimation of the former have been based upon this reaction. Some of the first work on the treatment of petroleum distillates was done by Molinari and Cucini[117] and Molinari and Fenaroli.[118] The last named investigators obtained from a Russian kerosene fraction, B.P. 295—300°C., a yield of 32% of ozonides.

More recently, Danaila, Andrei and Melinescu[119] have described an analytical method which they claim to give accurate and reliable results for light oils containing less than 5% of unsaturated hydrocarbons. According to this method, oxygen is passed successively through a gas meter, a sulphuric acid wash bottle, a single element Siemens-Halske ozoniser and a wash bottle containing 35—40 ccs. of the oil and 30—40 ccs. of 30 per cent. aqueous caustic soda, cooled to −10°C. to −15°C. After the gas has passed through the oil for six hours, at a rate of 4—14 litres per hour, the mixture is distilled in steam and the distillate washed with caustic soda and sodium bisulphite solution and, finally, dried over sodium. The unsaturated hydrocarbons are then estimated by determining the loss to 98 per cent. sulphuric acid before and after such treatment.

The accuracy of the ozone method is doubtful because very little reliable date exists regarding the action of ozone on hydrocarbons other than the olefines. According to Bone and Drugman,[120] ethane is attacked by dilute ozone at a temperature of 100°C., the initial oxidation products being ethyl alcohol and acetaldehyde, while benzene forms a highly explosive triozonide, $C_6H_6O_9$. Tausz[121] reports that, in the presence of aromatics, the aliphatic hydrocarbons are attacked by ozone at ordinary temperatures. Naphthalene is also attacked by ozone.

578. The Estimation of Unsaturated Hydrocarbons by means of Perbonzoic Acid. Prileschaef[122] first observed that ethereal or chloroform solutions of benzoyl peroxide react with hydrocarbons containing double bonds to give addition compounds. The initial products readily decompose to give oxides of the original olefines, which compounds are, generally, very easily hydrolysed to glycols. Prileschaef's experiments were done on hydrocarbons of the terpene series and also on di-isobutylene and decylene.

At a later date, Nametkin and Brussof[123] found that the reaction was quantitative with perbenzoic acid in chloroform solution. The method adopted by Nametkin and Brussof has been examined by Nametkin and Abakumovsky,[124] who claim to be able to obtain consistent and accurate results. The procedure adopted was as follows :—

The spirit to be examined is mixed with more than twice the theoretical amount of perbenzoic acid in chloroform solution and the mixture allowed to stand in the dark at ordinary temperatures for 40—48 hours.

At the end of this time, a solution of potassium iodide and sulphuric acid is added and the liberated iodine is titrated with thiosulphate. By this method is obtained the " oxygen value " (O.V.) of the oil, corresponding to the " iodine value " (I.V.), which is defined as the quantity of active oxygen from the perbenzoic acid required for the ozidation of 100 grams of the oil. The ratios

$$\frac{100 \times (\text{O.V.})}{16} \quad \text{and} \quad \frac{100 \times (\text{I.V.})}{254}$$

then represent the same value, the " unsaturated coefficient."

As a method of quantitative analysis for the usaturated content of petroleum spirits, however, this method has nothing to commend it. It involves a tedious technique and the results obtained are only empirical.

579. The Estimation of Unsaturated Hydrocarbons by means of Thiocyanogen. In the chemical examination of fats and fatty acids, Kaufman[125] has used thiocyanogen for the estimation of unsaturation. The basic reagent used is "Rhôdan" solution, a solution of free thiocyanogen $(SCN)_2$ in glacial acetic acid and is prepared by the action of bromine on a solution of lead thiocyanate, thus

$$Pb(CNS)_2 + Br_2 = PbBr_2 + (CNS)_2.$$

An excess of lead thiocyanate and bromine is added to anhydrous acetic acid and the mixture is shaken until it loses its colour. The lead bromide and excess lead thiocyanate are then filtered off through a filter, giving a perfectly clear and colourless solution of thiocyanogen.

Thiocyanogen in solution behaves very much like the halogens; in fact, it is sometimes called a pseudo-halogen and, in reactivity, stands midway between bromine and iodine; it is freed from its salts by bromine, but it liberates iodine from iodides. It is immediately decomposed by water, the end products being HSCN, HCN and H_2SO_4, while, in most solvents, it polymerizes more or less rapidly, although Kaufman found that the tendency to polymerize was less in acetic acid solution than in other solvents. It is of the utmost importance, however, that all reagents and glassware used be absolutely dry, as traces of moisture greatly reduce the stability of the solution, and it is advisable to follow the special procedure of Kaufman and prepare a perfectly dry acetic acid by distilling glacial acetic acid over phosphorus pentoxide. Solutions prepared in this way lose less than 1 per cent. of their titration value during the first week after preparation.

The use of thiocyanogen for the estimation of unsaturated hydrocarbons and the nature of the reactions involved has been examined by Hugel and Krassilchik.[126] These investigators have found that sulphocyanide dissolved in glacial acetic acid gives only addition products

with hydrocarbons which easily form substitution products with bromine, e.g., the terpenes and the aromatic hydrocarbons and shows no traces of substitution reactions, even with concentrated solutions. Diolefines, such as isoprene, react with one molecule of sulpho-cyanide in the 1·4 position and the reaction then ceases. Hugel and Krassilchik also state that the reaction velocity curve follows the law of bimolecular reactions and the velocity constants are the same for all the members of any given series of hydrocarbons, e.g., the mono-olefines. There are other reaction coefficients depending upon the position of the double bond in the chain (e.g., octene −2), or in the ring (e.g., cyclohexene).

The value of this method of estimating the unsaturation of light mineral oils is doubtful, and it is difficult to see what advantages it possesses over the McIlhiney and Hanus bromine and iodine titration methods. The instability of the reagent used is a great disadvantage, as also is the fact that the method does not give theoretical results with diolefinic and acetylenic substances.[127] The use of thiocyanogen in the determination of the unsaturation of lard oils has recently been discussed by Zeleny and Bailey.[128]

580. The Estimation of Unsaturated Hydrocarbons by means of Sulphur Monochloride. Ethylene reacts with sulphur monochloride to yield mainly two types of compounds; mustard gas (dichloro diethyl sulphide) and dichloro diethyl disulphide. Lorand[129] has shown that sulphur monochloride reacts vigorously with unsaturated hydrocarbons and also, at a moderate rate, with saturated hydrocarbons, the reaction in the latter case probably being a chlorination. Meigs[130] has stated that the reaction, in the case of the saturated hydrocarbons, is a time reaction, since the evolution of hydrochloric acid gas continues for many hours; the unsaturated hydrocarbons react readily and are not responsible for the time element. This was the basis of the original method of estimating hydrocarbons, using this reagent, proposed by Lorand in 1927.

The chemical reactions involved in the case of paraffins are probably as follows:

$$\text{(i)}\quad \mathrm{R{-}CH_2{-}CH_2{-}} + \begin{matrix}\mathrm{S{-}}Cl\\ |\\ \mathrm{S{-}}Cl\end{matrix} \rightarrow \mathrm{H}Cl + \mathrm{S_2} + \mathrm{R{-}CH_2{-}CH}Cl.$$

$$\text{(ii)}\quad \begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{CH{-}CH_2{-}} \rightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{C{-}}Cl\mathrm{{-}CH_2{-}} \rightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{C{=}CH{-}}$$

and the resulting unsaturated hydrocarbons may react thus

$$\mathrm{{-}CH{=}CH{-}} \rightarrow \mathrm{{-}C{\equiv}C{-}} + 2\mathrm{H}Cl + \mathrm{S_2},$$

finally condensing and polymerizing.

In the analytical method proposed by Lorand, the oil to be examined is dissolved in carbon tetrachloride and refluxed with sulphur monochloride. After subsequent hydrolysis and washing, the oil is redistilled to its original end point and either the amount of residue or distillate is suggested as a comparative basis for the degree of unsaturation, since the condensation products have much higher boiling points than the original oil.

There is little published data available on the action of this reagent with hydrocarbons of other types. Anthracene has been reported[131] to react quantitatively under certain conditions, while, in the presence of aluminium chloride[132, 133] or an aluminium-mercury couple,[134] aromatics react to yield sulphides. On the other hand, sulphur monochloride has been used to purify commercial benzene by warming the mixture on the water bath for a long time,[135] and this suggests that there is little or no reaction with the benzene itself under these conditions.

Recently, however, Faragher, Morrell and Levine[78] have described a method of hydrocarbon analysis in which the possible objections of sulphur monochloride are claimed to have been overcome. According to this method, unsaturated and aromatic hydrocarbons are estimated together by treatment with sulphuric acid : the oil is also treated with sulphur monochloride to remove olefines and the olefine free oil is examined for aromatic hydrocarbon content by means of a nitration method (see paragraph 595, for complete details). The olefine and aromatic hydrocarbon contents are then calculated as follows :—

$$U = \frac{100\,(S - A')}{100 - A'}$$

$$\text{and } A = S - U$$

where U and A are the actual percentages of olefine and aromatic hydrocarbons, respectively, S is the sum of the olefine and aromatic hydrocarbons as determined by sulphuric acid treatment, and A′ is the aromatic content of the olefine free oil as determined by treatment with the nitration mixture.

The removal of unsaturated hydrocarbons by treatment with sulphur monochloride is carried out by Faragher, Morrell and Levine by allowing 30 ml. of the latter to be added, drop by drop, to 100 ml. of the oil to be examined, and allowing the mixture to stand overnight. The solution is then cooled by addition of ice and washed two or three times with 10 per cent. caustic soda and, finally, with water. The resulting oil, which does not smell of hydrochloric acid, is dried over calcium chloride and filtered. It is then distilled to 120—125°C. at atmospheric pressure, allowed to cool to 30°C., and, finally, distilled under reduced pressure until decomposition begins or until a fall in temperature occurs. The distillate obtained is claimed by Faragher, Morrell and Levine to

contain less than 1 per cent. of olefines, the exact quantity of which may be estimated by bromine titration.

581. Other Methods for the Determination of Unsaturated Hydrocarbons.

Aluminium Chloride.—The removal of unsaturateds from light oils by means of aluminium chloride has been used by Heusler.[136] Such a procedure is, however, of little value, because, in the condensation and polymerization reactions which occur, new hydrocarbons of various types, including naphthenes and paraffins, are formed.

582. Hydrogen Peroxide.—Tausz[107] attempted to use hydrogen peroxide for the selective oxidation of unsaturated hydrocarbons, according to the method of Cross, Bevan and Heiberg, in which the hydrocarbon mixture is warmed with 3 per cent. hydrogen peroxide in the presence of ferrous sulphate. Tauz found that pentene, hexene, heptene, cyclohexene and methyl cyclohexene were easily oxidized in a vigorous reaction, but that aromatic hydrocarbons were also attacked.

583. Nitric Acid.—Heusler also tried to use this reagent for the estimation of unsaturateds, but was unable to perfect a method. Nitric acid is far too vigorous in its action for the selective removal of olefines because it attacks hydrocarbons of other series. Thus, Garner[137] claims that fuming nitric acid reacts completely with aromatic hydrocarbons at temperatures as low as −10°C. to −15°C. Manning[138] has described a method for the estimation of both unsaturated and aromatic hydrocarbons, in which a mixture of 10 per cent. of nitric acid (sp. gr., 1·4) in 98 per cent. sulphuric acid is used. Both unsaturated and aromatic hydrocarbons are said to be absorbed quantitatively (see paragraph 595).

584. Potassium Permanganate.—Heusler[139] attempted to remove the unsaturated hydrocarbons from brown coal tar by the action of acidic permanganate, but found that this reagent only effected a smaller removal of unsaturated hydrocarbons than did 1 : 3 dilute sulphuric acid. The reaction involved is mainly an oxidation, in which the oxidation products are glycols, acids, aldehydes and ketones, but Markownikoff and Oglobin[140] obtained, by the slow oxidation of a crude oil fraction, B.P. 185—190°C., a saturated hydrocarbon of B.P. above 340°C. This reaction is reminiscent of the action of potassium persulphate on aromatic hydrocarbons, which, although normally proceeding in such a way that alkyl groups are converted into carboxyl or aldehyde groups, sometimes eliminates hydrogen from alkyl groups, whereupon two molecules of the hydrocarbon become condensed. In this way, Moritz and Wolffenstein[141] obtained dibenzyl from toluene.

Benzene and toluene are stated by Norton[142] to be stable to alkaline permanganate at ordinary temperatures but, on the other hand, Howes and Nash[143] found that both these hydrocarbons were appreciably attacked at a temperature of 14—15°C. Under similar conditions, the xylenes are also attacked,[144] particularly ortho xylene. With regard to the action of permanganate on fully saturated hydrocarbons, Meyer and Saam[145] found that methane and ethane are attacked by this reagent, whereas propane is very stable. On the other hand, Zelinsky and Zelikow[146] state that 2-ethyl butane, which contains a tertiary carbon atom, decolourizes a 1% permanganate solution instantly, whereas, according to Morgan, Carter and Duck,[147] 3·3-diethyl pentane (tetra-ethyl methane) is not attacked. Kishner[148] found that although 2·6 dimethyl octane itself was quite stable towards permanganate, when in the presence of unsaturated hydrocarbons it was readily oxidized, while, in investigating the action of permanganate on 2-butyl hexane, Levene and Cretcher[149] found that this hydrocarbon is slowly oxidized to butyric acid, even at 25°C.

A few attempts have been made to use potassium permanganate as a reagent for use in the estimation of unsaturated hydrocarbons. Colman[150] found, however, that the absorption of oxygen varied for the same spirit, according to variations in the excess of permanganate used, time of reaction, amount of agitation and other factors.

Howes and Nash[143] also attempted to use permanganate in this way, but found that the rate of oxidation of the higher boiling unsaturated hydrocarbons was very slow, while at temperatures above −10°C., aromatic hydrocarbons were attacked. These investigators found, however, that the low boiling unsaturateds, such as trimethyl ethylene and cyclohexene were readily and completely oxidized.

585. Liquid Nitric Oxide.——Smirnov[151] has described a method for the estimation of unsaturated hydrocarbons which makes use of liquid nitric oxide at a temperature of −15°C. to −20°C. After treatment with this reagent, the oil is made alkaline and distilled in steam. The distillate, after separation, is dried and filtered through silica gel, which is washed with ether. After centrifuging, the ether is removed by distillation. The difference between the volumes of the original and treated oil represents the unsaturated content.

586. The Estimation of Aromatic Hydrocarbons.—As already pointed out, the hydrocarbon analysis of light oils and motor fuels is usually carried out by, first of all, estimating and removing the unsaturated hydrocarbons, which are the most active constituents, and then examining the olefine free oil for aromatics and other hydrocarbons. The following methods of estimating aromatic hydrocarbons are, there-

fore, only applicable for use with oils not containing unsaturateds. Special methods for the estimation of aromatic and unsaturated hydrocarbons together as one class are dealt with separately.

The estimation of aromatic hydrocarbons has been carried out by the following methods.

1. By specific gravity and refractive index measurements.
2. By treatment with concentrated sulphuric acid.
3. By means of critical solution temperature (C.S.T.) measurements in various solvents.
4. By treatment with nitric acid and other nitrating agents.
5. By means of solvents and other methods.

587. Methods based on Specific Gravity and Refractive Index Measurements.—Such procedures are based on the fact that, of the four main classes of hydrocarbons, the aromatics possess the highest specific gravities and refractive indices. Consequently, the removal of aromatic hydrocarbons from an oil causes a reduction in both these properties, and, if the relation between aromatic hydrocarbon content and either of these properties is known, then an analytical method can be devised.

Thole[152] has proposed such a method, based on specific gravity measurements, in which the oil to be examined is divided into three portions, (*a*) 40°—95°C., (*b*) 95°—122°C., and (*c*) 122°—150°C., it being assumed that these three fractions contain all the benzene, toluene and xylenes, respectively. These fractions are separately sulphonated (see later) and the differences in specific gravities of the fractions, before and after sulphonation and removal of the aromatics, are used for the calculation of the aromatic content. The formulæ used for the calculation of aromatic content are, usually, as follows :—

$$(i)\ \text{Percentage of aromatics by weight} = \frac{100\mathrm{D}\,(d_1 - d_2)}{(\mathrm{D} - d_2)d_1}$$

$$(ii)\ \text{Percentage of aromatics by volume} = \frac{100\,(d_1 - d_2)}{\mathrm{D} - d_2}$$

in which

D = specific gravity of aromatics only,
d_1 = specific gravity of oil under test,
d_2 = specific gravity of oil after removal of aromatics,

but these formulæ are only approximate, because, in the process of mixing aromatic with non-aromatic hydrocarbons, a certain increase in volume always takes place. To compensate for this, Thole has advised the

addition of the following corrections to the percentages of aromatics, calculated from formula (*ii*) above.

TABLE 117.

Calculated % Benzene by Volume	Correction to be added % by Volume	Calculated % Toluene by Volume	Correction to be added % by Volume
5	0·3	5	0·2
10	0·6	10	0·4
15	0·8	15	0·6
20	1·0	20	0·7
25	1·2	25	0·9
30	1·3	30	1·0

It has been pointed out by Tilitsheyew and Dumskaya,[153] however, that the corrections to be applied are dependent upon the composition of the non-aromatic portion, since, in mixing aromatic with paraffinic hydrocarbons, the corrections assume their minimum values, whereas, in mixing aromatics with naphthene hydrocarbons, the corrections reach maximum values. Thus, when mixing together equal weights of benzene and hexane, the correction is $\pm$ 1·75 per cent., but, in mixing equal weights of benzene and cyclohexane, the correction is as much as $\pm$ 5·35 per cent.

Consequently, the only correct procedure by which aromatic hydrocarbons may be estimated in this way is to determine, by means of synthetic mixtures, the functional relationship between the specific gravity of the non-aromatic portion and the value of the correction. Tilitsheyew and Dumskaya (loc. cit.) have published such figures, and their original paper should be consulted for further details. These investigators state that, for oil fractions of boiling point below 150°C., the above specific gravity method gives greater accuracy than that based on refractive index measurements and is very little inferior in accuracy to the aniline or nitro-benzene critical solution temperature methods (see later).

The use of refractive index measurements for the determination of aromatic hydrocarbons in light oils has been proposed by Hoyte.[154] According to this method, the oil under test is freed from aromatics by means of sulphuric acid and a 50/50 benzene-toluene mixture added to the residual spirit until the initial refractive index is restored. This added amount is then taken to be equal to the original aromatic content of the spirit. This method, however, is only capable of giving approximate results, because the elevation of refractive index by a given concentration of aromatics is dependent upon the refractive index of the non-aromatic portion[153] (c.f., the specific gravity method). If suitable corrections for this effect are employed, the refractive index method of

estimating aromatics is claimed by Tilitsheyew and Dumskaya to give accurate results.

An interesting and valuable contribution to our knowledge on the determination of hydrocarbon oil composition, particularly in the case of oils having molecular weights above 200, has recently been made by Vlughter, Waterman and van Westen.[155] These workers have developed a method of determining the composition of oils based upon Lorentz specific refraction $\left(\frac{N^2 - 1}{N^2 - 2}\right)\frac{1}{d}$ and aniline point measurements.

The original paper should be consulted for further details.

588. Methods Based on the Measurement of other Physical Properties, Magnetic Rotary Power and Specific Inductive Power.—Javelle[156] has measured the magnetic rotary powers of various hydrocarbons and has shown that different classes of hydrocarbons have different values, e.g., benzene 3·38, heptane 1·51, cyclohexane 1·47, cyclohexene 1·747. Individual members of the same hydrocarbon series also exhibit small variations. Javelle also observed that, in the case of binary mixtures of hydrocarbons, the values for the magnetic rotary power are linear functions of the compositions of the mixtures. Such measurements may, therefore, form the basis of an analytical method.

With a view to the possible application of the determination of specific inductive power to the identification and analysis of hydrocarbons, Touissant[157] has devised a method for such measurements, based on the electrometric determination of the capacity of a given condenser with air as the dielectric, and then with the liquid under investigation as the dielectric. The following values were obtained at 23°C. :—benzene 2·275, heptane 1·978, hexane 1·884, cyclohexane 2·026. A study of the variation of the specific inductive power of mixtures of hydrocarbons as a function of their compositions showed, however, that this variation is not a linear function.

589. The Estimation of Aromatic Hydrocarbons by the use of Concentrated Sulphuric Acid.—Concentrated sulphuric acid (98-100%) has been used for a long time for the determination of aromatic hydrocarbons.[158, 159, 160] In this case, the reaction involved is a sulphonation, the chemistry of which has been fully described by Wieland and Sakellarios.[161] The aromatic sulphonic acids so formed are soluble in the sulphuric acid and are eliminated therein, while the concentration of aromatics is determined by a measurement of the loss of volume sustained, by the measurement of the excess acid by titration,[162] by the conversion of the sulphonic acids in the acid sludge to

barium sulphonates and the precipitation of barium sulphate, or by the use of aniline points (see paragraph 590).

As in the estimation of unsaturated hydrocarbons by the use of sulphuric acid, much controversy exists regarding the most suitable strength of sulphuric acid to employ for the determination of aromatics. In this case, the controversy concerns the strength of acid necessary to remove the aromatic hydrocarbons completely, but be without action on saturated hydrocarbons. The general opinion[71] is that 100% sulphuric acid is the strongest that can possibly be used for this purpose, free SO_3 having a pronounced action upon straight chain and cyclic saturated hydrocarbons. On the other hand, Sentke[163] states that normal octane is attacked by concentrated sulphuric acid at ordinary temperatures. This statement, however, has not been confirmed.

Krieger[164] found it necessary to use sulphuric acid containing 8 per cent. of excess SO_3 to extract the aromatics from a kerosene and, later, Pritzker and Jungkung[165] used an acid containing 4 per cent. excess anhydride, and made use of a centrifuge to accelerate the settling out of the oil and acid into two layers after agitation. Similarly, Manning[138] found that 100 per cent. sulphuric acid failed to absorb benzene and toluene completely from light spirits, but also observed that, although acid containing 5 per cent. excess SO_3 effected complete removal, it also attacked saturated hydrocarbons. Manning recommends the use of 98 per cent. sulphuric acid containing 2 to 3 per cent. of silver sulphate, which he claims to give theoretical results in aromatic estimations but be without action on saturated hydrocarbons. In this case, silver sulphate acts as a sulphonation catalyst. Kattwinkel[166] has demonstrated that the action of sulphuric acid upon aromatic hydrocarbons may be catalysed by the presence of phosphorus pentoxide, and claims that, by the use of this compound, 98 per cent. sulphuric acid can be made to remove aromatics, even in concentrations up to 40 per cent. The method of Kattwinkel has since been recommended by Winkler.[167]

The use of 100 per cent. sulphuric acid for the determination of aromatics is advocated by Riesenfeld and Bandte,[167A] but these investigators have pointed out that, at temperatures of 40°C., paraffins containing tertiary carbon atoms are appreciably attacked by this strength of acid, so that it is essential to work at ordinary room temperatures. Faragher, Morrell and Levine[78] quote results, however, to show that treatment with 3 volumes of 98 per cent. sulphuric acid gives good results on synthetic mixtures containing benzene, toluene and xylene, for the determination of aromatic hydrocarbons. The standard method adopted by the Institution of Petroleum Technologists[168] consists of treating the oil to be examined with twice its volume of 98 $\pm$ 1 per cent. sulphuric acid for fifteen minutes, preferably in a

mechanical shaker. The acid layer is then withdrawn and the acid treatment repeated for two further periods of 15 minutes each, using in each of these cases one volume of acid. The aromatic hydrocarbon content is determined by measuring the difference in "aniline point" of the spirit before and after such treatment (see later).

Appreciable errors can also arise from the solubility of saturated hydrocarbons in the acid solution of the sulphonated aromatic compound. To illustrate these facts, the following experimental results of Manning and Shepherd[169] may be quoted: A mixture of benzene and aromatic-free petroleum ether, containing 20 per cent. of benzene, was shaken for half an hour with two volumes of 98 per cent. sulphuric acid. The loss in volume was 17 per cent., but the residual oil, on analysis, was found to contain 6·5 per cent. of benzene. The acid liquor, therefore, had dissolved 3·5 per cent. of the petroleum ether. On shaking the same mixture for half an hour with three volumes of 98 per cent. acid, the loss in volume was 20 per cent., but the residual oil still contained 3-4 per cent. of benzene.

590. The Applications of Critical Solution Temperatures to Hydrocarbon Analysis.—It was Chavanne and Simon[170] who first observed that the presence of aromatic hydrocarbons decreased the critical solution temperature (C.S.T.) of a hydrocarbon mixture with aniline, and, moreover, that the C.S.T. depression was proportional to the weight of aromatics present. Chavanne and Simon also observed that, of the four main classes of hydrocarbons, the paraffins have the highest critical solution temperature in aniline and aromatics the lowest, naphthenes and olefines occupying intermediate positions. As a result of these observations, Chavanne and Simon suggested the determination of C.S.T.'s in aniline for the estimation of aromatics in hydrocarbon mixtures, and also suggested a similar method for the determination of naphthenes in mixtures of saturated hydrocarbons.

Tizard and Marshall[160] later placed this new method of analysis on a sound experimental basis and, in the course of their work, they dispensed with the somewhat elaborate and time-consuming critical solution temperature measurements of Chavanne and Simon and used instead measurements of "Aniline Points," which may be defined as the temperatures at which equal volumes of hydrocarbon mixture and aniline are just completely miscible. By this modification the method lost none of its accuracy for aromatic concentrations up to 20 per cent. Tizard and Marshall found that benzene, toluene and ortho-xylene, in equal proportions by weight, produced identical depressions of aniline point within the limits of experimental error, but that meta and para xylenes lowered aniline points rather less than the same weight of benzene or toluene. As an analytical procedure, Tizard and Marshall

proposed that the difference in aniline points of a spirit before and after sulphonation with 98-100 per cent. sulphuric acid should be used as a basis for the determination of aromatic content, the following conversion factors being employed in the equation :

$$A = \alpha (T - T_1)$$

Where A = % aromatic hydrocarbons by weight
α = constant
T = aniline point after removal of aromatics
T_1 = aniline point before removal of aromatics.

	α
Benzene	1·19
Toluene	1·20
Xylenes	1·23

For a spirit containing all three aromatics in admixture, the figure 1·2 was suggested as a satisfactorily accurate mean value. Unfortunately, the value of α in the above equation is not truly constant, but depends upon a number of factors, the most important of which are :

(i) The nature of the aromatic hydrocarbons concerned.
(ii) The concentration of the aromatic hydrocarbons.
(iii) The nature of the non-aromatic hydrocarbon fraction.

Tarassof and Azerbaidz[171] found, for instance, that the value of the coefficient α in the above equation was twice as great for the high boiling point aromatic hydrocarbons found in turpentine spirit as for toluene. Tilitsheyew and Dumskaya[153] have reported similar, but much smaller variations in the value of α, but lay greater stress upon the variation of α with changes of the nature of the non-aromatic portion of the oil, first pointed out by Chavanne and Simon.[170]

It will therefore be obvious that in order to obtain accurate results in aromatic determinations by the aniline point method, the value of the coefficient α must be accurately known. Only approximate results will be obtained if mean values for α are applied. If the aromatic content of the spirit to be examined is more than 20 per cent. by weight, the spirit should be diluted with an aromatic free petroleum ether, to bring the aromatic content of the mixture down to 20 per cent. before it is examined by this method, otherwise the results obtained will be too high. Care must also be exercised in the choice of aniline for these determinations. In particular, the aniline must be perfectly dry as, according to Ormandy and Craven[172] the presence of 1 per cent. of water raises the aniline point of *n*-heptane by 6·2°C., and that of cyclohexane by 5·6°C. It is advisable to use an " A.R." or " C.P." grade

aniline for all such determinations ; this should be allowed to stand over potassium carbonate for 24 hours and then filtered. It should then be redistilled and only the fraction B.P. 181-182°C. collected. This should be stored in a dark glass bottle fitted with a ground glass stopper. Only freshly distilled aniline should be used. It is also usual to standardise each batch of aniline used, by determining its miscibility temperature with an equal volume of a pure hydrocarbon. Normal heptane is the hydrocarbon normally used for this purpose, because it may easily be obtained 99·9 per cent. pure from Pinus Sabiniana oil.[173, 111] The aniline point of pure *n*-heptane is 68°C.,[172] when perfectly dry aniline is used. Because of the fact that aniline is hygroscopic and, therefore, kept absolutely dry only with difficulty, an aniline point of 70°C. for *n*-heptane is sometimes taken as standard. This, however, is not sufficiently accurate for important work.

591. The aniline points of pure hydrocarbons are shown in Table 118, and it will be observed that, in general :

(1) The aniline points of *n*-paraffins increase with rise in molecular weight. (This, however, is not true in the case of *n*-pentane and *n*-hexane, although the relationship appears to hold with the higher hydrocarbons).

(2) The aniline points of iso-paraffins are higher than those of the corresponding normal paraffins. (This appears to be universally true except in the case of 3-ethyl pentane, which has a lower aniline point (66·3°C.) than *n*-heptane (68°C.))

(3) The aniline points of naphthenic hydrocarbons are lower than those of the paraffins. They are very irregular and range from about 20°C. to 60°C., for those hydrocarbons of the petrol boiling range (20-200°C.).

(4) The aniline points of the α-olefines are considerably lower than those of the corresponding paraffins and rise regularly with increase in boiling point.

TABLE 118.—ANILINE POINTS OF PURE HYDROCARBONS

PARAFFINS.					
Pentanes —				*Heptanes* —	
n-Pentane	72°C.	(*a*)	*n*-Heptane	68°C.	(*c*)
2-Methyl butane	77°C.	(*b*)		70°C. and 71°C.	(*d*) and (*a*) (*c*)
Hexanes —					
n-Hexane	69°C.	(*a*)	2-Methyl hexane	72·8°C. and 74·1°C.	(*a*) and (*e*) (*d*)
2-Methyl pentane	73·8°C.	(*a*)			
	74·7°C.	(*b*)			
3-Methyl pentane	69·4°C.	(*b*)	3-Methyl hexane	70·5°C. and	(*d*) (*e*)
2·2 Dimethyl butane	80·75°C.	(*b*)			
2·3 Dimethyl butane	72·3°C.	(*b*)	3-Ethyl pentane	66·3°C.	(*d*)

PARAFFINS.

Heptanes —		
2·2 Dimethyl pentane	77·7°C.	(*d*)
2·3 Dimethyl pentane	68·1°C.	(*d*) and (*e*)
2·4 Dimethyl pentane	78·8°C.	(*d*)
3·3 Dimethyl pentane	71·0°C.	(*d*)
2·2·3 Trimethyl butane	72·4°C.	(*d*)
Octanes —		
n-Octane	72·0°C.	(*a*)
2-Methyl heptane	74·0°C.	(*a*)
n-Nonane	74·5°C.	(*e*)
n-Decane	77·5°C.	(*e*)
n-Undecane	77·78°C.	(*f*)

NAPHTHENES.

Cyclo Pentanes —		
Cyclo pentane	18°C.	(*a*)
	16·8°C.	(*k*)
Methyl cyclopentane	33·0°C.	(*k*)
	35·0°C.	(*a*)
Ethyl cyclopentane	36·7°C.	(*k*)
	39·0°C.	(*g*)
1·3 Dimethyl cyclopentane	45·0°C.	(*a*)
	46·4°C.	(*k*)
n-Propyl cyclopentane	44·5°C.	(*k*)
	45·0°C.	(*g*)
1·2·3 Trimethyl cyclopentane	41·0°C.	(*e*)
n-Butyl cyclopentane		(*g*)
	48·7°C.	(*k*)
Cyclohexanes —		
Cyclohexane	31°C.	(*a*)
	30·2°C.	(*k*)
Methyl cyclohexane	41°C.	(*a*)
	39·5°C.	(*k*)
Ethyl cyclohexane	43·8°C.	(*k*)
1·2 Dimethyl cyclohexane	42·1°C.	(*a*)
	48·3°C.	(*k*)
1·3 Dimethyl cyclohexane	49·7°C.	(*a*)
	47·8°C.	(*k*)
1·4 Dimethyl cyclohexane	48·0°C.	(*a*)
	47·8°C.	(*k*)
1·3·5 Trimethyl cyclohexane	56-57°C.	(*m*)
n-Propyl cyclohexane	49·8°C.	(*k*)
1·2·4 Trimethyl cyclohexane	53·6°C.	(*e*)
n-Butyl cyclohexane	54·4°C.	(*k*)
1-Methyl 4-isopropyl cyclohexane	56·5°C.	(*k*)
Hexa-Methyl cyclohexane	65-66°C.	(*m*)

BICYCLIC NAPHTHENES.

Decahydronaphthalene	34°C.	(*e*)
Tetrahydronaphthalene	Below −20°C.	(*e*)
Cyclohexyl-cyclohexane	12°C.	(*e*)
Methyl cyclohexyl-cyclohexane	15°C.	(*e*)

CYCLIC OLEFINES.

Cyclopentene	Below −10°C.	(*k*)
Methyl cyclopentene	−7·0°C.	(*k*)
Ethyl cyclopentene	+1·2°C.	(*k*)
n-Propyl cyclopentene	+14·2°C.	(*k*)
n-Butyl cyclopentene	+25·0°C.	(*k*)
Cyclohexene	−20°C.	(*a*)

OLEFINES.—

Pentene-1	19·3°C.	(*l*)
Hexene-1	22·9°C.	(*l*)
Heptene-1	26·6°C.	(*l*)
Octene-1	32·8°C.	(*l*)
Nonene-1	38·6°C.	(*l*)
Isohexene	24°C.	(*e*)
Heptene	36°C.	(*e*)
Hexene	17°C.	(*e*)
Pentene-2	18°C.	(*e*)
Trimethyl ethylene	11°C. (*j*), 10°C.	(*e*)
Octene	26·5°C.	(*e*)
Cetene	68°C.	(*e*)

(*a*) Chavanne and Simon, Compt. rend., **1919, 168, 111, 1,324.**
(*b*) Chavanne, Bull. Soc. Chim. Belg., 1922, **31**, 331.
(*c*) Ormandy and Craven, J. Inst. Petr. Techn., 1926, **12**, 89.
(*d*) Edgar, Calingaert and Marker, J.A.C.S., 1929, **51**, 1,483.
(*e*) Garner, J. Inst. Petr. Techn., 1928, **14**, 713.
(*f*) Carpenter, J. Inst. Petr. Techn., 1926, **12**, 562.
(*g*) Chavanne, Bull. Acad. roy. Belg., 1926, (5), **12**, 105.
(*h*) Chavanne and Becker, Bull. Soc. Chim., 1927, **36**, 591.
(*i*) Konowalow, Ann. Phys., 1903, (4), 375.
(*j*) Brame, J. Inst. Petr. Techn., 1927, **13**, 794.
(*k*) Garner and Evans, J. Inst. Petr. Techn., 1932, **18**, 751.
(*l*) Wilkinson, J.C.S., 1931, 3,057–62.
(*m*) A. Dros, A. J. Tulleners and H. I. Waterman, J. Inst. Petr. Techn., 1933, **19**, 784.

592 Aniline points have also been used as the basis of methods for estimating the naphthene hydrocarbon content of naphthene-paraffin mixtures.[170] Thus, Ormandy and Craven[174] have described a procedure in which the naphthene concentration is given by the expression.

$$N = \frac{70 - T}{0{\cdot}3}$$

where N = % naphthenes,
T = aniline point of spirit after removal of aromatics and unsaturateds.

In this method it is assumed

(*i*) That all paraffin hydrocarbons (of whatever type) have an aniline point of 70°C.

(*ii*) That all naphthenes, whether of five or six ring structure, lower the aniline points of paraffins with which they are mixed by 0·3°C. per 1 per cent.

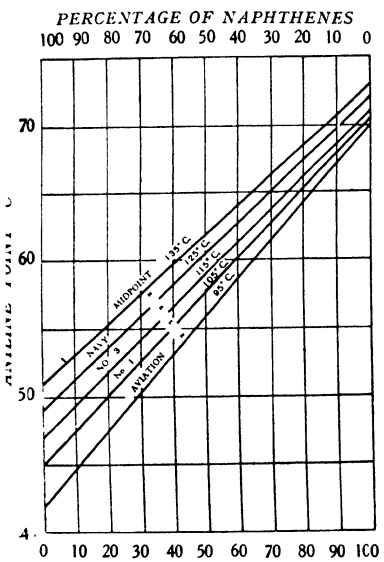


FIG. 147.—GRAPHS SHOWING ANILINE POINTS OF NAPHTHENE-PARAFFIN HYDROCARBON MIXTURES. (GARNER.)
(Courtesy of the Institution of Petroleum Technologists.)

But these assumptions are so far reaching and so far removed from the actual truth that the method gives but very approximate results. This opinion is shared by Schaarschmidt, Hofmeier and Leist,[175] who state that the method only gives accurate results in the case of simple binary mixtures of one paraffin and one naphthene, and that, in the case of complex mixtures of a number of different hydrocarbons, only roughly approximate results are obtained.

An attempt has been made by Garner[137] to overcome the objections against the above procedure, who has characterised petrols by their mid-points, i.e., temperatures at which 50 per cent. is distilled, and proposed a different relationship between aniline point and per cent. naphthenes for different mid-points (See Fig. 147).

Such a method as this, of course, must involve various assumptions, but it is reasonable to suppose that it gives more accurate results than the older method of Ormandy and Craven (loc. cit.).

593. It will be observed that all the foregoing methods of analysis, based on aniline point determinations, depend for their accuracy

upon the efficiency with which aromatic hydrocarbons may be removed from hydrocarbon mixtures. Obviously, in the determination of aromatics, if these are not completely removed, the figure obtained for the aromatic content will be too low and the figure obtained for the naphthenes will be too high. To overcome this difficulty, Aubrée[176] has developed a method for the estimation of aromatic hydrocarbons based upon critical solution temperature measurements in which the removal of these hydrocarbons by chemical means is rendered unnecessary.

If T = C.S.T. of original spirit,
T' = C.S.T. of spirit after removal of aromatics,
θn = C.S.T. of naphthenes,
θp = C.S.T. of paraffins,
A = % aromatics,
N = % naphthenes,
and P = % paraffins,
then $A = K(T' - T)$

$$\text{and } N = \frac{\theta p - T'(100 - A)}{\theta p - \theta n}$$

$$\text{or } \frac{N(\theta p - \theta n)}{100 - A} = \theta p - \frac{A}{K} + T,$$

an equation in which T^1 does not occur.

If a second solvent is now used, therefore, and the corresponding values for K', $\theta' p$ and $\theta' n$ obtained in a second equation, then, from the two equations, the two unknowns A and N can be calculated. As a second solvent, Aubrée has suggested benzyl alcohol.

Aromatics are soluble in all proportions in benzyl alcohol, as in aniline, at ordinary temperatures, while the C.S.T.'s of other hydrocarbons are lower in benzyl alcohol than in aniline. For the two saturated series of hydrocarbons, however, the variation in C.S.T., from one member to another of the same series, is more accentuated than in the case of aniline, and this fact makes the use of benzyl alcohol not well adapted to approximate analyses of petrols, but only to the precise analysis of narrow cuts separated by careful fractionation.

In view of the fact that unsaturated hydrocarbons also have very low aniline points, almost as low as those of the aromatics, the presence of these bodies will materially affect the accuracy of any results obtained in the determination of the latter. It is, therefore, necessary to remove olefines completely before an estimation of aromatics, by means of aniline points, is attempted. According to Garner,[137] a given weight of unsaturateds will depress the aniline point of a hydrocarbon mixture to two-fifths the extent of that caused by the same weight of aromatics.

594. Critical solution temperatures in nitro-benzene.— A method has been described by Erskine[177] for the determination of aromatic hydrocarbons in which C.S.T.'s are determined in nitro-benzene instead of in aniline. In this case, the miscibility temperatures are much lower and, as shown in the following table, decrease with rise in molecular weight of the paraffin hydrocarbon, whereas with aniline they increase.

TABLE 119.—CRITICAL SOLUTION TEMPERATURES OF PARAFFIN HYDROCARBONS IN NITRO-BENZENE

	C.S.T. °C.
n-Pentane	24·5
Iso-Pentane	31·25
n-Hexane	14·8
Iso-Hexane	24·05
n-Heptane	11·5
Iso-Heptane	18·05

Erskine claims that the use of nitro-benzene offers advantages over the use of aniline in this way, in that (*a*) a given percentage of aromatics gives a greater depression of C.S.T., and (*b*) the lower C.S.T.'s enable evaporation losses to be very much reduced.

According to Erskine, the values of the coefficient α, in the equation :

$$A = \alpha (T - T^1)$$

are, with nitro-benzene as the solvent,

Benzene	0·845
Toluene	0·890
Xylene	0·938

but Dobryanskii and Khesin[178] state that the value of the coefficient increases rapidly with increase in concentration of the aromatics, i.e., from 0·75 at 1·5 per cent. aromatics to 1·08 at 14 per cent. of aromatics. The nitro-benzene method of estimating aromatic hydrocarbons has been critically examined by Tilitsheyew and Dumskaya,[153] who state that it has many undoubted advantages over the more common aniline method.

595. The Estimation of Aromatic Hydrocarbons by Methods involving Nitration.—Owing to the ease with which aromatic hydro-

carbons may be nitrated, it is not surprising to find that many methods for the estimation of aromatic hydrocarbons make use of this reaction.

In one method,[179] fuming nitric acid has been used and the nitrated products dissolved in a known volume of sulphuric acid, the content of aromatic hydrocarbons being calculated from the increase in volume of the acid layer. This method is, however, not accurate, as a change in total volume occurs when nitro-aromatic compounds are dissolved in sulphuric acid, and each nitrated hydrocarbon not only gives a different volume change but also a different volume of nitrated products. For similar reasons, methods in which the nitro-compounds are removed and weighed are also inaccurate.[180, 181]

The method of Hess[182] does not possess these inherent faults and is more reliable. The aromatic hydrocarbons are nitrated in a vessel with a narrow graduated neck and the resulting nitro-bodies are then dissolved in sulphuric acid (95%), added in such quantity that the unchanged oil appears in the graduated portion, where its volume can be read.

A unique method is that of Egloff and Morrell,[65] in which a nitration mixture, consisting of nitric acid 25 per cent. sulphuric acid 58 per cent. and water 17 per cent. is used. This mixture does not dissolve the resulting nitro-compounds and they separate as a distinct layer, the volume of which is proportional to the amount of aromatic hydrocarbons originally present. This method suffers from the disadvantage that the volume of nitro-compounds formed varies with the particular aromatic hydrocarbons reacting, as shown in the following table.[78]

TABLE 120.

	Volume of Nitro Layer.		
	12% Solution ml.	20% Solution ml.	30% Solution ml.
Benzene ..	0·90	4·41	6·44
Toluene ..	1·06	4·45	7·86
Xylene ..	2·55	5·44	8·78
Cymene ..	1·55	3·93	—

Moreover, for low aromatic concentrations the method gives low results, due to the solubility of the nitro-compounds in the oil, and for high aromatic concentrations it gives high results, due to the solubility of the non-aromatic oil in the nitro-compounds.[167A] To compensate for these defects, Faragher, Morrell and Levine[78] have developed five equations for use with oils containing from 8 to 80 per cent. of aromatics, which they claim to give substantially accurate results.

(1) A = 2·609V + 7·8 .. .. 8-20% aromatics.
(2) A = 2·806V + 6·95 .. .. 20-30% ,,
(3) A = 3·2V + 3·8 .. .. 30-40% ,,
(4) A = 2·888V + 7·0 .. .. 40-70% ,,
(5) A = 2·3V + 19·8 .. .. 70-76% ,,

In which

A = volume of aromatics.
V = volume of nitro compounds.

Fuming nitric acid at a temperature of − 10° to − 15°C., is used by Garner[137] in a method in which aromatic and unsaturated hydrocarbons are estimated together as one class. The petrol to be examined is shaken with fuming nitric acid at the above temperature and the nitro-bodies which dissolve in the residual petrol are washed out by means of more fuming nitric acid. From the difference in aniline points of the petrol before and after such treatment is obtained the "aromatic hydrocarbon equivalent," i.e., aromatics and olefines together calculated as aromatics on the aniline point basis. From this figure is obtained the aromatic hydrocarbon content by subtracting from it the olefine content, determined by other means, assuming that unsaturated hydrocarbons depress aniline points to an extent two-fifths that due to the aromatics.

Then if A = % aromatics,
B = % unsaturateds,
a = aromatic equivalent,

$$A + \frac{2}{5} B = a$$

and $A + B = b$ = loss to nitric acid,

$$\text{or } B = \frac{5}{3}(b - a) \text{ and } A = b - B.$$

Aromatic and unsaturated hydrocarbons are also estimated together as one class in a method involving nitration devised by Manning[138] and later described by Manning and Shepherd.[169] This method is especially suitable for use when only small quantities of oil are available for test, as a small sample of oil is vapourised by drawing through it a stream of air or nitrogen and the vapours passed through absorbing reagents contained in small "potash" bulbs. For the estimation of aromatic and unsaturated hydrocarbons, a nitrating mixture is used, consisting of a mixture of 10 per cent. nitric acid (sp. gr. 1·4) or, preferably, 16 per cent. of potassium nitrate in 98 per cent. sulphuric acid. The petrol or hydrocarbon mixture vapour is slowly passed through this in a current of air and the increase in the weight of the bulbs represents

the amount of unsaturated and aromatic hydrocarbons absorbed. A small correction is necessary for the retention of a small amount of saturated hydrocarbons. To determine the aromatic hydrocarbons separately, they are then isolated in the form of their nitro derivatives. The solution in the acid mixture is heated for 2-3 hours on a boiling water bath in order to complete the nitration of the aromatics and the oxidation of the unsaturateds. After cooling, the acid solution is poured into excess of water and the nitro compounds are extracted with three portions of benzene. The benzene solution is then extracted with dilute caustic soda solution, washed with water, evaporated to dryness and weighed after thoroughly drying. The aromatic hydrocarbon content is calculated from the weight of the nitro compounds, obtained by the use of conversion factors. Under the experimental conditions employed, the unsaturated hydrocarbons are oxidised almost completely to carbon dioxide, water and products soluble in water or caustic soda. However, the value obtained for the aromatic content is always slightly high owing to contamination of the nitro compounds with products from the unsaturated hydrocarbons and the error due to this may amount to one unit on the percentage for every 20 per cent. of unsaturated hydrocarbons present. This method is not recommended for use with oils containing large amounts of unsaturated hydrocarbons.

596. The Use of Preferential Solvents in the Determination of Aromatic Hydrocarbons.—The most widely used solvent for the extraction of aromatic hydrocarbons from mineral oils is sulphur dioxide, originally suggested by Edeleanu,[183] and used commercially for the extraction of aromatics from kerosenes and illuminating oils. This solvent has been applied to the quantitative determination of aromatics by numerous investigators,[184] and its solvent action has been studied by Moore, Morrell and Egloff.[185] The critical solution temperatures of hydrocarbons in sulphur dioxide have been reported by Seyer and Huggett,[186] Seyer and Gill[187] and Seyer and Todd.[188]

Another solvent used for the determination of aromatic hydrocarbons is dimethyl sulphate, originally proposed by Valenta,[189] who claimed that it had no solvent action on naphthenes and paraffins. This claim is refuted by Graefe[190] and by Harrison and Perkin[191] Graefe conducted very complete tests and came to the conclusion that dimethyl sulphate had a very definite solvent action on saturated hydrocarbons. He also found that the solubility of an oil in this reagent was proportional to the amount of solvent used. Harrison and Perkin arrived at the same conclusions and proved that dimethyl sulphate cannot be used in this way for quantitative determinations. Taylor[192] has suggested the use of diethyl sulphate instead of dimethyl sulphate because of the poisonous properties of the latter.

Riesenfeld and Bandte[167A] have pointed out that the dimethyl sulphate method gives results for aromatic hydrocarbons which are too high, indicating that other hydrocarbons are also dissolved. Gohre[193] has investigated other preferential solvents. Laevulic acid is, apparently, suitable for oils containing up to 90 per cent. of aromatics; phenylhydrazine was found suitable for oils of high boiling point and glycol monoacetate suitable for light oils, except when the aromatic content is high, when the mixture must be cooled in ice. Furfuraldehyde was found suitable if used at − 10°C. Kattwinkel[194] has recommended the use of sulphoacetic acid mixed with acetic anhydride, which is capable of dissolving benzene hydrocarbons from light oils under special conditions.

Unfortunately, methods based on preferential solubilities are not to be recommended. The results obtained are greatly affected by the ratio of solvent to oil used.

597. The "Formolite Reaction" and its Use in the Examination of Light Hydrocarbon Oils.—The "formolite reaction" is of historical interest only and is extremely little used at the present time. Discovered by Nastjukoff,[195] it depends upon the fact that mineral oil products, when mixed with formaldehyde and then treated with concentrated sulphuric acid, yield yellow to brown precipitates, which are fairly reproducible when similar materials and a fixed procedure are employed. The precipitates were supposed to contain the aromatic and unsaturated constituents of the oil, at least for fractions of low molecular weight. According to Holde,[196] the different classes of hydrocarbons react with formaldehyde and sulphuric acid as follows:

(*i*) Paraffins and naphthenes are not attacked.
(*ii*) Olefines give a brown-red, syrupy liquid.
(*iii*) Unsaturated naphthenes (cyclic olefines) give a red-brown precipitate readily soluble in water.
(*iv*) Aromatics give a bright red or green precipitate insoluble in water.

The reaction is, however, not quantitative and the yields of the solid precipitates ("formolites") vary with the proportions of the reagents used.[197] The reaction is not suitable as the basis of a quantitative method of estimation. The use of methylal instead of formaldehyde has been advocated by Herr,[198] Radcliffe[199] and Dobryanskii,[200] but this modification does not make the reaction of analytical value.

598. The Estimation of Naphthene and Paraffin Hydrocarbons.—This is, perhaps, the most difficult step in the chemical analysis of motor

fuels, and no method has yet been proposed which gives anything but approximately accurate results.

The most widely used method of estimating naphthenes in the presence of paraffins is that based upon aniline point determinations,[160, 201] and which has already been described. This method must, however, be used with caution and it is probably preferable to employ the modified procedure of Garner.[137]

A further important analytical method is that of dehydrogenation of the cyclohexane naphthenes to aromatics which may be estimated by the methods already described. It should be noted that only those six membered ring compounds which can be regarded as hexa-hydro aromatics can be dehydrogenated in this way. Thus, 1·1-dimethyl cyclohexane cannot be dehydrogenated. The cyclopentane naphthenes are not affected by this treatment and cannot be estimated in this way.

The dehydrogenation is usually carried out by passing the oil vapours two or three times over platinum black, platinised charcoal or palladium black.[202] The reaction is usually complete and, according to Zelinskii and Kazanskii[203] can be applied to oils boiling as high as 200°C. On the other hand, statements have been made to the effect that the method is only applicable to light fractions, because of side reactions, formation of unsaturated hydrocarbons, poisoning of the catalyst, etc.

Manning and Shepherd[169] have applied the dehydrogenation methods to the estimation of the cyclohexane hydrocarbons occurring in spirits obtained by the carbonisation of coal. These investigators found that, at a temperature of 350°C., in a current of nitrogen, a 94 per cent. conversion of cyclohexane into benzene was obtained. However, attempts to dehydrogenate cyclohexane when mixed with petroleum ether (B.P. 40°-60°C.) failed. It was then found that the difficulties could be overcome by replacing the nitrogen by hydrogen and working at a slightly lower temperature, viz., 320-330°C. Under these conditions, the paraffin hydrocarbons were quite stable and cyclohexane was completely dehydrogenated. It was found, however, that, under these conditions, the higher homologues of cyclohexane were not so readily dehydrogenated as cyclohexane itself, and, moreover, that more than one passage over the catalyst had a slight decomposing action on paraffin hydrocarbons.

According to Tausz,[204] the separation of paraffins from naphthenes may be effected by the somewhat novel, if not useful, application of certain bacteria. These bacteria, β aliphaticum, β aliphaticum-liquefaciens and the paraffin bacteria, may be isolated from garden mould by culture in organic and inorganic media, containing *n*-hexane, cyclohexane or paraffin oil. Paraffin bacteria are without action on

naphthenes, benzenoid hydrocarbons and some paraffins (*n*-hexane and *n*-octane), but attack higher paraffins such as hexadecane. The other two species are inert towards cyclic hydrocarbons and hexylene, but attack paraffins and *n*-octene and hexadecene. Tausz claims that the destruction of the reactive hydrocarbons is complete even in the presence of hydrocarbons which are not attacked, but gives no information regarding the time required for the reaction.

Oxidation of naphthenes by a current of air in the presence of alkalies, at a temperature which will not permit attack of paraffin hydrocarbons, has been suggested by Charitschkoff.[205] The oxidation may be carried out with dry air at 150°C., in the presence of 1 per cent. of powdered caustic soda as a catalyst. The naphthenic acid so produced may be recognised by the green colour which the copper salts impart to a benzene solution. This cannot be considered an analytical method, however.

Nitric acid acts upon both paraffin and naphthene hydrocarbons, prolonged treatment with concentrated acid causing oxidation, while treatment with weaker acid causes the formation of nitro compounds. The nitration occurs the more readily the greater the size of the hydrocarbon molecule, and it appears that strong nitric acid is also capable of splitting and nitrating the molecules of secondary and tertiary paraffins at the same time.[206] The normal and quaternary paraffins are scarcely attacked at ordinary temperatures by concentrated, or even by fuming, nitric acid, but, on the other hand, secondary and tertiary paraffins react easily with the evolution of heat and the formation of carbon dioxide, lower carboxylic acids and tertiary nitro derivatives.[207] Fuming nitric acid is reported to attack some naphthenes and, of these, those with branched chains are the most easily attacked. Heusler[208] has removed naphthenes from a crude nonane cut by dropping the latter into four times its volume of fuming nitric acid. This method of freeing paraffins from naphthenes has also been recommended by Ubbelohde,[209] but it cannot be considered as quantitative.

Young[210] has used chlorosulphonic acid to produce pure normal paraffins from mixtures of saturated hydrocarbons and, according to Aschan, [211] this reagent reacts readily with branched chain paraffins at ordinary temperatures, di-isopropyl and isopentane dissolving completely with a brisk evolution of hydrochloric acid gas.*

599. Recommended Methods for the Hydrocarbon Analysis of Petrols and Light Hydrocarbon Oils.—It is, undoubtedly, true to

* By repeated treatment with chlorosulphonic acid, R. A. Virobyantz and S. M. Gabrielyantz (Foreign Petr. Techn., 1934, 2, (3), 87) have isolated *n*-heptane, *n*-octane, *n*-nonane and *n*-decane from Grosny and Maikop gasolines.

say that no method of hydrocarbon analysis can be recommended as being suitable for the examination of all kinds of light hydrocarbon oils of the motor fuel boiling range, and none of the analytical methods described above can be regarded as of universal applicability.

In the case of simple binary hydrocarbon mixtures of known constituents, analysis is comparatively simple. In this case, unsaturated hydrocarbons may be estimated with an accuracy sufficient for most purposes by means of bromine number determinations and aromatics by either the specific gravity, refractive index or aniline point methods, preferably the latter. In the case of binary mixtures of a paraffin and a naphthene, aniline points may be used to advantage, and results will, in this case, be accurate to within $\pm$ 1 per cent.

In the case of ternary hydrocarbon mixtures, the constituents of which are known, analysis becomes rather more difficult, but if an aromatic or unsaturated hydrocarbon is present, it is usually found that sulphuric acid can be used to effect a fairly accurate separation, if a suitable strength is employed. This should be determined by actual experiment. In any case, it is much easier to effect an accurate separation between one olefine and one aromatic than between the whole range of unsaturated and aromatic hydrocarbons found in motor fuels.

It is difficult to recommend any particular method of analysis for the examination of the hydrocarbon constituents of motor fuels, but the authors' choice falls upon the procedure of Faragher, Morrell and Levine[78] for the determination of unsaturated and aromatic hydrocarbons, and upon the method of Garner[137] for the *estimation* of naphthenes and paraffins.

600. The Isolation of Pure Hydrocarbons from Petroleum Light Distillates.—Much work dealing with the isolation of pure hydrocarbons from petroleum light distillates is described in the literature. Of this the most important, and by far the most reliable, is that conducted at the Bureau of Standards and listed Project No. 6 of the American Petroleum Institute Research Programme.

In this research the work has so far been confined to a single sample of crude oil obtained from well No. 6 of the South Ponca Field, Kay County, Oklahoma.[212] This oil was submitted to preliminary distillation in a semi-commercial still and the fractions so obtained further fractionated by distillation in a 15 litre still provided with a 20 plate bubble cap column,[212] followed by repeated distillations in a battery of all-glass laboratory stills. The latter were of various types and sizes ranging from 1 to 11 metres in height and fitted with either chain packing or bubble caps.[213] All the stills were electri-

cally heated and all distillations were carried out in an atmosphere of carbon dioxide with automatic control of pressure. Each still was provided with a Cottrell boiler through which the distillate flowed continuously to the condenser and receiver. The Cottrell boiler shewed at any moment the true boiling point of the fraction being collected.[214]

Distillation was continued until all the material had been fractionated into a set of constant boiling liquids—i.e., liquids which distilled at substantially constant temperatures. These azeotropic mixtures were then separated by various methods depending on circumstances. In some cases chemical methods were adopted such as (1) carefully controlled nitration and (2) fractional sulphonation and hydrolysis. Nitration was employed for the removal of benzene[214] and toluene,[215] since it was found that under properly controlled conditions the reaction was quantitative for these two substances, and no reactions with other constituents took place. The nitration procedure was applied only to those mixtures which had been so thoroughly fractionated by distillation that the only aromatic hydrocarbon present was benzene in one instance and toluene in the other. Fractional sulphonation followed by fractional hydrolysis was utilized in separating the three xylenes from one another and from ethyl-benzene.[216] These four substances were obtained mixed together in the material extracted from certain fractions by means of liquid sulphur dioxide. Separation was effected by a combination of fractional crystallisation with fractional distillation and sulphonation. These four aromatic hydrocarbons have different rates of sulphonation, and their sulphonated products have different rates of hydrolysis, so that a fractionation procedure based upon the differences of the rates of these chemical reactions was successfully employed in separating these substances from one another.

Other methods employed for separating azeotropic mixtures included fractional extraction with solvents such as aniline or liquid sulphur dioxide in a special counter-current flow apparatus,[214, 217] and fractional crystallization—sometimes in the presence of solvents.

Table 121 gives a list of the hydrocarbons isolated from the sample of Oklahoma crude oil in this investigation. Up to the present it has been possible to identify the various hydrocarbons by comparing their measured properties with those recorded in the literature for the synthetic hydrocarbons. The properties employed in this comparison have been freezing point, boiling point, density, refractive index and aniline point, supplemented when necessary by molecular weight and hydrogen-carbon ratio. Infra-red absorption spectra have also been determined. The general methods of establishing identity and demonstrating purity have been discussed by Washburn.[218]

TABLE 121.

HYDROCARBONS ISOLATED FROM AN OKLAHOMA PETROLEUM AT THE U.S. BUREAU OF STANDARDS IN A.P.I. PROJECT No. 6

	Amount in Crude Oil Per Cent.	Purity of Best Sample Mole Per Cent.
Paraffinic—		
Ethane	*a*	*a*
Propane	*a*	*a*
Butane	*a*	*a*
Pentanes (Two isomers)	*a*	*a*
n-Hexane	0·5	98·3
2·3-Dimethyl butane	0·3	>95
2-Methyl Pentane		>95
3-Methyl Pentane		>95
n-Heptane	0·9	>99·9
2·2-Dimethyl Pentane	>0·03	54
2-Methyl Hexane	0·25	99·9
3-Methyl Hexane	*b*	*b*
n-Octane	1	99·1
2-Methyl Heptane	0·16	*b*
n-Nonane	1	99·9
n-Decane	0·8	>99·79
Naphthenic—		
Cyclopentane	*a*	*a*
Methyl cyclopentane	0·2	98·9
Cyclohexane	0·3	99·98
Methylcyclohexane	0·3	>99·9
1·1-Dimethyl cyclopentane	>0·03	95
Nona naphthene	*b*	*b*
Aromatic—		
Benzene	0·08	99·8
Toluene	0·3	*a*
p.Xylene	0·04	>99·9
o.Xylene	0·12	>99
m.Xylene	0·12	>99·9
Ethyl benzene	0·03	94
Hemi mellithene	*b*	*b*
Pseudo-cumene	*b*	*b*
Mesitylene	*b*	*b*

a Not determined.
b Determination in progress.

601. Aromatic Hydrocarbons in Petroleum.—The presence of aromatic hydrocarbons in crude oil was first shewn by de La Rue and Müller in an examination of Burmese petroleum.[219] Several tons of "Rangoon Tar" were steam distilled, a further separation effected by repeated fractional distillation, and the aromatic hydrocarbons converted into nitro-compounds by means of a mixture of sulphuric and nitric acids. These workers shewed the presence of benzene, toluene,

xylene and cumene. Shortly afterwards, the presence of aromatic hydrocarbons was shewn in Galician crude by Pebal,[220] in Pennsylvanian crude by Schlorlemmer,[221] and in Hanoverian crude by Bussenius and Eisenstock.[222] At a later date, Markownikoff, Mabery and other workers shewed that aromatic hydrocarbons were normal constituents of petroleum, and in 1907, H. O. Jones and Wootton[223] drew attention to Borneo petroleum, which contains an exceptionally large proportion of aromatic hydrocarbons. The amount of aromatics present in various oils may vary from about 2 per cent. in natural gasolines up to 80 per cent. in the gasoline fractions of some Far Eastern crudes. Figures referring to the gasoline fractions (up to 150°C.) of various crude oils are given in Table 122.

TABLE 122.—AROMATIC HYDROCARBON CONTENTS OF GASOLINES (BY WEIGHT). (GARNER AND EVANS).[224]

	Yield of Gasoline	Benzene	Toluene	Xylenes	Total Aromatics up to 150°C
Hardstoft (England)	4%	0·15	0·5	1·3	1·95
Powell	16%	0·4	1·2	2·9	4·5
Reagan	35%	0·1	0·2	1·5	1·8
Seminole	36%	0·1	0·6	1·5	2·2
Grosny	13%	0·4	1·4	2·0	3·8
Peruvian	20%	0·3	1·6	2·5	4·4
Mexican	10%	0·5	1·5	3·0	5·0
Panuco	3%	0·7	1·9	4·0	6·6
Venezuelan ..	7%	0·9	1·5	3·7	6·1
Colombian ..	20%	0·2	0·8	1·3	2·3
Californian	20%	0·6	2·4	3·7	6·7
Persian	30%	1·5	4·5	5·1	11·1
Heavy-Smackover ..	—	0·15	0·4	1·5	2·05
Mexia	—	5·0	8·0	4·5	17·5
Roumanian ..	—	1·8	3·6	4·2	9·6
Baku	—	0·04	0·8	0·6	1·44
Borneo	—	7·0	14·0	15·0	36·0
Miri	—	0·4	1·9	1·5	3·8
Burmah	—	2·9	6·0	6·8	15·7
Badapur	154	1·0	1·6	2·9	5·5

The general conclusion which can be drawn from Table 122 is that in gasolines from paraffin and naphthene base petroleums, the percentage of aromatic hydrocarbons is low. Higher percentages are generally present in mixed base crude petroleums and petroleums of high asphalt content. The Borneo crude must be considered as being a separate category as nearly 40 per cent. of aromatic hydrocarbons is present in the gasoline fraction. In nearly all cases the concentration of aromatic hydrocarbons in individual fractions of crude oils increases with increase

in boiling point, i.e., the gasolines contain a larger proportion of xylenes than toluene and a larger proportion of toluene than benzene. Exceptions to this general rule are, however, known, e.g., Mexia crude, as shewn in Table 122.

A very large number of individual aromatic hydrocarbons have been shewn to be present in various petroleums, such as benzene, toluene, *o*-, *m*- and *p*-xylenes, pseudo-cumene, *p*-cymene, diethylbenzene, etc., etc. In Persian kerosene, toluene, *m*- and *p*-xylene, *p*-ethyl toluene, mesitylene, pseudo cumene, hemimellithene, an ethyl xylene and a diethyl benzene have been detected but not ortho xylene. Naphthalenes have also been identified.[225]

602. Naphthene Hydrocarbons in Petroleum.—There occur in all known petroleum the cyclic saturated hydrocarbons to which Markownikoff and Oglobin applied the name "Naphthenes." These hydrocarbons are chiefly the alkyl derivatives of cyclopentane and cyclohexane and represent a considerable proportion of the light fractions of petroleum. A great deal of confusion existed at first regarding the constitution of even the simpler naphthenes in petroleum. It was first thought that these compounds were all derivatives of cyclohexane and it was not until after 1895 that it was realized that at least two ring systems (penta- and hexa-) occur in petroleum. Napthenes containing rings of four, five, six, seven, eight and nine carbon atoms have been stated at various times to have been identified in petroleum. Thus cycloheptane was considered to occur in Caucasian naphtha by Markownikoff. The same worker also thought cyclobutane occurred in the pentane fraction of a Russian petroleum, but on very slender evidence. A dimethyl cyclobutane has also been reported to occur in Californian crude oil. It has been shewn that various hydrocarbons, termed "heptanaphthenes" and "octanaphthenes" by Markownikoff on purely analytical data, are in reality alkylated penta- or hexa-methylenes; e.g., Markownikoffs "octanaphthene" B.P. 119°C. is 1·3-dimethyl cyclohexane.

Petroleum, formed under conditions involving long heating under pressure, may naturally be expected to contain ring compounds. According to the strain theory of Baeyer, the most stable of the unsubstituted polymethylenes is cyclopentane, with cyclohexane not quite so stable and cyclobutane and cycloheptane in a state of considerable strain. According to this theory and the work of Thorpe[226] it may be anticipated that substituted cyclobutanes are of more probable occurrence in petroleum than cycloheptane derivatives. The majority of the compounds present, however, are likely to be of the less-strained five or six carbon atom ring types.

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Chapter XII

SULPHUR IN MOTOR FUELS FROM THE AUTOMOTIVE STANDPOINT

604. Much discussion has taken place during recent years regarding the maximum amount of sulphur and sulphur compounds allowable in petrols, and at the moment a controversy exists in the United States concerning the present upper limit of 0·1% total sulphur imposed in U.S. government specifications. Many, including some of those who are cracking high sulphur content heavy oils and who, consequently, have difficulty in meeting this specification, are of the opinion that a much higher sulphur content could be tolerated and that no corrosion troubles would be caused thereby, but others, principally the users of the motor fuels, are anxious for the present specification to continue in force. It is therefore of interest to examine this question and attempt to reach an impartial conclusion regarding these conflicting opinions.

It must be admitted, at the outset, that all sulphur compounds present in petrol are potential causes of corrosion, for all of them produce sulphur dioxide on combustion. Not all sulphur compounds, however, possess a corrosive action as such, for thiophene and the alkyl sulphides, carbon disulphide and the alkyl disulphides do not markedly attack the metals commonly used in engine construction at ordinary temperatures. On the other hand elemental sulphur,[1,2] sulphuretted hydrogen, mercaptans, sulphoxides[3] and polysulphides[3] definitely possess corrosive properties, though to varying extents.

The corrosive action of sulphuretted hydrogen need not be considered here because refined petrols do not normally contain even traces of this material.

605. The Corrosive Action of Elemental Sulphur.—The corrosive action of elemental sulphur has been studied by many investigators and the general concensus of opinion appears to be that this substance renders a fuel containing it corrosive to various metals, unless it be present only in very small concentrations. Corrosion encountered in fuel systems is generally due to the presence of elemental sulphur. The corrosion takes the form of a black deposit which has been shown to be mainly a mixture of copper sulphides.[4,1] This deposit is formed on carburettor floats, jets and filter gauzes and in severe cases the fuel flow has been completely prevented by its accumulation.

In 1925, Hoffert and his co-workers[1] recorded the results of experiments on the corrosive nature of benzoles and confirmed the earlier observation of Ormandy and Craven[4] that elemental sulphur was the substance chiefly responsible for the attack. With elemental sulphur dissolved in benzoles they found that blackening of copper occurred within six hours at room temperatures with concentrations down to 0·5 mgs. (0·0005*g*) per 100 ml. With brass, however, even as much as 0·01*g* sulphur per 100 mls. in pure benzene caused in two months only slight tarnishing of the surface.

Wood, Sheely and Trusty[2] also observed the corrosive action of free sulphur, but used in their experiments considerably greater concentrations of sulphur than those likely to occur in most motor fuels, e.g. 0·26 per cent. They found that elemental sulphur is especially corrosive to copper, silver and mercury, but not as markedly so to other metals investigated. Tin was the least attacked of all the metals.

A valuable contribution to our knowledge on this subject has recently been made by Garner and Evans.[5] These investigators have examined a range of petrols, benzole mixtures and benzole-toluole mixtures for elemental sulphur content, and have conducted on each the copper dish test and the United States Bureau of Mines copper strip tests at 50°C. and 100°C.,[6] these corrosion tests being those which are, at the moment, the most widely used. As a result of these experiments they conclude that, in general, the U.S. Bureau of Mines tests give fairly good agreement with the free sulphur content in the case of petrols. Exceptions were found however; e.g., a petrol which gave no corrosion at 50°C. gave very heavy corrosion at 100°C.; but such exceptions were more frequent with benzoles and toluoles and blends containing these substances. Thus one benzole gave a good corrosion test at 50°C. in spite of containing 4·5 mgs. of free sulphur per 100 mls. Discrepancies of this kind are stated by Garner and Evans to be probably attributable to the presence of inhibitors or similar substances which modify the course of the corrosion. Hoffert[1] has also pointed out this possibility.

The effect of temperature on the corrosive action of petrols, etc., on copper and other metals is of importance. Elemental sulphur has a definite corrosive action on copper at ordinary temperature and this attack is accelerated by a rise in temperature. On the other hand, the above results tend to shew that at some temperature between 50°C. and 100°C. the reaction between copper and some sulphur compounds, possibly polysulphides, becomes very noticeable. This is apparently due to the decomposition of the polysulphides under the action of heat with the formation of elemental sulphur. In this connection it is of interest to note that in a recent survey of fuel line temperatures in connection with vapour locking tendencies conducted by Bridgeman and White,[7] it was found that the average maximum temperature attained

in the fuel system after idling or hill climbing is 15°C. above atmospheric, while in extreme cases the rise may be as much as 32°C. This means that in warm weather temperatures of about 60°C. are attained, and temperatures of 71°C. may be reached in bad cases. The importance of this observation in matters connected with corrosion is obvious. As a result of their investigations, Garner and Evans concluded that elemental sulphur is not the only active corrosive agent present in petrols and benzoles, but that in the absence of other compounds fuels containing up to 0·5 mgs. free sulphur per 100 mls. may be regarded as non-corrosive, while fuels containing much more than 1 milligram are liable to give rise to trouble which, in some circumstances, may be serious. It would appear, from these conclusions, that the maximum allowable content of elemental sulphur lies somewhere between 0·5 mgs. and 1 mg. per 100 mls.

606. The Corrosive Action of Mercaptans.—Mercaptans may be considered the most active from the corrosion point of view, of all sulphur compounds.[8] These substances are more active than either sulphuretted hydrogen or elemental sulphur. In general the corrosion is caused by the formation of metal mercaptides through the direct chemical reaction between mercaptans and the metal, these mercaptides then decompose (particularly on heating) forming the metal sulphide and an alkyl sulphide. Mercaptans are much more corrosive in petrol solution when in the presence of water, presumably because of the increased ionization of the mercaptan which results. The same is true with regard to elemental sulphur and sulphuretted hydrogen.

607. The Corrosive Action of Other Sulphur Compounds.—Of the remaining types of sulphur compounds the alkyl sulphides and alkyl disulphides are not markedly corrosive when present in petrols, while carbon disulphide has only a very slight corrosive action. On the other hand, Birch and Norris[3] state that both sulphoxides and polysulphides have definite corrosive properties. Thiophenes are not corrosive. As in the case of mercaptans, the corrosive action of sulphides, disulphides, etc., is increased by the presence of water, but according to Wood, Sheely and Trusty[2] this is probably due to the establishment of anodic and cathodic regions of influence between the two dissimilar liquids and the metal in contact with both.

608. General Observations on The Corrosive Action of Sulphur Compounds Present in Petrols.—It will be seen from the foregoing details regarding the action of sulphur compounds of various types, that corrosion need only be feared in the case of petrols containing appreciable quantities of either sulphuretted hydrogen, elemental

sulphur or mercaptans, or sulphur compounds which decompose at moderate temperatures to give either of these substances, such as sulphoxides or polysulphides. Petrols are very rarely marketed (especially in Great Britain) containing either sulphuretted hydrogen or mercaptans, and the only corrosion that need be feared, in this country at any rate, is that resulting from elemental sulphur. Of course potential trouble from sulphoxides and polysulphides is always present, but these compounds only give corrosion at elevated temperatures.

It may be concluded that a spirit containing less than 1·0 mg. elemental sulphur per 100 mls. will be non-corrosive as far as the fuel feed pipes, carburettors and gauzes are concerned. The presence of sulphoxides and polysulphides in appreciable quantities may cause corrosion of inlet valves, etc., if present in appreciable quantities.

609. Corrosion of the Crank Case, Bearings, Exhaust System, Etc.—The presence of sulphur compounds in motor fuels can also lead to corrosion of engine crank cases, bearings, pistons and cylinders ; exhaust pipes and silencers may also be affected. In such cases, however, although sulphur in the fuel is the prime cause, the corrosion itself is due to sulphuric acid.

In the combustion of any sulphur compound sulphur dioxide is always formed, consequently this substance is present in the exhaust gases of engines running on fuels containing sulphur compounds. A portion of the exhaust gases finds its way into the crank case via the piston rings and the clearance space between piston and cylinder. At the same time steam is also present in the exhaust gases and this also finds its way into the crank cases. No harm is done until the sulphur dioxide comes in contact with the water resulting from the condensation of the steam, because perfectly dry sulphur dioxide exhibits no corrosive properties. When, however, this gas comes in contact with water, a dilute solution of sulphurous acid (H_2SO_3) is formed and is oxidized readily by the air present in the crank case to sulphuric acid (H_2SO_4), which has very vigorous corrosive action on most metals. No corrosion could occur if the condensation of water within the crank case could be prevented.

As pointed out by Diggs[9], the sulphuric acid formed in the crank case is nearly insoluble in lubricating oils and such oils tend to wet the surface of metals to a greater extent than aqueous solutions. Therefore those metal parts on which the oil film is allowed to remain intact will be very little corroded. However, in bearings and cylinder walls there is a continual tendency to rub off, or squeeze out, the oil more or less completely, particularly in stopping or starting the engine. Where the oil film is thus broken the acid suspended in the oil has a chance to attack the metal directly and does so with vigour.

The essential reactions which take place in crank case corrosion are therefore as follows:—[9]

(1) *During explosion.*

S compound + air in cylinder → $SO_2 + H_2O + CO_2$

(2) *In cool crank case.*

$SO_2 + O$ (air) + H_2O (condensed steam) → H_2SO_4

(3) *On bearings where the oil film breaks.*

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

(4) *On bearings as secondary reactions.*

$FeSO_4 + H_2 \rightarrow FeS + H_2O.$

and possibly

$FeSO_4$ + Fe (Finely divided) → $FeS + 4\,FeO.$

There is, however, no evidence that such corrosion occurs in warm weather when condensation of water in the crank case is prevented, such as when the engine is kept running during the day and kept in heated garages at night or when adequate crank case ventilation is employed, as suggested by Thorne.[10]

Evidence regarding the maximum allowable quantity of total sulphur in petrol before bearing corrosion occurs is somewhat lacking, but the following conclusions of Diggs[9] are of interest.

(*a*) When using a gasoline of 0·04% sulphur content there was no corrosion of wrist pins, gudgeon pins, etc., and the water condensed in the crank case contained no free acid, although it did contain ferrous sulphate.

(*b*) When using a gasoline of 0·151% sulphur content the corrosion was very appreciable and the water in the crank case contained free sulphuric acid in small quantities.

(*c*) When using a gasoline of 0·458% sulphur content the corrosion was very serious and the crank case water was quite acid.

These conclusions are based upon tests carried out on a Jordan engine fitted with new wrist pins, pistons and piston rings for each experiment. The experiments were conducted in such a way that the engine was allowed to run for one hour and then allowed to stand idle for one hour; each test was continued over 60—75 running hours. Each experiment was carried out at a temperature below freezing point "though not very cold."

It will thus be seen that the conditions employed in these experiments were unusually severe, and that the accumulation of water in the crank case was definitely encouraged; for this reason the tests do not represent true service conditions, except possibly for automobiles operated in the north part of the United States and in other very cold regions, during the winter season. Such conditions very rarely occur

in Great Britain, although condensed water in the crank cases of automobiles is often found. Morrell and Egloff[11] make the following statement :—

" Tests conducted over periods of months upon cracked gasoline of California origin containing 0·4% of sulphur have shewn no signs of corrosion in the various parts of the motor."

It has also been pointed out[12] that two thirds of the petrol sold in the United States is consumed in warm weather, when there is no chance for corrosion to occur. Egloff and Lowry[12] do not agree with the findings of Diggs[9] and, indeed, found in their experiments that corrosion within the crank case occurs only at atmospheric temperatures below 0°C. ; moreover, they indicated that in all American States in summer, and in many all the year round, petrol of high sulphur content could safely be marketed. The contention that appreciably higher sulphur contents than 0·1% could be tolerated with safety is supported by Egloff, Lowry and Truesdell,[13] who quote the opinions of a large number of experts in different countries of the world.

610. It is evident that it is extremely difficult to arrive at a definite conclusion from the above conflicting opinions. The work of Diggs indicates that a sulphur content of 0·15% is capable of causing " appreciable " corrosion at atmospheric temperatures below 0°C., but does not reveal to what level the sulphur content may be raised with safety for operation at higher temperatures. One can only conclude therefore, that for atmospheric temperatures of 0°C. and below, it is advisable to limit the sulphur content to 0·1%, whereas for higher operating temperatures the sulphur content may be appreciably higher without causing ill effects.

It is of interest to compare European and English motor fuel specifications with those existing in the United States, a selection of which are as follows :—

	Max allowable Sulphur content (% by weight).
U.S. Federal Government Specifications for all fuels	0·10
U.K. Air Ministry Specifications D.T.D. 224 and 230 Fuel for Aircraft Engines	0·1
B.E.S.A. Specifications No. 121 Aviation Spirits ..	0·05
Aviation Fuel Specification Belgian Army	0·10
B.E.S.A. Specification No. 135, Motor Benzole ..	0·40
N.B.A. Specification, Motor Benzole	0·40

Of these specifications only those relating to benzole tolerate a sulphur content very much higher than 0·1%. However, benzole is

rarely used as a fuel in an undiluted state, but in blends with petrol containing up to 50% benzole and which contain, normally, not more than 0·2% sulphur.

It should be noted that no limitation on sulphur content exists in Austria, Switzerland, Spain, France (except freedom from mercaptans), Czechoslovakia or Italy.

Further research on the subject is obviously needed, and it is highly probable that this would, if carried out, save the petroleum industry enormous sums of money in reducing the amount of sulphur removal necessary in the case of petrols consumed at average atmospheric temperatures.

611. The Effect of the Sulphur Contents of Motor Fuels on Exhaust System Corrosion.—The presence of sulphur dioxide in the exhaust gases of engines operating on sulphur containing fuels causes corrosion of exhaust pipes and silencers whenever the steam in the exhaust gas is allowed to condense. After the exhaust system gets warm no corrosion occurs, but on starting the engine and also on stopping it, condensation of the steam occurs and corrosion proceeds. Similarly on stopping the engine it may happen that combustion products are left within the engine cylinder and also cause corrosion of valve heads, etc.

612. The Economic Aspects of the Desulphurization of Motor Fuels.—It has been estimated by Egloff, Lowry and Truesdell[13] that it costs the American petroleum industry 50 million dollars per year to meet the existing sulphur specifications of 0·1%. In some cases no difficulty is met in complying with this requirement, as in the case of Mid-Continent crudes. But in Texas, Oklahoma and California however, the sulphur content of cracked spirits is only reduced to 0·1% by very drastic refining treatments, in which large volume losses are incurred, together with an appreciable falling off in anti-knock value.

Morrell and Egloff have dealt with a cracked distillate from a California fuel oil in detail. This distillate had a sulphur content of 8·5%, but the usual plumbite, acid, plumbite, rerun with steam, treatment was particularly ineffective in reducing this figure, a treatment of 40 lbs. sulphuric acid per barrel (6·4% by volume or 11·2% by weight) only reducing the sulphur content to 0·19%. This treatment gave a spirit loss of 19·1% and a 25·5% decrease in anti-knock value on the basis of Benzole-value in straight-run Pennsylvanian gasoline.

Nevertheless the United States Bureau of Mines twenty-first semi-annual survey conducted during January, 1930, shewed that of 150 samples of petrol collected in various parts of the country and examined for total sulphur content, 91·5% contained 0·1% sulphur or less

and complied with the Federal Specifications, while 85·6 per cent. contained 0·08% or less. Only 8·5% contained more than 0·1% sulphur, as compared with 5·4% in July, 1927.[14]

Now if a refiner is confronted with the necessity of reducing the sulphur content of his motor fuel in order to meet trade requirements, it is logical to assume that he will reduce this content only to a point that will allow a small margin of safety, in this case to about 0·09%. Thus, as 85·6% of the samples analysed in this survey contained 0·08% or less of sulphur it may be assumed that few of these were treated especially to reduce sulphur ; in other words, the reduction of sulphur content was not a problem with the refiners of these fuels. With regard to the 5·9% of the samples examined which contained 0·09 to 0·10% sulphur it may be assumed that only some of these required extra treatment. In other words between 85·6% and 91·5% of the samples did not constitute a problem in reduction of sulphur content. The statements made by Morrell and Egloff and by Egloff, Lowry and Truesdell do not, therefore appear to apply to the whole American petroleum industry but only to those parts concerned with the treatment of high sulphur crudes, e.g., Oklahoma.

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Chapter XIII

THE FORMATION, ESTIMATION AND SIGNIFICANCE OF GUM IN MOTOR FUELS.

614. Introduction.—In the early days of the petroleum industry, when motor fuels consisted entirely of straight-run distillates, trouble due to gum formation was rarely encountered but the demand for anti-knock motor-fuels and the extended use of cracking to meet this demand has resulted in the production of spirits which, unless carefully refined, are liable to deteriorate in storage.

The formation of gum in motor fuels has an adverse effect upon engine operation and can lead to the seizure of inlet valves in their guides and to the deposition of non-volatile resins in the fuel-feed system, the carburettor and the inlet manifold. Opinion as to the maximum permissible gum content for satisfactory engine operation is divided, mainly because of the lack of uniformity in testing methods.

In particular vapour-phase cracked spirits are the most liable to give trouble due to gum formation and in storage often suffer severe deterioration in colour and anti-knock value simultaneously, though it is probable that the development of satisfactory inhibitors to prevent such deterioration will partly solve the problem involved.

615. "Actual Gum" and "Potential Gum."—In any considerations on the gum contents of motor fuels it is necessary to appreciate the difference between the gum actually present in a spirit, and the ease with which gum may be formed on storage. No relationship is known to exist between these two separate properties. The "actual" gum content of a petrol is the amount of gum present in the fuel at the moment of test, whereas the "potential" gum content is the amount of gum formed, or liable to be formed, on further storage. The former is sometimes termed "existent" or "dissolved" gum.

It is, however, by no means a simple matter to define "existent gum." The word "gum" is generally used in the sense of a solid or semi-solid, non-volatile or almost non-volatile (though not necessarily heat stable) substance, which remains as a resinous or gummy residue when the volatile constituents of the spirit are removed by evaporation, and which may be deposited from solution at ordinary temperatures if sufficient accumulates in the spirit. In general, when the word "gum" is used, it is implied that the petrol is evaporated by some means not necessarily specified and that any solid or semi-solid, resinous or gummy

residue is "gum." "Potential gum" is the term used to denote the amount of gum likely to form on storage and has no connection whatever with that already present. It is obviously necessary to have these two separate definitions because a spirit may be "gum-free to-day and full of gum to-morrow." Moreover it has been shewn more or less conclusively that the amount of gum deposited in an engine induction manifold is only a function of the "actual" gum content and is in no way dependent upon the stability or otherwise of the motor fuel used; i.e., "potential" gum is of no consequence in this case. The time required for evaporation in an engine manifold is very short and no opportunity for the accelerated conversion of potential gum into actual gum occurs. Thus Hoffert and Claxton[1] have stated "The resinified or partially resinified constituents already present in solution in the benzole (motor benzole) before use are chiefly responsible for the troubles experienced when using benzoles in an internal combustion engine. Very little resinification of volatile unsaturated constituents takes place in the engine itself. It is previous resinification therefore, on which gumming in the engine primarily depends." It would appear that unstable motor fuels liable to form gum on storage would give satisfactory engine operation if consumed immediately after manufacture.

The potential gum content of a petrol may be estimated in a number of ways. Perhaps the simplest, and the most foolproof method, is to store the petrol for a given period of time and then determine the amount of "dissolved" or "existent" gum present. This is, however, a time-consuming and therefore inconvenient procedure and it is customary to use artificial devices whereby the changes brought about in storage are accelerated to such an extent that deterioration caused by months of storage can be brought about in a few hours. This is accomplished by heating under a super-atmospheric pressure of air or oxygen, commonly the latter. As will be shewn later, gum formation is essentially an oxidation process which is accelerated by increase in temperature and by an increase in oxygen partial-pressure.

Contrary to general belief, the colour of a gasoline is no indication of its gum content. Many samples having a very yellow colour have been found gum-free while others which have been +25 Saybolt colour, or better, have contained large amounts of gum. On the other hand yellow gasolines are usually regarded with some suspicion and are frequently, without real justification, termed gummy. The gum formed in unstable gasolines on storage usually remains in solution and is rarely deposited, but different petrols vary enormously in their solvent power for gum, cracked spirits containing olefines and spirits rich in aromatic hydrocarbons exerting a greater solvent effect than fully saturated straight-run spirits. Gum deposited from a petrol is relatively insoluble in petroleum spirits.

616. Factors Affecting Gum Formation.—It is generally agreed that oxidation reactions are responsible for the development of colour and deposition of gum that takes place when cracked-spirits are submitted to storage. When kept in contact with air most gasolines containing unsaturated hydrocarbons suffer chemical change to a certain degree and after a time acquire a smell resembling that of varnish. At the same time as deposition of gum or formation of gum takes place, traces of organic acids, aldehydes, peroxides and also water may be found in the spirit. At the present time the exact chemical mechanism of these changes is not completely understood, but sufficient evidence has accumulated to shew that certain unstable unsaturated hydrocarbons are partly responsible for the phenomenon, and that the process is essentially one of oxidation that is autocatalyzed.

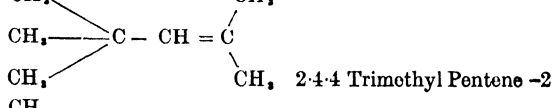
The first essential for gum formation is obviously the presence of air (oxygen). Under normal storage conditions air gains access to a petrol by means of the tank breathing caused by the escape of petrol vapours from the tank during the warmer hours of the day and the resulting entry of air into the tank during the colder part of the night to take the place of the escaped vapours. Moreover the solubility of air in gasoline is quite high and sufficient to cause normal gum formation. As in many other auto-catalytic reactions, colour deterioration and gumming are greatly influenced by the action of active radiations, particularly sunlight and ultra-violet light. Generally sunlight accelerates the formation of gum to a remarkable extent but it does not always cause a deepening in colour, and cases have been met in which crude unwashed gasolines have been rendered colourless by exposure to light. Satisfactory explanations as to why sunlight has a bleaching effect upon some gasolines and a colour deepening effect upon others have not yet been advanced. Higher boiling petroleum products behave similarly, although in general it is found that the effect of sunlight is to produce a deepening in colour. Under normal storage conditions the effect of sunlight upon colour and gum formation is of no import, but after bulk distribution, when the petrol is frequently required to be exposed to sunlight in the bowl of a petrol pump, deterioration is possible and frequently occurs, especially in sparsely populated districts where the petrol remains exposed for long periods before use. It would appear that special glass capable of acting as an ultra-violet light filter could be used with advantage in the construction of petrol pump bowls and all glass gauges, etc., used on petrol pumps.

Temperature has a marked effect on the rate of gum formation, an increase of a few degrees increasing the rate to a very noticeable extent. Thus in summer time, under the combined effect of sunlight and summer temperature petrol deterioration can be very rapid, and in the tropics the satisfactory storage of cracked spirits in tanks is often a matter of

some difficulty. The autocatalytic reactions responsible for colour and gum formation are also very susceptible to positive and negative catalysts. Traces of acids or alkalies have an accelerating action while many substances are known to have a retarding effect. This subject is dealt with in more detail later.

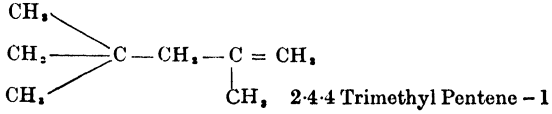
617. The Chemistry of Gum Formation.—As already mentioned, spirits containing appreciable amounts of unsaturateds are generally less stable in storage than straight-run petrols, but although all unsaturated hydrocarbons are potential gum formers it is an established fact that some unsaturateds, e.g., the pentenes and hexenes, can be stored for a very long time in diffused daylight and in the presence of air without undergoing oxidation reactions to more than a minute extent. On the other hand the more unstable unsaturateds, especially cyclopentadiene and styrene, etc., undergo oxidation and condensation reactions very readily and finally form hard glassy resins of a deep colour. The chemical reactivity of the unsaturated hydrocarbons is a function of their molecular configuration and in general the conjugated diolefines polymerize and resinify much more easily than other hydrocarbons whereas few, if any, of the straight chain mono-defines form gum on standing. Thus one of the Authors [2] stored pure samples of pentene -2, trimethyl-ethylene, octene-1 and diethyl-methyl-ethylene for six months in diffused daylight in the presence of air and at ordinary temperatures, and except for the formation of traces of organic peroxides no other deterioration was observed. No gum was precipitated in any of the samples. Cyclohexene was found, however, to behave rather differently, in that the rate of formation of oxidation products such as peroxides and aldehydes was much quicker than in the case of the other unsaturated hydrocarbons, but even in this case no gum deposition occurred. Exposure to ultra-violet light shewed quite definitely that cyclohexene suffered autoxidation much more rapidly than the pentenes, while the olefines of higher molecular weight, the so called "di-isobutylene" and "diamylene"* were definitely less reactive than the olefines of lower molecular weight. These observations have since been confirmed by

* The samples of "di-isobutylene" and "diamylene" were prepared by the standard methods of Butlerow[4], Edgar[5] and Norris and Joubert[6] respectively. They were almost certainly mixtures of isomeric hydrocarbons since Tongbert, Pickens, Fenske and Whitmore[7] have shewn that "Di-isobutylene" is a mixture of the isomers



2·4·4 Trimethyl Pentene -2

and



2·4·4 Trimethyl Pentene - 1

other workers and Flood, Hladky and Edgar[3] have stated that for olefines of similar structure those of low molecular weight are less stable than those of high molecular weight. Blends of pure unsaturated hydrocarbons in a straight-run gasoline have been examined for gumming properties by the same workers and they have shewn that none of the mono-olefines tested shewed appreciable oxygen absorption or gum formation when heated under oxygen pressure for four hours in 10 per cent. concentration in gasoline. At higher concentrations gum formation was observed. Straight chain olefines containing the double bond at the end of the chain were found to be more stable than those having the double bond elsewhere, while the data obtained on cyclohexene indicated that a double bond in a cyclic ring is somewhat less stable than in a straight-chain hydrocarbon. Compounds containing a double bond in their side chain appear to behave like simple olefines but the attachment of a double bond to a benzene ring, as in styrene or 1-phenyl propylene, decreases the stability to gum formation very markedly. As a class, di-olefines are much less stable than mono-olefines but the position of the double bond is important in determining the stability, conjugated double bonds introducing extreme instability while a compound containing two double bonds widely separated is almost as stable as an average mono-olefine. Cyclic di-olefines containing conjugated double bonds appear to be somewhat less stable than the comparable aliphatic di-olefines. Similar work has been carried out by Cassar[8] who has determined the actual gum contents of blends of various pure unsaturated hydrocarbons in an olefine free petrol, both before and after accelerated ageing by heat treatment under 100 lbs. per sq. inch oxygen pressure. The results obtained are summarized in Table 123, and shew that, of the olefines tested, only dimethyl-butadiene in 20 per cent. concentration gave large amounts of gum prior to treatment; while the simple mono-olefines, though stable to 4 hours accelerated ageing, gave fairly large amounts of gum after 24 hours similar treatment. The unstable nature of some di-olefines is also evident in the following cases :—

1·5-*Hexadiene.* $CH_2 = CH - CH_2 - CH_2 - CH = CH_2$
Develops a sharp odour and deposits a yellow oil on standing.

4-*Methyl* 2-*Ethyl cyclopentadiene.*
Boils at 135°C., but on distilling at ordinary pressure about one third is polymerized, the tendency to polymerize being abnormally great.

Dimethyl 2·4-*cyclohexadiene.*
Polymerizes easily on exposure to the air and ultimately sets to a pale yellow gelatinous mass.

Cyclopentadiene.

Spontaneously polymerizes in thirty days at 20°C., and in the presence of oxygen dicyclopentadiene diperoxide is readily formed. A resinous material is quickly deposited and a yellow brown colour develops.

1·3-*Cyclo-octadiene.*

Polymerizes so readily that when it is distilled polymerization occurs with explosive violence at 130—140°C. and a resinous mass is formed. Resinification also takes place rapidly on standing in air at ordinary temperatures.

TABLE 123.—GUMMING PROPERTIES OF PURE OLEFINES (CASSAR).

	Gum contents mgs/100ccs (Porcelain dish tests)		
	No accelerated ageing	Accelerated ageing	
		4 hours	24 hours
Olefine free petrol	0	0	1
Ditto + 20% Pentene-2	0	0	38
„ + 20% Trimethyl ethylene ..	0	1	35
„ + 20% Cyclohexene	0	0	45
„ + 20% Hexene	1	2	—
„ + 20% Heptene	1	1·5	—
„ + 20% Di-isobutene	0	1	—
„ + 20% Diamylene	0	1	—
„ + 20% Dimethyl butadiene ..	70	—	—
„ + 20% 2-methyl hexadiene ..	2	—	—
„ + 20% Limonene	8	236*	—

Not all diolefines polymerize rapidly. Thus Fischer and Chittenden[9] have found that 3-methyl 1·3-pentadiene does not possess a marked tendency to polymerize, and is unlike butadiene, isoprene, piperylene and 2·3-dimethyl—1·3-pentadiene in that it does not polymerize to an elastic resilient solid product.

Of saturated hydrocarbons, 1·4-dimethyl cyclohexane and 1·3-dimethyl cyclopentane are unique in their behaviour towards oxygen. At ordinary temperatures and in diffused daylight both of these hydrocarbons absorb oxygen readily, the latter to a greater extent than the former.[10]

It would appear therefore, that gum formation in cracked spirits may be caused, in the first place, by the instability of certain highly unsaturated hydrocarbons. The mono-olefines, except when present in large quantities, are not, in general, responsible for gum formation during

* Accelerated ageing of 1·5 hours.

normal storage. The responsibility of di-olefines for gum formation in cracked spirits was first suggested by Brooks and Humphrey in 1918.[11]

618. With regard to the exact mechanism of the oxidation reactions responsible for gum formation comparatively little is known. Probably the first product of the oxidation of an unsaturated hydrocarbon by air or oxygen is an organic peroxide,

$$>C=C< + O_2 \rightarrow >C(-O-O)-C<\rightarrow$$

which is subsequently converted into other oxygenated products, such as aldehydes, alcohols, ketones, fatty acids and resinous materials. The formation of gum by the condensation of aldehydes formed by the decomposition of peroxides has also been proposed, but although this may take place to a certain extent, it does not appear to be the main reaction. Brooks[12] has shewn that gums isolated from cracked spirit contain substantial amounts of explosive organic peroxides, an observation supported by Mardles and Moss[13] and other investigators who have stated that many residual gums decompose violently when heated on a water bath.

The hard non-volatile gum obtained by the evaporation of petrols in glass dishes in the normal method of estimating "existent" or "actual" gum does not necessarily exist in this form in solution in the petrol before evaporation, and there is much evidence to shew that the end-product obtained is the result of further oxidation and polymerization reactions accelerated by the action of heat during evaporation. It has already been shewn that the presence of oxygen is necessary for the initiation of the gum forming reactions, but the conversion of the gum in solution in a petrol to the hard mass obtained on evaporation does not require the presence of oxygen. Thus it has been suggested to designate gum in petrol solution as "pseudo" gum, implying that this material is transformed into "true" gum by the action of heat. It is evident, therefore, that the chemical structure of the "pseudo" gum is the key to the mechanism of gum formation.

619. The Peroxide Theory of Gum Formation.—It has been shewn by many investigators that peroxides are formed very quickly in cracked spirits and evidence is accumulating which shews that pseudo gum is composed largely of such bodies. Peroxides also have a catalytic effect in promoting gum formation. Of particular interest are some experiments by Story, Provine and Bennett[14] in which samples of cracked spirits were exposed to sunlight at an average temperature of 27·2°C. (81°F.), and tests carried out at intervals to determine the peroxide contents, acidities and gum contents of the samples.

After the samples had been exposed for about 100 hours under these conditions they become cloudy and deposited an almost colourless liquid gum which had a specific gravity of 1·0932 at 20°C. The results of the periodical examinations are reproduced in Table 124.

TABLE 124.—FORMATION OF PEROXIDES, ACIDITY AND GUM BY THE EXPOSURE OF CRACKED GASOLINE TO SUNLIGHT. (STORY, PROVINE AND BENNETT).

Total exposure Hours	Sunlight Hours	Peroxide oxygen (mgs Iodine per 100ccs spirit)*	Acidity (mgs KOH per litre spirit)	Gum content (copper dish test)† mgs/100ccs
0	0	0·0	0·0	400
24	12	15·0	0·0	400
72	28	53·0	0·8	450
128	46	24·0	2·5	500
152	58	50·0	4·5	550
170	62	44·0	7·0	600
240	94	53·0	9·8	650
296	106	54·0	18·0	750
344	110	54·0	24·0	950
400	134	60·0	27·0	1100
432	140	54·0	31·0	1350
500	176	140·0	49·0	1600
572	208	158·0	54·0	1800
672	224	148·0	67·0	2050

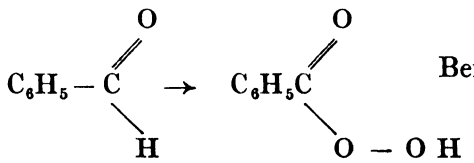
These figures shew that with increasing exposure to sunlight the peroxide oxygen content of the spirit increased and that after a short time, when presumably the peroxides reached the required concentration, acidic bodies began to appear. As the peroxide content and the acidity of the spirit increased so did the copper dish gum content increase. That sunlight is an important factor in this phenomenon is shewn in Table 125.

TABLE 125.—EFFECT OF SUNLIGHT ON THE PEROXIDATION OF CRACKED GASOLINE. (STORY, PROVINE AND BENNETT).

	Peroxides (milligrams iodine per 100 ccs)			
Exposure Hours	Sunlight and Oxygen	Sunlight and Air	Sunlight without Oxygen	Dark with Oxygen
0	0	0	0	0
2	22·0	12·0	4·0	Trace
4	44·0	24·0	4·0	Trace
10	102·0	36·0	4·0	Trace
14	232·0	60·0	8·0	Trace
36	548·0	300·0	8·0	Trace

* The peroxide oxygen was estimated by washing the spirit with water and estimating the amount of iodine liberated by the water solution from potassium iodide in acetic acid solution.
† For full description see this Chapter, paragraphs 625 and 626.

620. Now in the oxidation of benzaldehyde to benzoic acid, for example, just as much oxygen is consumed as is required for the formation of benzoic acid. If, however, some other oxidisable substance, such as indigo or acetic anhydride, is also present, twice as much oxygen is consumed in the conversion of the same amount of benzaldehyde into benzoic acid, as when this substance is absent, the indigo or acetic anhydride also being oxidized. Numerous theories have been advanced to explain this autoxidation, but of these the most generally accepted is that of Engler, Bodländer and others[15] who have assumed the formation of a peroxide, thus :—



Benzoyl hydrogen peroxide.

Thus if benzaldehyde is exposed alone to oxygen, the peroxide formed reacts with another molecule of benzaldehyde to give benzoic acid. If, however, some other oxidisable substance is present, the peroxide may lose one atom of oxygen to this substance instead, so that although the final product of the oxidation of benzaldehyde is, in each case, benzoic acid, twice as much oxygen has been consumed in the presence of the second oxidisable substance. The initial peroxides formed in cracked spirits might be expected to break down in a similar way, yielding half the oxygen content originally taken up to other oxidisable constituents, e.g., olefines. In this way secondary oxidation products would be formed, which presumably would condense finally with the formation of gum. Thus the gum finally produced when a cracked spirit is stored may arise not only from the peroxides themselves, which may break up giving oxygen and condensing to resins, but also from the interaction of peroxides with other unsaturated hydrocarbons. As an instance of this Brooks[12] has shewn that a small proportion of a readily oxidisable hydrocarbon (limonene) in a cracked spirit can cause the gumming of a relatively very large proportion of other unsaturated hydrocarbons, thus :—

	Residue (copper dish) *mgs/100ccs.*
Straight run petrol + 2 per cent. limonene ..	46
Refined cracked petrol + ditto	634
Refined cracked petrol alone	7

621. With a view to indicating the effect of peroxides on gum formation, Hoffert and Claxton[16] have carried out experiments in which various peroxides have been added to pure benzene and to unrefined

benzoles and the gum contents of the mixtures determined. Benzoyl peroxide $(C_6H_5CO)_2O_2$ was first used, but this stable peroxide had very little effect upon the gum content, whereas acetyl peroxide $(C_2H_3O)_2O_2$, which is a strong oxidizing agent and which explodes violently on heating, caused the formation of large amounts of gum in unrefined benzoles. It did not, however, promote the formation of gum in pure benzene. The results obtained by Hoffert and Claxton are reproduced in Table 126

TABLE 126.—EFFECT OF ACETYL PEROXIDE ON THE GUM CONTENTS OF PURE BENZENE AND UNREFINED BENZOLES. (HOFFERT AND CLAXTON).

	Evaporating dish	Residue on evaporation (mgs/100ccs)	
		No peroxide	5 ccs of ether solution of acetyl peroxide added
1. Pure Benzene ..	Glass	0·0	0·5
Do.	Iron	0·5	0·0
2. Unrefined Benzole A	Glass	1·5	58·5
Do.	Iron	0·5	64·0
3. Unrefined Benzole B	Glass	2·0	20·5
Do.	Tin	—	24·0

and confirm the contention that unstable peroxides can cause gum formation. The suspicion that acetic anhydride or acetic acid, formed by the hydrolysis of the peroxide, was responsible for the gum formation was shewn to be unfounded.

The above findings on the effect of peroxide additions on gumming tendency have been checked in the case of petroleum distillates by Cassar,[8] who has prepared the peroxides by oxidizing olefines in bombs and found that while unstable vapour phase cracked spirits are markedly affected by peroxides, relatively stable liquid phase cracked spirits are much more resistant. The catalytic effect of peroxides upon gum formation is also evident from the following table.

TABLE 127.—CATALYTIC EFFECT OF DI-OLEFINES AND PEROXIDES (CASSAR)

Sample	Porcelain Dish Gum (mgs/100cs.)
1. 70% olefine free stock, 30% unstable gasoline ..	18
2. Ditto + 10% pure limonene	36
3. Ditto + 10% peroxidised limonene	302
4. 90% olefine free stock, 10% peroxidised limonene ..	161

As a general rule the distillates from cracking plants are entirely free

from peroxides when fresh, since any oxygen present in the charge reacts completely with the oil at the high temperature at which cracking takes place. Peroxides formed at these temperatures immediately decompose. However, in a straight distillation the temperatures are not high enough, on the one hand, to cause the oxygen to combine completely with the oil or, on the other hand, to decompose all the peroxides formed, so that peroxides and free oxygen may come over with the distillate. If the distillate is not cooled immediately and thoroughly, the free oxygen gives rise to further peroxide formation and the distillate may cause extensive gumming in a cracked spirit with which it is blended. Special precautions should be taken to prevent the introduction of air when re-running a cracked distillate.

622. The effect of peroxides on gum formation has also been considered by Yule and Wilson,[17] who have developed a quantitative test for estimating peroxides based upon the oxidation of ferrous sulphate in the presence of ammonium thiocyanate. When a gasoline containing peroxides is shaken with a solution containing these reagents a red colour due to the formation of ferric thiocyanate from ferric sulphate is produced.

$$>C-C< \quad +2FeSO_4 \quad +H_2SO_4= \quad >C-C< \quad +Fe_2(SO_4)_3$$
$$\quad\;\; | \;\; | \qquad\qquad\qquad\qquad\quad | \;\; | \qquad\qquad$$
$$\quad O-O \qquad\qquad\qquad\qquad\quad OH \;\; OH \qquad\qquad$$

The ferric salt so formed is titrated immediately with 0·01N titanous chloride solution, and the result is expressed in gram equivalents of active oxygen per 1,000 litres of gasoline, i.e. "peroxide numbers." This method of analysis, however, always gives somewhat low results, especially for high concentration of peroxides. Thus certain types of peroxides are catalytically decomposed by ferrous salts, e.g. diethyl peroxide, which is decomposed with the formation of ethyl alcohol and acetaldehyde[18]

$$CH_3-CH_2-O-O-CH_2-CH_3 \rightarrow CH_3-CH_2-OH+CHO-CH_3$$

Moreover, a small proportion of the peroxides cannot be reduced by ferrous sulphate. The most widely used test for peroxides is the potassium iodide test of Marks and Morrell.[19]

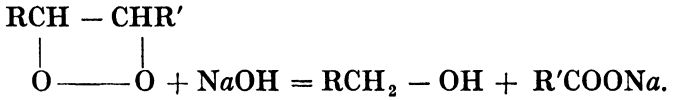
The effects of various reagents upon the peroxides present in a sample of cracked spirit have been described by Yule and Wilson[17] whose results are reproduced in Table 128. Water was found to have a very

TABLE 128.—EFECT OF VARIOUS REAGENTS ON PEROXIDES CONTAINED IN GASOLINE. (YULE AND WILSON).

Test	Treatment	Peroxide Number	Colour (Saybolt)	Gum mgs/ 100 ccs.*
1.	Original Sample Untreated	19·4	+18	40
2.	Shaken with Water	19·0	+18	30
3.	Refluxed with Water 2 Hours	14·6	—	129
4.	Refluxed without Water 2 hours	15·0	Yellow	88
5.	Distilled in Steam	6·0	—	11
6.	Shaken with 5% $NaOH$ for 1 min.	17·0	—	—
7.	Shaken with 5% $NaOH$ for 5 min.	15·2	—	—
8.	Shaken with 5% $NaOH$ for 15 min.	14·6	+18	56
9.	Shaken with 5% $NaOH$, slight excess H_2SO_4 added and reshaken	16·8	+17	57
10.	Shaken with 5% $NaOH$ Containing 2% Formaldehyde	7·3	+17	51
11.	Shaken with 5% $NaOH$ Containing Lead Sulphide in Suspension	2·8	+17	30
12.	Shaken with Water Containing Lead Sulphide in Suspension	4·4	+19	37
13.	Shaken with Sodium Plumbite Solution	14·0	Yellow	128
14.	Shaken with Sodium Plumbite Soln. plus 0·1% Cymene Hydrosulphide	1·4	—	75
15.	Allowed to Stand with 0·1% Cymene Hydrosulphide	17·5	—	—
16.	Shaken with Satd. $NaHSO_3$ Soln. then with 5% $NaOH$	2·8	+15	133
17.	Shaken with 10% Weight of Silica gel	0·8	+19	5
18.	Shaken with 1% of 25% H_2SO_4, then with 5% $NaOH$	9·0	—	—
19.	Shaken with 1% of 50% H_2SO_4, then with 5% $NaOH$	2·2	—	—
20.	Shaken with 1% of 75% H_2SO_4, then with 5% $NaOH$	0·4	+17	31
21.	Shaken with 1% of 98% H_2SO_4, then with 5% $NaOH$	0·3	—	—
22.	Previous Sample Distilled in Steam, Saturated with H_2S, and allowed to stand 5 mins.	0·4	—	—
23.	Saturated with H_2S, allowed to stand 5 mins., Shaken with 5% $NaOH$	14·2	—	—
24.	Saturated with H_2S, Allowed to Stand 5 mins., Shaken with 5% $NaOH$.	15·2	—	—
25.	Saturated with H_2S, Allowed to Stand 30 mins., Shaken with 5% $NaOH$	14·4	—	—
26.	Saturated with SO_2, Allowed to Stand 5 mins., Shaken with 5% $NaOH$	0·8	—	—
27.	Saturated with SO_2, Allowed to Stand 30 mins., Shaken with 5% $NaOH$	0·4	—	—

* Determined by the method of Norris and Thole (see paragraph 631).

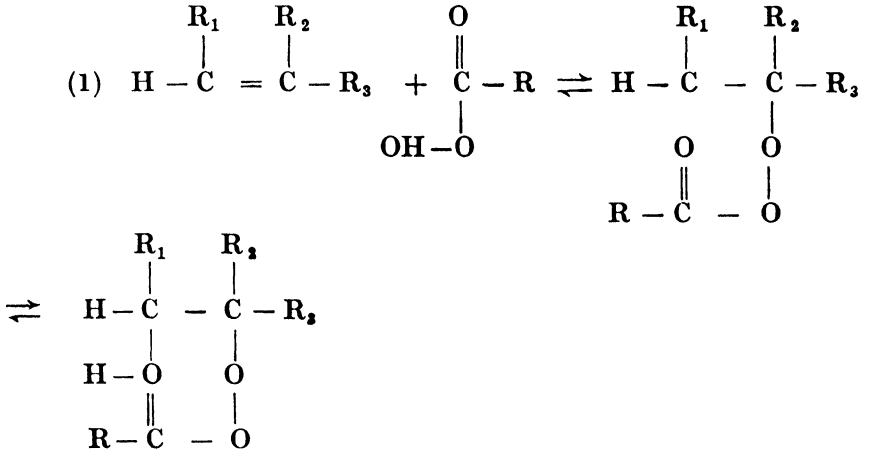
slight solvent action upon peroxides but did not cause any hydrolysis, despite various reports to the contrary.[12] Thus it was found that a sample of petrol containing peroxides could even be refluxed with water for several hours, or distilled in steam, with little more decomposition than would be expected from the action of heat alone. Caustic soda immediately removes a small amount of the peroxides, thus :—



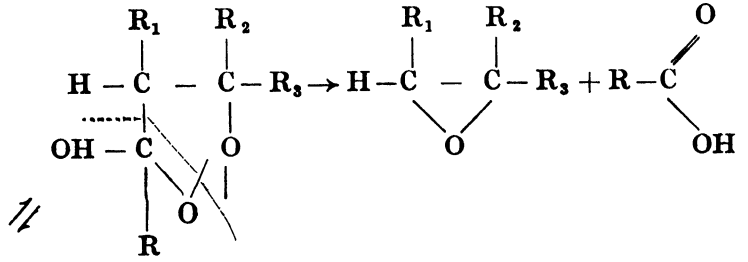
while concentrated sulphuric acid readily effects decomposition. Peroxides have an oxidizing action upon sulphuretted hydrogen, mercaptans, lead sulphide and mercury.

The phenomenon of gumming in cracked spirits is considered by some investigators to be similar to that oxidation responsible for knocking in engines, in that peroxide formation is considered to be the primary cause of both. The analogy must not be pursued too far, however, as it only covers the formation of peroxide bodies during the initial stages of the oxidation. There is no relationship between the tendency of a spirit to gum and its tendency to knock except when it contains appreciable amounts of already formed peroxides.

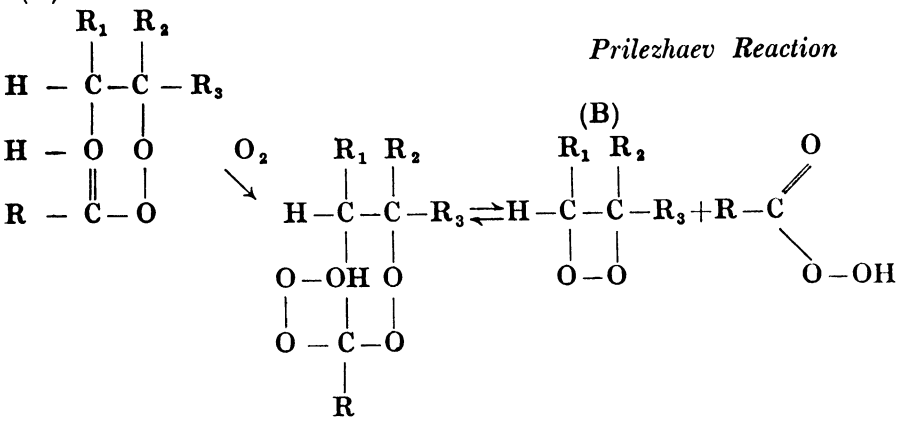
623. The Per-Acid Theory of Gum Formation.—While admitting the formation of peroxides in the first stage of the oxidation of hydrocarbons, Wagner and Hyman[20] favour the idea of per-acids as catalysts in actual gum formation, and have postulated the following chain of reactions for the production of pseudo-gum



(2)



(A)



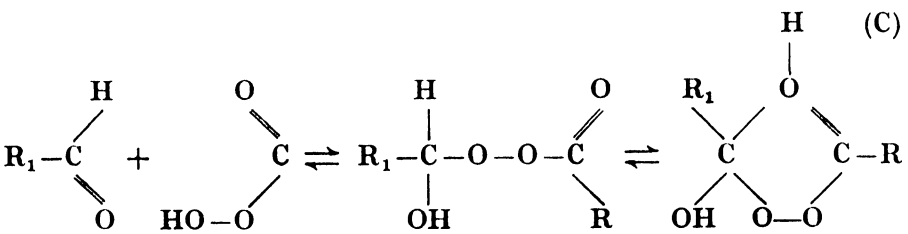
Prilezhaev Reaction

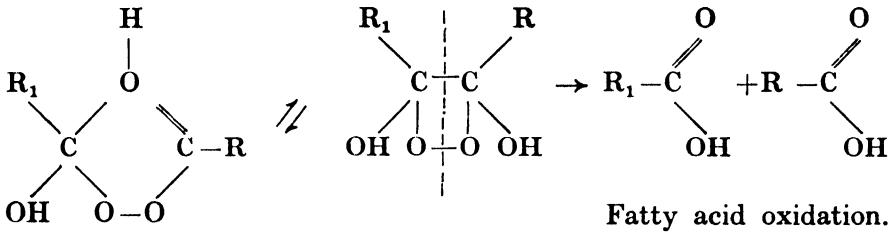
(B)

Atmospheric oxidation.

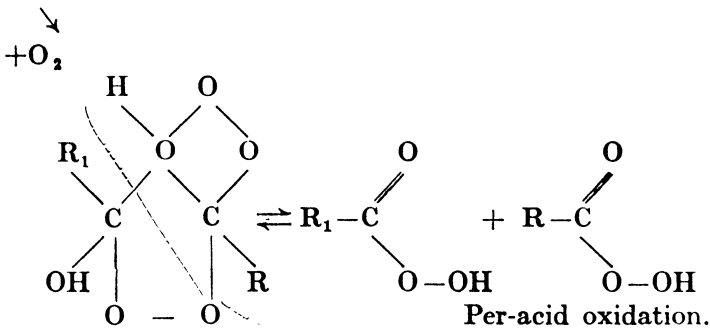
There is in the scheme a certain resemblance with the Prilezhaev reaction, but autocatalysis requires an increase in the amount of the catalyst (assumed to be a per-acid) with time, whereas the Prilezhaev reaction would lead to a decrease in the amount of catalyst. Furthermore the latter reaction does not take account of atmospheric oxygen. The above equations shew that through the medium of reactive oxonium compounds of type A the per-acid would be regenerated, along with the peroxide B, which latter may break into an aldehyde and a ketone, the aldehyde being then further oxidized in the presence of the acid, somewhat as follows :—

(C)



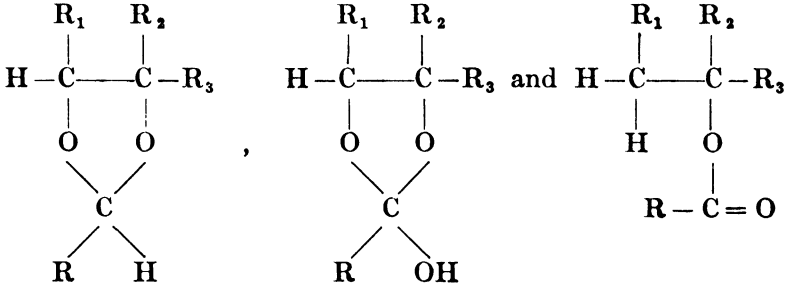


Fatty acid oxidation.

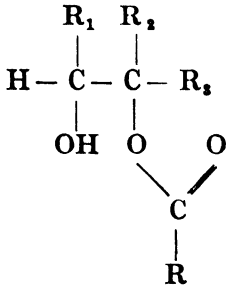


Per-acid oxidation.

Wagner and Hyman are of the opinion that pseudo-gum consists of compounds of type (A) and its degradation products, i.e. esters and acetals,



That compounds of type (C) can play but a minor rôle in residual gum formation may be shewn, according to Wagner and Hyman, by exposing to sunlight acetaldehyde dissolved in an inert hydrocarbon solvent, when, it is stated, the solution shews an intense peroxide reaction and no gum. Type A compounds, when heated in non-aqueous solutions would tend to form glycol esters of the type :



which could then polymerize with the expulsion of water to form esters, olefines and furan-derivative gums. Condensation might also occur with the less volatile aldehydes and ketones, while in aqueous solution hydrolysis would occur to form di- and poly-hydric alcohols, i.e., sugar derivatives.

According to this theory of gum formation, if the acid strength or oxidising activity of the per-acid is suppressed, and if external agents, such as light, heat or peroxides are absent, then the oxidation of the petrol should be retarded indefinitely. Such considerations are held to explain the gum inhibiting effect of both hydroquinone and ammonia, the former acting by reducing the per-acid to an inactive organic acid, whereas the ammonia keeps down the hydrogen-ion concentration.

Yule and Wilson[17] do not support this per-acid theory, in view of the fact that a small quantity of a gummy spirit added to a cracked distillate was found to have just as great a catalytic effect upon gum formation, whether washed with sodium carbonate or not.

Comprehensive reviews of the general subject of autocatalysis have been presented by Kondakow[21] and by Milas,[22] while the catalytic effect of cobalt oleate on the autoxidation of pentene −2 has also been considered.[23]

624. The Chemical Composition of Residual Gums.—Wagner and Hyman[24] have analysed a sample of gum obtained from a highly unsaturated spirit after exposure to an oxidising atmosphere for some months. The spirit was distilled in vacuo to a 28 per cent. residue, which had an acid-number of 0·75, a saponification number of 13·4, and contained 0·2 per cent. oxygen and which gave a very strong test for peroxides. When the residue was being distilled a series of violent explosions occurred and with each explosion vapours of acrolein were evolved. A heavy resinous mass was thus obtained which did not give a positive peroxide test but which gave a strong test for acrolein, indicating that evaporation had caused the decomposition of the peroxides and that acrolein, among other substances, was formed during the process.

Gums obtained by the evaporation of gasolines in small glass dishes on water baths were examined by Smith and Cooke[25] in 1922. As first formed the gums were soft and sticky and entirely soluble in acetone, but on heating they became hard and brittle and were no longer soluble in acetone. Their analyses were as follows:

	Soluble gum	Insoluble gum		Soluble gum	Insoluble gum
Hydrogen ..	7·39	6·75	Ash ..	2·78	1·00
Carbon ..	69·48	70·62	Sulphur	0·28	0·50
Oxygen ..	19·93	21·06	Nitrogen	0·14	0·07

Bakelite resins, formed by the condensation of phenol and formaldehyde, contain 5·4 to 5·96 per cent. hydrogen, 76·4 to 77·9 per cent. carbon and 16·4 to 18·1 per cent. oxygen.

Gums obtained by the evaporation of gasolines in copper dishes have been examined by Story, Provine and Bennett[14] after drying and grinding to a powder. The gums were brown in colour, insoluble in water and almost completely soluble in acetone, alcohol and chloroform. The constituents of the gum were separated by saponification, steam distillation and filtration, followed by acidification, distillation, filtration and evaporation. The residue was taken up in solvents. In this way a separation into unsaponifiable matter, insoluble acids and soluble acids was effected. No volatile matter was detected. The results of the examination are detailed in Table 129.

TABLE 129.—COMPOSITION OF GUM FROM COPPER DISH EVAPORATION TESTS. (STORY, PROVINE AND BENNETT).

	Original gum	Unsaponifiable matter	Insoluble acids	Soluble acids
% Carbon	70·73	64·2	73·22	66·70
% Hydrogen	6·95	6·32	6·81	7·20
% Oxygen	19·51	13·81	18·58	24·23
% Nitrogen	0·13	Trace	Nil	Nil
% Sulphur	0·68	0·29	0·41	1·07
% Ash*	2·00	15·38	0·98	0·80
Hanus Iodine Value ..	73	—	89	84
Molecular Weight ..	200	—	119	—
Saponification equivalent	191	—	104	94
Neutralization equivalent	732	—	460	241
Physical nature	Dark brown and resinous	Dark brown solid	Light brown solid	Brown viscous liquid
Melting Point °C. ..	98—105°C.	—	192—195	—
Per cent. of total gum ..	100	13·0	55·0	30·5

625. Tests for Actual and Potential Gum Contents.—The ultimate criterion of the satisfactory nature of a laboratory test for "actual" or "existent" gum content is that it shall indicate the relative amounts of gum which motor spirits will deposit in engines. Reproducible methods are available but there is at present insufficient evidence to shew that any of these is significant with regard to actual engine results.

Many methods have been proposed for determining "actual" gum contents, but with varying success. The oldest of these is the well known copper dish test, devised by F. C. Robinson and his associates of the Atlantic Refining Company as one of the tests for aviation

* Composed largely of dust accumulated during the evaporation of the gasoline in dishes.

gasolines, and used extensively for this purpose during the late war, when it found a place in United States government specifications. The test is still used to a small extent but has recently been described as "obsolescent if not obsolete." It has been fully described in publications of the United States Bureau of Mines.[26, 27]

The copper dish test for gum content makes use of a freshly polished hemispherical dish of spun copper approximately 3½ ins. (9 cms.) diameter. 100 mls. of the spirit to be tested are placed in this dish and evaporated to dryness on an actively boiling water bath in such a way that no steam is allowed to come in contact with the outer surface of the dish higher than the level of the spirit. The amount of gum is determined by the difference in weight of the dish before filling with petrol and after evaporation.

This test has now fallen into disfavour because of its lack of reproducibility and because the results obtained by its use do not agree with engine results. Gum contents determined by evaporation in copper dishes are usually very much higher than those determined in dishes of glass or porcelain, and in extreme cases the figures obtained are about a hundred times greater. This suggests that the copper has an accelerating or catalytic effect upon the formation of gum and that the method of test is consequently incapable of differentiating between actual gum and that formed during the evaporation. This is shewn in the results of Story, Provine and Bennett[14] reproduced in Table 130.

TABLE 130.—THE CATALYTIC EFFECT OF COPPER UPON GUM FORMATION. (STORY, PROVINE AND BENNETT).

	Total acidity (mgs/KOH) For various amounts evaporated				Gum Residue				
	30%	50%	70%	90%	Weight mgs	Total acidity mgs/KOH	Free acids mgs/KOH	Saponification equivalent*	Neutralisation equivalent*
Untreated cracked spirit evaporated in a copper dish ..	7·8	14·0	19·3	25·3	24·3	71·6	18·6	191	730
Same spirit evaporated in a glass dish	Trace	Trace	2·1	2·8	10	3·5	1·8	160	312

626. The inability of the copper dish gum test to give results which bear any relation to engine performance has been pointed out by

* Numbers of grams of gum saponified or neutralised by 1 equivalent (56·1 grams) of caustic potash (KOH).

Voorhees and Eisinger[28] who have quoted the case of a spirit which gave 351 milligrams of gum per 100 mls. in this test and only 6 milligrams per 100 mls. in a modified glass dish test, and which gave perfectly satisfactory engine operation over 1,068 miles. When the copper dish test was first introduced it was stated that a motor fuel should not give a gum content higher than 22 milligrams per 100 mls., and an aviation fuel should give no weighable residue. A further difficulty with the copper dish test is that certain sulphur compounds, e.g., mercaptans, sulphuretted hydrogen, polysulphides and also elemental sulphur have a corrosive effect upon the dish, covering it with a layer of copper sulphide. Thus, with fuels containing any of these substances, the increase in weight of the dish after evaporation is not only caused by the gum in the fuel but may be considerably augmented by the corrosion deposit. This prevents accurate results being obtained. The copper dish test has also been extensively used for detecting corrosive sulphur in fuels.

Because of these various short-comings, the copper dish test for the determination of gum content is rapidly being replaced by more reliable methods. The results obtained by its use mean very little, and gum contents by this test of the order of 100—300 milligrams may indicate troublesome engine operation and they may not. There is, however, one thing that can be said in its favour, i.e., *no gasoline which is free from gum by the copper dish test will ever cause trouble in an engine if used immediately.*

627. Glass Dish Evaporation Tests for "Actual" Gum Contents.—In 1922 Smith and Cooke,[25] recognizing the disadvantages of the copper dish test, adopted a procedure in which 30 ml. glass evaporating dishes were employed. Twenty millilitres of the spirit to be examined were placed in one of these dishes and heated on an actively boiling water bath for four hours followed by drying in an air oven for 24 hours at a temperature of 105°C. This method was followed by a modification by Cooke[29] in 1925, in which the evaporation was carried out in a steam oven to avoid contact with air and it was claimed to give more accurate results than the water bath method and to require less time for evaporation.

The oven used was double walled, and had glass shelves and a gas-tight door. Steam is admitted by a pipe between the walls of the oven and then passed into an inner chamber through small perforations in the floor of the chamber, which were placed near the oven door so that the path of travel of the steam was across the sample dishes to the outlet pipe. This pipe passed through the outer chamber formed by the double walls, to a trap so placed that the vapours could be led off to a ventilator, while liquids resulting from condensation drained away. An outlet pipe carried away condensed steam. Valves were

placed in the outlet lines so that a slight pressure could be maintained within the oven if desired. The glass shelves were placed about 5 inches apart, vertically, so that there was working space above the sample dishes.

Weighed glass, porcelain or silica dishes of 30 ml. capacity were placed on the shelves in the oven and 20 ml. samples of gasoline added from pipettes. The oven was closed and steam allowed to enter it, the outlet valves being so adjusted that all the condensate was removed and a small amount of excess steam escaped. After two or three hours the steam was cut off, the oven was opened, and the dishes transferred to a drying oven of the conventional type and maintained at a temperature of 105°C. for 24 hours or until constant weight was obtained.

With regard to the relative merits of the above steam oven method and the glass dish steam bath method, little can be said, as both are capable of giving reproducible results if sufficient attention to detail is given. Generally the gum figures obtained with the latter method are somewhat higher than those obtained by the use of the steam oven, indicating that for normal petrols of end-point about 200°C some oxidation during the test takes place when the evaporating spirit is exposed to the air. According to Wagner and Hyman [20] the water bath method gives results 3 to 6 times more gum, and according to Auld [30] 2½ to 5 times more gum, than the steam oven method. In the case of benzoles of end-point about 150°C., unless air is actually streamed over the surface of the evaporating spirit in the glass dish test, the vapour evolved effectively "blankets" the surface of the liquid and prevents air oxidation. When, however, petrols (of higher end-points) are evaporated, vapour is evolved comparatively slowly towards the end of the test and the petrol is exposed to air oxidation.[31]

A comparison of the results obtained by the steam oven and glass-dish water-bath methods is shewn in the following figures by Wagner and Hyman.

TABLE 131.—COMPARISON OF GUM TEST METHODS (WAGNER AND HYMAN.)

Sample No.	Grams of Gum			
	1	2	3	4
Steam Oven Test (20 ccs Spirit) ..	0·0003	0·0033	0·0115	—
Copper Dish Test (100 ccs Spirit) ..	0·0009	0·0190	0·0660	0·1205
Water Bath Test (20 ccs Spirit) ..	0·1930	—	—	0·7500

A disadvantage of the steam oven method is that it involves the use of a somewhat troublesome steam oven and the water bath test is unquestionably more simple in operation. A further criticism is that

steam is not without some action on gums and that steam reacts with organic peroxides.[13,32]

The test using a glass dish heated on a boiling water bath is now finding general acceptance throughout the industry, though many modifications of the original Smith and Cooke procedure are used. Thus Wagner and Hyman have used 30 ml. pyrex-glass dishes, 50—52 mm. wide and 21—22 mm. deep in conjunction with 20 ml. samples of spirit. The dishes are placed on an actively boiling water bath so that the greatest possible immersion is obtained. After evaporation of the sample the dish is placed in an air oven at 105°C. for thirty minutes, after which it is cooled in a dessicator and weighed.

However, all gum tests involving the evaporation of petrols in open dishes are open to objections, which may be summarized as follows[32]:—

1. The time of evaporation is long and differs for samples of varying volatility.
2. The degree of oxidation (if the evaporation is conducted in contact with air) is not under control and the degree of heat polymerization also varies with the rate of evaporation of the particular sample.
3. The results are affected by the thickness and thermal conductivity of the material of which the dish is constructed, which greatly influence the rate of evaporation.
4. The material of the dish probably exerts a specific catalytic effect when evaporation is conducted over a long period with exposure to oxygen.
5. The usual " final temperature " of the gum (a few degrees below 100°C.) differs considerably from the normal temperature of an inlet valve, upon which gum deposits usually accumulate in an engine to the most serious extent.
6. Evaporation in a current of steam, which eliminates some of these objections, still involves a considerable period of heating which cannot easily be standardized.

628. Air-Jet Evaporation Tests.—Perhaps the most important modification of the Smith and Cooke glass dish steam bath gum test is that which makes use of a jet of air directed vertically downwards on to the centre of the spirit in the dish to assist evaporation. This was first employed by Hunn, Fischer and Blackwood,[33] who used as much air as possible without splashing spirit over the rim of the dish. A suitable jet for the air was found to be a tube ½ inch I.D. loosely packed with cotton, the open end being covered by a fine mesh wire screen. Complete evaporation of a 400°F. (204·4°C.) end-point spirit was found to take place in 12 to 15 minutes, while normal gums could be dried to

constant weight at 105°C. in 2—3 hours. The method was checked by replacing the air stream with the inert gases nitrogen and carbon-dioxide, and it was found that the air did not cause any perceptible increase in the amount of gum by oxidation. The air-jet hastens evaporation and so prevents the oxidation which occurs in the normal glass dish test.

At a somewhat later date (October, 1930) Littlejohn, Thomas and Thompson[34] described a similar procedure after finding that the normal glass dish test gave, on occasions, discordant results, and with cracked spirit blends did not give figures the arithmetic mean of the gum contents of the constituents of the blends. These workers used a steam bath 24 in. long by 12 in. wide and 4½ in. deep, provided with two rows of 7 holes (2 in. diam.), and fitted with two brass headers $\frac{5}{8}$ in. internal diameter, adjustable for height and running horizontally over each row of holes. Over the centre of each hole was a jet from the header and each jet was closed with $\frac{1}{16}$ in. brass plate through which was bored a single hole 0·036 inch diameter. The rate of air flow was varied by adjusting the air pressure applied to the header, this being measured with a manometer. The results obtained with this apparatus are of sufficient importance to merit a complete description. It has already been stated that the normal glass dish test gave somewhat discordant results, but a marked improvement was noted using the air-jet, as shewn in the following figures.

TABLE 132.—COMPARISON OF AIR-JET EVAPORATION WITH PLAIN EVAPORATION IN GLASS DISHES. (LITTLEJOHN, THOMAS AND THOMPSON.)

		Hole number in bath						
		1	4	7	9	11	13	14
No Air Jet	Gum. mgs /100 mls.	40	46	47	62	—	82	—
		32	—	44	68	69	74	—
Air Jet	Gum. mgs /100 mls.—							
	Spirit A	6	7	6	6	6	—	6
	Spirit B	38	37	36	36	37	—	35
	Spirit C	263	265	265	262	262	—	263

629. The effect of varying the height of the air-jet above the spirit surface was determined at constant air pressure by inclining the brass header from the horizontal, but was found to have little influence upon the results whereas alteration in the air pressure had a profound bearing on the results. Increased temperature of evaporation and increased supply of air, although accompanied by decreased time of evaporation,

brought about increased gum formation. Attempts were made to decrease the time of evaporation by using dishes of copper and aluminium but the results obtained indicated that the higher temperatures of the spirit during evaporation due to the high conductivity of the metals outweighed the effects of the shorter time of evaporation. It was found that the use of an inert gas instead of air did not give any lower results. The conditions of drying the gum obtained on evaporation were also examined and as a result a drying time of 1½ hours at a temperature of 150°C. was selected as giving a consistent result with reasonable speed of drying. It was found that when the actual weight of gum deposited in the dish is such that the gum is evenly and thinly distributed over the glass surface, reasonably complete drying of the gum is effected, but amounts greater than 10 milligrams became deposited in the form of a small surface in the bottom of the dish. On drying, the surface of the pool acquires a skin of polymerized or dried material and it is very likely that this skin reduces the possibility of evaporation, with the result that the material which would normally be removed is retained beneath the surface skin and polymerized by the heat of drying. Thus it was found, in the case of one spirit, that evaporation of 25 ml. gave an amount of gum equivalent to 322 milligrams per 100 ml., but by evaporating such a quantity of spirit that the gum obtained did not exceed 10 milligrams, a result of 80 milligrams per 100 ml. was obtained. The air-jet method of gum determination has also been investigated by Bridgeman and Aldrich[35] who used flat-bottomed pyrex glass dishes approximately 80 mm. diameter and 45 mm. depth heated on a steam bath. The air-jet consisted of a plain glass tube of 8 mm. inside diameter, the end of which was approximately 2·5 cm. above the centre of the original surface of the liquid. The air was filtered to remove dust particles by passage through a tower packed alternately with fine mesh copper screen and absorbent cotton. After evaporation, the dishes were placed in an air oven at 102°C. (216°F.) for a period of 16 hours, after which they were cooled in a dissicator and weighed. Successive 2 hour periods of heating, followed by cooling and weighing, were then employed until the weight reached a constant value. On the average, constancy of weight was only obtained after 22 hours of heating (*cf.* the much shorter drying time of 1½ hours at 150°C. adopted by Littlejohn, Thomas and Thompson.) A comparison of the reproducibility of results by the air-jet, glass dish and copper dish tests is shewn below, from which it is evident that, whereas on the percentage basis there is not much difference between the reproducibilities of the first two methods of test, the actual deviations indicate that the air-jet and glass dish methods give much more reliable results than the copper dish test, and the air-jet method gives slightly more reproducible results than the glass dish test.

TABLE 133.—COMPARISON OF GUM TESTS. (BRIDGEMAN AND ALDRICH.)

Method	Average deviation per cent.	Average absolute deviation mgs.
Copper Dish	22·5	23·8*
Glass Dish	13·0	2·5
Air Jet	13·2	1·7

However, despite the improvement obtained by the use of the air-jet method, Bridgeman and Aldrich found that even this method of test did not give results on blended fuels in direct proportion to the gum contents of the blend constituents determined in the same manner. They therefore inferred that the method did not give "true" gum contents, but involved the effects of three variables apart from the idiosyncrasies of gasoline composition, (*a*) time of evaporation, (*b*) temperature, and (*c*) atmosphere surrounding the spirit during evaporation. These variables were investigated and it was found that the weight of

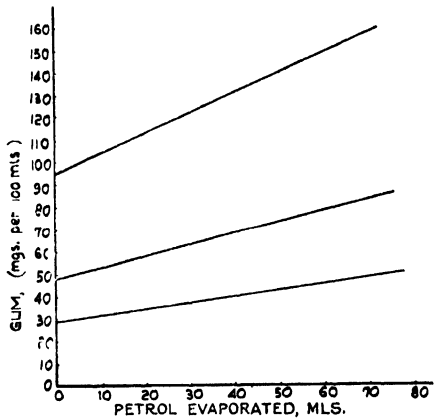


FIG. 148.—GRAPH SHEWING CHANGE IN APPARENT GUM CONTENT IN THREE GASOLINES WITH CHANGE IN VOLUME EVAPORATED (BRIDGEMAN & ALDRICH.)

gum obtained (in mgs. per 100 mls.) by the air-jet method increased with the volume of gasoline evaporated as shewn in Fig. 148 in which :—

$$G = V(a + bV) \quad \ldots \quad (1)$$

$$\text{and } \frac{100G}{V} = a_1 + b_1 V \quad \ldots \quad (2)$$

where G = the actual weight of residue formed on evaporation of volume V of gasoline,

$\frac{100G}{V}$ = the gum content in milligrams per 100 mls.,

a_1 = the gum content corresponding to instantaneous evaporation.

b_1 = the quantity of gum formed during evaporation.

* Excluding the worst 3 cases, this figure becomes 12·9 mgs.

Littlejohn, Thomas and Thompson also found an analogous decrease in gum content with decrease in volume of spirit evaporated.

630. The use of a high temperature air-jet has been recommended by Mulligan, Lovell and Boyd[36] as approximating in some respects the conditions which exist during the deposition of gum in the intake system of an automobile engine. The apparatus used is shewn in Figure 149. The evaporating dish is a Berzelius type of beaker of heat resistant glass and of 100 ml. capacity and is placed inside a bath containing 500 to 750 ml. of ethylene glycol (B.P. 195° —200°C.) which is fitted with a reflux condenser having a drying tube attached to its upper end. The bath is insulated and heated by means of an electric hot plate. The air supply is fed from a low pressure air system through cotton wool filters to a preheater situated in the bath where it is heated to the required temperature. The gum test is carried out by allowing a predetermined volume of spirit to be evaporated from the dish in the usual way. Drying is carried out *in situ* by means of the hot air-jet, or in an air oven at 150°C. for one hour.

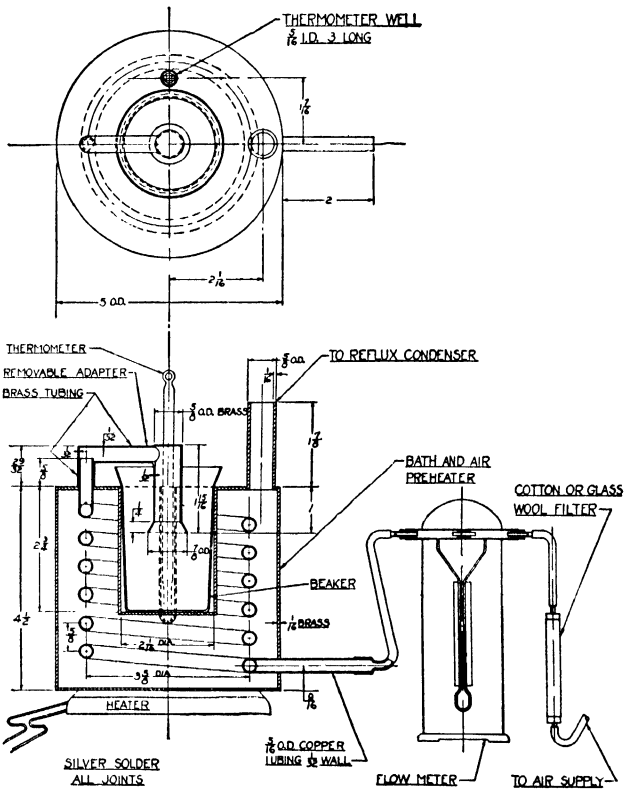


FIG. 149.—DIAGRAM OF HIGH TEMPERATURE AIR JET GUM APPARATUS.
(Courtesy, Editor, Industrial and Engineering Chemistry.)

These workers also examined a so called " hot drip " method in which spirit was allowed to drip into the evaporating dish from a capillary tube attached to a funnel. Hot air was introduced simultaneously through a larger tube surrounding the capillary at the rate of about one litre per minute. No splashing occurred and no creeping of the

gummy deposit up the sides of the beaker was observed, there being not more than 1 ml. of unevaporated gasoline in the beaker at any one time. Under these conditions the evaporation of a 50 ml. sample of gasoline required about 10 minutes.

Various gasolines were examined for gum contents by these methods and also by the conventional air-jet and steam oven methods with the results obtained in Table 134. These shew that, in general, the values obtained in the high temperature air-jet method are near those of the hot-drip and the steam oven methods but only about half those obtained by the conventional air-jet and 100°C. drip tests.

The effect of the atmosphere in the high temperature air-jet method was also examined but it was found that the use of air gave practically the same results as nitrogen or carbon dioxide. The effect of temperature was also determined.

TABLE 134.—COMPARISON OF GUM CONTENTS DETERMINED BY VARIOUS METHODS. (MULLIGAN, LOVELL AND BOYD).

Gasoline	High Temp. Air-Jet. 190°C. mgs.	Hot drip 190°C. mgs.	Steam oven 155°C. mgs.	Conventional Air-Jet 100°C. Evaporation 150°C. Drying mgs.	100°C. Drip Test 100°C. Evaporation 150°C. Drying mgs.	Modified Air-Jet 175°C. Evaporation 150°C. Drying mgs.
A (original)	—	118	135	313	319	153
	—	127	138	316	323	162
	—	137	—	—	—	—
A (later)	174	—	193	474	—	—
	172·5	—	—	—	—	—
B ..	2·5	2·9	2·9	4·8	5·2	3·5
	2·4	3·0	2·8	4·6	5·1	2·7
C ..	5·3	6·3	5·6	10·4	11·9	6·6
	5·2	6·2	6·0	10·1	11·4	6·5
D ..	10·0	10·6	11·4	18·7	17·6	11·0
	9·9	10·3	12·5	18·2	19·8	—
	10·4	—	—	70	68	40·4
	10·3	—	—	78	79	41·2
E ..	38·1	39·0	40·4	90	85	—
	37·8	—	13·8	95	105	—
	—	—	45·7	111	—	—
F ..	20·7	21·7	25·7	—	44·1	—
	21·0	19·9	25·9	—	—	—
	21·0	—	—	—	—	—
Time in minutes to obtain dry sample of gum ..	20—25	25—30	Several hours	70—80	70—80	70

631. The main feature of the above "hot drip" gum test, namely flash vaporization, was first suggested by Norris and Thole[32] who also had in mind the development of a test reproducing, as near as possible, the conditions existing in an engine induction system. This type of evaporation has much to commend it and in particular prevents the exposure of the higher boiling fractions of the spirit to the polymerizing action of heat for a much longer period than the lighter constituents. In ordinary dish tests this causes the amount of gum formed to increase with increase in the average boiling point of the spirit. Norris and Thole used a spiral tube of pyrex glass, 45 cm. long and 6 mm. internal diameter mounted in an air oven at 220°C. and fitted at the inlet with a tube through which nitrogen was passed through the system at a controlled rate, and a tap funnel by means of which a measured sample of spirit was introduced at a definite rate. Vapour from the exit of the spiral tube, mixed with nitrogen, was led off through a condenser. The gum content was determined by weighing the tube before and after the experiment. A sample of petrol which gave 30 milligrams of gum per 100 mls. by evaporation of 25 ml. in the steam bath glass dish test only gave 8—9·6 milligrams of gum in this improved method. In the words of the originators of this method, "it would appear that—the results so far obtained have convinced them that the method—is fundamentally more sound as well as superior in accuracy and rapidity to dish tests."

632. Other Tests for "Actual" or "Preformed" Gum Contents.—In 1930 Hunn, Fischer and Blackwood[37] described a gum test that had been developed by the Ethyl Gasoline Corporation and in which the fuel air mixture from a Holley Vaporizer was drawn by a vacuum over an iron plate heated to 400°F. (204·5°C.), which could be removed from the apparatus and weighed. One quart of fuel was used for each test, the time required being about one hour. Tests indicated that virtually all the dissolved gum in a spirit (as estimated by the conventional low temperature air-jet method) was deposited in this apparatus, as contrasted with a deposition of only 10—25 per cent. when the same fuels were tested in a Delco engine.

A comprehensive review of all the known methods of gum determination has recently been made by Egloff, Morrell, Wirth and Murphy.[38]

633. Proposed Standard Tests for the Determination of the Preformed Gum Contents of Motor Fuels.—The American Society of Testing materials have been enquiring into the question of standardization of gum tests for some time with the aid of a special sub-committee. Most of the methods described above have been critically examined in a

general testing programme and attempts have been made to correlate these tests with engine performance. At the present time sufficient work has been carried out to justify the standardization of a suitable tentative test procedure. This is a hot air-jet method involving evaporation at a temperature of 155°C., and full details have been published in the 1932 Report of Committee D 2, on Petroleum Products and Lubricants. (A.S.T.M. D381—34T)

634. Recently the Institution of Petroleum Technologists appointed a sub-committee to standardise a method for the estimation of gum present in cracked spirits and a report has appeared.[38A] This committee has drafted the following standardised method :

General

It is important that special precautions with regard to sampling should be taken :

1. The sample must be placed in a glass-stoppered bottle, the stopper of which is suitably retained in position.
2. The bottle must be filled to the neck.
3. The sample must be kept in a cool place and in the dark until required for testing.

The gum determination should be carried out as soon as possible after receipt, and immediately the bottle is opened.

Apparatus

Dishes.—The dishes shall be hemispherical in shape and made of a suitable resistance glass, e.g., Kavalier, Jena, Pyrex. Dish *a*, for a 25 ml. sample, shall be approximately 6 cm. in diameter, 3 cm. in height, and 12 grams $\pm$ 3 grams in weight. Dish *b*, for a 50 ml. sample, shall be approximately 9 cm. in diameter, 5 cm. in height, and 30 grams $\pm$ 5 grams in weight.

Steam-Heated Bath.—The holes in the steam-heated bath for accommodating the dishes shall be of such a size that the dish is immersed to within about 10 mm. of the rim. Over the centre of each hole there shall be placed vertically an air-jet at a distance of 4 cm. from the surface of the sample at the commencement of the test. The bath should be provided with a shield for protection from extraneous draughts.

Air-Jets.—The hole in the air-jet shall be $\frac{1}{16}$ in. (1·6 mm.) diameter and shall be drilled through a plate $\frac{1}{16}$ in. (1·6 mm.) in thickness. The pressure of filtered air passing through the jet shall be maintained at the equivalent of 1 cm. of water for dish *a* and 2 cm. of water for dish *b*.

Method

The dish shall be cleaned by immersion in concentrated sulphuric acid, preferably for at least one hour, rinsed with distilled water, then with acetone and wiped and finally dried in a suitable oven at 150°C. for 20 minutes. All subsequent handling of the dish shall be by means of metal forceps.

When required for the test the dish shall be removed from the oven and allowed to cool in a dust-free place for 15 to 20 minutes. The dish shall then be weighed to an accuracy of $\pm$ 0·1 mgm., all weighings being made by tare against a similar dish which has been subjected to exactly the same treatment (omitting the sample) at exactly the same time as the test dish. The same dish may be used as a tare for more than one test dish, but not for more than six test dishes, provided all are heated at the same time. Strict attention shall be given to these details of weighing in order to provide the accuracy necessary when low gum contents are involved.

The dish shall then be placed on the vigorously boiling steam bath with the air-jets in operation, and 25 ml. of the sample to be tested shall be measured out into the dish. The dish and its contents shall remain on the steam-bath for 60 minutes or such longer period as is necessary to ensure that no further evaporation takes place. The dish shall then be removed from the bath, wiped carefully outside, and transferred to an oven, the temperature of which is 150°C. $\pm$ 5°C. The dish shall remain in the oven for 1 hour, the temperature being maintained at 150°C. $\pm$ 5°C. The dish shall be allowed to cool in a dust-free place for 15 to 20 minutes and then be weighed to an accuracy of $\pm$ 0·1 mgm. as described above.

If the actual weight of gum finally obtained is less than 5 mgm. the test shall be repeated, using dish *b* and 50 ml. of the sample.

Care should be taken to avoid the condensation of steam on the jet, and in the event of any water dropping into the sample under test, the test shall be rejected.

Expression of Results

The gum content shall be calculated and expressed as milligrams of gum per 100 ml. of gasoline.

ACCURACY

With care and proper attention to details, duplicate determinations made in the same laboratory should not usually differ by more than 10 per cent.

In the event of this accuracy being unobtainable, owing to instability of the sample, a larger number of tests should be carried out and the mean of all the determinations recorded.

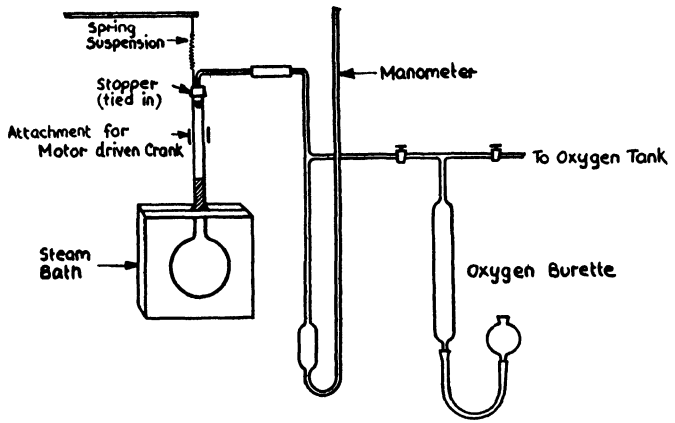


FIG. 150.—OXYGEN ABSORPTION APPARATUS OF VOORHEES AND EISINGER.

635. The Determination of the Gum Stability of Gasolines.—The foregoing gum tests are only of use in indicating the amount of gum present in a spirit at the time the test is carried out and they give no information whatever regarding the stability of spirits on further storage; therefore, in order to obtain this information other tests are required.

Naturally, the best way in which to obtain information regarding the stability of a spirit towards gum formation in storage is to submit it to such storage under the appropriate temperature conditions and to examine it for dissolved gum content after the desired time has elapsed; but such a procedure is cumbersome, as the result is only known after a long elapse of time. It is not surprising, therefore, to find that attempts have been made so to accelerate the chemical changes taking place in a spirit in storage that they may be made to occur to a measurable extent within a few hours in a small laboratory apparatus. The accelerating agents proposed are (1) Catalysts, (2) Heat and (3) High pressures; but of these only the latter two have been used to any great extent. In general an increase in pressure (of air or of oxygen) alone

is not sufficient to cause a measurable amount of gum formation within a reasonable time and combinations of heat and pressure have accordingly been used.

Perhaps the first attempt to predict the behaviour of petrol in storage by means of a laboratory accelerated ageing test was that made by Voorhees and Eisinger in 1928, and in which 25 ml. samples of petrol were heated at 210°F. (98·9°C.) in the presence of oxygen in the apparatus shewn in Fig. 150. The rate of oxidation could be followed by observing the fall in pressure registered by the manometer and the

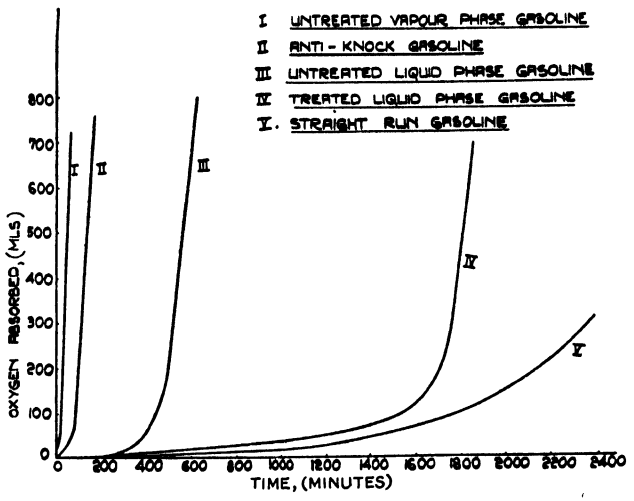


FIG. 151.—CURVES SHEWING OXYGEN ABSORPTION BY GASOLINE (VOORHEES AND EISINGER.)

extent of gum formation could be determined by a glass dish or similar dissolved-gum test on the oxidised spirit. Different petrols varied widely in their susceptibility to oxidation when tested in this way, but in all cases there was observed at the beginning of the test a distinct induction period, during which time the oxidation rate was very low. After the induction period, the extent of which varied to a marked extent with different spirits, oxidation proceeded at an ever increasing rate and the time required for the formation of a large amount of gum was very short. Typical results obtained for petrols of different types are reproduced in Fig. 151. Voorhees and Eisinger suggested that the stability of a spirit in storage could be predicted from a knowledge of the amount of gum it formed or by the length of its induction period in the test, and experiments which they conducted indicated that a spirit which formed less than 10 milligrams of gum when heated to 210°F.

for five hours in the presence of oxygen, would not form enough gum on storage for at least a year to impair its value.

The apparatus and method of test developed by Voorhees and Eisinger was later used by Herthel and Apgar[39] in a general study of gumming behaviour, when it was found that the use of rubber stoppers in the flask containing the petrol should be avoided, because they are attacked by the petrol and that moisture should be vigorously excluded because it accelerates oxidation.

636. The next workers in this field were Hunn, Fischer and Blackwood[37] to whom credit is due for the accelerated ageing test now in wide use. These workers used much higher oxygen pressures than had been customary in previous work and carried out the oxidation in a glass bottle enclosed in a steel bomb. The temperature chosen was 100°C. (212°F.) and the oxygen pressure 100 lbs. sq. inch, and it was found, in general, that a gasoline having a "break-down" time (i.e., time required to give a sharp drop in oxygen pressure) in this test of 1½ to 2 hours was sufficiently stable for normal storage conditions.

More recently the oxygen bomb test has been thoroughly investigated by Ramsay[40] who has adopted the following apparatus and method of procedure.

Apparatus.—Bombs were constructed of chrome-vanadium steel of about ¼ inch wall thickness, and inside diameter such that they would accommodate 8 ounce oil sample bottles with about $\frac{1}{16}$ inch clearance. The inside height of the bombs was about 2 inches greater than the height of the bottle. The bombs were machined out of the solid and were provided with flanges at the top to which the covers were bolted with ½ inch bolts. The joint between the bomb and the cover was made tight by means of a lead gasket squeezed down into a circular recess by means of the bolts. Each bomb was fitted with a pressure gauge attached to the bomb through an intermediate coil of ⅛ inch copper tubing, to minimize condensation of petrol vapours in the gauge. The oxygen inlet pipe to each bomb was fitted with a fine adjustment needle valve.

In order to investigate the effect of temperature in these oxygen bomb tests, Ramsay made use of a large oil-filled bath capable of holding six bombs. This was thermostatically controlled and efficiently stirred and was filled with water-white transformer oil to which 0·1 per cent. β-naphthol had been added to reduce oxidation and corrosion. The standard procedure adopted for charging the bombs was as follows:

"After thoroughly cleaning and drying the inside of the bombs

they were placed in an ice bath for at least 45 minutes with the covers in place. At the end of this time the covers were removed, a cork pad was placed in the bottom of each bomb and an 8 ounce bottle containing 100 ml. of the gasoline to be tested was inserted in each. Before use each 8 ounce bottle was cleaned with sulphuric acid and dichromate mixture, washed with distilled water and dried in an oven. Over the neck of each bottle was placed a parchment cap, made from a Soxhlet extraction thimble, in order to prevent contamination of the sample, and the covers were then put in place and made tight. The bombs, with the samples inside, were allowed to stand in an ice bath until the petrol samples dropped to approximately 0°C. and at this point the bombs were connected to an oxygen cylinder, and oxygen 10 lbs. in excess of the desired pressure, was admitted. After cooling for 15 minutes, the pressure was lowered to the exact experimental pressure, the bombs were placed in the high temperature bath and the experiment started. At the completion of the experiment, the bombs were again placed in the ice bath for about 15 minutes, after which the pressure was released and the samples removed." Experiments were always run in duplicate.

637. Using such an experimental procedure Ramsay examined the relation between gum stability and the length of the induction period and determined the effect of oxygen pressure and temperature. The same ground was covered a little later by Aldrich and Robie[41] and it is convenient to consider the results obtained in these two parallel investigations at the same time.

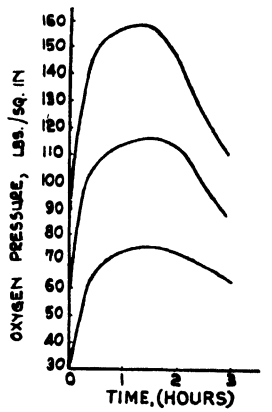


FIG. 152.—TYPICAL PRESSURE-TIME CURVES AT DIFFERENT INITIAL OXYGEN PRESSURES. (ALDRICH AND ROBIE.)

When the bombs charged with petrol samples and oxygen to the desired pressure are placed in the high temperature bath, the pressure first of all rises while the bomb attains the temperature of the bath. The pressure then remains essentially constant for a length of time which depends upon the stability of the petrol sample and upon the initial oxygen pressure and finally drops as the oxidation and absorption of oxygen proceeds. The interval between the time of introduction of the bombs into the oil bath and the time at which the pressure begins to drop is taken as the " induction period." However this is not the *true* induction period because obviously it is dependent upon the rate of heating, and should be corrected to give the " true induction period " at the bath temperature.

Typical pressure—time curves are given in Fig. 152 and these shew the above separate stages.

It has been logically assumed by various investigators that during the induction period no gum is formed and that this only occurs when the oxygen pressure begins to fall. The validity of this assumption is shewn in Fig. 153, which refers to tests carried out at three oxygen pressures by Aldrich and Robie and in which the arrows indicate the measured induction periods.* Similar results are obtained for other spirits. It would appear however, that the quantity of gum formed during the induction period becomes smaller as the pressure is decreased. Hence a measurement of the induction period at various pressures and extrapolation to an oxygen concentration equivalent to an air pressure of one atmosphere might give a true indication of stability at the temperature employed. The relationship between the induction period at 100 lbs. oxygen pressure and the induction period at 1 atmosphere air pressure is given by the equation :

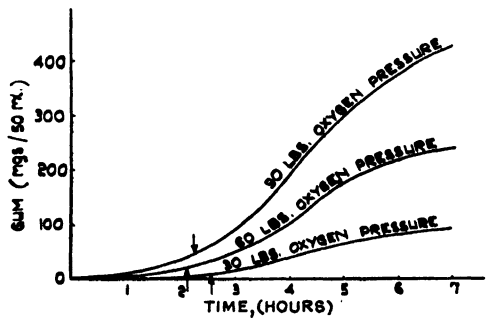


FIG. 153.—CURVES SHOWING GUM CONTENTS AT VARIOUS TIMES DURING THE ACCELERATED OXIDATION TEST FOR THREE OXYGEN PRESSURES. INDUCTION PERIODS DENOTED BY ARROWS. (ALDRICH AND ROBIE.)

$$I_{1\,atm} = K\ I_{100} \quad . \quad . \quad . \quad . \quad (3)$$

in which K has a value of from 1·38 to 1·41, while the general equation representing the relation between the induction period at any pressure and the value at an air pressure of 1 atmosphere, for the same temperature in both cases is :

$$I_{1\,atm} = \frac{154{\cdot}6}{150 - 0{\cdot}40\,P}\ I_P \quad . \quad (4)$$

where P is the initial oxygen pressure in pounds per square inch gauge.

The induction period at any given pressure changes markedly with change in temperature and it has been found that if the logarithm of the induction period is plotted against the logarithm of the Centigrade temperature, a straight line reproduces the plotted points within the experimental error. The slope of this line varies with different spirits and may be represented by the general equation :

$$\text{Log } I = a + b \log T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which a and b are constants characteristic of each gasoline and whose values vary from 13·0 to 20·0 and from − 0·03 to − 0·05 respectively.

In the light of the above relationship it would appear to be very

* There is, however, some difference of opinion on this point and Bridgeman[44] states that extensive oxidation of the fuel may occur although the pressure in the bomb may remain substantially constant.

unlikely that a rigid connection should exist between the induction periods at elevated temperatures and pressures, and length of stability in storage at normal temperatures and pressures. Thus, before test in the oxygen bomb, the petrols may be stored for a considerable time and may have passed their period of stability so that the observed induction periods may change comparatively little with decreasing temperature, i.e., the slopes of the lines connecting temperature with induction period vary for different spirits. It is possible to have two petrols which have the same induction periods at 100 lbs. oxygen pressure and 100°C. but have quite different induction periods under normal storage conditions.

It is necessary therefore, in determining the length of storage for which a spirit is suitable without forming gum, to conduct oxygen bomb gum tests at different pressures and temperatures and to extrapolate the observed results to normal storage conditions. No two gasolines may be assumed to behave alike and it is therefore necessary to do experiments at at least two pressures and two temperatures before an accurate extrapolation is obtained.

However, despite these failings of the oxygen bomb test for petrol stability, it has already found a place in certain motor-fuel specifications. Thus the Air Corps of the U.S. Army have tentatively adopted such a procedure for judging the stability of aviation spirits[43] (see Chapter 14, paragraphs 839 and 840) and the same kind of test is used by the U.S. Naval Engineering Experimental Station at Annapolis, who have claimed that the amount of gum produced by a four hour accelerated ageing test is approximately equal to that produced by ninety days storage.[44] Thus :

	Ordinary Gum Test		
Gasoline No.	When received	After 90 days storage.	Four hour accelerated ageing test
	mgs./100 mls.		mgs./100 mls.
1	none	3.0	4·2
2	none	none	3·0
3	none	none	none
4	none	2·5	1·8
5	none	none	1·5
6	1·0	2·0	3·0
7	none	none	1·0
8	none	1·3	none
9	none	none	none
10	none	none	1·8
11	none	2·0	4·0
12	none	2·2	2·4

638. Thomas[45] has recently described an accelerated ageing test which has been developed in the laboratories of The Anglo Persian Oil Company and in which 50 ml. samples of spirits are treated with oxygen at 10 pounds per sq. inch pressure at 100°C. for 20 minutes in a Standard type of Mahler bomb used in calorific value determinations. After treatment in this way the sample is removed from the bomb and its existent gum content determined in the usual manner by an evaporation test. Thomas has also described a similar ageing test, in which 400 ml. samples are used, for the estimation of general stability (e.g. colour, gum and knock rating). In this case also an oxygen pressure of only 10 pounds per square inch is used. The bombs employed are vitreous-enamelled on the inside and the use of glass bottles inside the bomb is thus rendered unnecessary. Furthermore the lag in heating the sample up to 100°C. is considerably reduced.

It is concluded that in view of the very considerable practical difficulties of correlating a potential gum test with storage, a suitable procedure would be to determine in the bomb, the gum stability curve of a bulk of refined material which is known to be satisfactory both as regards lack of gum formation and in actual use in the engine, and about which no complaints have been received. By refining finished spirits to conform to this agreed gum stability curve, the gum stability of the materials would be assured (within limits) whatever the subsequent conditions of storage.

Tests for determining the potential gum contents of spirits by treatment with ultra-violet light[46] and stannic chloride[47] (which polymerises unsaturated hydrocarbons with an evolution of heat) have recently been proposed, but these are not likely to find extended application.

639. Accelerated Gum Tests for Motor Benzoles.—Motor benzoles differ from cracked spirits in the important respect that they contain only very small amounts of unsaturated hydrocarbons (up to about 5 per cent. by volume). Consequently in an oxygen bomb gum test they absorb a smaller quantity of oxygen and the drop in oxygen pressure at the end of the induction period is masked by slight variations in temperature and barometric pressure, unless these factors are very carefully controlled. For these reasons the measurement of the induction period has not been found satisfactory in the case of benzoles and measurement of the amount of gum formed during an oxidation test has been found to be the only practical method of assessing gum stability in storage.

In 1928 Hoffert and Claxton[1, 16] described an oxidation test for benzoles, in which oxygen was bubbled at a definite speed through 100 ml. of benzole contained in a 150 ml. glass flask and maintained at

refluxing temperature for four hours at atmospheric pressure. The benzole was then evaporated from a glass dish on a boiling water bath and the residue weighed. It was claimed that a benzole stable to this test was stable under ordinary storage conditions and that the results of the test usually gave a rough indication of the extent of gum formation on storage. These claims appear to be justified by the figures given in Table 135, which shew that benzoles giving up to 10 to 15 mg. of gum per 100 ml. do not increase in gum content on storage.

TABLE 135.—COMPARISON OF OXIDATION TEST RESULTS WITH THE RESULTS OF STORAGE AND LABORATORY TESTS ON BENZOLES. (HOFFERT & CLAXTON[48]).

Oxidation Test Mgs/100ml.	Time of Storage (months)	Gum in Benzole after storage Mgs/100ml.	Oxidation Test Mgs/100ml.	Time of storage (months)	Gum in Benzole after storage mgs/100ml.
0·5	4	2·0	55·5	6	25·5
0·5	4	4·5	67·0	4	70·5
1·0	4	0·5	70·5	3·5	10·0
1·0	4	2·5	72·0	4	2·5
1·0	4	4·0	82·5	4	11·5
1·0	4	5·0	89·5	3	15·5
1·0	4	6·5	102·0	3	130·0
1.5	3	0·5	111·5	2·5	44·0
4·5	2	5·5	112·0	3	155·0
5·0	4	2·5	127·5	4	373·0
5·5	6	4·0	129·5	4	84·5
6·5	2·5	2·5	135·5	4	60·0
7·5	7	2·0	196·5	4	113·5
10·0	2·5	3·0	206·5	4	167·5
13·0	7	1·0	226·0	3	33·0
22·0	4	7·0	266·5	3	94·0
30·5	6	8·0	282·0	4	111·0

TECHNICAL SCALE TESTS.

Oxidation Test mgs/100mls.	Time of Storage months	Gum in Benzole after storage mgs/100mls.
1·0	4	0·5
3·5	3	2·0
3.5	18	3·0
5·0	4	3·0
6·0	4	3·5
7·0	5·5	4·0
10·0	4	21·0
21·0	4	19·0
23·0	4	7·0
33·5	4	42·5
52·5	5·5	36·5
70·0	5·5	67·0

This type of test has now been standardised and included in the National Benzole Association specifications for motor benzole. It has also been approved by the Technical Committee of the International Conference of Benzole Producers. Details of the standardised test are as follows[48]:

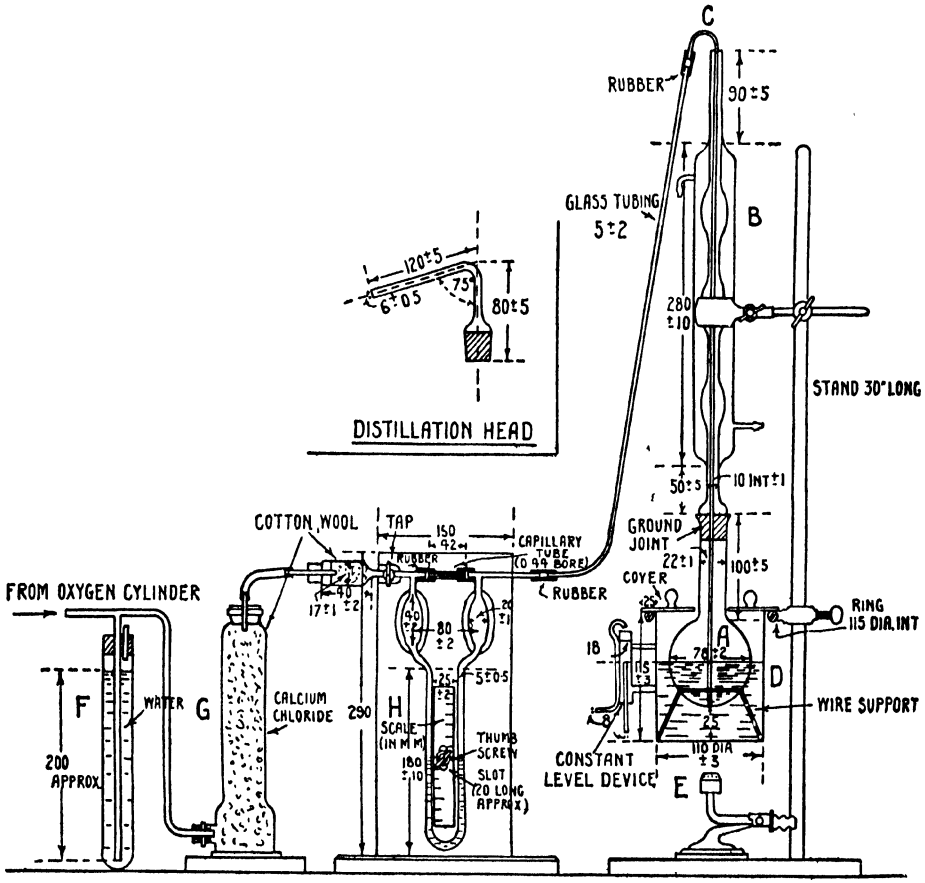


Fig. 154. Oxidation Test Apparatus for Benzoles.

The apparatus is shewn in Fig. 154 and consists of a 250 ml. round bottomed flask attached by a ground glass joint to a reflux condenser and contained in a water bath. A current of oxygen is passed from an oxygen cylinder through the constant pressure device F, a calcium chloride drying tube (G) a cotton wool filter and a flow meter (H) to a tube passing down the inside of the reflux condenser and dipping under the surface of the benzole contained in the flask. 100 ml. samples of benzole are used in the test, and oxygen rates of 35 ml. per minute. The temperature of the benzole in the flask is kept at 100°C., by

maintaining the water in the water bath in a state of active boiling. The duration of the oxidation is standardised at 3 hours. After the oxidation, the oxygen stream is turned off, and the flask disconnected from the remainder of the apparatus. The flask is then fitted with a distillation head (as shewn in Fig. 154) and 75 per cent. of the benzole is distilled off. The residue is then evaporated from standard pyrex dishes (66·5 mm. ± 2 mm. diameter and 18 grams ± 3 grams in weight) on a water bath for a period of 1½ hours, followed by drying at 98° to 105°C. for one hour, after which it is weighed. The gum content is expressed in the usual way, i.e., milligrams per 100 ml.

It should be noted that this test was developed especially for benzoles. It is not suitable for petrols.

640. The Effect of Gum in Motor Fuels on Engine Operation —Permissible Limits for gum Content.—That gum in petrols may cause serious trouble in engine operation has been generally recognised since about 1915 when Hall[49] stated that " a spirit with such (gumming) tendency will eventually clog and stick up the valves of any engine in which it may be used." Experiences are also on record in which about 10 gallons of vapour-phase cracked spirit stored for about seven years were used in a car which at the time had already been driven over 80,000 miles and which had rather loose valves and valve guides. The use of this spirit very quickly resulted in sticking of the valves and the deposit on the inlet valve guide was $\frac{1}{16}$ inch thick and extremely sticky. Another car, which was also using the same fuel and which was rather new, was more unfortunate in that it was almost impossible to remove the inlet valves, in fact, a crow-bar was resorted to and, in one or two cases, the valve stem guide came out with the valve.[28]

In 1928 Voorhees and Eisinger conducted an investigation with the object of determining to what extent a fuel should be free of gum in order to avoid repetitions of the above experiences, and used for this purpose a single cylinder air cooled Delco model 850 engine. The engine was operated usually at about 1250 r.p.m. and was thoroughly cleaned before each test, making sure that there was no carbon in the combustion chamber and that there was no deposit in the inlet manifold. The valves were also ground in and their stems and guides cleaned. The engine was then run on a measured quantity of fuel under certain standard conditions and after the tests the cylinder head and inlet valves were removed and photographed. Carbon deposits were removed and weighed. Fifteen different tests were thus made on various kinds of spirit with the results reproduced in Table 136. Inspection of these results brings out very clearly the important fact (which has already been mentioned) that a spirit may have a high potential gum content

TABLE 136.—SUMMARY OF ENGINE GUM TESTS (VOORHEES & EISINGER)

Run No.	Fuel Used.	Gum by steam oven test, mgs./100ml.	Gum by oxygen gum test, mgs./25ml.	Gum by copper dish test, in mgs./100ml.	Weight of deposit inlet manifold, grams.	Weight of Carbon deposit on Cylinder head, Grams.	R.P.M.	Load H.P.	Length of test, Hours.	Remarks
1	Commercial Spirit No. 1.	4	3	10	0·00	—	1260	0·45	16·25	No gum deposit in inlet passage or in cylinder.
2	Vapour-phase gasoline No. 2.	7	6	65	0·00	—	1370	0·45	16·75	Ditto.
3	Vapour-phase gasoline (one year old) No. 3.	120	520	665	3·99	3·29	1240	0·75	17·25	Much gum in cylinder head and on valve. Valve sticking.
4	Vapour-phase spirit No. 4.	22	380	188	0·94	1·57	1230	0·80	21·25	Some gum deposit inside of Cylinder head.
5	Vapour-phase spirit No. 5	17	360	237	0·41	3·38	1220	0·83	23·75	Ditto.
6	Fuel No. 6 (50% of Fuel No. 4) and 50% of Fuel No. 1.	11	—	110	0·17	1·93	1240	0·85	19	Slight trace of gum on inlet valve.
7	Commercial Spirit No. 2	4	—	19	0·00	—	1310	1·10	16·75	No gum deposit in inlet manifold or in cylinder.
8	Fuel No. 8A (Fuel No. 1 with dissolved gum).	39	—	69	0·29	4·84	1230	0·93	17·75	Considerable gum inside cylinder head.
9	Fuel No. 8B (ditto)	12	—	46	0·12	3·09	1260	0·87	17·25	No gum deposit in cylinder head.
10	Vapour-phase spirit No. 9	4	150	51	0·00	—	1280	0·98	15·75	No gum deposit in cylinder head or in inlet manifold.
11	Vapour-phase spirit No. 11 (freshly distilled).	8	850	712	0·00	1·29	1280	1·01	19·75	Ditto.
12	Fuel No. 8C (Fuel No. 1 with dissolved gum).	18	—	32	Trace	1·17	960	0·00	28	Trace of gum on inlet valve.
13	Same as fuel No. 8C.	18	—	32	0·27	1·24	1220	0·98	19·5	Some gum deposit inside of cylinder head.
14	Vapour-phase spirit No. 10.	12	170	453	0·09	3·04	1240	0·71	19	No gum deposit inside cylinder head.
15	Fuel No. 12A (Fuel No. 1 with dissolved gum).	76	—	81	0·20	2·88	1230	0·75	19·5	Considerable gum deposit inside cylinder head.

as shewn by the oxygen gum test (and also partly by the copper dish test) and yet give satisfactory performance in the engine. This is most strikingly illustrated in the case of Test No. 11, which was made

on a freshly distilled vapour-phase cracked spirit. This fuel, which gave 712 mgs. of gum by the copper dish test, but only 8 mgs. of preformed gum by the steam oven test, gave good performance in the engine, with absolutely no deposit in the inlet manifold. On the other hand, a spirit which contained a somewhat larger amount of actual or preformed gum as shewn by the steam oven test (Fuel No. 5) gave an appreciable gum deposit in the engine. These results support the contention that the spirit is not in the manifold sufficiently long to permit oxidation and formation of gum, and only gum which has been previously formed can be deposited on the hot surfaces. The temperature of the inlet manifold appears, from the results of Voorhees and Eisinger, to have a measurable effect on both the amount of gum deposited and the nature of the deposit. Thus Run No. 12 made under conditions such that the intake manifold wall temperature was 135°F. (57·2°C.), gave only a small trace of gummy deposit, whereas Run No. 13, on the same fuel, at an intake temperature of 175°F., shewed a much greater deposit which was decidedly hard and brittle. The engine used in these tests was of the overhead-valve type and this was probably the reason why gum deposits, which were in some cases excessive, did not cause any great trouble in sticking of valves, as the gum formed ran down the valve stem and collected mostly on the under side of the valve head instead of on the stem, sometimes running into the combustion chamber. It therefore appeared logical to assume that valve sticking would manifest itself sooner in an "L" head engine than in an engine fitted with overhead valves.

641. Further work on this important subject has been carried out by Hunn, Fischer and Blackwood[37] on two water-cooled Delco engines and on a Buick 6 cylinder car. The former engines were fitted with special intake manifolds, 5 inches long, horizontally placed and electrically heated, while thermocouples at the cylinder ends of the intake manifolds recorded the air-fuel mixture temperatures. Fixed carburettor jets were used and the running conditions were as follows: Spirit per test 25 gallons; engine speed 1,200 r.p.m.; water outlet temperature 180°F. (82·2°C.); mixture temperature 170°F. (76·7°C.); maximum possible throttle opening. The two Delco engines used were not identical and it was consequently found that Engine No. 2 gave heavier gum deposits than Engine No. 1. The results obtained on these engines are reproduced in Table 137.

The results shew that only a fraction of the dissolved gum in the gasoline, as determined by the usual laboratory evaporation tests, is deposited in the intake system, the percentage of the total depending upon the design and the operating conditions of the engine. The undeposited gum is carried into the combustion chamber and burnt

TABLE 137.—DELCO ENGINE GUM TESTS. (HUNN, FISCHER & BLACKWOOD).

Sample	Gum Content of Sample. Mgs per 100 ml			Total gum deposit. Mgs	
	Copper Dish	Porcelain Dish	Air-Jet Test	Per 100 ml Fuel	Per gallon Fuel
Engine No. 1.					
1. Anti-Knock Gasoline plus 1% High Gum Content Spirit ..	180	17	16	4·4	168
3 2 parts Anti-Knock Naphtha plus 1 part of Vapour Phase Spirit	212	13	17	1·5	56
5. Acid Treated Vapour-Phase Spirit	258	19	8	0·3	12
7. Anti-Knock Spirit plus Copper Oleate	277	130	19	3·3	124
9. Untreated Cracked Spirit ..	320	20	14	1·7	64
10. Anti-Knock Naphtha ..	29	5	5	0·5	20
10A. Anti-Knock Naphtha plus 2ccs Tetra-Ethyl Lead ..	46	15	6	0·4	16
10B. Anti-Knock Naphtha Blend..	18	6	6	1·6	60
13. California Spirit	15	5	3	0·4	16
14. Anti-Knock Spirit plus 5% raw Vapour-Phase Gasoline ..	172	19	19	4·9	184
Engine No. 2.					
1. Anti-Knock Naphtha plus 1% High Gum Content Spirit ..	180	17	16	6·5	248
4. Untreated Vapour-Phase Spirit	243	968	122	29·0	760
6. Anti-Knock Naphtha plus Copper Oleate	240	126	11	5·8	220
8. Anti-Knock Naphtha plus 1cc Tetra-Ethyl Lead ..	15	4	3	0·7	28
9A. Untreated Cracked Gasoline	365	50	36	8·0	304
11. Anti-Knock Naphtha plus 1cc Tetra-Ethyl Lead ..	12	3	3	0·8	32
12. Vapour-Phase Gasoline after 2½ months storage	170	33	8	3·8	144
15. Vapour-Phase Gasoline blend after 4 months storage ..	17	10	6	3·1	116
16. Acid Treated Vapour-Phase Spirit after 5 months storage	493	232	51	1·0	72
17. Acid Treated Vapour-Phase Spirit	9	2	1	0·4	16

with the fuel charge. The results also shew the futility of the copper dish test for gum (cf. samples 3, 5 and 9 with samples Nos. 10B and 12) and indicate that the air-jet gum figures are in rough agreement with engine test data. Sticking valves were not common in these tests.

Engine No. 1 gave no trouble in this way, but Engine No. 2 developed a sticking inlet valve on samples Nos. 4 and 9A, both containing large amounts of gum by the air-jet method.

In tests on a Buick six cylinder car a fuel containing 10 mgs./100 mls. of gum by the air-jet method gave perfect operation throughout a run of 5,000 miles while a fuel containing 25 mgs. of gum gave a perceptible loss of power after 3,000 miles though it gave no valve trouble. A fuel containing 50 mgs. of gum gave marked loss in power and slight trouble from sticking inlet valves.

642. Further work has been recently carried out by Marley, Ridenour and Gruse[50] on three different single-cylinder engines, one of which was an experimental outfit built round a Delco generator and crankshaft, and of which the other two were single cylinders of full normal engine size and design, one being of the overhead valve type and the other an L-head engine. The first engine was provided with an electrically heated straight tubular intake manifold, eight inches long and one inch in diameter, in which a thermometer was inserted for temperature measurements. The L-head engine was fitted with a Stromberg DX-3 down-draft carburettor mounted just above the manifold and close to the exhaust port, while the temperature of the fuel air mixture was controlled by a flutter valve which served to control the path of the mixture over the exhaust heated manifold. The time of heating of the fuel-air mixture was artificially increased to such an extent that the amount of mixture for only one cylinder passed through a heater large enough to take care of six or eight cylinders. The valve-in-head engine was provided with an intake manifold in which the time of heating was increased still further.

The results obtained on these engines with fuels of normal A.S.T.M. distillation curves and varying gum contents are particularly interesting in that they shew the effects of inlet manifold heating and mixture strength upon the extent of gum deposits.

These indicate that at intake temperatures up to and including 50°C., even a 35 mg. gum content fuel produces little gum deposit, but as soon as the mixture is heated to 65°C. the gum deposits increase rapidly with rise in gum content. A 3 mg. gum content fuel gave practically no gum deposit at any intake temperature examined but an 18 mg. gum content fuel gave increasing deposits at temperatures above 50°C. In general, for a fuel of any gum content, raising the intake temperature causes more of the gum to be deposited in the intake system and less to be deposited in the combustion chamber; but at low intake temperatures, the gum content of the fuel appears to have a noticeable effect in raising carbon deposits within the engine cylinder. It will be noticed that at high intake temperatures rich mixtures give larger gum deposits

than lean mixtures, this is also true at lower intake temperatures though to a less extent.

Tests were also carried out on a fuel of very high gum content (265 mgs./100 ml). A series of runs was first made in the small overhead valve engine, each being continued until the engine stopped itself with a gummed up inlet valve. Tests were also conducted in the larger L-head engine at an air fuel ratio of 13 to 1. The results obtained in these tests are reproduced in Tables 138 and 139 and shew the large effect of manifold temperature. Moreover they indicate that by lowering intake temperatures, volatile spirits of moderate gum content (say up to 30 mgs./100 mls.) might perhaps be used without serious trouble from gum deposits. Under actual road conditions Mock[51] found mixture temperatures to be as low as 26·0°C. (80°F.) in winter, about 48·9° to 65·5°C (120 to 150°F.) in spring and as high as 93·3°C. (200°F.) in summer, while under extreme conditions they may rise to 160°C. (320°F.) Experiments by Brown[52] indicate winter temperatures of 43·3°C. to 57·2°C. (110 to 135°F.) and summer temperatures of up to 93·3°C. (200°F.)

TABLE 138.—FUEL OF 265 MGS/100 ML. GUM CONTENT IN SMALL OVER-HEAD VALVE ENGINE. AIR FUEL RATIO = 12 TO 1. (MARLEY, RIDENOUR & GRUSE).

(Duplicate tests).

Intake mixture Temp. °F. ..	127·4	127·4	86	86
°C.	53·0	53·0	30·0	30·0
Time till engine stopped ..	3hr. 50min.	3hr. 38min.	5hr. 43min.	5hr. 10min.
Intake deposit (grams.) ..	1·3	1·9	1·1	0·8

TABLE 139.—TESTS IN L-HEAD ENGINE. AIR FUEL RATIO 13 TO 1. (MARLEY, RIDENOUR AND GRUSE.)

Gum content of fuel.	Intake temp.	Intake deposit	Combustion chamber deposit
265 mgs/100 ml. ..	86°F. (30·0°C.)	0·53 grams.	8·5 grams.
265 mgs/100 ml. ..	176°F. (80°C.)	29·60 grams.	6·5 grams.

643. It may reasonably be inferred from the above results that although correlation may be obtained between gum contents as determined by the air-jet evaporation test or any other approved test for actual gum content, and the results obtained on one particular engine operating under certain conditions, it is a much more difficult matter to give a definite opinion regarding the maximum permissible gum content of a spirit intended for general distribution and use in a large variety of

engines under a multitude of different conditions. There appears to be only one safe course to adopt, and that is to limit the gum content of a fuel to such an extent that it will not give serious trouble under the most exacting conditions to which it is likely to be subjected in service. It is admitted that this may increase the cost of refining unnecessarily, but only in this way is it possible to give satisfaction to all users.

644. Gum Inhibitors.—Considerable research work has been done in studies of the inhibition of various oxidation reactions, and in recent years this has been applied to the prevention of gum formation in cracked spirits. Among the leaders in this work are Moureau and Dufraisse who were among the first to record the important observation that small amounts of certain materials when added to readily oxidisable substances prevent their oxidation, and these workers have studied the subject in detail as applied to the oxidation of individual chemical compounds, e.g., benzaldehyde and styrene.[53] A comprehensive review of this work has been given by Milas.[22]

Smith and Wilson[54] investigated the action of inhibitors on the rate of oxygen absorption by unsaturated organic compounds, while Backstrom,[55] Alyea[56] and Christiansen[57] have all suggested a chain reaction to account for the anti-oxidation effects of inhibitors.

645. At the present time, considerable interest is being shewn in the inhibition of gum formation in cracked spirit by the use of so called "anti-oxidants" or "inhibitors." Universal Oil Products Co., the owners and licensors of the Dubbs cracking process, have announced the development of a successful inhibitor which they are prepared to license to users. A new company called Anti-Oxidants, Ltd., has been formed to market similar substances covered by the patents of The Standard Oil Co., of Indiana, Du Pont Ammonia Corporation and The National Benzole Company (England).

The advantages attending the use of such inhibitors are far reaching, in as much as they permit the employment of less drastic refining methods, thus reducing refining losses and cost of refining. Moreover, because of this, they partly prevent the high loss in anti-knock value caused by drastic refining, especially in the case of vapour-phase cracked spirits. Furthermore they allow the spirits to be stored with much less trouble from gum formation. However, whether or not inhibitors find ready application in the petroleum industry is purely a matter of economics. If they are made available to the petroleum refiner at very low royalty charges, their use may expand rapidly, but if their cost is so high as completely or nearly to offset any other economies occasioned by their use, then obviously their adoption will be on a very limited scale.

646. Perhaps the first published work on the stabilisation of motor fuels against gum formation in storage is that of the National Benzole Association, which is described in detail in the Annual Reports of the Benzole Research Committee from 1926 onwards. This work was chiefly concerned with the stabilisation of motor benzoles and resulted in the discovery that " tri-cresol," a mixture of ortho-, meta- and para-cresols, and many other substances, could be used in very small concentrations to prevent gum formation. In 1926, the first patent on gum inhibition in motor fuels appeared in the names of Hoffert and Somerville, of the National Benzole Association, covering the use of aromatic amines, phenols and nitro bodies, but specifically tri-cresol for this purpose.[58] Prior to this date patents had appeared on the inhibition of sludge and resin formation in transformer and lubricating oils by the addition of other similar anti-oxidants.[59, 60]

Since 1926 many patents have been granted covering the use of inhibitors in motor fuels and much information has been published in the literature concerning their relative efficiencies.

It is appropriate to consider the work of the National Benzole Association first. Their original patent detailed the desirable characteristics of an inhibitor as follows :

1. It must be capable of preventing or reducing the formation of resin (gum).
2. The amount added must leave little or no residue on evaporation of the fuel.
3. It must not react with any of the constituents of the fuel to an extent which will give rise to any residue on evaporation or to objectionable by-products.
4. When added to the fuel it must have little or no effect upon any metal or other engine parts with which it is likely to come in contact.
5. It must be capable of dissolving or uniformly dispersing in the fuel.

It was noted that the inhibitors need only be added to the fuel in very small quantities (up to about 0·05 per cent.) and that (in some cases at least) there was an upper limit to the amount which could usefully be employed. Tendency to gum formation was found to be increased by certain substances, e.g., acids, aldehydes and mercaptans ; to be decreased by others, such as the compounds specified, while other substances such as water, alcohols, ethers, thiophene and carbon disulphide appeared to have little or no effect.

It has already been pointed out that in the case of cracked spirits, the length of the induction period in the oxygen accelerated gum test is approximately related to the length of permissible storage before

gumming occurs, but that in the case of motor benzoles containing comparatively small amounts of unsaturated or gum forming bodies, it is difficult to determine the length of these induction periods accurately. However, it has been found that if the length of the induction period of a benzole has not been passed at the end of three hours oxidation in the N.B.A. standard oxidation test the benzole is stable under the usual conditions of storage for periods of at least six months. In indicating the value of inhibitors, Fig. 155 reproduced from the published work of Hoffert and Claxton,[61] is of interest and shews that as little as 0·01 per cent. by weight of p-cresol is sufficient (with the particular benzole under test) to cause an induction period of this duration.

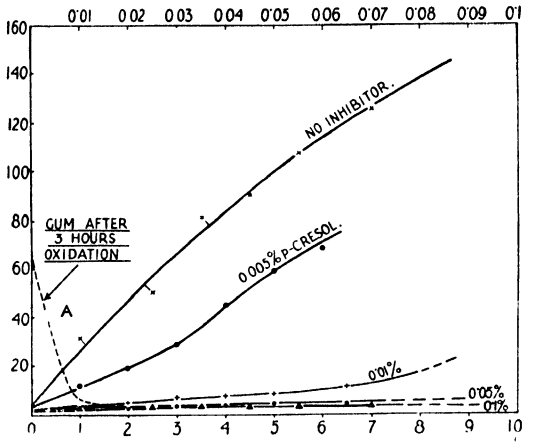


FIG. 155.—CURVES SHEWING THE EFFECT OF PARA-CRESOL AS AN INHIBITOR IN BENZOLE. (HOFFERT AND CLAXTON.)
(Courtesy, Editor, "Journal of the Society of Chemical Industry.")

647. The conditions of storage, such as temperature, material of the containing vessel, the presence of water, the accessibility of air, etc., vary so widely that the exact correlation of the quantities of gum formed in an accelerated gumming test with the quantities of gum formed on storage, or even of the length of the induction period with the behaviour of a fuel on storage, is extremely difficult. It is therefore necessary to provide a factor of safety by adding sufficient inhibitor to ensure that the induction period in storage is far longer than the time of storage to which the fuel is to be submitted. In the case of benzoles produced by high temperature carbonisation processes 0·03 to 0·05 per cent. by weight of ortho- or para-cresol is usually sufficient for normal storage.

It has been found, in the case of some inhibitors, that when very small amounts are added to motor fuels, the tendency to gum formation rapidly decreases to a minimum at some critical concentration of

inhibitor and then increases when more inhibitor is added. The most suitable concentration varies according to the nature of the particular inhibitor used and also according to the character of the fuel to which it is added.

Thus with benzoles, *p*-methyl amino phenol and *p*-phenylene diamine give the smallest quantity of gum when their concentration is about 0·001 per cent. by weight, whereas with ortho- and para-cresols the corresponding concentration is about 0·05 per cent. by weight. The optimum concentration of benzylamino-phenol is about 0·001 per cent. by weight with benzoles and about 0·005 per cent. in the case of spirits obtained by low temperature carbonisation (Hoffert and Claxton).

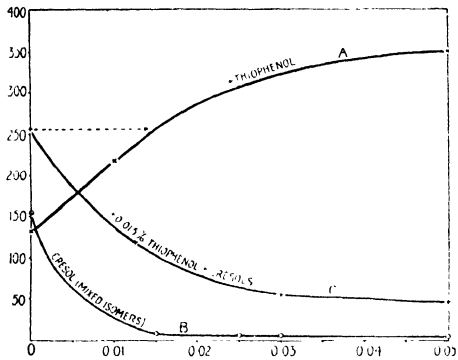


FIG. 156.—CURVES SHEWING THE EFFECT OF THIOPHENOL UPON THE EFFICIENCY OF MIXED CRESOLS AS A GUM INHIBITOR. (HOFFERT AND CLAXTON.)

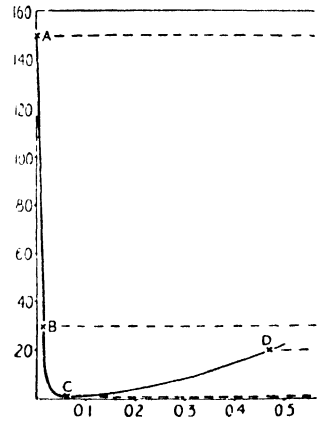


FIG. 157.—CURVE SHEWING THE EFFECT OF INHIBITOR CONCENTRATION UPON ITS EFFICIENCY. (HOFFERT & CLAXTON.)

Courtesy, Editor "Journal of the Society of Chemical Industry."

648. Many of the most efficient inhibitors, such as the poly-phenols and amino-phenols, tend, under certain conditions, to cause colour formation during the induction period. This tendency to colour formation increases as the concentration of inhibitor is increased and is greater when basic or acidic impurities are present in the fuel. Obviously acidic bodies are objectionable for the reason that they tend to neutralise the inhibitor and decrease its effectiveness. The relative solubility of an inhibitor in a motor fuel and also in water has also been shewn to be important, because in storage and distribution it is impossible to ensure absolute freedom from water, and any water with which the fuel comes in contact will tend to dissolve out the inhibitor. This difficulty is not so serious with benzoles as with petrols because inhibitors such as the phenols and amino-phenols are more soluble in the former than in the latter. For petrols, special inhibitors have been developed, such

as benzyl-amino-phenol, which are more soluble in petrols than in water. The poly-hydroxy types of inhibitor are less satisfactory, in that they are sparingly soluble in petrol but comparatively readily soluble in water. For benzoles, fractions prepared from technically pure cresylic acid are quite suitable as inhibitors if they contain only small amounts of sulphur.

The addition of an inhibitor to a benzole or petrol that contains impurities which accelerate gum formation is ineffective and may even increase the gumming tendency in storage. This is shewn in Fig. 156. Curve A shews that the accelerating effect of thiophenol increases with its concentration, while curves B and C shew that the effectiveness of cresols as inhibitors is markedly decreased in the presence of 0·015 per cent. of thiophenol. The addition of an inhibitor such as phenol to a petrol or benzole already containing a certain amount of inhibitor may also result in an increase in gumming tendency. This is shewn in Fig. 157.

649. The National Benzole Association have carried out numerous large scale tests on the storage stability of benzoles containing inhibitors, of which the following examples are typical.[61]

A batch of 6,000 gallons of inhibited benzole made from a gas works once-run benzole, containing 8·5 per cent. by volume of unsaturated hydrocarbons, when first produced gave a gum content of 2 mgs. per 100 ml. After six months storage the gum content did not rise above 3 mgs. During one year's production of inhibited benzole from this gas works once-run benzole, the gum content averaged 3 mgs. and the oxidation test (4 hours oxidation) gave 7 mgs./100 mls.

This benzole was blended with straight-run petrol and used under the normal conditions of storage and distribution without any trouble due to gum formation. Extensive engine tests, including fleet trials, on inhibited benzoles or inhibited benzole-petrol-blends have been made on different types of private cars and commercial vehicles. In these tests the normal procedure of storage and distribution has been adopted, or the benzoles have been stored for periods of up to 18 months before use. In no instance has any abnormal deposition of gum in the induction system or on the inlet valves been found.

650. **Efficiencies of Different Inhibitors.**—In Dec. 1930, Egloff, Faragher and Morrell[62] presented the results of experiments on the stabilisation of the knock-ratings, gum contents and colours of cracked spirits by the use of various inhibitors. They found that aniline, hydro-quinone, naphthalene and anthracene were effective in this direction. Two years later Egloff, Morrell, Lowry and Dryer[63] published the results of comprehensive tests on a very wide range of

inhibitors and established relationships between chemical structure and inhibiting effectiveness.

In the latter research, inhibitor effectiveness was determined in a series of comparative tests in which 0·01 per cent. of the inhibitor was added to a Pennsylvanian cracked spirit which had been treated with fullers earth and which had an induction period in the oxygen bomb test of only 45 minutes.

Each inhibited spirit was then tested by the oxygen bomb test and its induction period determined. In those cases where the inhibitor was insoluble in the spirit, a solvent was used, usually benzene, acetone, methanol or ethyl alcohol.

The results obtained may be summarised as follows :

Phenols.—Phenol itself has moderate inhibiting action, but the effect of the hydroxyl group in phenol is intensified by the introduction of alkyl radicals, particularly when they occupy an ortho or para position. Thus ortho- or para-cresol are much more effective inhibitors than phenol. Alkyl groups occupying the meta position are of less value, as *m*-cresol is no more effective than phenol and considerably less effective than its other isomers ; *p*-tertiary butyl phenol is about as effective as *p*-cresol. Two alkyl groups are considerably more effective than one, but in compounds containing two such groups, those in which the substituents are in the para and ortho positions are the most effective. When additional hydroxyl groups are introduced into a phenol, the inhibiting power is again increased, but a hydroxyl group in the ortho or para position is more effective than one in the meta position. Catechol gave slightly the longest induction period of all the inhibitors examined. The results obtained by Egloff and his co-workers on various phenols are reproduced in Table 140.

Amino and Nitro Phenols.—An amino group in any position in a compound already containing a phenolic hydroxyl group increases its inhibiting power, but there are marked differences among individual compounds. Thus *o*-amino phenol gave an induction period of 1320 mins., *m*-amino phenol 330 mins., and *p*-amino phenol 2340 minutes. In general the introduction of a nitro group into phenols is disadvantageous. In contrast to the behaviour of phenols, alcohols have little or no inhibiting power.

Amines.—As a class amines are not so effective as phenols. Aniline was ineffective under the conditions examined and nitro-aniline, the toluidines and a number of other primary and tertiary aromatic amines were ineffective. The diamines were rather more effective than the mono-amines but aliphatic amines were of no value. Only one halogen compound was found of any practical use, i.e., 4 chloro-2 amino phenol, which gave an induction period of 955 minutes. Ethers, ketones,

quinones, acids and acid derivatives, nitrogenous compounds and sulphur compounds were generally ineffective though thiodiphenylamine gave an induction period of 1440 minutes.

TABLE 140.

THE PHENOLS AS GUM INHIBITORS. (EGLOFF, MORRELL, LOWRY AND DRYER).

	(0·01% concentrations of inhibitor). Induction Period (mins.)	Solvent
Cracked Gasoline alone	45	—
Monohydroxy—		
Phenol	75	—
o-Cresol	135	—
m-Cresol	75	—
p-Cresol	210	—
Tricresol (tech.)	135	—
Butyl-phenol (para & ortho mixed)	195	—
tert-Butyl Phenol (ditto)	210	—
4-Hydroxy-1·3 Dimethyl Benzene	420	—
2-Hydroxy-1·3 Dimethyl Benzene	420	Benzene
4-Hydroxy-1·2 Dimethyl Benzene	255	,,
2-Hydroxy-1·4 Dimethyl Benzene	285	,,
Thymol	300	—
Carvacool	180	—
Polyhydroxy—		
Catechol	2400	Benzene
Resorcinol	150	Acetone
Orcinol	150	Methanol
4-Butyl-resorcinol	360	Benzene
4-Hexyl-resorcinol	390	,,
4-Heptyl-resorcinol	300	,,
Hydroquinone	85	Acetone
Toluhydroquinone	70	Methanol
Pyrogallol	2185	Ethyl Alcohol
Phloroglucinol	90	Methanol
Condensed Ring Systems—		
α-Naphthol	2250	—
β-Naphthol	330	—
1·5-Dihydroxy Naphthalene	1705	Acetone
o-Hydroxy Diphenyl	60	—
p-Hydroxy Diphenyl	135	Benzene
Nitroso β-Naphthol	135	—

651. Patents on Gum Inhibitors.—No discussion on gum inhibitors would be complete without reference to the many patents which have recently been issued in this field. The following are of interest.

English Patents.

E.P. 289,347, P. G. Somerville and W. H. Hoffert, 26/10/26.

E.P. 312,774, Johnson, 30/4/28.

E.P. 318,521, Standard Oil Development Co., 3/9/29.
E.P. 319,362, Standard Oil Development Co., 19/9/29.
E.P. 319,363, Standard Oil Development, Co., 19/9/29.
E.P. 336,515, D. A. Howes, R. Scott and I.C.I., Ltd., 22/7/29.
E.P. 347,627, Standard Oil Development Co.
E.P. 348,011, Standard Oil Co. (N.Y.), 29/10/29.
E.P. 349,427, Standard Oil Co. (N.Y.). 21/11/29.
E.P. 350,438, Wade and Standard Oil Co., 5/3/30.
E.P. 364,533, J. Hyman, 28/7/30.
E.P. 366,041.
E.P. 383,511, Standard Oil Development Co., 11/3/32.

Other Patents.

U.S.P. 1,748,507, Brooks and Gray Processes Corpn., 10/10/25.
U.S.P. 1,789,302, Calcott, Lee and Dupont Ammonia Corpn., 23/8/29.
Ger. P. 545,720, Burchard, 18/1/31.
Can.P. 325,188, Rogers, Voorhees and Standard Oil Co., 16/8/32.
Can.P. 325,189, Rogers, Voorhees and Standard Oil Co., 16/8/32.
Can.P. 302,371, Lewis, Mead and Standard Oil Development Co., 22/7/30.
Can.P. 302,372, Lewis, Gustafson and Standard Oil Development, Co., 22/7/30.
Can.P. 302,373, Fischer, Gustafson and Standard Oil Development Co., 22/7/30.

652. Methods for the Removal of Gum From Motor Fuels.—Occasionally it happens that a batch of motor spirit, through lack of refining treatment or other such cause, prematurely forms gum during storage and it is necessary to treat it in some way to render it saleable. This may usually be accomplished by redistillation, preferably at low temperatures in the presence of steam, but it is sometimes necessary to refine again to ged rid of the colour developed. Various methods have been patented whereby gummy residues may be removed from motor fuels in such a way that unsaturated and aromatic hydrocarbons are not attacked. The following examples may be quoted: U.S.P.'s 1,789,413; 1,867,697; 1,886,261.

653. The Use of Dyes in Motor Fuels.—An interesting development during the past two or three years is that of artificially dyed motor fuels, a development which has grown so rapidly that at the present time, probably more than 25 per cent. of the motor fuels sold in the United States are treated in this way. In other countries the idea has not, as yet, been widely adopted.

The reasons for dyeing a motor fuel may be summarised as follows :

1. To give it a distinctive appearance so that it can be readily identified and thus promote sales.
2. To mask a yellowish or brownish tinge and hence improve the appearance of the fuel in bowls of visible pumps.
3. To neutralise coloured compounds, when they are present in the fuel in small amounts, in order to give the fuel the appearance of water-whiteness. In such cases only enough dye is used to overcome the colour forming substances in the fuel, but not enough to give the latter the distinctive colour of the dye.
4. To lower the cost of refining and refining losses by obviating the need of marketing a water white product.

Of these reasons, Nos. 2, 3 and 4 are the most important, but No. 1 is, in some cases, sufficient reason in itself from the sales point of view. However this need not concern us here.

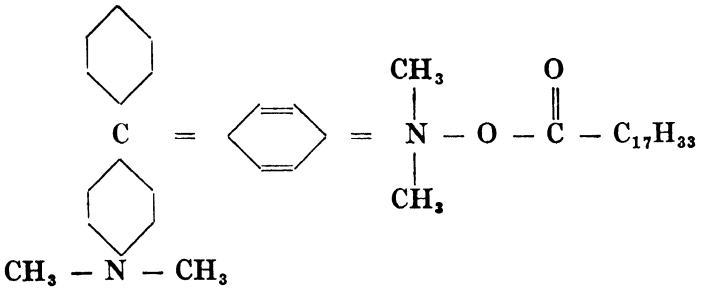
It has already been shewn in Chapter 5 (Volume I), th at the refining of cracked spirits, especially those produced by cracking in the vapour-phase, to a water white colour, is often a very expensive and wasteful procedure and the resulting product is frequently inferior to a similar spirit less drastically treated and having a slight yellow colour. Colour, *per se*, in a motor fuel is not an undesirable property, but the buying public has become so accustomed to the water white product that it regards a yellow spirit as impure, dirty or gummy. Because of these considerations dyed motor fuels have been adopted by many sales organisations and refining companies so that they may market a spirit not refined to water whiteness, and hence refined more cheaply.

One of the most important money saving possibilities of dyed spirits is the fact that slightly yellow fuels can be converted to water whiteness by the use of very small quantities of blue dye, the principle involved being similar to that underlying the addition of minute quantities of methylene blue to sugar in order to whiten it, and the use of blue in laundering white clothes. It has been stated that the cost of such treatment is about 0·4 cents per barrel of 42 U.S. gallons, compared with a figure of 8 cents per barrel for refining to water whiteness.[64]

In actual practice it is sometimes advisable to use sufficient dye to give the spirit a slightly blue tinge immediately after dyeing, so that there is some margin for fading to occur before actual loss of colour becomes noticeable. The amount of blue dye required to neutralise a slight yellow tinge in a cracked spirit varies from 0·05 to 2·0 mgs. per 100 mls. or from 0·175 to 7·0 pounds per 1,000 barrels.

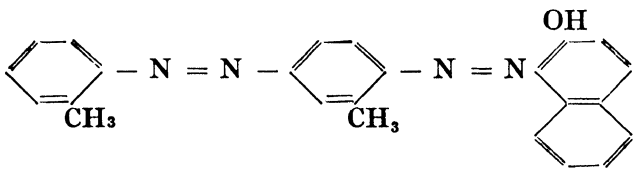
The use of a blue dye in this way is an effective remedy for the poor selling qualities of those spirits which tend slightly to go off colour during normal distribution without forming appreciable quantities of gum.

654. Kinds of Dyes Used for Colouring Motor Fuels.—The fatty acid salts of the triphenylmethane dyes were among the earliest types of dyestuffs used for colouring motor fuels. A typical example of this class is the oleate of malachite green.



Such dyes are now rarely used for this purpose because, although they give exceedingly bright and brilliant shades, they are very fugitive, especially in cracked spirits.

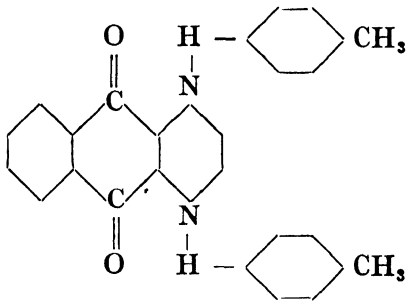
The dyes which are principally in use at present are the azo dyes and the anthraquinone derivatives. These may also be classified by colour since most of the red and yellow dyes are of the first class and most of the blues and violets belong to the second. Of the two classes, the anthraquinone colours are the more expensive, but they are also the more stable to light. In azo dyes, which are characterised by the group $-N=N-$ the particular shade of the dye is controlled by the other groups present and by the number of azo groups in the molecule. These dyes are prepared by treating an aromatic amine with nitrous acid and coupling the so called diazotised base with a phenol or with an aromatic amine. Thus Du Pont oil yellow is obtained by coupling diazotised ortho-toluidine with ortho-toluidine and Du Pont oil orange is obtained from diazotised aniline and beta-naphthol.[65] Naturally there are many such combinations possible, each differing slightly from the others in shade, strength, fastness and solubility. The oil reds are usually a little more complex than the simple yellow dyes, frequently containing two or more azo groups. An example of this is Du Pont oil red, the formula of which is



This is made by coupling diazotised ortho-amino azo-toluene with β-naphthol and is known, in its pure form, as Biebrich Scarlet. In some cases oil soluble orange dyes, instead of being chemical individuals, are

mixtures of red and yellow dyes. The use of such dyes in motor fuels offers the advantage that the shade can be varied to give any appearance desired but the disadvantage is ever present, unless great care is taken in selecting the two dyes, of one of the dyes fading in light to a greater extent than the other. This causes a change in tint.

As already mentioned the anthraquinone dyestuffs are more stable to light than the azo dyes. The most widely used blue dye in America is 1 : 4 di-toluido anthraquinone.



Violet shades are produced either with pure anthraquinone compounds or by the use of one of the ordinary anthraquinone blue dyes mixed with an azo red. The mixed dyes in this class are usually less satisfactory than the pure dyes because they are less brilliant. Purple shades are nearly always obtained by shading a violet or reddish blue anthraquinone dye with an azo red.

A number of peculiarities are noted in the green dyes. First, no satisfactory greens are known which are pure compounds. The only method of obtaining greens of adequate fastness is by mixing a greenish anthraquinone-blue with an azo-yellow. Many times it has been found that although the blue alone is faster than the yellow the mixture will fade to an extremely yellowish green, i.e., the blue fades more rapidly than the yellow. This phenomenon is connected with the composition of the motor fuel since the same dye mixture will exhibit this property in some fuels and not in others. An objection to the use of green dyes of this type is that nearly all the oil yellows on the market have a pronounced reddish cast which makes the resulting greens dull and more of an olive shade then an emerald. The latter is considered more appealing.

With regard to the dyestuffs available for colouring motor fuels in the United Kingdom, Messrs. Imperial Chemical Industries, Limited, market a range of Waxoline dyes, several members of which may be used for this purpose. For example :

Waxoline Blue 4044.
Waxoline Green G.
Waxoline Blue 10109.

Waxoline Purple A.
Waxoline Yellow A.D.S.
Waxoline Red III.S.

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Chapter XIV

INTERNAL COMBUSTION ENGINES.

657. Introduction.—All heat engines which are required to function as prime movers consist of certain rigid parts which go through regular cycles of movement, and, associated with them, a "working substance" (i.e., fuel) which is constantly consumed and which must be continually renewed in order to obtain continuous operation. The sole function of the heat engine is to produce mechanical effort by the conversion of heat energy into mechanical energy. The heat energy is taken into the engine by the fuel, part of which the engine is able to convert to useful effort and part of which it rejects. The fraction of the total heat supplied that is usefully converted is the thermal efficiency of the heat engine, and on the grounds of fuel cost and other considerations this should be kept as high as possible.

The theory of the internal combustion engine is intimately connected with Carnot's ideal heat engine. In such an imagined engine all the heat taken by the engine to convert into work is received at a single high temperature T_1 and all the heat that is rejected is rejected at a single low temperature T_2. The highest efficiency attainable is then given by

$$\frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the greater the difference between these two temperatures, the higher the efficiency. Of course, the conditions visualized by Carnot in his thermodynamical reasonings cannot be realized in practice, but the importance of a wide temperature range as forecasted by the Carnot analysis is fully confirmed in practice. From this viewpoint, it is of interest to compare the working temperature ranges and efficiencies of various types of prime movers. The steam engine suffers from the disadvantage that all the heat has to be got into the working fluid (steam) through metal walls capable of withstanding high pressures. The upper temperature limit of such an engine is about 470°C., equivalent to a steam pressure of approximately 1,500 lbs. per square inch. Such a temperature is about 2,000°C. below that commonly found in internal combustion engines. With regard to the lower temperature limit, many attempts have been made to utilize the heat carried away in internal combustion engine exhaust gases, but, generally, these are not

cooled usefully to below 500°C., under normal conditions. In steam using engines, however, the working fluid may be rejected at temperatures as low as 40°C. (313° absolute) when using a high vacuum condenser on a steam turbine. We have, therefore, the following comparative figures.[1]

Internal combustion engines,	$T_1 = 3073°$	absolute.
	$T_2 = 773°$	,,
Steam turbines,	$T_1 = 743°$	,,
	$T_2 = 313°$	,,

The corresponding Carnot efficiencies are,

Internal combustion engine,	75 per cent.
Steam turbine,	58 per cent.

Such a comparison, however, is not a complete one. The figure of 58 per cent. is the efficiency of the turbine itself. With even the most efficient boilers, not more than 85 per cent. of the heat of the fuel reaches the turbine in the form of steam, so that the Carnot efficiency of the whole plant is $58 \times 0{\cdot}85 = 49{\cdot}3$. The highest brake thermal efficiencies (see later) achieved in practice are, for a steam turbine, 33·8 per cent., and for an internal combustion engine operating at full load, 40 per cent. Assuming a boiler efficiency of 85 per cent., the former figure falls to $33{\cdot}8 \times 0{\cdot}85 = 28{\cdot}7$ per cent.

The steam turbine, however, has its peculiar advantages. Of these, perhaps the most important is that concerning the fuel which it consumes, i.e., coal, the cost per ton of which is only a fraction of that of fuels required for internal combustion engine operation. For this reason, steam turbines are of great value in large power stations and are not likely to be replaced for this purpose by internal combustion engine for some long time to come. The latter are ideally suited for smaller stationary and mobile power units, of which frequent starting and stopping is required and from which a large power output is demanded, combined with a limitation upon size and weight.

It is not intended to deal with the theoretical principles of interna combustion engine operation in detail in this Chapter, as this ground has been adequately covered in the well known treatises of such authorities as H. R. Ricardo,[2] D. R. Pye[1] and A. W. Judge.[3] The following discussion is limited mainly to various practical considerations.

The Ideal Air Cycle

658. A simplified idea of what actually takes place in normal internal combustion engine operation is obtained by a consideration of the ideal air cycle in which ideal air, obeying the perfect gas laws and having a constant specific heat at all temperatures, is employed, and in

which it is assumed that no heat transfer between the working substance and the cylinder walls occurs.

A pressure-volume diagram of the so called " constant volume " cycle is shown in Figure 158, in which the working substance is supposed to be instantaneously heated at constant volume (2—3) after adiabatic compression (1—2) by the inward movement of the piston and cooled again at constant volume (4—1) after adiabatic expansion. A further pressure-volume diagram is shown in Figure 159, in which there is no

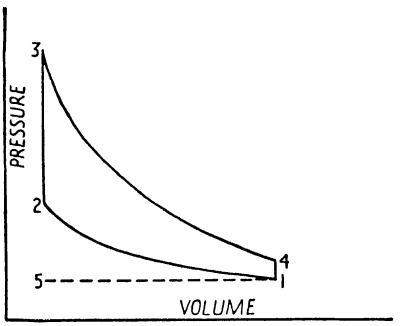


FIG. 158.—THEORETICAL DIAGRAM FOR CONSTANT VOLUME CYCLE.

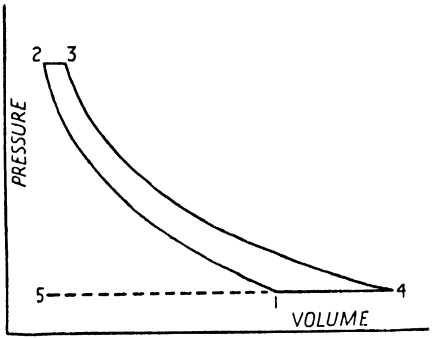


FIG. 159.—THEORETICAL DIAGRAM FOR CONSTANT PRESSURE CYCLE.

(Reproduced from " The Internal Combustion Engine," by D. R. Pye. Courtesy of The Clarendon Press.)

further pressure rise after the adiabatic compression (1—2) is complete, the heat being added at such a rate during the early stages of expansion that the pressure remains constant until combustion is complete, after which it drops according to the ordinary law of adiabatic expansion of a perfect gas, down to atmospheric pressure. A complete diagram of the operations taking place in a real engine cylinder must show the processes of getting the gases into and out of the cylinder, but a consideration of this may be deferred until later.

The thermal efficiency of the ideal engine working on the cycle shown in Figure 158 may be calculated as follows. Let the pressure, volume and absolute temperature at the point 1, i.e., before compression begins, be represented by P_1, V_1 and T_1 and, similarly, for other points in the cycle. The only gains or losses of heat by the working substance take place while it is heated from T_2 to T_3 and cooled from T_4 to T_1, processes 1—2 and 3—4 being adiabatic. The area of the diagram represents the work done by the piston and is equivalent to the difference between the heat supplied to, and given up by, the working substance. In other words, the heat equivalent of the net work done per cycle is

$$K_V (T_3 - T_2) - K_V (T_4 - T_1) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K_V = the specific heat at constant volume, and the efficiency of the cycle $= \frac{\text{heat equivalent of net work done}}{\text{heat supplied}}$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad \ldots\ldots\ldots \quad (3)$$

If the common ratio of compression and expansion $\frac{V_1}{V_2} = \frac{V_4}{V_3}$ is denoted by r, then it follows from the well-known expression $PV^\gamma =$ constant, or $T\,V^{\gamma-1} =$ constant, that

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} = \left(\frac{1}{r}\right)^{\gamma-1} \quad \ldots\ldots\ldots \quad (4)$$

$$\text{also } \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{1}{r}\right)^{\gamma-1} \quad \ldots\ldots\ldots \quad (5)$$

and the efficiency of the cycle reduces to

$$E = 1 - \left(\frac{1}{r}\right)^{\gamma-1} \quad \ldots\ldots\ldots \quad (6)$$

In the constant pressure cycle of Figure 159, the heat supplied to working substance after compression is $K_p\,(T_3 - T_2)$ and the heat abstracted from it after expansion is $K_p\,(T_4 - T_1)$. Compression and expansion again being adiabatic and these expressions identical with those for the constant volume cycle, except for the substitution of K_p for K_v, it follows that an identical expression gives the thermal efficiency of the cycle as was found for the other, r being in each case the ratio of adiabatic compression and expansion.

The most important fact brought out in equation (6) is that the thermal efficiency depends upon nothing but the ratio in which the working fluid is compressed and expanded. Thus, of two engines of the same compression ratio, in which the temperatures are very different, owing either to a different initial temperature T_1, or to different amounts of heat being added during the process 2—3, the thermal efficiencies are the same in each case. One engine might do more work than the other, but that amount of work is always the same fraction of the total heat supplied during the process 2—3.

659. No real engine can, of course, follow these cycles very closely, for the following reasons :—

(1) No compression or expansion can be made truly adiabatic.
(2) The working substance is not a perfect gas.
(3) Heat cannot be supplied at strictly constant pressure or constant volume.

However, what is true of the ideal engine, is also true of all real engines, namely, that the compression ratio is of primary importance and that the higher we can make it, the higher will be the thermal efficiency. The ideal engine affords a standard by which real engines may be compared, but which they can never hope to reach. In Table 141 are given the values of the air standard efficiency calculated for a range of compression ratios using a value of $\gamma = 1{\cdot}396$, which is the value for air at ordinary temperatures.

TABLE 141. AIR STANDARD EFFICIENCIES

Compression Ratio	Thermal Efficiency $1-\left(\frac{1}{r}\right)^{\gamma-1}$
	($\gamma = 1{\cdot}396$)
2	0·240
3	0·354
4	0·424
5	0·473
6	0·509
7	0·539
8	0·563
10	0·600
12	0·628
14	0·651
16	0·671
18	0·683
20	0·695

These values are plotted in Figure 160, from which it may be seen that there is a rapid gain of efficiency as the compression ratio is increased up to about 5 to 1 and that above this point the gain becomes progressively less.

Despite its undoubted value, however, it has been recognized that the "ideal air" cycle is sometimes too far removed from practical possibilities to form a satisfactory basis of comparison for real engines. An ideal cycle should afford a guide to engine designers in the sense that it should show what is to be expected as a result of a modification in design, such as raising the compression ratio, any fundamental physico-chemical conditions being taken into account, but the processes in the engine being legitimately simplified by the neglect of practical imperfections, so as to allow results to be calculated with reasonable ease and to make the conditions of calculation independent of any particular engine.

660. In this connection, the important pioneer work of Tizard and Pye[4] is of the greatest importance. These workers made a detailed study of the conditions existing in actual engines with the object of

investigating the process of combustion, the chemical changes occurring, and the limits of thermal efficiency resulting therefrom. Subsequent tests by Ricardo[2] on a variable compression engine and with various fuels confirmed the conclusions arrived at by Tizard and Pye. These conclusions may be summarized as follows :—

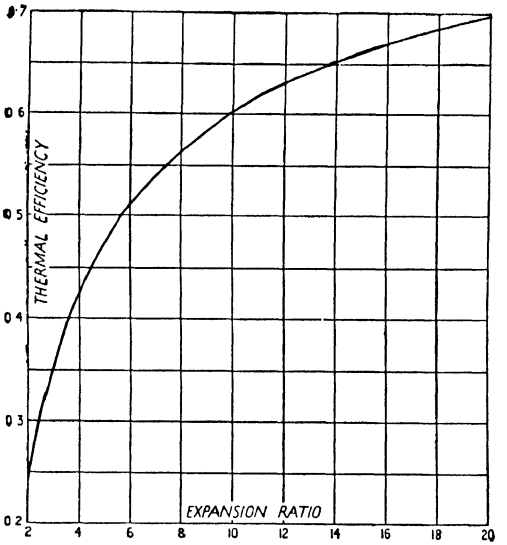


FIG. 160.—AIR STANDARD EFFICIENCIES AT DIFFERENT COMPRESSION RATIOS.
(Reproduced from "The Internal Combustion Engine," by D. R. Pye. Courtesy of The Clarendon Press.)

(1) The relative increase in thermal efficiency to be expected from an increase in the compression ratio is distinctly higher than the "air standard" efficiencies would suggest. Thus, the theoretical efficiency for the correct mixture strength (see later), at 5 : 1 compression ratio, is about 33·8 per cent. or about 71 per cent. of the air standard efficiency. The theoretical efficiency for a 10 to 1 compression is 45 per cent., or nearly 75 per cent. of the air-standard efficiency.

(2) When both change in specific heat and dissociation are taken into account, the maximum temperature obtained with economical mixture strengths is practically the same in the case of all available hydrocarbon fuels, but with alcohols it is appreciably lower.

(3) The theoretical thermal efficiency for the correct mixture strength may be expressed by the following formula :—

$$E = 1 - \left(\frac{1}{r}\right)^{0.258} \quad \ldots\ldots\ldots \quad (7)$$

(4) For 20 per cent. weak fuel-air mixtures, the theoretical efficiency is given by the equation.

$$E = 1 - \left(\frac{1}{r}\right)^{0.295} \quad \ldots\ldots\ldots \quad (8)$$

This mixture strength corresponds very closely to the conditions under which the maximum observed efficiencies are now obtained and Tizard and Pye have proposed equation (8) to replace the air standard efficiency formula. Experiments conducted on a Ricardo variable compression engine confirmed the calculated relative increase in thermal efficiency on raising the compression ratio, as shown in Table 142.

TABLE 142

Compression Ratio	Maximum Thermal Efficiency		Ratio Observed / Calculated	Air Standard Efficiency	Ratio Observed / Air Standard
	Calculated from Equation	Observed			
4 to 1	0·337	0·277	0·82	0·425	0·65
5 to 1	0·380	0·316	0·83	0·475	0·665
7 to 1	0·440	0·372	0·85	0·540	0·685

In Figure 161 are shown three curves, (*a*) the air standard efficiency for a range of compression ratios from 4 : 1 to 7·5 : 1, (*b*) Tizard and

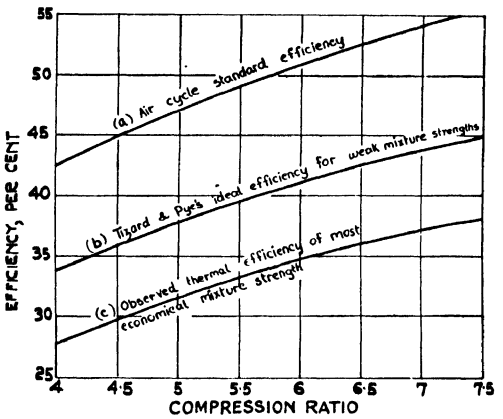


FIG. 161.—GRAPH SHEWING THERMAL EFFICIENCIES AT DIFFERENT COMPRESSION RATIOS.
(*Courtesy of The Institution of Petroleum Technologists.*)

Pye's ideal thermal efficiency corresponding to the same range of compression and (*c*) the observed results on the Ricardo variable compression engine with the most economical mixture strength based on the net calorific value of the fuel and including the latent heat of vaporization. It will be observed that throughout the whole range the relation between the experimental results and the calculated ideal efficiencies is constant to within very narrow limits. The difference between the two represents the heat loss to the cylinder walls during combustion and ex-

pansion and the small loss due to the early opening of the exhaust valves. Ricardo's tests showed that the gain in efficiency with increase in compression was almost exactly the same in the case of all fuels tested.

Explosion and Combustion in Engines

661. When an inflammable vapour or gas is mixed with air (or oxygen) in certain proportions, the resulting mixture is explosive and the presence of a small flame or spark will cause the elements of the mixture chemically to combine with more or less violence. If the mixture ignites slowly and the resultant flame takes a comparatively long time to spread through the mixture from particle to particle until the whole volume is combusted, the process is termed "inflammation." On the other hand, the much more violent form of combustion which readily occurs with certain mixtures (e.g., hydrogen and oxygen) is called "detonation." These two modes of combustion are very important in petrol and other engines.

In the case of mixtures of petrol vapour and air, if the proportion of air to petrol by weight exceeds about 22, or if the mixture is so "rich" in petrol vapour that this ratio is below about 8, it is impossible to obtain an explosion in the ordinary petrol engine. Moreover, if the mixture proportions between 22 and 8 are brought very close to these limits the type of combustion that results approaches that of inflammation and a weaker explosion occurs. On the rich mixture side, the weaker explosion is caused by the excess fuel which cannot take part in the reaction and which acts as an inert diluent. It is, therefore, necessary in petrol engine operation to supply the engine cylinders with a fuel-air mixture of fairly limited proportions, a fact which decidedly limits possible improvements in operating efficiency, as will be shown later.

662. The Effect of Mixture Strength upon Flame Velocity, Etc. —Dugald Clark,[5] from experiments on mixtures of coal gas and air, found that the point where inflammability ceases, when the gaseous mixture is diluted with air, is fairly sharply defined; he found that whereas a mixture of 14 parts by weight of air to 1 of gas would explode on the application of a spark, a mixture of 15 parts of air to 1 of gas would not do so; and that if this "critical proportion" of gases was subjected to a slight increase of temperature or of pressure, the mixture became inflammable. At the same time, it has been shown that in passing from the explosive mixture in which the exact proportions of the gases for chemical combination are present, to the mixture of the "critical proportion" by successive dilutions, the inflammability slowly decreases until, at the critical proportion, the rate of flame travel is

very slow and the noise of the explosion practically unheard. This is shewn in Figure 162, in the case of mixtures of air and hydrogen taken from the results of Le Chatelier and Mallard.[6] Generally, the mixture of hydrogen and air (namely, 1 : 2·5) in which the hydrogen and oxygen are present in the correct proportions for complete chemical combination, does not give the greatest flame speed. But when the hydrogen is increased beyond this proportion to 1 volume of hydrogen to 1½ volumes of air, the velocity is a maximum. The same is true with regard to petrol-air mixtures.

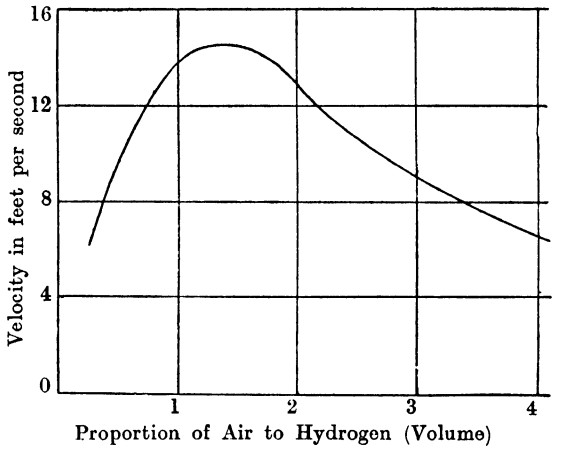


FIG. 162.—CURVE SHEWING FLAME SPEEDS IN HYDROGEN-AIR MIXTURES.

The flame velocity is much greater when a mixture is exploded under conditions of constant volume than when under constant pressure. This is probably due to the fact that the particles of gas as they ignite increase rapidly both in temperature and pressure and thus greatly assist the flame propagation which takes place from particle to particle. In the case of a petrol engine, ignition at constant volume can only occur at the dead centre position, when the piston is momentarily stationary, so that for maximum flame velocity it is important to ignite as near the top dead centre as possible, at the same time bearing in mind the necessary time interval elapsing between the moment of ignition and the attainment of maximum pressure.

663. Combustion Data.—The chemical basis of the working of every type of internal combustion engine is the chemical combination of the elements carbon and hydrogen present in the fuel with the oxygen content of air. The former elements are found in the combined state in all liquid fuels and when completely combusted yield carbon dioxide and water, respectively, thus

$$C + O_2 \rightarrow CO_2 \quad \ldots\ldots\ldots\ldots \quad (9)$$

$$2H_2 + O_2 \rightarrow 2H_2O \quad \ldots\ldots\ldots\ldots \quad (10)$$

or $$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O \quad \ldots\ldots\ldots\ldots \quad (11)$$

Hydrogen + oxygen → carbon dioxide + water.

Such combinations are strongly exothermic, i.e., they take place with the evolution of heat, and engine fuels may be considered as the media by which the heat converted by the engine into mechanical work is supplied. Naturally, the greater the amount of heat liberated by a given quantity of fuel, other things being equal, the greater the fuel economy for a given power output.

The energy content of a hydrocarbon in this sense is usually referred to as its " calorific value." This is determined by burning unit weight of the fuel in air in a calorimeter, cooling the products down to atmospheric temperature and measuring the amount of heat generated in the process. Heat of combustion is another term used to denote the same thing. In expressing the heat of combustion of hydrocarbons, allowance is generally made for the fact that the water formed during combustion is either condensed to the liquid state, or is present as water vapour or steam. If present as a liquid, the water vapour in condensing yields up an extra quantity of heat equal to its latent heat of vaporization which is 966 B.T.U.s per lb., or 537 calories per gram at 100°C. Thus, by the " higher heating value " of a fuel is meant the actual heat of combustion plus the latent heat of condensation of the water formed during combustion. By the " lower heating value " of a compound is meant the heat of combustion alone. Analogous terms are " gross calorific value " and " nett calorific value," respectively.

When a sample of liquid fuel is tested in a calorimeter, some at least of the heat liberated during combustion is devoted to overcoming the latent heat of evaporation of the liquid. Thus, in the case of such a calorimeter when a sample of liquid fuel is placed in the bomb only a trifling proportion is evaporated before combustion commences. During the process of combustion, the remainder of the fuel is evaporated, and the heat required for overcoming the latent heat of evaporation is supplied by combustion. Now, when used in an engine, the whole, or very nearly the whole, of the fuel is evaporated before the end of the compression stroke, such small proportion as escapes evaporation usually passes through the cylinder unburnt. In practice, the proportion of liquid fuel which both evaporates and burns during the combustion stroke may be considered as negligible, so that the heat required for evaporation may be regarded as being supplied either outside the cylinder or at least outside the heat cycle. In other words, the heat

absorbed in the evaporation of the fuel would not otherwise be made use of. It is, therefore, proper and customary to add the latent heat of evaporation to the heat of combustion for use in engine calculations. Furthermore, in the case of petrol engines, the uncondensed steam passes into the exhaust and therefore does not yield up its latent heat of condensation as useful heat inside the cylinder. The lower heating value, plus the fuel latent heat of vaporization, is, therefore, used in engine calculations.

E.g., Consider the case of a petrol of the empirical formula C_8H_{18}, containing 84·6 per cent. carbon and 15·4 per cent. hydrogen.

$$\text{Nett heat of combustion} = (\cdot 846 \times 14{,}540) + (\cdot 154 \times 52{,}500)$$
$$= 20{,}380 \text{ B.T.U.s per lb.}$$

The amount of steam formed on combustion is $(0{\cdot}154 \times 9)$ lbs. = 1·386 lbs. The latent heat of this amount of steam is $1{\cdot}386 \times 966 = 1{,}338$ B.T.U.s.

$\therefore$ the lower heating value $= 20{,}380 - 1{,}338 = 19{,}042$.

To this value should be added the latent heat of vaporization of the fuel which we may take as 132 B.T.U.s per lb. Thus, we arrive at a value of $19{,}042 + 132 = 19{,}174$ B.T.U.s per lb.

The foregoing argument applies only to carburettor engines employing volatile liquid fuel. In engines of the Diesel type, where the fuel is injected into the cylinder in the liquid state, the available heat per pound of fuel supplied is simply the lower calorific value.

664. Volumetric Proportions in Combustion.—It has been shewn in equation (11) that, in ideal combustion, 1 volume of hydrocarbon vapour C_nH_m combines with $\left(n + \frac{m}{4}\right)$ volumes of oxygen to form n volumes of CO_2 and $\frac{m}{2}$ volumes of water vapour. Since the composition of air by volume is approximately 79·1 per cent. nitrogen and 20·9 per cent. oxygen, it follows that 4·78 cubic feet of air contains 1 cubic foot of oxygen and 3·78 cubic feet of nitrogen. Hence, 1 volume of C_nH_m will require $4{\cdot}78\left(n + \frac{m}{4}\right)$ volumes of air for complete combustion, and if the water formed be regarded as occupying no appreciable volume, the volume of the products of combustion will be

$$n + 3{\cdot}78\left(n + \frac{m}{4}\right)$$

$$\text{or} \qquad 4{\cdot}78n + 3{\cdot}78\frac{m}{4} \quad \ldots\ldots\ldots \quad (12)$$

If, however, as is actually the case, no condensation within the cylinder occurs during the expansion stroke, then an increase in volume due to combustion will occur in the ratio

$$\frac{\text{Initial volume}}{\text{Final volume}} = \frac{4{\cdot}78\left(n + \frac{m}{4}\right)}{4{\cdot}78n + \frac{m}{\cdot 2} + 3{\cdot}78\frac{m}{4}}$$

$$\text{or } \frac{4{\cdot}78n + 1{\cdot}19m}{4{\cdot}78n + 1{\cdot}44m} \quad \ldots\ldots\ldots \quad (13)$$

This ratio is frequently termed the " Volume Ratio."

The conditions obtained with a typical petrol may be illustrated with sufficient accuracy by a consideration of pure normal heptane, C_7H_{16}.

The equation then becomes

$$C_7H_{16} + \left(7 + \frac{16}{4}\right) O_2 = 7CO_2 + \frac{16}{2} H_2O \quad \ldots \quad (14)$$

It follows from this equation that 1 cubic foot of heptane vapour will require for complete combustion $4{\cdot}78 \times 11$ cubic feet or 52·58 cubic feet of air, and that the volume of the exhaust products, including that of the water vapour, will be 56·58 cubic feet.

$$\text{Hence, } \frac{\text{Initial volume}}{\text{Final volume}} = \frac{52{\cdot}58}{56{\cdot}58}$$

so that the volume is about 7·6 per cent. greater after combustion than before.

665. Weight Proportions for Complete Combustion.— From the equation

$$C_7H_{16} + \left(7 + \frac{16}{4}\right) O_2 = 7CO_2 + 8H_2O,$$

it is evident that $\frac{11 \times 32}{(7 \times 12) + (16 \times 1)} = \frac{352}{100} = 3{\cdot}52$ pounds of oxygen are required for the complete combustion of 1 pound of heptane. This quantity is equivalent to $3{\cdot}52 \times 4{\cdot}31 = 15{\cdot}17$ pounds of air or 199·3 cubic feet. If we take the lower calorific value of heptane as 20,700 B.T.U.s per lb., we find that the calorific value per cubic foot of combustible mixture is $\frac{20{,}700}{199{\cdot}3} = 103{\cdot}8$ B.T.U.s. A convenient value often employed in such calculations is to assume the calorific value to be 100 B.T.U.s per cubic foot.

666. Composition of Exhaust Gases.—From the preceding figures referring to the case of heptane mixed with air in the proportions for complete combustion, namely, 15·17 pounds of air per pound of fuel, it follows that theoretically the composition of the exhaust gases should be

85·6 per cent. carbon dioxide
14·4 per cent. nitrogen
100·0

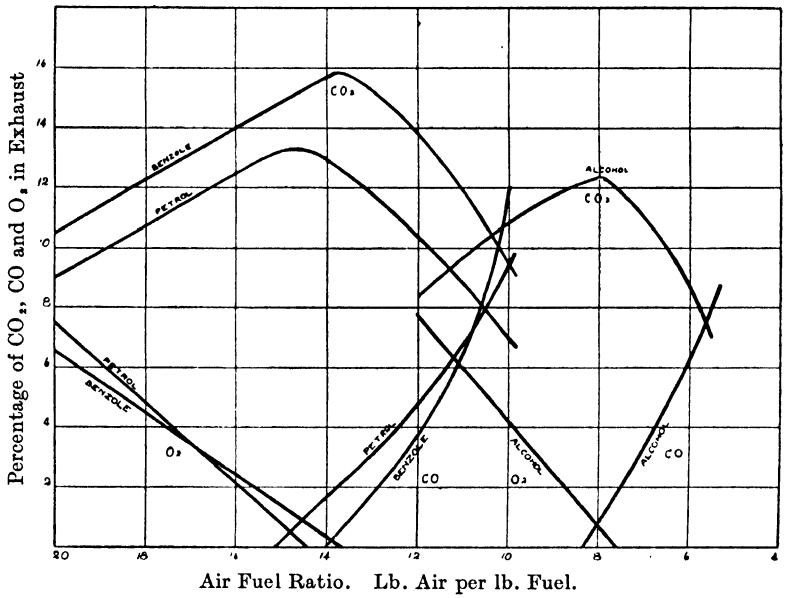


FIG. 163.—GRAPHS SHEWING COMPOSITION OF EXHAUST GASES OF THE PETROL ENGINE.
(Courtesy of the National Benzole Association.)

the water formed being considered to be condensed. Such a theoretical state of affairs is, however, never met in practice, although under certain conditions the exhaust gases have compositions closely approximating these figures. When weak petrol-air mixtures are supplied to an engine, there is more than a sufficiency of oxygen necessary to complete the combustion and free oxygen is found in the exhaust gases. When rich mixtures are supplied, there is an insufficiency of oxygen present completely to combust the fuel and carbon monoxide appears in the exhaust gases.

The variations in exhaust gas compositions obtained by altering the air-fuel ratio supplied by the carburettor are as shown in Figure 163, in the case of a typical petrol, benzole and ethyl alcohol. The curves for the oxygen concentrations are almost straight lines and the curves for oxygen and carbon monoxide overlap by a small amount near the

mixtures approaching correct proportions. It will be observed that the mixture strength giving almost complete combustion of benzole is slightly more rich than that for petrol and that the corresponding mixture strength for ethyl alcohol is much richer. This is determined solely by the chemical compositions of the three fuels, thus :—

TABLE 143

	Composition. Per Cent. Weight.			Air-Fuel Ratio for Complete Combustion (By Weight)
	Carbon	Hydrogen	Oxygen	
Petrol	85·3	14·7	—	15·0
Benzole	91·65	8·05	—	13·44
Ethyl alcohol ..	52·1	13·11	34·8	9·09
Methanol	37·5	12·5	50·0	6·53

Combustion in a petrol engine is not perfect although the incompleteness, as evidenced by the presence of carbon monoxide in the exhaust gases, is not very marked. In addition, chemical tests on the condensed water from the exhaust often reveal the presence of traces of aldehydes and other partly oxidized organic materials. For this reason, the air-fuel ratio supplied to the engine cannot be computed from the exhaust gas composition with any great accuracy. In general, it is found that the discrepancy becomes greater as the supplied air-fuel ratio is made weaker. This subject has been dealt with in detail by Best.[7]

Since combustion within the cylinder is incomplete and combustible gases are found in the exhaust, it is obvious that the whole of the calorific value of the fuel is not liberated during the combustion process and that an amount of available energy, dependent upon the efficiency of the combustion, is not used. Knowing the composition of the exhaust gases and the amount of available energy they contain in virtue of their content of carbon monoxide, hydrogen and methane, it is possible to calculate the percentage of the fuel heat usefully employed.

The combustion of a rich or a weak fuel-air mixture may be represented by an equation such as :—

$$2(a-1)C_6H_6 + 15\,O_2 + 56{\cdot}4N_2 = A{\cdot}CO_2 + B{\cdot}CO + C{\cdot}H_2O + D{\cdot}H_2 + E{\cdot}O_2 + 56{\cdot}4\,N_2 \quad . \quad . \quad . \quad (15)$$

which refers to benzene, where a = degree of richness.[1] The values of the coefficients A, B, C, D and E and, consequently, the composition of the exhaust gases, depends, for a given supplied air-fuel ratio, upon the temperature and to a less extent the pressure, produced by the combustion. Were it not for the phenomenon of dissociation, there would never be in the same exhaust gas mixture pure oxygen together with

hydrogen and carbon monoxide, but this accounts for a proportion of the carbon dioxide and water molecules to be split up into CO, H_2 and O_2 when temperatures are high. The proportion dissociated increases rapidly above 2,700°C., at which temperatures the three gases exist together in chemical equilibrium. As soon as the temperature in the cylinder falls, due to expansion, recombination takes place, so as finally to leave only free oxygen if the mixture is weak and carbon monoxide if it is rich. Free hydrogen is never left in appreciable quantity, even in a rich mixture, because of its extreme affinity for oxygen. The amount of dissociated water vapour even at the maximum temperature is not great under ordinary engine conditions, but the dissociation of carbon dioxide is an essential factor in explaining certain well known features of engine behaviour.

667. Calculation of the Products of Combustion allowing for Dissociation.—It was shown by H. T. Tizard and D. R. Pye in 1923[4] that the well known characteristic of a petrol engine, that it gives its maximum power when running on a fuel-air mixture about 10 to 20 per cent. richer in fuel than that giving complete combustion, is just what would be expected from theory when dissociation is taken into account. Methods of calculation were developed and results worked out for typical fuels. Since that date, however, experimental work by Fenning[8] has enabled Pye to repeat these calculations with greater accuracy,[1] whose latest conclusions may be summarised as follows:

The equilibrium existing between carbon dioxide, carbon monoxide, oxygen and hydrogen may be expressed by the following equations:

$$K_1 = \frac{(P_{CO})^2 \times (P_{O_2})}{(P_{CO_2})^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which $\log_{10} K_1 = 8{\cdot}46 - \frac{28{,}600}{T}$

$$\text{and} \quad \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\text{in which } \log_{10} K = 1{\cdot}405 - \frac{1{,}550}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In equation (15), the constants A, B, C, etc., require to be evaluated. Three equations can be written down at once by equating the number of atoms of the various elements before and after combustion, assuming the theoretical mixture strength is supplied (i.e., $a = 0$). Thus:

$$\begin{aligned} A + B &= 12 \\ 2A + B + C + 2E &= 80 \\ 2C + 2D &= 12 \end{aligned}$$

Now the partial pressure of a gas is proportional to the number of molecules of it present, hence, from equations (16) and (17), we obtain :

$$\frac{B^2}{A^2} \times (P_{O_2}) = K_1 \quad \ldots\ldots\ldots \quad (19)$$

$$\text{and } \frac{B \times C}{A \times D} = K \quad \ldots\ldots\ldots \quad (20)$$

If X is the total number of molecules present at the maximum explosion temperature,

$$X = A + B + C + D + E + 56{\cdot}4 \quad \ldots\ldots \quad (21)$$

and (P_{O_2}) in equation (19) can be regarded as the fraction $\frac{E}{X}$ of the maximum explosion pressure.

In the case of a typical combustion such as that represented by the equation.

$$2C_6H_6 + \underbrace{15O_2 + 56{\cdot}4N_2}_{71{\cdot}4} = \underbrace{12CO_2 + 6H_2O + 56{\cdot}4N_2}_{74{\cdot}4} + 1{\cdot}52 \times 10^6 \text{ CHU} \quad (22)$$

Vols. 2

the following relationship exists between P_e, the maximum pressure developed, and T_e, the maximum temperature, assuming a compression ration of 5 to 1 and an initial temperature of 100°C.

$$P_e = \frac{X}{73{\cdot}4} \times 5 \times \frac{T_e}{373} \text{ atmospheres.}$$

To evaluate the five constants A, B, C, etc., a guess is made of the maximum temperatures and the values of the five constants calculated. With these solutions, it must then be determined whether the amount of heat generated plus the volumetric heat of the products result in the temperature originally guessed. If this is not the case, a new temperature nearer to the calculated one must be guessed and the operations repeated until the final temperature calculated coincides with the original temperature proposed.

The following example, worked out by Pye,[1] will make the method clear. Suppose the guessed maximum temperature in benzene-air combustion is guessed to be 2,500°C. Then :

$$T_e = 2{,}773$$
$$K_1 = 0{\cdot}014$$
$$K = 7{\cdot}0$$

$$P_{O_2} = \frac{E}{X} P_e = \frac{E \times 5}{73{\cdot}4} \times \frac{2773}{373} = 0{\cdot}506E$$

$$\frac{B^2}{A^2} E = \frac{K_1}{0{\cdot}506} = 0{\cdot}0277$$

$$\frac{B \times C}{A \times D} = 7{\cdot}0$$

From these equations the five constants may be evaluated as follows :

$$A = 10{\cdot}25$$
$$B = 1{\cdot}75$$
$$C = 5{\cdot}85$$
$$D = 0{\cdot}15$$
$$E = 0{\cdot}95$$

The heat generated during the formation of these products from air and benzene will be the heat of combustion of 2 molecules of benzene vapour less the heat of combustion of 1·75 molecules of carbon monoxide and 0·15 molecules of hydrogen. This may be easily calculated to be 18,950 C.H.U. per molecule of original fuel-air mixture. The mean volumetric heat of the products of combustion between 2,500°C. and 100°C. is 7·11 C.H.U. per mole. of original mixture. During compression in the ratio of 5 to 1 from the starting temperature (100°C.), 1,590 C.H.U. per mol. are communicated to the mixture. The total temperature rise will, therefore, be :

$$\frac{18{,}950 + 1{,}590}{7{\cdot}11} = 2{,}889°\text{C.}$$

and the final temperature nearly 3,000°C., which is far too high, the guessed temperature having been 2,500°C.

A guess of 2,750°C. for the final temperature leads to the composition of the products of combustion at the maximum temperature

$$8{\cdot}98\ CO_2 + 3{\cdot}02\ CO + 5{\cdot}75\ H_2O + 0{\cdot}25\ H_2 + 1{\cdot}64\ O_2 + 56{\cdot}4\ N_2$$

In this case, the greater degree of dissociation, due to the higher guessed temperature, makes the heat generated less, being 17,690 instead of 18,950 C.H.U. per mol. The mean volumetric heat of the mixture over the higher temperature range will be greater, 7·26 against 7·11, and on both accounts, therefore, the finally calculated temperature becomes

$$\frac{17{,}690 + 1{,}590}{7{\cdot}26} + 100 = 2{,}755°\text{C.}$$

which is close enough to the guessed temperature for all practical purposes and which may be accepted as the true final temperature when the correct mixture of benzene and air is compressed in the ratio 5 : 1 and then burned at constant volume. Examination of the products of combustion shows that of the carbon in the benzene, 25·8 per cent. is burned to carbon monoxide at the maximum temperature and that 2·7 per cent. of the hydrogen is uncombined.

In the case of weak or rich fuel-air mixtures, the appropriate value of a may be used and it follows, that

$$A + B = 12(1 + a)$$
$$2C + 2D = 12(1 + a)$$

In other respects the calculation is identical with that given

above. The manner in which the maximum temperature varies with the fuel-air ratio is shown in Figure 164. It will be observed that owing to dissociation the highest calculated temperature on the curve is that for a mixture strength some 20 per cent. richer in fuel than that giving complete combustion and that over a wide range of mixture strength on the rich side the temperatures only vary slightly. Under comparable conditions, the power of an engine will vary with the maximum temperature reached by the combustion and will form the lower curve in Figure 164, which "reproducing as it does the well known power characteristic of a petrol engine when the fuel-air ratio is varied, affords substantial confirmation of the calculations and of the theory on which they are based."[1]

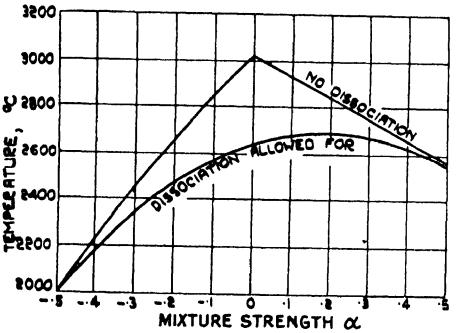


FIG. 164.—CALCULATED MAXIMUM EXPLOSION TEMPERATURES IN BENZENE-AIR MIXTURES AT DIFFERENT MIXTURE STRENGTHS.
(Courtesy of The Institution of Petroleum Technologists.)

TEMPERATURES AND PRESSURES IN INTERNAL COMBUSTION ENGINES

668. The pressure and temperature conditions existing in internal combustion engines when under load may be arrived at by calculations, but the figures so obtained are only approximate because of the many assumptions that have to be made. However, actual measurements of temperature and pressure have shown that such calculations are accurate enough for most purposes.

TEMPERATURES

Suction Temperature.—The suction temperature is one of the most important temperatures in engine operation. It determines volumetric efficiency and serves as the starting point from which other temperatures may be determined. The temperature at this point is influenced by the final exhaust temperature, owing to the admixture of the fresh charge with the residual exhaust products in the clearance space. The temperature of these may be taken as about 2,100°F., in an engine operating at a compression ratio of 5 to 1 and at a speed of 2,000 r.p.m., using petrol as a fuel with a mean jacket temperature of 60°C.

The incoming charge consists of air at ordinary atmospheric temperature (or a little higher) and a small proportion of fuel, entirely or partly vaporized. Knowing the weight of air entering the cylinder per induction stroke, the weight of residual exhaust products with which it becomes contaminated, the amount of heat picked up from the hot walls of the cylinder and the piston, etc., and the latent heat of the fuel, it is possible to approximate the temperature of the fuel-air charge at the moment when the inlet valve closes, i.e., when the suction stroke is complete. In the case of petrol, assuming the engine conditions given above, the charge picks up about 0·0005 B.T.U.s per cubic inch from the hot cylinder walls, etc. This is equivalent to 0·05 B.T.U.s per cycle when the cylinder has a volume of 100 cubic inches. The final result is that the total charge, including residual products, at the end of the suction stroke, is at a temperature of about 720°F. absolute or 260°F.

The effect of the fuel used upon the final suction temperature is important. Fuels with high latent heats give lower temperatures than ordinary petrols. Thus, under the same conditions benzene gives a temperature of 235°F. and ethyl alcohol a temperature of 150°F. or below. Methanol gives a still lower temperature. In the same way, fuels with higher latent heats give higher volumetric efficiencies.

669. Compression Temperature.—During the compression stroke, the fresh charge of fuel and air is compressed under nearly adiabatic conditions to a smaller volume as determined by the compression ratio. At the beginning of compression, the fresh charge (when either petrol or benzole is being used as a fuel) is at a temperature slightly lower than that of the cylinder walls, etc., and hence absorbs heat from the latter. As, however, the gas is heated by compression, heat is later lost to the cylinder walls. With alcohol fuels, the final suction temperature is considerably below the mean wall temperature, so that the mixture is heated to a quite appreciable extent during the earlier part of compression. On the other hand, however, alcohol fuels, especially methanol, are not completely evaporated at the end of the suction stroke and some of the heat of compression is used up in completing the evaporation.

For the engine conditions mentioned above, i.e., compression ratio 5·0, engine speed 2,000 r.p.m., jacket temperature 60°C., the following compression temperatures are representative :—[2]

Petrol, correct mixture	1,258°F. abs. = 407°C.
20 per cent. weak mixture ..	1,267°F. abs. = 412°C.
Benzole, correct mixture	1,220°F. abs. = 386°C.
20 per cent. weak mixture ..	1,232°F. abs. = 393°C.
Ethyl alcohol, correct mixture	968°F. abs. = 246°C.
20 per cent. weak mixture ..	998°F. abs. = 280°C.

Pye (loc. cit.) has arrived at slightly lower figures by taking an average value of γ in the equation PV^{γ} = constant, equal to 1·33. He gives the following figures for the pressures and temperatures obtained on compression at different ratios, assuming a constant temperature of 100°C. before compression.

TABLE 144.—COMPRESSION PRESSURES AND TEMPERATURES, ASSUMING γ = 1·33 AND A CONSTANT SUCTION TEMPERATURE OF 100°C. (PYE.)

Compression Ratio	Maximum Compression Pressure Lbs. Per Square Inch	Maximum Compression Temperature. °C
4	92·5	313
5	125	362
6	159	399
7	195	434

When allowance was made for the varying amounts of exhaust products left in the engine cylinder at the various compression ratios, assumed to be at a constant temperature of 850°C., in all cases, the following figures were derived on the basis of 1 cubic foot swept volume.

TABLE 145

Compression Ratio	Volume Residual Exhaust at 850°C. Cu. Ft.	Volume Residual Exhaust at N.T.P.	Volume Fresh Charge at N.T.P.	Temperature of Mixture before Compression °C	Maximum Temperature of Compression °C
4	0·33	0·08	0·82	139	376
5	0·25	0·061	0·82	122	399
6	0·20	0·049	0·82	111	419
7	0·166	0·04	0·82	102	437

A comparison of these two sets of figures shows that the allowance for the diminished proportion of hot exhaust gases at the higher ratios has narrowed the difference in compression temperatures between 4 to 1 and 7 to 1 from 121°C. to 61°C. It must be remembered, however, that the residual exhaust gases at the higher ratio will, in addition to being smaller in volume, also be cooler, although this will not affect the above figures to any noticeable extent.

670. Combustion Temperatures.—The temperature rise on combustion might be calculated by dividing the heat output by the specific heat of the gaseous reactants at normal temperatures, but such a procedure is, of course, only capable of giving very rough figures. The calculated result is far too high because no allowance is made for dissocia-

tion, because heat is lost by radiation and conduction to the walls of the combustion chamber and because the specific heat of the gases increases with increase in temperature. A much more accurate result is obtained by making allowance for the first and last of these effects as has been done by Tizard and Pye[4]; the effect of heat loss to the combustion chamber can only be guessed, it cannot be calculated. Tizard and Pye have thus arrived at the explosion temperatures reproduced in Table 146.

TABLE 146. EXPLOSION TEMPERATURES. (TIZARD AND PYE.)

Degree of Richness (a)	−0·5	−0·2	0	0·1	0·2	0·3	0·4	0·5
Benzene	1994	2470	2655	2690	2701	2681	2630	2561
Heptane	—	—	2591	2623	2603	2527	2448	2366
Ethyl Alcohol ..	—	—	2507	2524	2505	2429	2348	2278

671. Engine Temperatures.—In 1904, Professor Callendar made various temperature measurements upon an air cooled petrol engine, the results of which are of interest. At a speed of 2,000 r.p.m., with a retarded spark and half throttle, the temperature of the combustion chamber on the exhaust side quickly rose to 570°C., but under road conditions with a cooling draught of air did not exceed 400°C. The highest exhaust valve temperatures were obtained at full throttle with the spark retarded. The inlet valve was found to keep comparatively cool at 70°C. with the cooling air blast and also partially due to the latent heat of the fuel. The difference in temperature between the exhaust and inlet sides of the engine was found to be about 80°C. In normal engine operation, the mean temperature of the inlet valve is probably between 100°C. and 200°C.

With regard to cylinder barrel temperatures, it was found that the lower end of the cylinder was only 20°C. cooler than the upper end. This has been ascribed to " piston convection " in which the piston absorbs heat at the top of its stroke and carries it quickly to the lower end, where it is absorbed by the cooler walls. The difference in temperature between the two ends becomes smaller as the speed increases; this effect is beneficial in equalising the cylinder barrel expansion and cooling effects. The temperature of the exhaust gases from any given engine depends upon the compression ratio, the engine speed and general design, but normally varies between 600 and 750°C. Exhaust valve temperatures are very much dependent upon valve and valve seat design but usually lie between 350°C. and 450°C. in normal engines operating at medium speeds with average loads. On the other hand, exhaust valve temperatures of 650°C. are occasionally met, but should not be allowed to rise above this figure under full load conditions.

Exhaust valves should have wide seats to get rid of the heat as efficiently as possible and also reduce the unit loading of the seat inserts. In this connection, the cam design is important, as "hammering" of the seat inserts, by the valves dropping on them under high temperature conditions, shortens their life appreciably. The choice of fuel is important in keeping exhaust valve temperatures as low as possible. Even among fuels of the same anti-knock value differences are obtained, benzole blends giving slightly higher exhaust valve temperatures than fuels of the same knock rating containing tetra-ethyl lead.[9]

Referring to piston temperatures, Judge (loc. cit.) has described the results of tests carried out by Professor A. H. Gibson on both cast-iron and aluminium alloy pistons in an air cooled aluminium cylinder, 100 mm. bore × 140 mm. stroke. The following conclusions were reached:

(1) "Under normal operating conditions at full load, the temperature at the hottest point of an aluminium alloy piston varies from 210°C. to 250°C., depending on the design of the piston and the composition of its alloy. This is with a clearance (cold) of about 25 thousandths of an inch. With such a clearance, the drop in temperature between the edge of the piston crown and the cylinder wall is from 25 to 30°C. An increase in the piston clearance increases the temperature of the piston."

(2) All aluminium alloy pistons working with the same clearance attain the same temperature to within very narrow limits. The difference between the best and the worst is only about 25°C., except in the case of an alloy containing 8 per cent. copper and 1 per cent. manganese which has a lower conductivity except when it has been annealed at 450°C. for a short time.

(3) Under the same conditions of operation, a cast iron piston of the same size has a maximum operating temperature of about 440°C. The advantage of using an aluminium piston depends upon circumstances, but is greater at higher compression ratios because, under these conditions, the lower piston temperature reduces the tendency to knock very appreciably.

672. Pressures in Internal Combustion Engines.—The pressures developed in petrol engine operation are inseparably connected with the temperatures and may be calculated approximately from the latter.

It is of interest to consider what pressure changes occur after the passage of the spark at or near the end of the compression stroke. Explosion or pressure rise is not instantaneous with the passage of the igniting spark but lags behind it at a definite time interval depending upon conditions. Thus, in a petrol engine running at 2,000 r.p.m., with a compression ratio of 5 to 1, during the time interval equivalent

to about 15 degrees of crank angle after the appearance of the spark, no noticeable pressure rise above that due to compression is observed. (c.f., the diesel engine.) During this period, small nuclei of combustion must be present in the explosive mixture, but these are, as yet, so small as to produce no heating effect or pressure rise. This occurs even though a state of violent turbulence exists.

Such a delay period preceding explosion after the passage of the spark is not affected to a marked extent by changes in temperature and pressure, when measured on a time basis. To compensate for this delay period, which increases in terms of crank angle with increase in engine speed, although on a time basis it remains substantially constant, it is necessary to advance the moment of passage of the spark, so that the spark advance necessary increases with rise in engine speed. The spark advance required to compensate for the delay period is only a part of the full advance necessary, for the time occupied by the pressure rise must also be allowed for, so that the peak of the pressure curve shall be reached before expansion has seriously begun. If the peak pressure is reached later than this, it means that some heat of combustion is not developed until a point when the remaining ratio of expansion is much reduced, and therefore also the efficiency with which this late-developed heat can be utilised in the engine. As soon as the delay period is over and general combustion has begun, the rate at which it proceeds is directly dependent upon turbulence. Without turbulence the rise of pressure would be so slow that it could not be completed in the time available. Fortunately, the degree of turbulence and rate of pressure rise increase with increase of engine speed.

Indicator diagrams afford a valuable means of studying the pressures obtained during the various phases of the engine cycle.

An interesting comparison, made by the aid of a high speed indicator, of the pressures developed in a petrol and a compression ignition engine has recently been given by Ricardo.[10] The former engine had a compression ratio of 6·2 to 1 and operated at 1,500 r.p.m., with 28° spark advance. Maximum pressure was attained 12° after top dead centre. The high speed C.I. engine had a compression ratio of 13·5 to 1, injection began at 16° before top centre and maximum pressure was attained at 12° after top centre. The B.M.E.P.s recorded were 139 and 112 pounds per square inch, respectively. The petrol engine gave a maximum pressure of about 650 pounds and the diesel engine a pressure of 800 pounds per square inch.

When the temperature at any point in the cycle is known, the corresponding pressure is, of course, easily calculated. Thus, if in the case of a petrol engine of 5·0 compression ratio, the compression pressure is 128 lbs. per square inch, the compression temperature 1,258°F. absolute, the temperature after ignition 4,946°F. absolute and the ratio of specific

volumes is 1·05, then the pressure at the beginning of the expansion stroke is

$$123 \times 1{\cdot}05 \times \frac{4946}{1258} = 508{\cdot}5 \text{ lbs. per square inch.}$$

This calculated explosion pressure is somewhat higher than that found in practice due to the finite speed of burning of the mixture, as compared with the piston speed, which causes a slight rounding of the peak of the indicator diagram.

Calculation shows that with benzene under these conditions the explosion temperature is 4,480°F. and the pressure 505 lbs. per square inch.

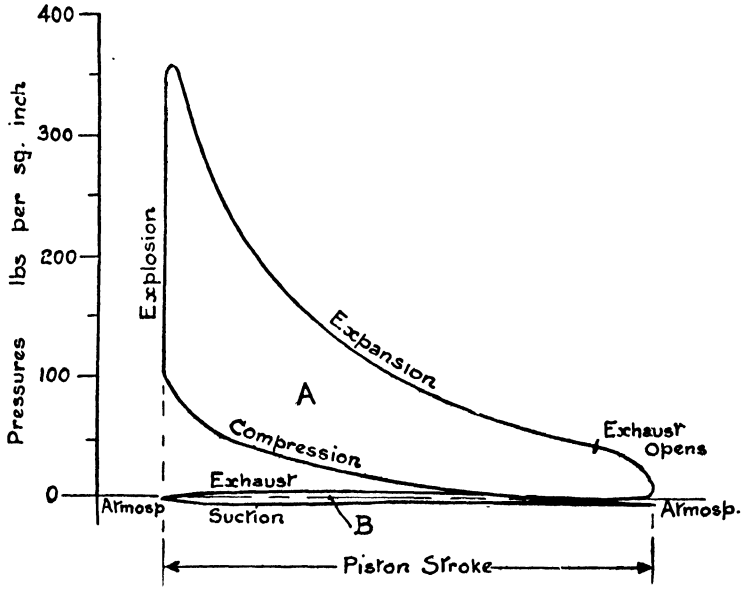


FIG. 165.—INDICATOR DIAGRAM TAKEN ON A PETROL ENGINE.

673. Mean Effective Pressures.—In the normal indicator diagram, shown in Figure 165, the area A represents the useful work and the exhaust suction loop B the wasteful work. The effective work per cycle is therefore represented by the difference in areas, A—B, and is therefore, a measure of the indicated horse power if the speed is known. The area of the diagram may conveniently be determined by the use of a planimeter, and from this may be determined the mean height, thus,

$$b = \frac{\text{Area in square inches}}{\text{Length of stroke (inches)}}$$

Then b, multiplied by the pressure scale gives a value known as the

"Indicated mean effective pressure." From this, the "indicated horse power" may be calculated.

If P_m = I.M.E.P. in lbs. per square inch,
l = length of stroke in inches.
a = piston area in square inches.
n = number of cylinders,
N = r.p.m.

$$\text{then Indicated Horse Power} = \frac{P_m l a N n}{66{,}000}$$

Alternatively, knowing the horse power of the engine, as determined by a brake or dynamometer (in which case it is known as the "Brake Horse Power" and differs from the Indicated Horse Power by an amount which depends upon the mechanical efficiency), the Brake Mean Effective Pressure may also be calculated

$$\text{B.M.E.P.} = 792{,}000 \frac{\text{B.H.P.}}{V N n}$$

where V = piston swept volume in cubic inches,
N = R.P.M.,
n = number of cylinders.

These concepts of mean effective pressures are of much importance in considerations of engine power outputs.

Volumetric Efficiency

674. There are two different ways in which the volumetric efficiency of an engine may be defined. Either

(*a*) the ratio between the swept volume of the piston and the volume of combustible material drawn in per stroke, reckoned at the pressure and temperature of the surrounding air; or

(*b*) the ratio between the quantity of combustible material drawn in per stroke and the quantity which would fill the swept volume at N.T.P.

The second definition is generally used as it is more accurate in its expression. If we consider an engine operating in such a way that its inlet valve closes exactly at the end of the suction stroke giving a pressure in the cylinder equal to that of the atmosphere, i.e., 760 mms., then the volumetric efficiency is obviously equal to

$$\frac{273}{\text{Temperature in °C. absolute of indrawn charge}}$$

If we assume the temperature of the indrawn charge to be 60°C., the volumetric efficiency is then 82 per cent.

In practice, the values obtained are usually less than this because the pressure at the end of the suction stroke is less than atmospheric. The time necessary to open and close the inlet valve makes it necessary to begin the closure about 35 degrees before the end of the stroke, which causes some throttling, and it is further necessary to delay completing the closure until about 25 degrees after the end of the stroke, so that the effective swept volume is slightly less than would be given by the full movement of the piston.

It is difficult to give a good average figure for the volumetric efficiency of a petrol engine, but it usually lies between 72 and 78 per cent., for a normally aspirated engine. Apart from such factors as valve timing, type of induction system, etc., the volumetric efficiency depends upon the breathing capacity of the engine, upon the mixture strength, the latent heat of vaporization of the fuel employed, upon the heat received by the ingoing charge during its passage through the induction system and upon the compression ratio.[1]

The effect of breathing capacity is such that it is more important to provide ample area for the inlet than for the exhaust valves, and in order to reduce pumping losses it is an advantage to use large valves. Other factors must, however, be taken into account, such as the beneficial effect of inlet charge velocity upon turbulence and the difficulty of cooling large valves. The best conditions are normally obtained with inlet mixture velocities of 120—140 feet per second. Figures higher than 160 feet per second cause a falling off in volumetric efficiency.

Mixture strength has an important effect on volumetric efficiency, which is intimately connected with that due to fuel latent heat. Due to the latent heat of the fuel, the temperature of the air is decreased as fuel becomes evaporated and it may be shown that, in the case of the theoretical fuel-air mixture, the temperature of the inlet air is lowered, if no extra heat is added, by about 21°C. For benzole the figure is 26°C., and for ethyl alcohol 86°C., all figures being based on the assumption that the fuel is entirely evaporated by the time the inlet valve closes and that no engine heat reaches the charge up to this point. In the case of ethyl alcohol, and particularly so in the case of methanol, the latent heat is so great that the mixture is unable to pick up sufficient heat for complete evaporation during the suction stroke and this continues during the compression stroke. Obviously, for the same amount of fuel evaporated before the inlet valve closes, the amount of cooling and, therefore, the quantity of air drawn into the cylinder is greater the greater the latent heat of the fuel used. This accounts for the high power outputs obtainable from alcohol fuels, despite their low calorific values. (See Chapter 9, Volume I.)

The effect of mixture strength upon volumetric efficiency is important. Changes in the latter are brought about by differences in

the amount of cooling caused by fuel evaporation and by alterations in the cylinder wall temperatures, caused by change in mixture strength. Fig. 166 shows the variation of volumetric efficiency with different mixture strengths for the E. 35 Ricardo engine at 5 : 1 compression ratio using petrol, ethyl alcohol and coal gas as fuels. When running on coal gas, no heat was added to the inlet air, but with the liquid fuels the air was heated to the extent of 0·024 C.H.U. per revolution, otherwise the volumetric efficiencies on the latter fuels would have been about 4 per cent. higher. Although the absolute values of volumetric efficiency obtained on the three fuels cannot therefore be usefully compared, the difference between the ways in which the volumetric efficiency is influenced by mixture strength is indicated.

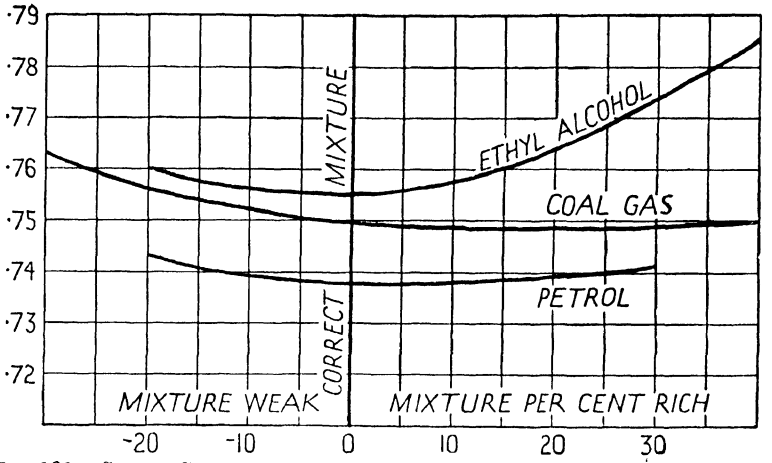


FIG. 166.—CURVES SHEWING THE EFFECT OF MIXTURE STRENGTH ON VOLUMETRIC EFFICIENCY WITH DIFFERENT FUELS.

(Reproduced from "The Internal Combustion Engine," by D. R. Pye. Courtesy of The Clarendon Press.)

In the case of each fuel, the volumetric efficiency falls a little as the mixture strength is varied from weak up to the theoretical value, after which ethyl alcohol gives a pronounced rise and petrol a slight rise. With coal gas there is some indication of a dropping tendency up to 20 per cent. rich, after which the value is substantially constant. The slight diminution in volumetric efficiency as more fuel is added at weak mixtures may be due to some extent to an additional displacement of air by fuel vapour, but the main cause is most probably a rise in the surface temperatures of the walls of the cylinder head and piston as the flame temperature increases with the richer mixtures. As the mixture is enriched beyond the theoretical composition, more fuel is evaporated and, consequently, the temperature of the inlet air decreases and the volumetric efficiency rises. This effect is most pronounced in the case of fuels of high latent heat, such as the lower alcohols, and is of consider-

able importance in considerations of power outputs obtainable with alcohol fuels. With alcohols, an appreciable amount of the fuel evaporates during the compression stroke, compression is more nearly isothermal, the temperature of the cycle, as a whole, is lower, and the efficiency is raised thereby. The power output is, therefore, increased somewhat, since a slightly greater proportion of the total internal energy available is converted into useful work.

Fuel Consumption and Power Output

675. The power output obtainable from an engine running on a given fuel is in no way dependent upon the calorific value of that fuel. The latter property only determines the fuel consumption necessary for the development of a given amount of work.

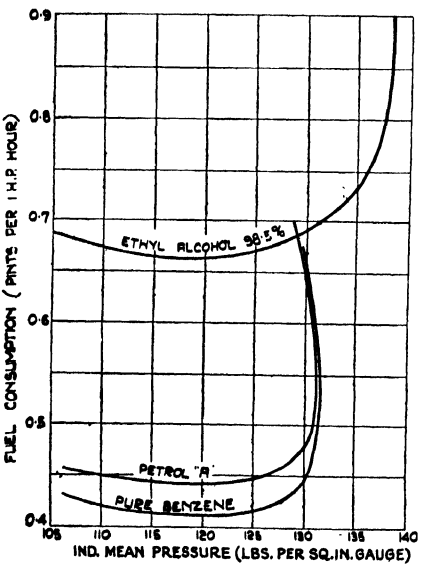


Fig. 167.—Consumption "Loops" Obtained with Different Fuels.
(*Courtesy of the Institution of Petroleum Technologists.*)

With hydrocarbons, the thermal efficiency obtainable at a compression ratio such that knocking does not occur is practically constant, irrespective of the type of hydrocarbon. Consequently, among hydrocarbons, the fuel consumptions for a given power output are practically constant with the one important exception of fuels containing large amounts of benzole, whose specific gravities and calorific values per unit volume are somewhat higher. Consequently compression ratio and the ability of withstanding knocking, rather than calorific value, are the important factors governing power output and fuel consumption.

The effect of mixture strength is of great importance in determining both fuel consumption and thermal efficiency. It has already been shown that over a large range of mixture strength on the rich side, the power output obtainable from an engine at constant speed varies but little, but is a maximum at about 20 per cent. rich. If, on an engine running on the maximum power mixture strength, or a richer mixture, steps are taken to reduce the supply of fuel while running, the fuel consumption is at first reduced with little alteration in power output and the fuel consumption per horse power will decrease in proportion. A point is ultimately reached when further fuel reduction causes a

more and more rapid fall in power and the fuel consumption, after reaching a minimum, begins to increase again.

Typical fuel consumption curves, often called "fuel consumption loops," are shown in Figure 167. The length of the horizontal portions of these curves is an important characteristic of the engine and fuel used, for it indicates the range of power over which a good fuel economy can be obtained before the limit is reached at which the air-fuel ratio is too weak for rapid and regular combustion. In a multi-cylinder engine, the economical range of fuel-air ratio is always narrow in comparison, because there is always some inequality in fuel distribution and as soon as the cylinder receiving the weakest mixture becomes starved of fuel, the limit of steady running is reached, even though the majority of the cylinders may still be receiving uneconomically rich mixture strengths.

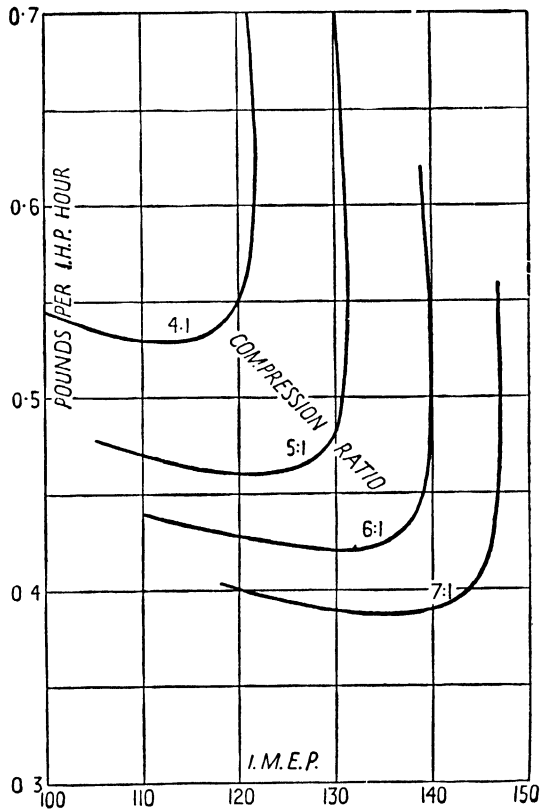


FIG. 168.—CURVES SHEWING THE EFFECT OF COMPRESSION RATIO ON POWER OUTPUT AND FUEL CONSUMPTION, USING BENZENE AS A FUEL.

(Reproduced from "The Internal Combustion Engine," by D. R. Pye. Courtesy of The Clarendon Press.)

It is only because the calorific values per pound of nearly all liquid hydrocarbon fuels are substantially the same that, for practical purposes, we can use the fuel consumption figures to express the heat economy of an engine. This is brought out in Figure 167, which refers to a single cylinder engine. The curve for pure benzene has been added in order to show that with this fuel, which gives almost the same thermal efficiency as petrol, the minimum consumption expressed in pints per horse power, is some 5 per cent. less. If the fuel consumption had been expressed in terms of weight instead of in terms of volume, the fuel consumption would have been 5 per cent. greater instead of less.

In spite of the fact that the lowest consumption on alcohol was

0·67 pounds per I.H.P. hour as against 0·43 for petrol, the thermal efficiency was actually rather higher, being 33·5 as against 32 per cent., due to the effects of fuel latent heat.

The effect of compression ratio upon power output and fuel consumption is shown in Figure 168 in which are given fuel consumption loops for benzene at compression ratios of 4, 5, 6 and 7 to 1.

Various Points Concerning High Compression Engines

676. The general increase in specific power output of engines during the last few years has been made possible by an increase in the anti-knock properties of available fuels and by the solution of several problems peculiar to high compression and supercharged engines. Among these may be mentioned the modification of the thermal charac-

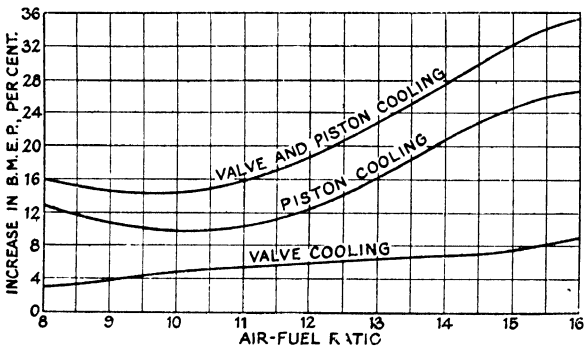


Fig. 169.—Curves Shewing the Effect of Abnormal Cooling of Piston and Exhaust Valve on Brake Mean Effective Pressure of Throttled Engine for Equal Knocking Tendency.
(*Courtesy of Ethyl Gasoline Corporation.*)

teristics of sparking plugs, and the development of well cooled exhaust valves which are highly resistant to oxidation, etc. Super-compression and supercharged engines introduce the problem of critical temperatures which is not present in low compression engines, and the elimination of localized hot spots is essential. Cooling is a vital question in supercharged engines because of the increased quantity of heat that has to be dissipated.

Recently a study has been made by the Ethyl Gasoline Corporation to determine the effect on power output of abnormal cooling of the exhaust valve and piston of a $3\frac{1}{4}'' \times 5''$ single cylinder engine. The compression ratio was so adjusted that when the engine operated without the special cooling, it was necessary to close the throttle partially to prevent knocking. An internally water cooled exhaust valve permitted an increase of B.M.E.P. of 8 per cent. at the theoretical mixture strength for the same freedom from knocking, as shown in Figure 169.

The use of soap-suds as a crankcase lubricant, in connection with spraying of the lubricant in copious quantities on the under side of the piston, permitted an increase of 25 per cent. in the B.M.E.P. A combination of these two types of cooling increased the B.M.E.P. by one-third at a 15 to 1 air-fuel ratio. It will be noted in Figure 169 that the increase in B.M.E.P., at rich mixtures is not nearly so great as at the leaner mixtures, hence it is apparent that the gains due to exceptional cooling are more pronounced in engines which are designed to operate most economically. Similar phenomena have been observed in aero engines.

The higher the compression ratio of a given engine, the cooler is its operation, because a smaller amount of waste heat is rejected and a larger amount converted into useful work. Figure 170 shows a heat balance for a small eight cylinder engine at compression ratios of 5·2, 6·0 and 7·0. The decrease in exhaust gas temperature with increase in compression ratio is contrary to popular belief. The facility with which high compression engines are cooled is of great importance in automobiles where conventional radiator size does not permit the ready dissipation of heat due to increased engine power. In aeroplanes, the smaller heat rejection of the jacket is of even greater importance because of the air resistance introduced by the frontal area of the radiator.

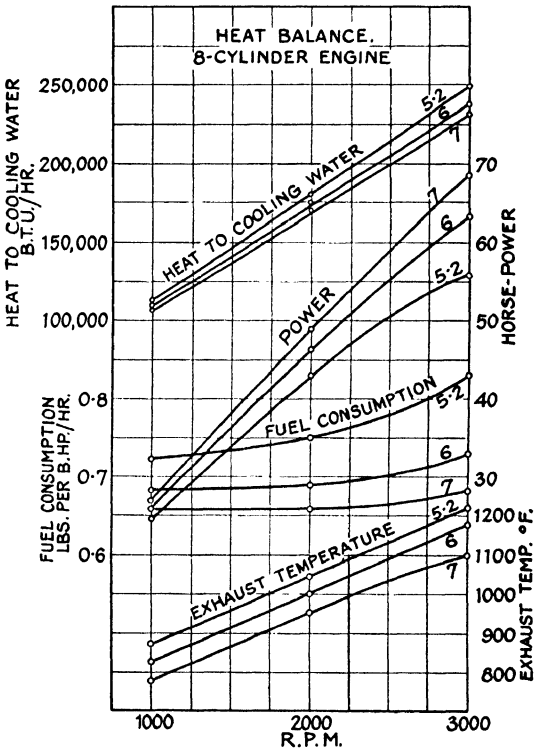


FIG. 170.—THE EFFECT OF COMPRESSION RATIO ON THE HEAT BALANCE OF AN ENGINE.
(Courtesy of Ethyl Gasoline Corporation.)

In high compression engines the accumulation of carbon presents a problem which is, in some cases, serious. By forming a coating of low thermal conductivity on the surface of the combustion chamber, it increases surface temperatures, reduces volumetric efficiency and promotes knocking and pre-ignition. The clearance volume of high compression engines is quite small and carbon accumulation may considerably in-

crease the compression ratio. Many so called carbon solvents have been recently introduced on the market which are claimed to loosen the carbon and enable it to be blown out of the exhaust ports. The solvents are periodically injected into the engine cylinder in small quantities.

677. Effect of High Compressions on Average Bearing Pressures.—The average bearing load can ordinarily be materially diminished by an increase in compression ratio. This seeming paradox is due to the fact that the inertia forces in engines are almost invariably larger than those due to gas pressures.

Figure 171 shows the pressures on the master crank pin of a Wright 8-cylinder cyclone engine, operating at compression ratios of 5·5 and 7·0 to 1, at 1,900 r.p.m. It will be noted that the actual average bearing pressures are less than the inertia forces alone. In other words, if the engine were rotated at a speed of 1,900 r.p.m. without compression or firing, the bearing pressures would be larger than during actual operation at full throttle. The increase in compression ratio from 5·5 to 7·0 to 1 reduces the average bearing pressure from 17,600 pounds to 16,300 pounds, or to the extent of 7·38 per cent. Bearing pressures for various American aircraft and automobile engines are summarized in Table 147.

TABLE 147.—EFFECT OF COMPRESSION RATIO ON MEAN CRANK PIN PRESSURE AT FULL THROTTLE

Engine	Speed	Compression Ratio	Bearing Pressure Full Throttle. Lbs.	Bearing Pressure Inertia Only Lbs.
Wright Cyclone 9 ..	1,900	5·5	17,600	20,050
,, ,, ..	1,900	7·0	16,300	20,050
Continental A–70 ..	1,485	5·5	3,710	3,485
,, A–70 ..	1,485	7·0	3,765	3,485
,, A–70 ..	1,800	5·5	4,710	5,760
,, A–70 ..	1,800	7·0	4,630	5,760
,, A–70 ..	2,200	5·5	6,715	7,700
,, A–70 ..	2,200	7·0	6,370	7,700
8-Cylinder Automobile	1,000	5·5	532	286
,, ,,	1,000	7·0	580	286
,, ,,	2,000	5·5	1,208	1,138
,, ,,	2,000	7·0	1,222	1,138
,, ,,	3,000	5·5	2,492	2,590
,, ,,	3,000	7·0	2,480	2,590
,, ,,	4,000	5·5	4,460	4,600
,, ,,	4,000	7·0	4,300	4,600
,, ,,	5,000	5·5	7,081	7,251
,, ,,	5,000	7·0	7,027	7,251

678. Factors Influencing Automobile Acceleration.—The ac-

celeration of an automobile is proportional to the accelerating force and inversely proportional to the mass. During the past five years the average accelerative ability of automobiles in America has increased only about 10 per cent., at the rate of about two per cent. per year. Engine torque has increased much more, but has been offset by increases in car weight due to greater engine weight and preference of the American public for larger cars.

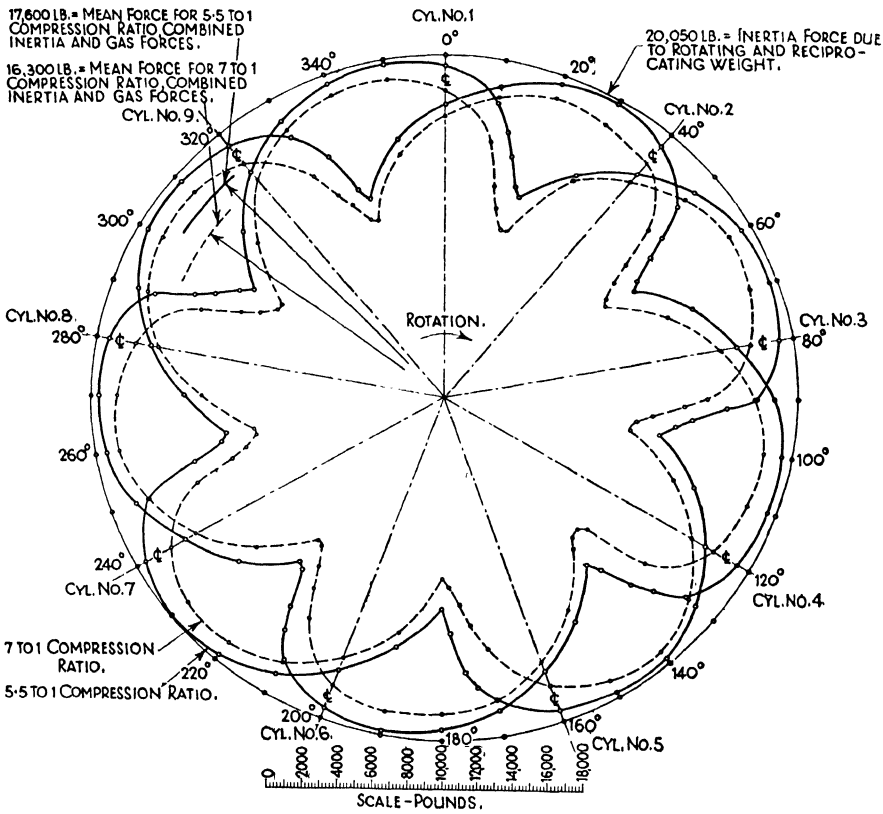


FIG. 171.—POLAR DIAGRAM SHEWING MAGNITUDE OF RESULTANT FORCE ON CRANK PIN AT VARIOUS CRANK ANGLE POSITIONS FOR ONE COMPLETE ENGINE CYCLE. WRIGHT R-1750 "CYCLONE" ENGINE. WIDE OPEN THROTTLE AT 1,900 R.P.M.
(Courtesy of Ethyl Gasoline Corporation.)

The power required to drive a vehicle at constant speed along a road is utilized in overcoming air resistance and road friction. Additional potential power of the engine at the corresponding speed is available for acceleration of the vehicle. Figure 172 shows a curve of the power required to drive a certain car at constant velocity over a range of speed. The power required to overcome wind resistance is a cubical function of speed, hence the rapid increase in power required at high speed for car

propulsion. The same figure also gives curves of wide open throttle engine power for the same car at compression ratios of 5 and 7·0 to 1. The top speed of the car in each case is determined by the intersection of the former curve with the engine power curve.

It will be noted that the increased compression ratio results in a substantial increase in maximum speed. Although the actual increase in engine power due to this increase in compression ratio is only about 15 per cent., the increase in accelerating ability is greater at all speeds, but especially so at the higher speeds, due to the fact that the increased power made available is a large percentage of the net power available for acceleration.

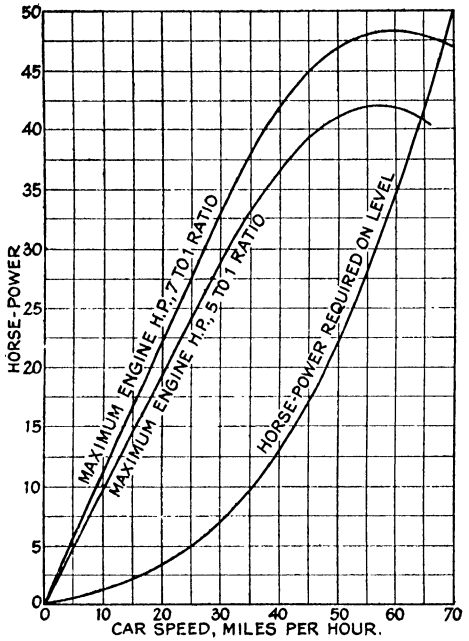


Fig. 172.
(*Courtesy, Ethyl Gasoline Corporation.*)

679. Carburettors and Carburation.—The primary function of a carburettor is to supply to the engine an ignitable mixture of fuel and air of constant proportions under all conditions of speed or load, but it must also perform the following duties :

(1) Pulverise the fuel as finely as possible in order to give a readily vaporisable air-fuel fog.
(2) Provide, momentarily, an over-rich mixture when the throttle is suddenly opened (see below).
(3) Provide an over-rich mixture for starting or running idle at low speeds.

In its simplest form a carburettor consists of a " metering " jet, to which liquid fuel is supplied at a constant level from a chamber, and which is situated in the centre of a venturi nozzle or choke tube, through which the whole of the air passes on its way to the engine. The reduced pressure in the choke tube is relied upon to draw fuel from the jet in the form of a spray which is pulverised by the rapidly moving air in the choke tube and carried in the air stream to the cylinders.

It can be shown that if :

V = velocity of the liquid fuel at the top of the jet (feet per second),
V_o = velocity of the air at the top of the jet (feet per second),
D = density of the liquid fuel (lbs. per cubic foot),
D_o = density of still air (lbs. per cubic foot),
h = difference between the fuel level and the top of the jet (inches), and
g = 32·2,

then these factors are related by the approximate formula

$$V^2 = \frac{D_o}{D} V_o^2 - 2gh,$$

and for fuel to flow at all, the air must have a velocity of at least

$$V_o = 2gh \frac{D}{D_o} \text{ feet per second.}$$

By reducing the choke tube area sufficiently, this air velocity can be attained, even when the engine is running at very low speeds. Moreover, a high air velocity through the choke is necessary in order to pulverise the fuel into a readily vaporisable fog. The obvious disadvantage of any such carburettor is the excessive pressure drop across the choke which reduces the volumetric efficiency of the engine.

A difficulty encountered in any type of jet carburettor is that as the speed at which the air flows through the choke tube increases, so the flow of fuel also increases, but at a considerably greater rate, with the result that if the proportional sizes of jet and choke tube diameters are chosen to give a " correct " mixture at any one speed, the mixture will be too weak at a lower speed and too rich at a higher speed. Some type of mechanism is therefore necessary to compensate for this effect.

Attempts to correct the tendency to over-richness at high speeds exhibited by the simple carburettor led to the early adoption of an auxiliary valve which came into operation at the higher speeds and admitted air to dilute the over-rich mixture formed in the choke tube. Such an arrangement is not at all satisfactory because it necessitates a moving part which soon gets out of adjustment.

Compensation is also effected in some carburettors by means of an additional jet fed by gravity from the float chamber and open to the atmosphere, the fuel flow through which is unaffected by choke tube depression. This type of compensation is very effective in giving fairly accurate metering under all conditions of load or speed.

A carburettor must also be capable of supplying a rich mixture when the throttle is suddenly opened, for the following reason. When an engine is running light with the throttle almost closed, the pressure in the induction system is much lower than it is when the throttle is opened suddenly. In the first case the pressure may be only 5 pounds per square inch absolute and in the second case will be nearly that of the atmosphere. At the lower pressure even a fuel of fairly low volatility will vaporise with ease, but at the higher pressure liquid fuel will be deposited on the walls of the induction manifold and the mixture that reaches the cylinders will be, in all probability, too weak to burn, unless the fuel used is very volatile, this state continuing until the walls of the induction manifold are thoroughly covered with a film of liquid fuel.

This can be overcome in two ways, either by raising the temperature of the induction manifold to make the fuel vaporise more easily or by arranging for an over-rich mixture to be supplied momentarily when the throttle is suddenly opened. The first method is used to a large extent by the use of induction manifolds heated from the engine or the exhaust system, but is to be avoided because of the lowering in volumetric efficiency that it brings about. The second method is satisfactory, it costs nothing in power output, and permits both of working normally with the most economical mixture strength and of reducing the heat input to the induction system. So called "pump carburettors" are now available to meet this requirement and incorporate a small pump element which injects a certain quantity of liquid fuel into the choke tube, whenever the throttle is suddenly opened. These carburettors are finding much popularity in sporting events because of the high engine acceleration which they allow. A simpler method, and one which has been in use for some years, is employed in carburettors using a gravity fed compensating jet. A well is provided, having a capacity sufficient to supply a 100 per cent. excess of fuel for, say, 3 or 4 cycles, and fed from the compensating jet. When running on full throttle, this well is normally dry, but when idling the well fills up to nearly the level in the float chamber. As soon as the throttle is opened, the sudden depression caused by the inflow of air to the induction system draws the whole of the contents of the well into the induction system and thus provides momentarily an over-rich mixture containing enough fuel sufficient for the formation of an ignitable fuel vapour-air mixture.

680. In all carburettors used for aircraft, it is necessary to provide some means of compensation for altitude effects. This is effected by means of what are termed altitude controls. The effect of diminished air density at altitude, assuming that the carburation is correct at sea level, is to reduce the weight of air passing through the carburettor, but the velocity of the air past the jet is not diminished in a like manner, so that there is approximately the same suction on the jet, and, therefore, relatively more petrol than air is drawn into the cylinders, and the mixture becomes richer in petrol.

A satisfactory method of compensation for altitude consists of reducing the pressure in the float chamber, so that the petrol pressure head on the jet is reduced, and less petrol flows at the higher altitudes. Figure 173 illustrates the principle of this method.

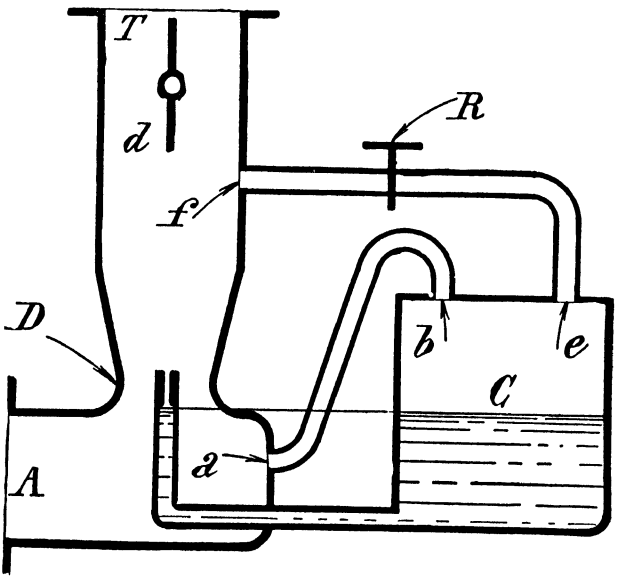


FIG. 173.—DIAGRAM SHEWING THE PRINCIPLES OF A CARBURETTOR COMPENSATING DEVICE.
(Reproduced from "Automobile and Aircraft Engines," by A. W. Judge. Courtesy of Sir Isaac Pitman & Sons, Ltd.)

The float chamber is hermetically sealed and is provided with a tube, *a b*, connecting it to the air inlet. A second tube, *e f*, joins the top of the float chamber with the mixing chamber, above the choke tube; and a hand controlled tap, R, is placed in this passage. When the engine is running with the tap R closed, there will be a certain vacuum in the mixing chamber at *d*, whilst at A and C practically atmospheric pressure will exist. Under these conditions, the discharge from the main jet is governed by the difference between the pressure at C and *d*. The effect of opening the tap R is to lower the pressure at C, and therefore to reduce the pressure difference so that less petrol flows. Auto-

matic control of the tap R is arranged for by means of an aneroid device consisting of an exhausted corrugated box, the sides of which open as the air density decreases. By means of a system of levers, the movement can be arranged to operate the vacuum control device to give more air in the fuel-air mixture as the altitude increases.

Variations in fuel viscosity with change in temperature are usually small, but are sufficient to cause definite alterations in mixture strength. At very low temperatures, marked weakening of the mixture strength is observed.[16] In view of all the above disadvantages of the carburettor, it is not surprising to find that work is being carried out in an attempt to devise some much simpler and more efficient apparatus for getting the fuel into the engine cylinder in the required proportions. In this connection, recent work on direct injection of fuel is of much interest. This is dealt with later (see Chapter XVIII).

Recently, so called " downdraft " carburettors have been introduced on some automobile engines. In the normal updraft carburettors, in which the point at which the fuel joins the air stream is a point above its level in the float chamber, a high air velocity is required in the choke tube to assure a flow of fuel from the jet and to carry the fuel into the engine without precipitation. On the other hand, in downdraft carburettors, the fuel outlet is below the fuel level and the air stream does not have to do work in carrying the fuel. Power output is thus increased by increasing the volumetric efficiency. Larger manifolds may be employed and the air flow capacity of carburettors increased. For reasons which need not be entered into here, the metering characteristics of the downdraft carburettor are superior to those of the conventional type.[11]

681. Fuel Mixture Distribution.—Successful carburation involves two separate phenomena, first the production of a petrol-air mixture of constant proportions in the carburettor and, secondly, the distribution of this mixture to the engine cylinders through the induction manifold. The latter is difficult to achieve, but it is necessary to provide to each cylinder of a multi-cylinder engine exactly equal amounts of fuel-air mixture of constant composition. Imperfect distribution causes uneven torque and unnecessary vibration, it increases fuel consumption and results in a loss of power output. It is often found on a six cylinder automobile engine fitted with only one carburettor that some cylinders operate with much richer mixtures than the others, and it is necessary to provide some cylinders with an uneconomical mixture strength so that the other cylinders get a mixture rich enough to fire.

The complexity of the problem of distribution is evident from a consideration of the numerous factors involved, which may be listed as follows :—(*a*) degree of atomization, (*b*) lack of homogeneity of the

mixture, (*c*) precipitation, (*d*) division of air flow, (*e*) application of heat, (*g*) manifold design and (*h*) port design. Each of these items is a separate problem.

The degree of atomization obtained with commercial carburettors varies markedly from one model to another, but it is evident that the better the atomization and the smaller the fuel particles carried by the air stream, the better is the chance of obtaining good distribution between the various cylinders without fuel precipitation. Some carburettors are very sensitive with regard to the position of the throttle valve, which often deflects the mixture to one side or other of the manifold depending upon the position of the throttle, causing the extreme cylinders to run with rich and lean mixtures alternately.

A detailed consideration of the problems underlying fuel mixture distribution in the inlet manifold is outside the scope of this book and the reader is referred to the references at the end of this chapter for further information. An important factor involved is, however, that of fuel volatility, which is described later. Another factor is the latent heat of vaporization of the fuel, which assumes considerable importance in the carburation of alcohol fuels, particularly methanol, which has a latent heat approximately 3·5 times as great as that of an average hydrocarbon fuel.

682. Adjustments necessary to a Carburettor in order to operate satisfactorily on Different Fuels.—Float chamber carburettors are susceptible to changes in the specific gravity of the fuel used, since when fuels of high specific gravity are used, e.g., benzoles or alcohols, the float rises to a greater height above the fuel level and cuts off the fuel supply early. The nett result of this is to lower the level of the fuel in the float chamber and jet and so cause a weakening of the mixture strength. Therefore the weight of the float must be readjusted to compensate for this effect, and made heavier for fuels of high specific gravity. It can be shown that if

W = weight of float mechanism,
D_p = specific gravity of petrol,
D_B = specific gravity of benzole,

then w, the additional weight required when running on benzole, is given by the expression

$$\frac{W\,(D_B - D_p)}{D_p}$$

For fuels of different calorific values, the size of the carburettor jet should be adjusted so as to deliver per unit time the same quantity of fuel heat units.

Automobile Engines

683. The modern automobile engine is an extremely efficient and reliable piece of mechanism which is constantly being improved and it is of interest to consider briefly the main features of recent designs.

On the Continent and in the United States, the present tendency in motor car engines is towards an increase in the number of cylinders, but in this country, because of the tax upon horse power, the 8-cylinder engine has practically disappeared and very few representatives of the 12 cylinder class remain. The 4 cylinder engine has, however, now been passed in numbers by the 6 cylinder engine in the United Kingdom, 60 per cent. of the total number of different models now being 6 cylinder engines. Nevertheless, in this country, the so called "Baby" car, of 7—9 horse power, fitted with a 4 cylinder engine, is extremely popular, due to the decreased purchasing power of the public caused by excessive taxation. Such cars are now finding their way on to the European and American markets.

This development, peculiar to the British market, has led to the use of high engine speeds and engines of high specific output.

Of the small car class, the 1933 Triumph "Super Nine" is typical. This car is fitted with a four cylinder engine of 60 mm. bore and 90 mm. stroke, giving a total swept volume of 1,018 ccs., and an R.A.C. rating of 8·9 h.p. The engine develops 21·5 B.H.P. at 2,500 r.p.m., 25·5 B.H.P. at 3,000 r.p.m., 28·5 B.H.P. at 3,500 r.p.m., and 30 B.H.P. at 4,000 r.p.m. An engine speed of 3,000 r.p.m. corresponds to a road speed of 41·8 m.p.h. in top gear. The compression ratio is 5·6 to 1. A one piece detachable cylinder head is fitted. The exhaust valves are arranged at the side, the inlet valves being overhead, arranged almost centrally over the cylinder bores, while the sparking plugs are almost directly over the exhaust valves. The result is a combustion chamber of pear shaped form comparatively free of any tendency to knock with present British fuels.

Another popular car in this class is the Hillman "Minx," having a four cylinder engine of 63 mm. bore and 65 mm. stroke. The swept volume is 1,184·5 ccs., corresponding to an R.A.C. rating of 9·84 h.p.

Among larger sized cars, the Morris range of automobiles are of interest, some particulars of which are given in Table 148, which has been compiled from information supplied by Morris Motors Limited.

Some figures have recently been published referring to the power outputs of Talbot car engines.[1,2] These are given in Table 149 and refer to (*a*) a $2\frac{1}{4}$ litre unsupercharged 6 cylinder engine, running on petrol-benzole with a compression ratio of 10 : 1, and (*b*) a $1\frac{1}{2}$ litre supercharged eight cylinder engine, running on alcohol fuel at a compression ratio of 6·2 to 1.

TABLE 148

MORRIS AUTOMOBILE ENGINES (1933)

Engine	Bore and Stroke. Mms.	Total Swept Volume Ccs.	Bore Stroke Ratio	Compression Ratio	B.H.P. under Road Conditions	R.P.M. at Maximum Torque	Petrol Consumption. M.P.G.	Petrol Consumption Pints/B.H.P./Hour at Maximum Torque
Isis 6 cylinder o.h.v.	69 × 110	2,468	1·594	5·5	49·2 at 3,200 r.p.m.	1,300	22	0·63
Major 6 cylinder s.v.	61·25 × 102	1,803	1·665	5·54	32·2 at 3,400 r.p.m.	1,400	27	0·60
Ten 4 cylinder s.v.	63·5 × 102	1,292	1·61	5·76	23 at 3,200 r.p.m.	1,600	35	0·61

TABLE 149. POWER OUTPUTS OF RACING CAR ENGINES

Touring Car Engine Tuned for Racing. 2½ Litre 6 Cylinder Unsupercharged. Flat Head			Racing Car Engine. 8 Cylinder, Supercharged. Hemispherical Head	
R.P.M.	B.M.E.P. Lbs. Per Square Inch	B.H.P.	B.M.E.P. Lbs. Per Square Inch	B.H.P.
2,500	125	55	227	64
3,000	125	66	233	79
3,5000	125	77	240	95
4,000	124	86·5	244	110
4,500	117	92·5	242	123
5,000	103	90·5	239	135
5,500	—	—	233	145
6,000	—	—	224	152
6,500	—	—	214	157
7,000	—	—	202	160

Concerning high powered lorry engines, the A.E.C. "Mammoth Major," 120 h.p. engine is a well known example of this class. Rated at 45 h.p., it develops, with an economical carburettor setting, 60 B.H.P. at 1,000 r.p.m., and acceleration is smooth and steady until a power output of 120 B.H.P. is attained at 2,400 r.p.m., at which speed a governor operates. Overhead valves are fitted and these are operated by an overhead camshaft. The crankshaft is of the 7 bearing type with bearings of 2¾ inches diameter. Partial balancing is provided by counterweights to relieve the main bearings of some of the dynamic loading. The power output characteristics of this engine are given in Chapter XIX (see paragraph 865).

Details of some 1933 American car engines are given in Table 150. In America, the compression ratios of such engines continue to rise slowly, chiefly as a result of fitting aluminium cylinder heads of the turbulent type and means for controlling temperatures.[17]

MOTOR CYCLE ENGINES

684. The motor cycle engine has undergone many changes during the past ten years, and at the present time motor cycles capable of speeds of over 90 miles per hour are quite common. Single cylinder engines are most popular and by far the larger number of these are air cooled. Two stroke engines are widely used on the smaller and lighter machines.

Motor cycle engines are mainly of three sizes, 250 ccs., 350 ccs. and 500 ccs. capacity, having nominal rated horse powers of 2·5, 3·5 and 5·0. respectively. Two stroke engines are mainly confined to the 250 ccs. capacity category.

Four stroke engines are mostly fitted with overhead valves, operated

TABLE 150

1933 AUTOMOBILE ENGINES (AMERICAN)

Car	Model	Number of Cylinders	Cylinder Arrangement	Bore and Stroke. Inches	Displacement Cubic Inches	Compression Ratio	Maximum H.P.	R.P.M. at Maximum H.P.
Buick	50	8	In line	$2\frac{5}{16} \times 4\frac{1}{16}$	230·4	5·25	86	3,200
Buick	60	8	do.	$3\frac{1}{16} \times 4\frac{5}{8}$	272·6	5·25	97	3,200
Buick	80 90	8	do.	$3\frac{5}{16} \times 5$	344·8	4·8	113	3,200
Cadillac 8	345C	8	V90°	$3\frac{3}{8} \times 4\frac{1}{16}$	353	5·4	115	3,000
Cadillac 12	370C	12	V45°	$3\frac{1}{8} \times 4$	368	5·6	135	3,400
Cadillac 16	452C	16	V45°	3×4	452	5·7	165	3,400
Chrysler 6	CO	6	In line	$3\frac{1}{2} \times 4\frac{1}{2}$	224	5·35	83	3,400
Chrysler Royal 8	CT	8	do.	$3\frac{1}{4} \times 4\frac{1}{8}$	273·8	5·2	90	3,400
Chrysler Imperial 8	CQ	8	do.	$3\frac{1}{4} \times 4\frac{1}{2}$	298·6	6·2	108	3,400
Chrysler Imperial 8	CL	8	do.	$3\frac{1}{2} \times 5$	384·8	5·8	135	3,200
Continental Beacon	C400	4	do.	$3\frac{3}{8} \times 4$	143·12	5·05	40	2,700
Continental Flyer	C600	6	do.	3×4	169·64	5·21	65	3,500
De Soto	SD	6	do.	$3\frac{1}{4} \times 4\frac{3}{8}$	217·7	5·35	79	3,400
Dodge 6	DP	6	do.	$3\frac{1}{8} \times 4\frac{3}{8}$	201·3	5·5	75	3,600
Dodge 8	DO	8	do.	$3\frac{1}{4} \times 4\frac{1}{4}$	282·1	6·2	100	3,600
Graham 6	Std. 6	6	do.	$3\frac{1}{4} \times 4\frac{1}{2}$	224	6·5	85	3,400
Graham 8	Std. 8	8	do.	$3\frac{1}{8} \times 4$	245·4	6·5	95	3,400
Hudson Super Six	SS6	6	do.	$2\frac{5}{16} \times 4\frac{3}{4}$	193	6·2	70	3,200
Pierce Arrow	836	8	do.	$3 \times 4\frac{1}{4}$	240·3	5·5	135	3,400
Pierce Arrow	1,236	12	V80°	$3\frac{3}{8} \times 4$	429	6·0	160	3,400
Studebaker 6	56	6	In line	$3\frac{1}{4} \times 4\frac{5}{8}$	230	5·5	85	3,200
Willys 6	99	6	do.	$3\frac{5}{16} \times 4\frac{1}{2}$	213·3	5·26	80	3,400
Willys 4	77	4	do.	$3\frac{1}{8} \times 4\frac{3}{8}$	134	5·1	45	3,200

either by an overhead camshaft or by push rods. Some models, such as those manufactured by Rudge Whitworth, have four valves, two inlet and two exhaust, while others are fitted with only one exhaust and one inlet valve. The valves are disposed radially in the cylinder head, giving a very efficient pent-roof combustion chamber of very good anti-knock characteristics. Sparking plugs are either placed in the centre of the head or at one side with a slight bias to the exhaust valve. Aluminium or aluminium alloy pistons are now standard and are often dome shaped so as to allow the attainment of high compression ratios. Standard models have compression ratios of 6—7 to 1, while racing models often have compression ratios as high as 10 to 1 when the use of alcohol fuels is allowed. With petrol-benzole fuels, compression ratios are usually limited to about 7·5 to 1.

Recent data concerning three motor cycle engines, manufactured by Messrs. Rudge Whitworth, Limited, Coventry, England, are reproduced in Tables 151 and 152.[12] Additional figures for the power outputs of motor cycle engines operating at various compression ratios on various fuels are given in Chapter IX (Volume I), paragraph 425.

TABLE 151. RUDGE WHITWORTH MOTOR CYCLE ENGINES

Capacity	500 ccs.	350 ccs.	250 ccs.
Bore, mm.	85	70	62·5
Stroke, mm.	88	90·5	81
Capacity, ccs.	499	349	246
Compression Ratio	7·25	8·0	9·0
Fuel	50% Petrol 50% Benzole	50% Petrol 50% Benzole	50% Petrol 50% Benzole
Valve Arrangement	2 Inlet Parallel 2 Exhaust Radial	4 Radial	4 Radial
Lubrication	Dry Sump		
Big End Bearing	Caged Roller	Plain	Plain
Piston	Aluminium Slipper		
Ignition	Magneto and centrally situated sparking plug.		
Weight, lbs.	85	80	55

AERO-ENGINES

685. Perhaps the most efficient internal combustion engines manufactured are those used in aircraft. The aero-engine must be efficient not only in relation to the fuel it consumes, but in every possible respect, including the material of which it is constructed, because the utmost reliability is demanded. For military aircraft, this high reliability must often be combined with very high power output.

TABLE 152. RUDGE WHITWORTH MOTOR CYCLE ENGINES

R.P.M.	500 ccs.		350 ccs.		250 ccs.	
	B.M.E.P. Lbs./sq. in.	B.H.P.	B.M.E.P. Lbs./sq. in.	B.H.P.	B.M.E.P. Lbs./sq. in.	B.H.P.
3,600	161·5	22·3	—	—	—	—
4,000	171	26·3	—	—	—	—
4,400	172	29·3	—	—	—	—
4,600	173	30·6	171	21·2	—	—
4,800	173	31·9	171	22·2	174	16·1
5,000	171·5	33·0	174	23·4	175	16·8
5,200	172·5	34·5	175·5	24·6	177	17·7
5,400	170	35·3	177	25·8	176	18·3
5,600	166·5	35·8	179·5	27·1	175	18·9
5,800	163	36·3	179·5	28·1	175	19·6
6,000	158	36·7	178	28·8	176	20·4
6,200	—	—	175·5	29·3	176	21·0
6,400	—	—	171	29·6	173	21·4
6,600	—	—	—	—	172	21·9
6,800	—	—	—	—	169	22·1
7,000	—	—	—	—	158	21·5

The late war gave a tremendous impetus to aero-engine development and since 1918 much progress has been made, culminating in the development of planes capable of speeds in excess of 300 miles per hour. Service planes are now in regular use which have normal speeds of over 200 m.p.h.

Development of aero-engines in this country has, for the most part, been directed along three avenues, the air cooled radial engine, the straight line multi-cylinder engine, one piston operating each crank, and the Vee type engine, in which two pistons are coupled to each crank.

Straight line multi-cylinder engines, usually of 4 or 6 cylinders, have been developed for both air cooling and liquid cooling.

686. Air Versus Liquid Cooling.—Much controversy exists as to which type of cooling is the most desirable in aircraft engines. The water cooled engine starts with the heavy handicap of a radiator and water connections, involving considerable additional weight, and what perhaps is even more serious for military purposes, much greater vulnerability ; but against these defects must be offset a very large advantage on the score of reliability, and the ability, owing to the lower cylinder temperature, both to consume less lubricating oil, to employ a higher compression and, therefore, to obtain a lower fuel consumption. However, the air cooled engine scores on the ground of greater simplicity and other points. Its first cost, for a given power output, is about 20 per cent. lower than the in-line water cooled engine, it contains about 20 per cent. fewer parts, and has a 30 per cent. lower weight.[13] Under

service conditions, the radial engine is claimed to give greater manœuvrability. An objection to the radial engine is that the heat is located in certain spots in the cylinders and cylinder heads and is difficult to remove, but owing to the disposition of its cylinders and its relation to the slip stream from the propellor, it offers the most ideal case for air cooling and it is in this type of engine that air cooling has been developed with the greatest success.

687. High Temperature Liquid Cooling.—Recently a considerable amount of work has been carried out, both in this country and in America, on the possible use of liquids of higher boiling point than water as cooling media for liquid cooled engines. There are several reasons for increasing the temperature of the coolant.

(1) Saving in weight.
(2) Higher air speed of the airplane by reduction of drag.
(3) Possibility of decreasing fuel consumption.
(4) Simplification of controls.

With reference to the first item, it has been found that a little over 0·2 lbs. per horse-power can be saved in weight, using an outlet cooling temperature of 300°F., obtained using ethylene glycol (Prestone) as the cooling liquid. On a Curtis persuit plane, the use of this material at this temperature allowed a 75 per cent. reduction in the size of the radiator, a 10 per cent. reduction in the air resistance of the entire plane and materially increased the maximum speed.[14]

It will be evident that it is not possible to take an engine which has been developed for water cooling with an exit temperature of 180°F., and run it at practically double this figure. There are a number of difficulties to be overcome. In the first place, the higher temperature lowers the strength of aluminium alloy materials very greatly. It increases the difficulty of cooling pistons and, therefore, more heat is transmitted to the lubricating oil, which in turn must be better cooled.

Ethylene glycol has the advantage of being an anti-freeze material so long as it contains 5 per cent. of water, but it has a tendency to leak very badly and extra precautions must be taken to prevent this. Lubrication problems on engine parts are more difficult, on account of the higher temperature, and more care must be taken in the construction of radiators on account of the reduction in strength of the usual solder. In general, the higher temperatures involved are somewhat similar to those experienced in air-cooled engines and it is therefore necessary to change clearances throughout the engine to correspond with these high temperatures.[15] It is probable that the development of high temperature liquid cooling will do much to reduce some of the inherent disadvantages of liquid cooled engines in the near future.

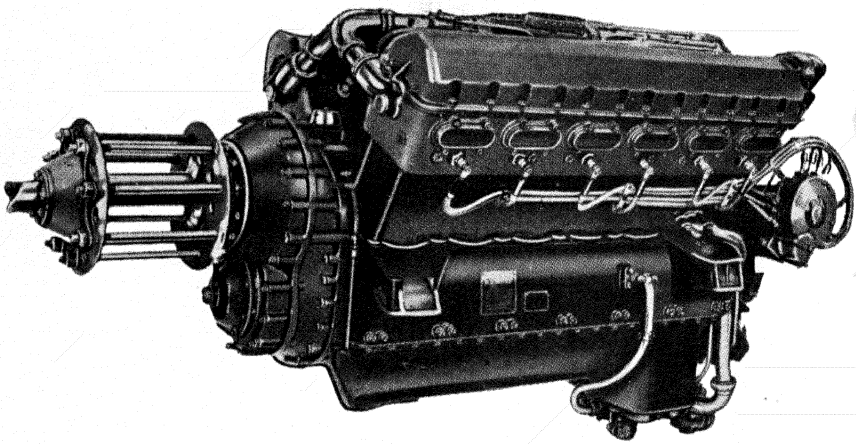


FIG. 174.—VIEW OF ROLLS-ROYCE "KESTREL" AERO ENGINE.
(Courtesy of Rolls-Royce, Ltd.)

Facing p. 209]

688. Types of Aero-Engines Now Employed.—For the smallest and lightest type of aircraft, the air cooled engine is practically supreme on the grounds of first cost, but the water cooled 6-cylinder in line engine is used to a considerable extent. The average engine capacity is approximately 6 litres. The four cylinder in-line engine is now entering into this class and is likely to prove a healthy competitor.

For small civil type planes, it appears that favour is gradually turning to the small twin engined passenger machine, carrying about six people. If expectations are realized, then the small civil type engine of 150 horse-power to 200 horse-power will become a really important category. The so-called medium size civil type engine is of 350—400 horse-power. Under the category of military and air liner type engines, the liquid cooled engine of 600 to 700 horse-power plays an important part, as instanced by the Rolls Royce range of 12 cylinder Vee type engines, while 800—900 horse-power high efficiency military planes are normally fitted with either 9 cylinder radial engines or Vee type water cooled engines.

In this country, the best known types of water cooled engines are those manufactured by Rolls Royce, Ltd., while the Bristol Aeroplane Company is well known for its air cooled engines. In America, the air cooled engines of the Pratt and Whitney Aircraft Co. have an enviable reputation.

Aero Diesel engines are dealt with in Chapter XIX.

Description of Typical Aero-Engine

689. Rolls Royce Water Cooled Engine.—The latest productions of the Rolls Royce Company are known as the " Kestrel " and the " Buzzard." These engines are of similar design and are of the Vee type, embodying two lines of 12 cylinders inclined at an angle of 60°. In both types, an effort has been made to reduce the frontal area to an absolute minimum so that the fuselage drag of the aircraft into which they are fitted can be made as low as possible.

The " Kestrel " engine is supplied in no less than twelve varieties, all incorporating the same main components. These twelve types are obtained by supplying the engine with three different gear ratios: ·632 : 1, ·552 : 1, and ·475 : 1. These three gear ratios can be applied to engines of two different compression ratios, namely 7 : 1 and 6 : 1, with normal aspiration, or, alternatively, by fitting superchargers either of what is known as the " moderate " type, that is to say, permitting a certain amount of supercharging at take off and maintaining 525 horse-power to 2,000 feet, or the " full " supercharger, which is capable of maintaining the ground level rate-power up to 11,500 feet. In connection with the high compression engines, the rated output of 480 horse-

power is developed at normal speed at ground level and maintained to an altitude of 3,000 feet by opening the throttle to the fullest extent.

The " Buzzard " engine is supplied fitted with a supercharger which can be fully used at ground level in order to facilitate taking off heavy aircraft from the ground. Two different propellor gear ratios are pro-provided, viz., ·553 to 1 and ·477 to 1.

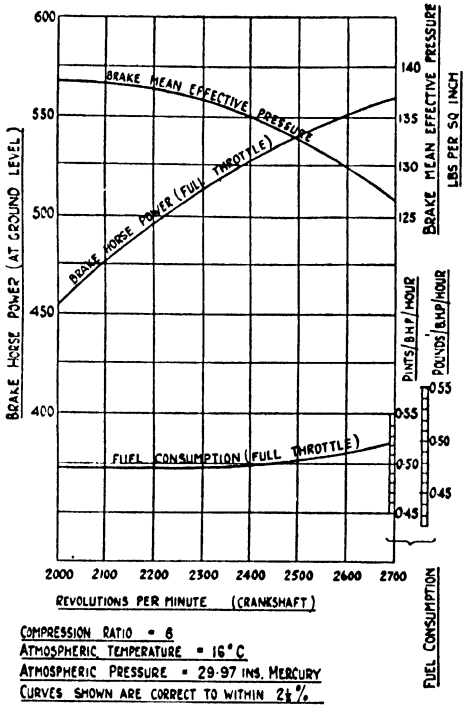


FIG. 175.

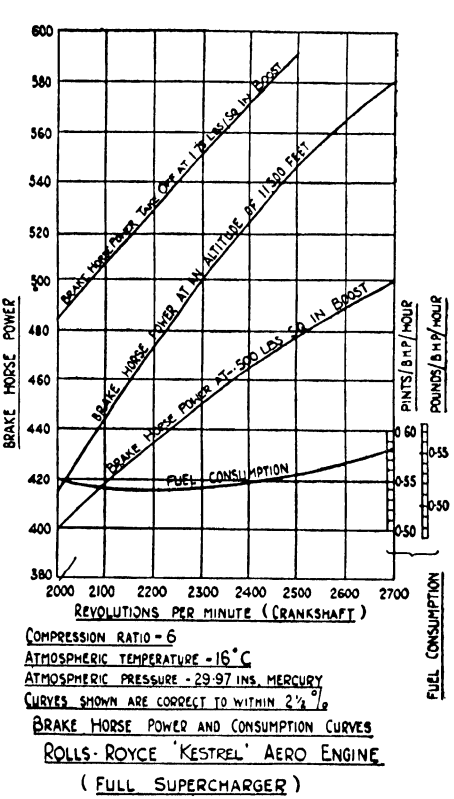


FIG. 176.

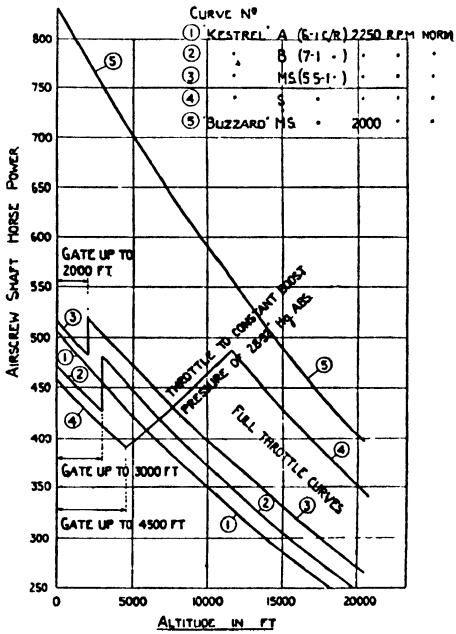
(*Courtesy of Rolls-Royce, Ltd.*)

In both the " Kestrel " and " Buzzard " engines, the cylinder construction is of an aluminium block design giving a very light and rigid engine. The cylinder blocks are aluminium castings and the cylinder heads with the necessary passages for the gas and exhaust are cast integrally with the walls forming the water jackets. Renewable valve seating rings are screwed into the heads and the valve guide bushes are of cast iron. There are two inlet and two exhaust valves per cylinder, the valves being operated by an overhead camshaft and a separate rocker being provided for each valve.

The pistons are made from forged " Y " alloy and are machined all

over. The connecting rods are of " H " section and are of forked type. Three lubricating oil pumps, of the geared type, are provided and the engine is lubricated on the dry-sump principle, the bulk of the oil being carried in a separate service tank, from which it is delivered to various parts of the engine.

In " Kestrel " engines of types " A " and " B ", two Rolls-Royce Duplex Carburettors are mounted between the cylinder blocks. The two throttles of each carburettor are connected, so that all four throttles are opened and closed simultaneously and to the same extent. The carburettors are fitted with a device by which the flow of petrol from the float chamber to the jet is automatically regulated in accordance with the altitude at which the machine is flying. Compensating passages are provided to maintain the same pressure in the float chamber as in the throat under all conditions. The compensating passages, in addition to reducing eddying, enable the float chamber cover to be sealed, thus reducing the risk of petrol leakage. Petrol is supplied to both carburettors by a small gear pump. Superchargers fitted to the " Kestrel " and " Buzzard " engines consist of high speed centrifugal fans mounted co-axially with the crankshaft at the near end of the engine and drawing their air supply through the carburettors.



COMPARISON OF B.H.P AVAILABLE FROM THE VARIOUS TYPES OF R.R ENGINES BASED UPON PERFORMANCE AT THE NORMAL R.P.M & TAKING THE FIXED BLADED AIRSCREW CHARACTERISTICS INTO ACCOUNT BY ASSUMING PROBABLE CHANGES IN R.P.M AT THE VARIOUS ALTITUDES

NOTE - GATE THROTTLE STOPS ARE EMPLOYED AT THE LOWER ALTITUDES FOR ALL ENGINES WITH THE EXCEPTION OF TYPES 'KESTREL' A & 'BUZZARD' MS.

ROLLS-ROYCE AERO ENGINES.

FIG. 177.
(Courtesy of Rolls-Royce, Ltd.)

Ignition is by two 12-terminal high tension magnetos mounted on opposite sides of the auxiliary gear casing.

Details concerning the " Kestrel " engines are given in Table 153, and power curves for unsupercharged and full supercharged engines are reproduced in Figures 175 and 176. Similar figures for the " Buzzard " engines are given in Table 154. The power outputs of these engines at various altitudes are given in Figure 177.

TABLE 153

ROLLS-ROYCE "KESTREL" ENGINES (*Courtesy of Rolls-Royce, Limited*)

Series	Unsupercharged						Moderate Supercharger			Full Supercharger		
	I A	II A	III A	I B	II B	III B	I MS	II MS	III MS	I S	II S	III S
Bore, inches	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00
Stroke, inches	5·50	5·50	5·50	5·50	5·50	5·50	5·50	5·50	5·50	5·50	5·50	5·50
Normal Rated B.H.P.												
Ground level	490	490	490	480	480	480	525	525	525	—	—	—
2,000 feet	—	—	—	—	—	—	525	525	525	—	—	—
3,000 feet	—	—	—	480	480	480	—	—	—	—	—	—
11,500 feet	—	—	—	—	—	—	—	—	—	408	480	480
Normal R.P.M.	2,250	2,250	2,250	2,250	2,250	2,250	2,250	2,250	2,250	2,250	2,250	2,250
Maximum B.H.P.	560	560	560	580	580	580	660	660	660	580	580	580
Maximum R.P.M.	2,700	2,700	2,700	2,700	2,700	2,700	2,700	2,700	2,700	2,700	2,700	2,700
Normal Air Screw, R.P.M.	1,422	1,242	1,668	1,422	1,242	1,068	1,422	1,242	1,068	1,422	1,242	1,068
Engine Compression Ratio	6	6	6	7	7	7	5·5	5·5	5·5	6	6	6
Fuel Consumption, Gallons per hour*	30	30	30	28	28	28	35	35	35	32	32	32
Oil Consumption, Pints per hour*	5	5	5	5	5	5	5	5	5	5	5	5
Weight of Engine, Lbs.†	884	884	884	884	884	884	922	922	922	922	922	922

* At normal B.H.P. and R.P.M.

† *Includes* carburettors, magnetos, engine feet reduction gear and air screw hub, but *excludes* exhaust manifolds, radiator, air screw oil, fuel and water.

TABLE 154.* ROLLS-ROYCE "BUZZARD" AERO-ENGINES

	Moderate Supercharger	
	Buzzard II MS.	Buzzard III MS.
Bore, inches	6·00	6·00
Stroke, inches	6·60	6·60
Normal rated B.H.P. (Ground level)	825	825
Normal Crankshaft R.P.M.	2,000	2,000
Maximum B.H.P.	920	920
Maximum Crankshaft R.P.M.	2,300	2,300
Normal air screw R.P.M.	1,106	954
Compression Ratio	5·5	5·5
Fuel Consumption, Gallons per hour	53	53
Oil Consumption, Pints per hour	9	9
Weight of Engine, Lbs.	1,530	1,530

690. Bristol Aeroplane Company.—Radial Air Cooled Engines.—The Bristol "Mercury" and "Pegasus" engines are of the air cooled radial type having nine cylinders arranged in a single row at 40° intervals around a forged duralumin crank case, the design having been arranged to produce an efficient but simple and compact high performance unit particularly suitable for air cooling.

The cylinders consist of open ended steel barrels closed by a screwed-on head of forged aluminium alloy carrying four overhead valves and rocker gear. The exhaust ports are located at the front of the head directly in the air stream in order to ensure an equable temperature distribution throughout the head with freedom from hot spots. The four overhead valves per cylinder are operated by push-rods from the two row eight lobe cam sleeve running concentrically with, and driven from, the front end of the crankshaft, compensating gear ensuring that the correct valve clearances are automatically maintained over the widest range of operating temperatures.

All types are provided with a centrifugal type blower in the induction system. The unit is mounted immediately behind the rear wall of the crank case, concentric with, and driven from, the tail end of the crankshaft around which it revolves. The drive from the crankshaft is through multiplying gears and incorporates flexible spring drive and friction clutches damping out cyclic shocks and protecting the high speed gears and impellor from any shock loads resulting from excessively rapid engine acceleration and deceleration.

The Duplex carburettor feeding the induction system is mounted on the intake side of the blower, the mixture being drawn axially into the impellor and discharged radially via a fixed diffuser into the annular induction chamber surrounding the blower. From this chamber, the

* Courtesy of Rolls-Royce, Limited.

mixture flows to the cylinders by the 18 radial pipes feeding each of the cylinder inlet ports.

Dual ignition is provided by two H.T. magnetos firing two sparking plugs in each cylinder, the magnetos with other auxiliary drives and accessories such as oil pump and filters, starter system and petrol pump being carried on the crank case rear cover ensuring the necessary protection for these components.

The Mercury Series V-S2. This is a compact engine of small overall diameter, intended for use in high performance scouts or similar aircraft having a speed at high altitude of some 200 miles per hour or more. The supercharger has a high gear ratio and maintains the normal pressure in the induction system up to an altitude of 12,000 feet, at which the power is 520 B.H.P. at the normal speed of 2,250 r.p.m.; the maximum power obtainable is 570 B.H.P. at 2,600 r.p.m., at an altitude of 16,000 feet.

The Pegasus II Types M2 and M3. These engines are alike except for the speed ratios of their airscrew reduction gears, the ratio of the type M2 engine being 0·666 to 1 and that of the type M3 0·5 to 1. The supercharger is in each case of the medium duty type and gives a rated altitude of 5,000 feet, at which 580 B.H.P. is developed at the normal speed of 2,000 r.p.m., or 635 B.H.P. at 6,500 feet at a maximum speed of 2,300 r.p.m. These engines are offered for use in general purpose service aircraft or for fast mail or passenger carrying civil aircraft operating at high altitudes on special services.

The Pegasus II Types L2 and L3. Generally similar to the Pegasus types M2 and M3, these engines have superchargers of lower output, so that their rated altitude is 2,000 feet. At this height, the power is 600 B.H.P. at the normal speed of 2,000 r.p.m., while at the maximum of 2,300 r.p.m., the power developed is 650 B.H.P. at 2,500 feet.

These engines are suitable for flying boats and commercial aircraft requiring good take off power and operating at moderate altitudes and for certain classes of military aircraft having similar characteristics.

Pegasus II Types V2 and V3. These engines are intended more particularly for commercial aircraft of the "Air Liner" class. With a rated speed of only 1,900 r.p.m., at which 550 B.H.P. is developed, the maximum power is 610 B.H.P. at 2,185 r.p.m. The full 550 B.H.P. is available for take off at normal speed.

The leading particulars of Bristol Mercury and Pegasus 1933 engines are detailed in Table 156. A front view of the Pegasus engine is shown in Figure 178 and a side view of the Mercury engine in Figure 179.

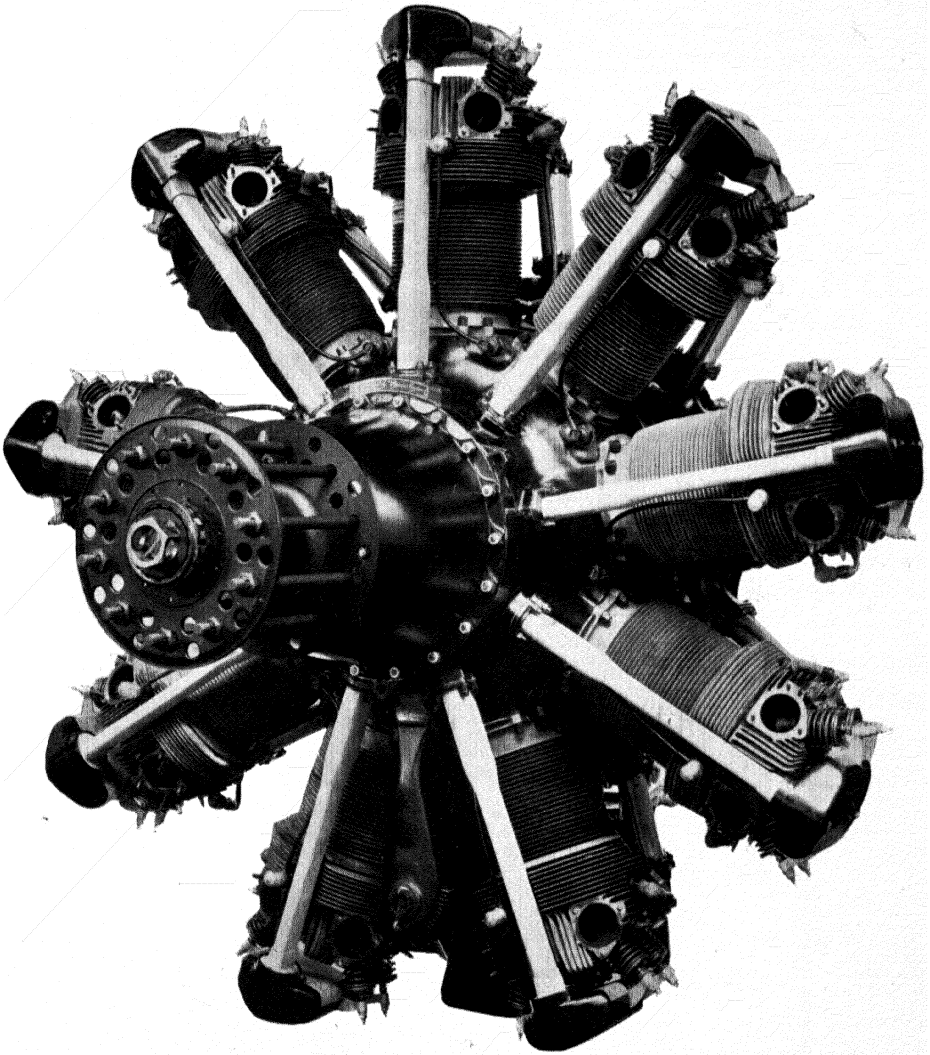


FIG. 178.—FRONT VIEW OF BRISTOL "PEGASUS" AERO ENGINE.
(Courtesy of Bristol Aeroplane Co.)

[*Facing p.* 214

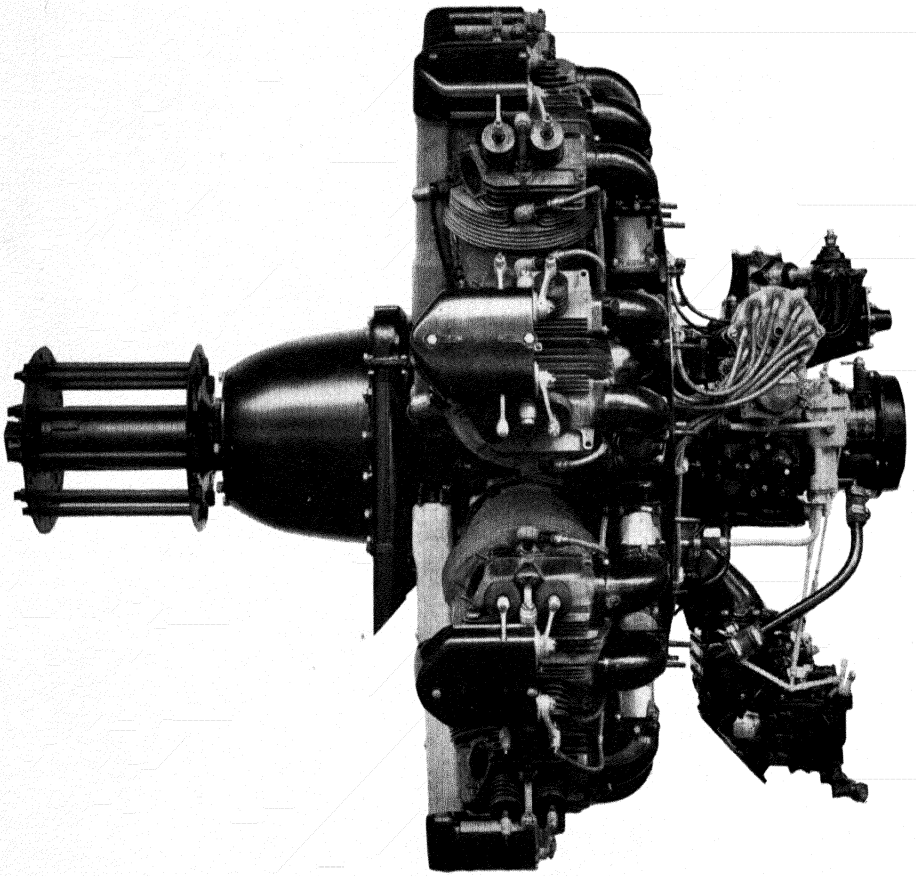


FIG. 179.—SIDE VIEW OF BRISTOL "MERCURY" AERO ENGINE.
(*Courtesy of Bristol Aeroplane Co.*)

Facing p. 215]

691. Pratt and Whitney Radial Air Cooled Aero-Engines.—Some particulars of the well-known engines manufactured by the Pratt and Whitney Aircraft Co., East Hartford, Connecticut, are given in Table 156. These are nine cylinder radial air cooled engines.

TABLE 155*

LEADING PARTICULARS BRISTOL MERCURY AND PEGASUS 1933 ENGINES

Engine Type	Mercury V-S2	Pegasus II M2	Pegasus II M3	Pegasus II L2	Pegasus II L3	Pegasus U 2	Pegasus U 3
Normal engine r.p.m.	2,250	2,000		2,000		1,900	
Maximum engine r.p.m.	2,600	2,300		2,300		2,185	
Ratio $\frac{\text{Airscrew}}{\text{Engine}}$ ..	0·666	0·666	0·5	0·666	0·5	0·666	0·5
Airscrew normal r.p.m.	1,500	1,330	1,000	1,330	1,000	1,270	950
Airscrew maximum r.p.m.	1,730	1,530	1,150	1,530	1,150	1,460	1,095
Take off B.H.P. Sea level at normal r.p.m.	570	620		635		550	
Rated B.H.P. at normal r.p.m.	520	580		600		500	
Rated altitude at normal r.p.m.	12,000	5,000		2,000		Ground level	
B.H.P. at maximum r.p.m.	570 at 16,000 feet	635 at 6,500 feet		650 at 2,500 feet		610	
Standard weight bare	945	980		970		970	

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* Courtesy of Bristol Aeroplane Company, Limited.

TABLE 156*

PRATT AND WHITNEY RADIAL AIR COOLED AERO-ENGINES

Type	Compression Ratio	Blower Ratio	Permissible R.P.M. at Sea Level	Critical Altitude	Rated R.P.M.	Rated H.P.	Minimum Octane Number of Fuel. (U.S. Army Specification Method).
Wasp Junior	6·0	10 : 1	2,000	7,500	2,300	375	86
Wasp C, C-1, D	5·25	10 : 1	1,950	6,000	2,100	450	80
Wasp C, C-1	6·0	10 : 1	1,850	8,000	2,100	450	83
Wasp S.D.	6·0	10 : 1	1,950	7,500	2,200	500	83
Hornet B, B-1, DD	6·0	12 : 1	1,850	8,000	1,950	575	86
„ 3 : 2 Red.	6·0	12 : 1	1,750	8,000	2,000	575	86
Hornet B1, DD	6·0	10 : 1	1,850	6,000	1,950	575	86
„ 3 : 2 Red.	6·0	10 : 1	1,850	6,000	2,000	575	86

* Courtesy of the Pratt & Whitney Aircraft Co.

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Chapter XV

THE EFFECT OF FUEL VOLATILITY CHARACTERISTICS ON ENGINE PERFORMANCE

695. Introduction.—Only a few years ago the oil refiners' interest with reference to motor fuel seemed to be limited to "initial-boiling-point," "end-point" and "gravity," (none of which has any relation to the performance of a fuel in an engine), while at the same time the automobile engineer did not regard the properties of fuels as of any great importance. There was, perhaps, some justification for this situation in the fact that little or no fundamental data existed relating the performance of a fuel in an engine to its physical characteristics. Eventually, however, the fact was recognized that the automobile engine and its fuel constitute a joint problem, concerning almost equally the automobile engineer and the refiner, and out of this recognition came the formation in the United States in 1922 of the Co-operative Fuel Research Steering Committee, representing the American Petroleum Institute, the Automobile Chamber of Commerce and the Society of Automotive Engineers. Under the direction of this Committee, fundamental research carried out at the U.S. Bureau of Standards has clarified many relationships of the properties of fuel to its engine performance, so that it is now possible to state with some confidence the properties which a fuel should have to meet given engine conditions, and to state certain fundamental principles of automotive engine design which are desirable for the type of fuel in general use. While the work of the Co-operative Fuel Research Steering Committee has been in progress, much valuable work along similar lines has been carried out by other bodies, the most important of which is that financed by the Natural Gasoline Association of America and conducted by Professor George Granger Brown and his associates in the Department of Engineering Research, University of Michigan. This work extended from June, 1926 to May, 1930, and the results obtained are described in detail in University of Michigan Engineering Research Bulletin No. 14, May, 1930. The results obtained by the Co-operative Fuel Research Committee have been published at frequent intervals in the American scientific press.

Apart from these researches and those carried out by a few American oil companies, practically no other work on these problems has been carried out. Consequently, the subject matter of this chapter has been drawn very largely from these sources, and the thanks of the authors are

due to Professor G. G. Brown and the U.S. Bureau of Standards for permitting such reproduction of their valuable work.

Engine operations can conveniently be divided into the following phases :—(*a*) starting from cold, (*b*) warming up, and (*c*) normal driving conditions. As will be shown in this chapter, different fuel characteristics are necessary for the satisfactory engine performance in these various phases. A further question, that of dilution of the lubricating oil by the less volatile portions of the motor fuel also requires consideration.

The Meaning and Significance of the Term Volatility as applied to Motor Fuels

696. Volatility may be defined as the degree to which a substance will vaporize, i.e., form vapour, under specified equilibrium conditions. Thus, the dictionary defines " volatility " as the property of a substance which causes it to be dispersed readily into the air. This term is used generally in a comparative sense, e.g., " as volatile as ether." Consideration of these definitions indicates that volatility is a quality of a material indicating the ability of the material to vaporize, or the degree to which it will vaporize at ordinary temperatures, as on exposure to the air. This conception of volatility will be made more clear by considering the volatilization process itself.

When a *pure* chemical compound is vaporized, the properties of the residue after partial vaporization are identical with the properties of the original material, and, in such a case, volatility relationships are comparatively simple. Thus, under a pressure of 1 atmosphere, pure normal octane boils at a temperature of 125°C. When placed in a distilling flask and boiled for some time to displace all the air from the flask so that the liquid octane is under a pressure of 1 atmosphere of octane vapour practically free from air, all the octane may be " caused to pass off in the form of vapour " at a temperature of 125°C. But if the temperature of the flask is lowered below the boiling point none of the liquid octane will pass off as vapour, except that very small amount which passes into the air in the flask to give a partial pressure equal to the vapour pressure of the liquid. Thus, under these specified conditions, normal octane, at temperatures below 125°C., will not vaporize, and such a test is not a true test for volatility. If, however, the same substance is placed in a vessel freely exposed to the atmosphere, it will be completely vaporized at practically any temperature so long as enough air is allowed to come in contact with the liquid. Thus, if a specified amount of air such as 12 pounds is mixed with one pound of octane, and this mixture is heated to 40°F. (4·4°C.), at atmospheric pressure, 35 per cent. of the octane will vaporize. If the temperature is raised to 70°F. (21·1°C.),

under conditions otherwise identical, 90 per cent. will be volatile. These figures clearly indicate the necessity of specifying conditions completely when speaking of volatility.

In order that the term may be used with quantitative significance in the present discussion, *volatility is here defined as the degree to which a fuel will vaporize under specified equilibrium conditions. Whenever equilibrium conditions do not obtain, the term effective volatility will be employed instead of volatility alone.*

697. Operating and Starting Volatility.—A motor fuel must be evaporated so as to form an air-fuel mixture before it can be burnt. Thus volatility is a most important property of a motor fuel. Volatility can be conveniently expressed as the percentage of the fuel which can be evaporated at a specified temperature into air at atmospheric pressure when the air and fuel are present in definite proportions by weight.

Another practical equivalent measure of volatility is the temperature at which the fuel in a given air-fuel mixture is evaporated completely, or to some definite extent, say 95 per cent. Such a measurement indicates the volatility characteristics of the fuel which affect complete utilization, crank case dilution and the like. As to starting volatility, an engine must be started before it can be operated, and, in general, starting temperatures are lower than operating temperatures. There must be supplied, at the prevailing temperature, a mixture with air that will burn, even at the expense of only partial evaporation, for once the engine starts the temperature rises rapidly and more complete evaporation takes place. A fuel that might be very satisfactory from the standpoint of continuous operation may not permit starting from cold. Starting volatility can be measured by the quantity of fuel which must be supplied to produce at some chosen low temperature a given mixture that will explode.

698. Tests for Fuel Volatility.—The usual distillation test applied to motor fuels consists in evaporating a charge of 100 mls. of fuel in a specified manner from a specified flask and observing the temperatures at which various percentages are distilled over. This type of test has long been recognized as unsatisfactory for indicating quantitatively the volatility of fuels in an engine induction system, for the following reasons :—

(1) This type of distillation is a " batch " distillation in which the fuel vapour is drawn from the system as it forms, and evaporation at any stage of the process is taking place in the presence of a vapour that has been formed at practically the existing temperature and which is not representative of the charge which has been evaporated previously.

(2) In an atmospheric distillation, evaporation takes place at a fuel vapour pressure of 1 atmosphere (760 mms. of mercury), whereas, in the engine, the vapour pressure of the fuel is in the neighbourhood of 15 to 20 mms. of mercury; that is, only 2—3 per cent. of atmospheric pressure. Vapour temperatures at 760 mms. vapour pressure for a given percentage evaporated may be 100°C. higher than the corresponding temperatures for evaporation under engine conditions, and the composition of the first 20 per cent. evaporated will be decidedly different in the two cases.

(3) In an engine, fuel vaporization takes place in a current of air and the vaporized portion remains in contact with the unvaporized portion, whereas the batch type of atmospheric distillation is carried out in the absence of air.

It should not be inferred from the foregoing statements that the atmospheric distillation test is worthless. It gives valuable information regarding the relative volatilities of fuels and permits the specification of types of fuels that have been found to give satisfactory performance. However, the results obtained by its use are not readily translatable into expected performance and do not permit a direct quantitative comparison of fuels. Consequently numerous attempts have been made to relate the two processes of complete and partial vaporization.

699. Early Work on Fuel Volatility.—In 1921, Wilson and Barnard[1] proposed a method of measuring fuel volatility which consisted in the preparation of an equilibrium solution at a vapour pressure of 1 atmosphere by feeding fuel continuously into a heated flask containing a fixed volume of solution at such a rate as just to replace that lost by evaporation. This process was continued until from 7 to 10 times the volume of the solution in the flask had been distilled over and the temperature had ceased to rise, indicating that a state of equilibrium between the liquid and the vapour of the whole fuel had been reached. The vapour pressures of the equilibrium solution were measured over a desired temperature range by a static method and the data obtained, together with the average molecular weight of the fuel estimated from its A.S.T.M. distillation curve, permitted the calculation of the dew-points of the fuel in various air-fuel mixtures. The expression " dew-point of the air-fuel mixture " denotes that temperature at which the vapour of the whole fuel will just begin to condense from the air-fuel mixture. The term " saturation temperature " is perhaps better, since it embodies the idea of the temperature at which the space occupied by the air-fuel mixture is just saturated with the fuel vapour.

A more direct method of arriving at a satisfactory criterion of fuel volatility was employed by W. A. Gruse,[2] who mixed air and fuel in definite proportions at a temperature well above the dew-point and

observed the temperature at which condensation just began to take place on a cooled mirror. Measurements were made on a number of fuels, but the method appears to be tedious.

Kennedy[3] also made measurements of the dew-points of air-fuel mixtures by a static method which consisted in evaporating a known weight of fuel in a large flask of known volume and observing the temperature at which condensation just began to take place on a portion of the flask, which was cooled slightly below the temperature of the surrounding bath. Molecular weights of the fuels were calculated from the pressure exerted by a known weight of fuel vapour in the flask at a definite temperature, and observed dew-points were extrapolated to various air-fuel ratios. Measurements thus obtained were in general agreement with those of Gruse.

Work on a static phase change method was also conducted by Stevenson and Stark.[4] This method consisted essentially in evaporating a known weight of fuel in a known volume of air, and observing the pressure on the system as the temperature was reduced. Similar observations were taken with increasing temperatures, and the transition in the rate of change in pressure was evaluated from a plot of the pressure-temperature data. The temperature corresponding to this transition point was taken as the dew-point of the air-fuel mixture. The agreement between the results obtained with increasing and with decreasing temperature was taken as an indication that the dew-point of the mixture was the same as the temperature of complete equilibrium vaporization. The average molecular weight of the fuel was determined, and this, together with the weight of fuel required to saturate a known volume of air at a known temperature (the dew-point), permitted the calculation of the corresponding vapour pressures of the completely vaporized fuel. Direct dew-point observations were made to give independent checks. The end-point of the equilibrium distillation at atmospheric pressure, as determined by the phase-change method, was emphasized as a unique fuel characteristic and was called by Stevenson and Stark the " Deppé end-point." Graphs were prepared showing the relationship between the Deppé end-point and the saturation temperatures in various air-fuel mixtures, from which the saturation temperatures of air-fuel mixtures of any fuel could be determined by a measurement of the Deppé end-point. In this work, an equilibrium distillation was carried out and the difference between such a distillation and the A.S.T.M. 100 mls. distillation particularly stressed. Equilibrium distillation was contrasted with fractional distillation and the equilibrium end-point of complete vaporization was shown to be about 60°C. (140°F.) below the A.S.T.M. end-point.

In 1926, James[5] conducted continuous vaporization of fuels in a miniature pipe still at feed rates sufficiently low to permit attainment

of equilibrium, and used the results obtained to calculate the temperatures at which the fuels would be completely evaporated into a given air-fuel mixture at any given pressure.

The work carried out by the above investigators was later reviewed by T. S. Sligh, Junr.[6], who made the following remarks :—

(*a*) Direct observations of dew-points of air-fuel mixtures are at best tedious, and a number of observations are necessary to establish a point definitely.

(*b*) Equilibrium-solution methods are applicable only when the solution can be prepared at or near the temperature for which data are desired.

(*c*) Static methods involving the use of small quantities of fuel require great care if adsorption effects of the walls of the containing vessel, or of impurities, are to be avoided.

(*d*) While empirical relations connecting some point on the A.S.T.M. distillation curve or on the equilibrium distillation curve with the dew-point of an air-fuel mixture have been proposed, no rational method of extrapolation has been developed.

700. Equilibrium Air Distillation.—At the same time Sligh described work carried out at the U.S. Bureau of Standards on a method of continuous fuel vaporization in the presence of a known amount of air, now called " equilibrium air distillation." This consisted in supplying air and liquid fuel at measured rates to an evaporating coil, observing the temperature corresponding to equilibrium, separating and measuring the unevaporated liquid, and from data obtained at the required temperatures, plotting the distillation curves of fuels in the presence of known amounts of air. Thus the distillation curve for a fuel in any desired air-fuel mixture could be obtained at the temperatures and fuel vapour concentrations corresponding to engine operation. Later work by the Co-operative Fuel Research Committee and by Professor Brown at Michigan showed that this new method of measuring fuel volatility was of the greatest importance.

A diagrammatic sketch of the air distillation apparatus developed by Sligh is shown in Figure 180.

It has been described by Bridgeman as follows.[7] The essential part of the apparatus is the vaporization coil (*a*) which is constructed of copper tubing $\frac{1}{16}$-in outside diameter, 16 feet long, bent into the form of a helix. Liquid fuel and air are fed into this coil at measured rates. The coil is immersed in a stirred bath containing water, the temperature of which is regulated by the heater (*f*) above room temperature, and by the addition of ice below room temperature. The flow of fuel is controlled by displacement from the reservoir by the hollow plunger (*i*) which is operated by clockwork. Partial stoppage of the overflow tube into (*a*)

is avoided by providing an offset in the reservoir wall at this point. The plunger is suspended by a fine nichrome wire, 0·008-in. diameter, which passes through the packing gland (*l*) at the top of the reservoir and thence over an idler pulley to connect to a drum (*k*) mounted on the spindle of the clock mechanism (*j*). The packing gland consists of a thin piece of leather pierced by a very fine hole for the wire and mounted between two metal discs which serve to compress the leather and force it tightly around the wire. A recess is provided at the top which can be filled with mercury to ensure absence of leakage. The mainspring was removed from the clock mechanism, which was driven by the weight of

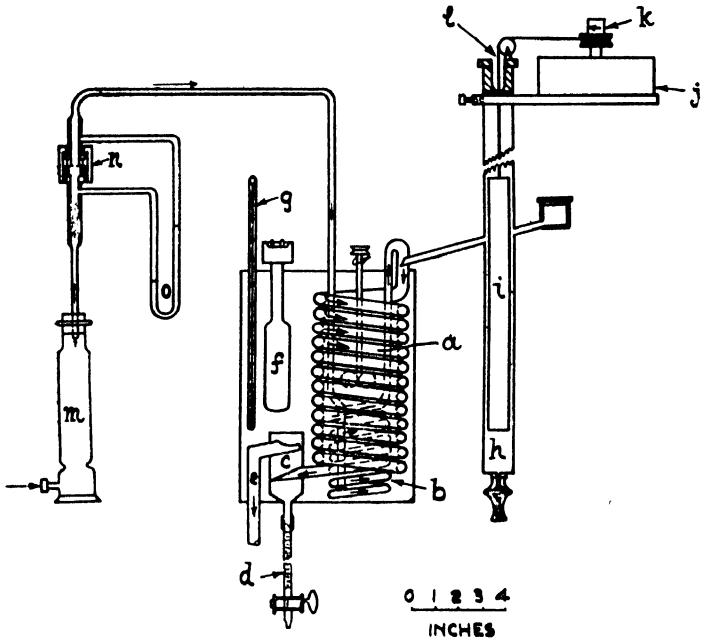


FIG. 180.—THE SLIGH APPARATUS FOR EQUILIBRIUM-AIR DISTILLATION.

the plunger acting through the drum mounted on the main shaft. The gear train and escapement served to regulate the motion and to maintain a constant rate of fall of the plunger. Four drums were fitted to the apparatus, permitting variations in the rate of fuel feed from 1 to 4 mls. per minute. The air, obtained from a low pressure supply, was dried by passage through a tower (*m*) containing calcium chloride and was passed through the calibrated meter (*n*). To reduce turbulence on the high pressure side of the orifice, a number of tubes were placed lengthwise in the air passage. After passage through the flow-meter the air was led to the bottom of the coil (*b*) so that it could be preheated or precooled to the temperature of the bath before coming into contact with the fuel.

At the bottom of the vaporization helix (*a*) the mixture flowed into a separating chamber (*c*) where the velocity was reduced. The air-vapour mixture passed out through the pipe (*e*) while the residual liquid drained out into the burette (*d*) where it was measured.

In the course of investigations conducted on behalf of the Natural Gasoline Association of America, Professor G. G. Brown used a similar type of apparatus, which, however, embodied various refinements over that described and used by Sligh and Bridgeman. Professor Brown's apparatus is shown in Figure 181.

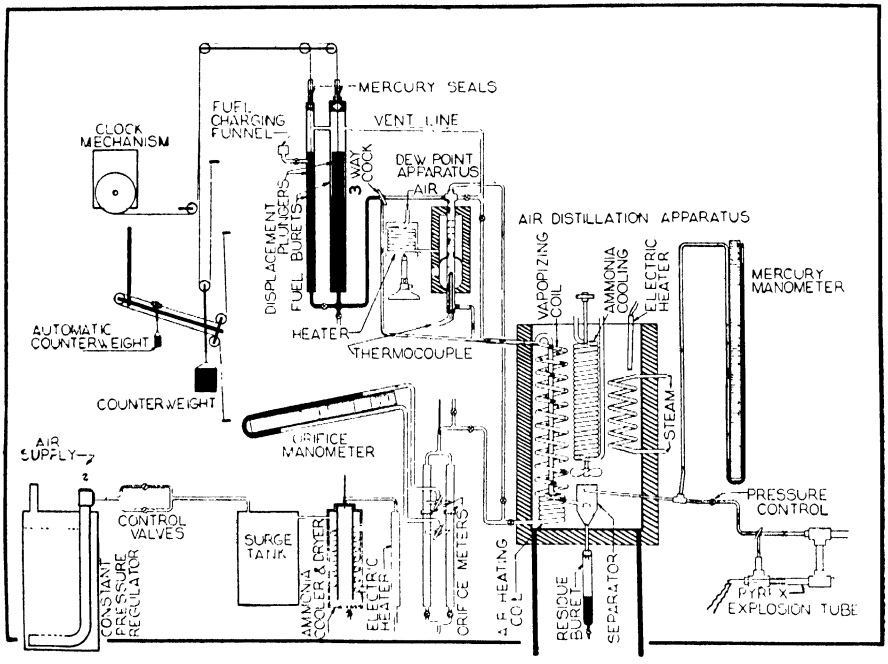


FIG. 181.—THE GRANGER BROWN APPARATUS FOR EQUILIBRIUM-AIR DISTILLATION.

In order to feed mixtures of different air-fuel ratios to the apparatus, displacement plungers of different diameters were used and, as the weights of different plungers were not the same, and that of each was too great to be supported entirely by the clock mechanism, a system of counter weights was provided. This also enabled a constant rate of fuel feed to be employed. Fuel was fed into the apparatus from the bottom of the burettes in order to avoid any change in composition due to surface evaporation. A Stevenson and Babor dew-point apparatus was also incorporated. The air used in the apparatus was conditioned by passage through an ammonia expansion cooler to precipitate moisture and then through an electric heater to bring it to constant temperature. Air-fuel vapour mixtures from the vaporizing coil could be passed into a

pyrex explosion tube. It was thus possible to determine the explosive limits of the fuel under test.

701. Results Obtained in Equilibrium Air Distillations.—In Figure 182 the curve A represents the air equilibrium distillation of a petrol in the presence of 15 times its weight of air. It should be noted that from 30 or 40 to 95 per cent. evaporated, the curve is practically a straight line and that the lower end breaks away rather sharply. Curve B is a calculated equilibrium air distillation curve, for a 15 to 1 air-

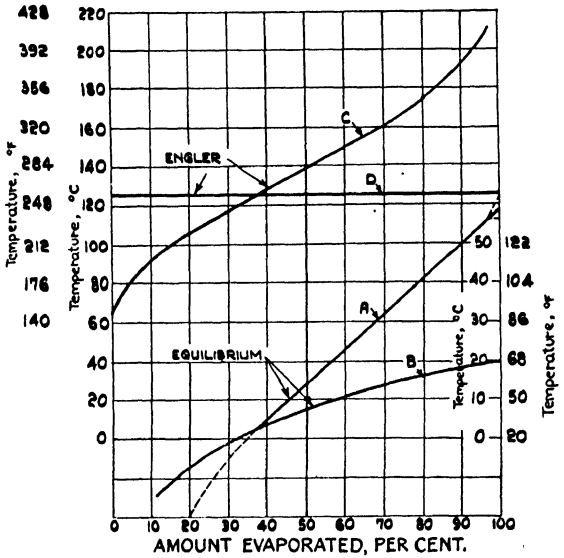


FIG. 182.—CALCULATED AIR-EQUILIBRIUM DISTILLATION CURVES OF A MOTOR FUEL AND NORMAL OCTANE IN THE PRESENCE OF 15 TIMES THEIR WEIGHTS OF AIR. (SLIGH.)

fuel mixture of *n*-octane, B.P. 125°C. Here the curvature decreases progressively as the distillation proceeds. The curves C and D show the A.S.T.M. distillations of these two substances plotted to a different temperature scale. The difference in temperatures for given percentages evaporated in the two types of distillation should be noted, also the fact that the petrol is almost completely evaporated in a 15 to 1 mixture at a temperature below that of the A.S.T.M. initial boiling point.

Figure 183 shows distillation data for the same motor fuel in various fuel air ratios. The lower dotted line marked 20 to 1 and crossing the distillation curves at an acute angle is drawn through points of 20 to 1 air-fuel vapour mixtures resulting from the partial evaporation of the fuel in the various air-fuel mixtures supplied. The *resultant air-fuel vapour mixture* is dependent upon the percentage evaporated : thus, 75 per cent. evaporated in a 15 to 1 air-fuel mixture supplied corresponds to

a 15 to 0·75 = 20 to 1 resultant air-fuel vapour mixture. Points above the dotted line marked 20 to 1 represent resultant mixtures richer than 20 to 1 and points below this line represent resultant mixtures weaker than 20 to 1. In like manner, the upper dotted line is drawn for a resultant 8 to 1 air-fuel vapour mixture. Assuming that these ratios mark the rich and lean limits of explosive mixtures, it is seen that the portion of the plot between these lines represents the operating range of an engine. For instance, an 8 to 1 supplied mixture at 70°C. would be barely lean enough to fire and a 3 to 1 supplied mixture at 3°C. would give a resultant mixture barely rich enough to fire. This is based on the assumption that the evaporation takes place in the presence of air at atmospheric pressure.

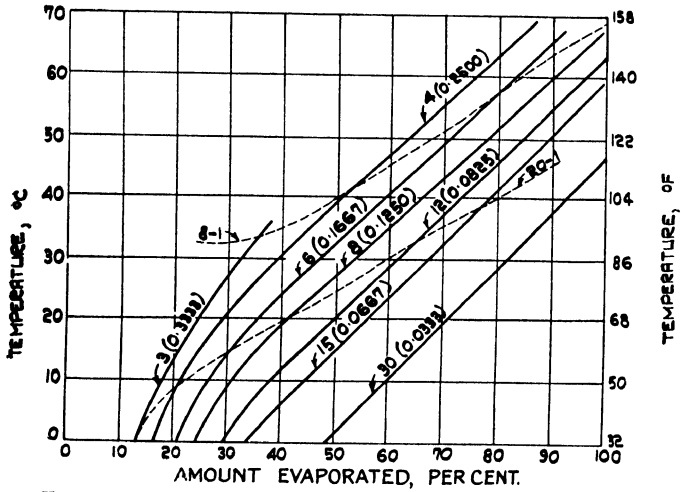


FIG. 183.—AIR-EQUILIBRIUM DISTILLATION CURVES FOR VARIOUS AIR-FUEL RATIOS IN THE CASE OF THE SAME MOTOR FUEL GIVEN IN FIG. 182. (SLIGH.)

N.B. The whole numbers in the curves indicate the parts by weight of air to one part of fuel and the figures in parenthesis indicate the corresponding parts of fuel to one part of air.

Figure 184 represents a corresponding plot for the pure hydrocarbon octane and, in this case, it will be seen that the constant resultant mixture lines are perpendicular to the temperature axis, indicating that no change in resultant mixture richness can be secured below 100 per cent. evaporated by supplying an excess of a pure compound.

The effect of reduced pressure upon equilibrium air distillation curves is important, because evaporation in engine manifolds takes place at pressures lower than atmospheric. Consider that evaporation takes place from a 3 to 1 air-fuel mixture supplied at an air pressure of 0·5 instead of 1 atmosphere. The quantity of a substance evaporated into a given space is independent of the weight of air or of any other inert gas which may be present in that space, and since the volume of a given

weight of air is, at a constant temperature, inversely proportional to the pressure, the evaporation takes place into a *volume* of air equivalent to that which would be occupied at one atmosphere pressure by the air in a 6 to 1 mixture. Thus, making observations of percentage evaporated in a 3 to 1 supplied air-fuel mixture at 0·5 atmosphere pressure, the 3 to 1 curve is displaced and superimposed on the 6 to 1 atmospheric curve. Thus, the data in Figure 142 can be transposed into 0·5 atmosphere plots by dividing the air weights by 2. The effect of reduction of air pressures on the mixture richness is obvious. This effect is solely due to the fact that the reduced air pressure results in a correspondingly reduced weight of air per unit volume and, for a given resultant air-fuel ratio, a proportionately smaller amount of fuel must be vaporized.

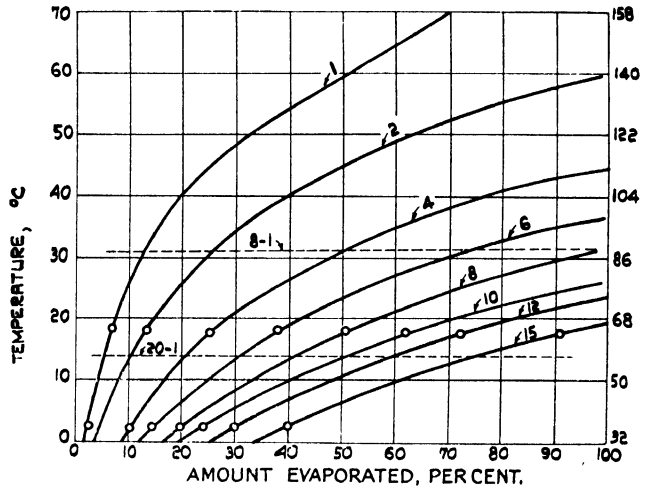


FIG. 184.—AIR-DISTILLATION CURVES FOR NORMAL OCTANE. (SLIGH.)

702. Departure from Equilibrium in Air Distillations.—In any dynamic system the question of the attainment of equilibrium is a serious one, consequently numerous tests have been carried out to determine the extent to which equilibrium is attained in air distillations. Bridgeman[8] conducted experiments on a range of motor fuels and on toluene under different conditions and found that there was a small progressive increase in the percentage of fuel evaporated with decrease in the rate of feed, other conditions remaining the same. This led to the following general relationship for determining the equilibrium percentage evaporated in terms of the determined percentage and the rate of fuel feed.

$$P = P_0 (1 + 0{\cdot}0125\ F) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_0 = experimentally determined percentage evaporated. This is equivalent to extrapolation to zero rate of fuel feed, and the validity

of this expedient was checked by Bridgeman by experiments with pure toluene at temperatures of 0°C. to 35°C. This correction appeared to be independent of the temperature, the air-fuel ratio and the particular fuel used.

On the other hand, Brown[9] found that in his apparatus, although the effect of feed rate on vaporization indicated a straight line relationship, the slopes of these lines were not independent of temperature, but decreased numerically as the temperature was lowered. At higher temperatures corresponding to over 50 or 65 per cent. vaporization, the apparatus appeared to give equilibrium results. Brown also found that the extrapolation of the experimental results to zero feed rate, although appearing logical, is not entirely reliable. Thus, resultant air-fuel ratio curves deduced from air distillation results and corrected in this way were found to be anomalous in the case of a natural gasoline aviation fuel. These curves suggested that less vaporization would occur in a 20 to 1 air-fuel ratio than in a 12 to 1 air-fuel ratio at a temperature of −50°C., a condition impossible under equilibrium conditions. Brown therefore concluded that little confidence could be placed in the method of obtaining equilibrium conditions by extrapolation of air distillation data to zero rate of feed, particularly at temperatures below −15°C., and made various investigations to determine the deviations from true equilibrium. As a result of these investigations, it was concluded that satisfactory results were obtained only when the equilibrium air distillation curve was computed from, or interpreted by, data obtained by continuous equilibrium vaporization of the fuel in the absence of air in an apparatus similar to that described by Leslie and Good.[10] If the molecular weight of the fuel vaporized in the continuous equilibrium vaporization process is known for the different pressures and temperatures corresponding to the partial pressure of the fuel vapour in the equilibrium air distillation, the air distillation curve can be accurately computed. The methods by which this computation is effected need not be discussed here, and for further details reference should be made to Brown's original publications bearing on the subject.[9]

703. Relationship Existing between Equilibrium Air Distillation Curves and A.S.T.M. Distillation Curves.—Although the equilibrium air distillation apparatus seems to be a satisfactory standard for the measurement of volatility characteristics when its results are corrected by the above method, nevertheless it is not convenient for testing a large number of fuels rapidly, due to the time required to obtain complete information on each sample. Since the A.S.T.M. distillation test is simple, reproducible and in common use, the interpretation of the curves obtained from it in terms of volatility data would permit the continuance of its use as an accepted test and the computation of volatility from it

directly. Consequently, attempts have been made to derive air distillation data from the A.S.T.M. curve.

According to Bridgeman,[8] a scheme of correlation of the results obtained by these two methods is suggested by the Clapyeron equation,

$$\frac{dp}{dT} = \frac{L}{T\,(V_1 - V_2)} \quad \ldots\ldots\ldots \quad (2)$$

where p = vapour pressure at the temperature T in °C. (abs.),
L = latent heat of vaporization per mol.,
V_1 = volume of vapour per mol.,
V_2 = volume of liquid per mol.

In general, V_2 is small compared with V_1 and can be neglected. Assuming that the vapour obeys the perfect gas law, namely, $pV = RT$, where R is the gas constant per mol., the Clapeyron equation can be written in the approximate form,

$$\frac{1}{p}\frac{dp}{dT} = \frac{L}{RT^2} \quad \ldots\ldots\ldots \quad (3)$$

and integration yields the relation

$$\log \frac{p}{760} = \frac{L}{RT_B}\left(1 - \frac{T_B}{T}\right) = a\left(1 - \frac{T_B}{T}\right) \quad \ldots\ldots \quad (4)$$

where L is assumed to be independent of temperature and T_B is the boiling point corresponding to a pressure of 760 mms. There is experimental evidence which shows that $\frac{L}{RT_B}$ is a constant for substances of similar properties such as the hydrocarbons, so that this expression can be replaced by the constant a. Hence, for a given value of p, the ratio T_B/T will be constant.

$$\frac{T_B}{T} = b \quad \ldots\ldots\ldots \quad (5)$$

It would appear probable that such a relation would hold for mixtures of hydrocarbons such as motor fuels. Since the equilibrium air distillation results are expressed on a weight basis, the partial pressure of the fuel vapour is dependent upon the molecular weight of the vapour, which changes with extent of evaporation. At any given percentage evaporated, the molecular weights of the vapours from different fuels should not be greatly different and hence their partial pressures should be roughly the same.

704. In the A.S.T.M. distillation test, the vapour is at a constant pressure of 1 atmosphere and hence fulfils the desired conditions in this respect. But the temperature of the liquid is considerably higher than

that of the vapour, and strict application of equation (5) implies that the two temperatures are identical. If the difference in temperature at a given percentage evaporated is approximately constant for all normal fuels, a rule analogous to that given in equation (5) for pure substances should be roughly applicable. If, as seems probable, the variations in partial pressures in a particular air-vapour mixture of different fuels obtained with the equilibrium air distillation apparatus, are compensated by corresponding variations in temperature between the liquid and vapour in the A.S.T.M. distillations for the same percentage evaporated, then such a rule should hold very closely. In this case, the constant would vary with the percentage evaporated in a regular manner.

Some verification of this prediction was obtained in the work of Cragoe and Eisinger,[11] who found that the ratio of the absolute temperature from the A.S.T.M. distillation curve at 5 per cent. evaporated to the absolute temperature of a 20 to 1 resultant air-vapour mixture at 5 per cent. evaporated was a constant independent of the fuel, and the same was true at 15 per cent. evaporated to form a 13·3 to 1 mixture.

705. In 1927, Brown[12] published some results obtained in a comparison of the temperatures for 30, 40 and 60 per cent. vaporized in the two kinds of distillation. It was found that the equilibrium air temperature with a fuel-air ratio of 12 to 1 was related to the A.S.T.M. temperature by the equation,

$$\text{E.A.T.} = \tfrac{3}{4}\,(\text{A.S.T.M.} - 200) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where E.A.T. = equilibrium air distillation temperature °F.,
A.S.T.M. = A.S.T.M. distillation temperature °F.

This equation enabled computation of the equilibrium air temperatures from A.S.T.M. data with an accuracy better than $\pm$ 10°F., except in extreme cases. Brown also found that the dew-point of a 12 to 1 air-fuel mixture was related to the A.S.T.M. 90 per cent. point by the relation

$$\text{Dew-Point (12 to 1 air-fuel ratio)°F.} = \tfrac{5}{7}\,(\text{A.S.T.M. 90\% point °F.} - 186) \quad . \quad . \quad . \quad . \quad (7)$$

In both these equations the A.S.T.M. distillation figure should be corrected for loss and residue.

During the early part of 1928, Bridgeman[7] made a general study of the relationship existing between the temperatures on the A.S.T.M. and equilibrium air distillation curves for the same percentages evaporated, and the results obtained indicated that the ratios of the absolute temperatures were constant and independent of the fuel for any given air-

fuel vapour mixture and percentage evaporated. The temperature ratio R_{16} for a 16 to 1 mixture was found to be related to the percentage evaporated as follows

$$R_{16} = 1{\cdot}372 \pm 45 \times 10^{-6} (P - 50)^2 \quad . \quad . \quad . \quad . \quad (8)$$

where P is the percentage evaporated. The plus sign applies to values of P above 50 and the minus sign to those below 50 per cent. The average deviation between the observed ratios and those calculated from this equation was found to be 0·003, which was within the experimental error. At any given percentage evaporated, the temperature ratio for any mixture was found to be given by the relation

$$R = R_{16} + 5 \times 10^{-3} (M - 16) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where M is the resultant air-fuel mixture.

Equations (8) and (9) can be combined to give

$$R = 1{\cdot}372 + 5 \times 10^{-3} (M - 16) \pm 45 \times 10^{-6} (P - 50)^2 . \quad . \quad (10)$$

from which R can be obtained for any value of P from 5 to 90 and for any value of M from 8 to 1 to 20 to 1. Values of the ratio for percentages less than 5 per cent. and greater than 90 per cent. are uncertain, due respectively to the effect of thermometer lag and the small amount of liquid in the flask towards the end of the A.S.T.M. distillation.

With regard to dew-points, Bridgeman admitted the relationship of Brown, given in equation (7) above, which may be written in the form.

$$\frac{90 \text{ per cent. A.S.T.M. temperature °F. (Abs.)}}{DP_{12} \text{ °F. (Abs.)}} = 1{\cdot}4 + \frac{2{\cdot}2}{DP_{12}} = 1{\cdot}404 \quad (11)$$

since $\frac{2{\cdot}2}{DP_{12}}$ is generally approximately 0·004. The value of 1·404 agreed well with the value of 1·399 deduced by Bridgeman.

706. For convenience in the computation of volatility from A.S.T.M. distillation data Bridgeman constructed an alignment chart, which is reproduced in Figure 185. The numerals on the three oblique scales to the left represent percentages evaporated on both the A.S.T.M. and the equilibrium air distillation curves, forming, in the case of the latter, *resultant* air-vapour mixtures of 20 to 1, 16 to 1 and 12 to 1, respectively. The three vertical scales on the right represent equilibrium air distillation temperatures in degrees centigrade for the same three temperatures. A.S.T.M. temperatures are marked on the middle scale. The following example will show how the chart may be used.

If it is desired to know the equilibrium air distillation (E.A.D.) temperature which will just give a 20 to 1 air vapour temperature at

50 per cent. evaporated from a fuel whose A.S.T.M. 50 per cent. temperature is 140°C., connect 50 on P 20 with 140 on the A.S.T.M. scale by a straight edge and extrapolate to the T 20 scale. This intersection gives the required temperature, which is 23°C. On the right of each P scale is an individual mark which can be used for evaluating the dew-points of these three mixtures for any motor fuel whose *A.S.T.M. 90 per cent. evaporated* temperature is known. For example, if the mark labelled DP on P 12 is connected to 200 on the A.S.T.M. scale, the intercept on the T 12 scale is 65°C., which is the dew-point of a 12 to 1 mixture formed

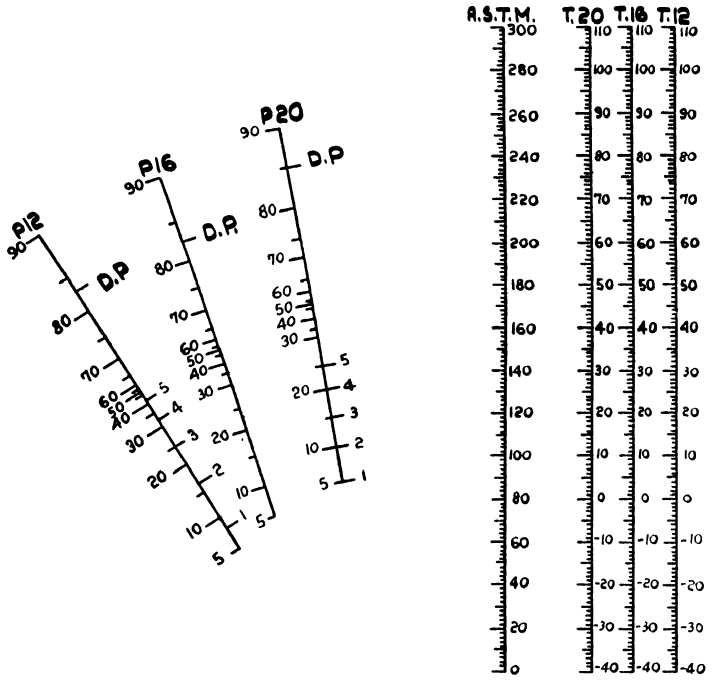


FIG. 185.—ALIGNMENT CHART FOR THE COMPUTATION OF VOLATILITY DATA FROM A.S.T.M. DISTILLATION CURVES. (BRIDGEMAN.)

from a fuel the A.S.T.M. temperature of which at 90 per cent. evaporated is 200°C.

707. During 1929, Bridgeman[13] published the results of further work and derived a relationship between the equilibrium air distillation temperature and the A.S.T.M. distillation temperature for any percentage evaporated between 0 and 100 per cent., which gave greater accuracy than those in use up to that time. This work may be briefly described as follows :—

When the curve representing any given air-vapour mixture is extra-

polated to cut the line of 0 per cent. evaporated, the point of intersection represents the temperature below which this given mixture cannot be formed and is termed by Bridgeman the " Bubble Point."

Determination of bubble points of air-vapour mixtures by extrapolation from the equilibrium air distillation curves is not feasible, in general, because of increasing curvature at the smaller percentages evaporated. Such points can, however, be computed from a knowledge of the vapour pressures and molecular weights of the vapour formed in vapour pressure measurements. Bridgeman determined molecular weights by a simple indirect method, that of computation from the molecular weights of residues obtained in air equilibrium distillation at various percentages evaporated, in each case to form a 16 to 1 resultant air-vapour mixture.

Thus, since the number of mols. of fuel in the residue plus those in the resultant mixture at any percentage evaporated is necessarily equal to the total number of mols. of fuel supplied, it follows that

$$\frac{(100 - P)}{M_e} + \frac{P}{M_v} = \frac{100}{M_f} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where P is the percentage evaporated and M_e, M_v and M_f are the molecular weights, respectively, of the fuel in the residual liquid, of the vapour and of the original fuel. Rearranging and writing $\triangle M = M_e - M_f$, this equation becomes

$$M_v = \frac{M_e}{\left(1 + \frac{100}{P} \times \frac{\triangle M}{M_f}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The corresponding value for M_v was computed for each value of M_e by equation (13) and these data were plotted against percentage evaporated. The extrapolated value at 0 per cent. evaporated was taken to be the desired molecular weight of the vapour. This method is not highly accurate but is sufficiently so for this purpose, since a variation of a few units in the molecular weight does not affect the evaluation of the bubble point appreciably.

For any mixture of air and fuel-vapour, the assumption of the perfect gas laws leads to the relation

$$\frac{760}{p_f} = 1 + M\left(\frac{M_v}{M_a}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where p_f is the vapour pressure of the fuel in millimetres of mercury, M is the mixture ratio and M_v and M_a are the molecular weights of the fuel vapour and air, respectively. From this relation, the vapour pressure of the motor fuel corresponding to a 16 to 1 mixture was computed for

various fuels, using the molecular weights of the vapours found above and taking the molecular weight of the air M_a as 28·96. It was also shown by Bridgeman[14] that the vapour pressure data on motor fuels could, in general, be represented by

$$\log\left(\frac{p_f}{760}\right) \quad A\left(1 - \frac{T_{nbp}}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where T = absolute temperature °C., corresponding to the vapour pressure p_f.
T_{nbp} = normal bubble point, °C.,
and A = specific constant for each fuel.

Using the values of p_f from equation (14) and the experimental values of A for the same fuels, the ratio $\frac{T_{nbp}}{T_{bp16}}$ was computed by means of relation (15) in each case. It was further shown that $T_{nbp} = T_{10\%\ A.S.T.M.}$ and that

$$\frac{T_{10\%\ A.S.T.M.}}{T_{bp16}} = 1{\cdot}5 - \frac{C}{T_{bp16}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which C is a number depending upon the slope (S) of the A.S.T.M. curve at the 10 per cent. point, according to the relation

$$C = -10\sqrt{S} + 39.$$

The effect of the slope of the A.S.T.M. curve upon the bubble point is marked. Bridgeman reported differences in the latter of 14°C. between fuels of the same 10 per cent. point but different slopes.

708. With regard to other percentages evaporated, numerous fuels were examined to determine the effect of the slope of the A.S.T.M. curve upon the equilibrium air distillation curve at various points. It was found that the ratio between the absolute temperatures for the same percentages by volume in the A.S.T.M. distillation as for percentage by weight in the equilibrium air distillation for a resultant mixture of 16 to 1 might be expressed by the equation

$$\frac{T_{A.S.T.M.}}{T_{E.A.D.16}} = 1{\cdot}5 - \frac{C}{T_{E.A.D.16}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\text{in which } C = \sqrt{460 \text{ slope}}\ \log_{10}\left(\frac{100 - \%}{50}\right) + 39 \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This latter equation applies between the limits of 10 to 90 per cent. vaporized.

In order to find corresponding temperatures for other air-vapour

mixtures, Bridgeman[13] assumed that the temperature differences between E.A.D. curves of different air-fuel ratios was constant for all percentages vaporized and that the temperature for any air-vapour mixture might be estimated from the temperature of the 16 to 1 air-vapour mixture by the relationship

$$T_{E.A.D.} = T_{E.A.D.16} + 51{\cdot}7 - 43 \log R$$

$$\text{or } T_{E.A.D.} = T_{E.A.D.16} + 51{\cdot}7 - 43 \log \frac{100FR}{\%} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

in which R = resultant air-vapour ratio by weight,
FR = feed ratio by weight.

According to Brown, the last assumption is not accurate, as the temperature differences become larger at higher temperatures, but he remarks that "these equations do not justify any attempt to correct for this relatively small error."

Combining equations (17), (18) and (19) gives, for the absolute temperature on the E.A.D. curve, the expression

$$T_{E.A.D.} = \frac{2}{3}\left(T_{A.S.T.M.} + \sqrt{460\,S} \log \frac{100 - \%}{50} + 39\right) + 51{\cdot}7 - 43 \log \frac{100FR}{\%} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

in which % = the per cent. by weight vaporized in the equilibrium air distillation and the per cent. by volume vaporized in the A.S.T.M. distillation.

The corresponding equation relating the initial vaporization temperature (bubble point) to the 10 per cent. point in the A.S.T.M. distillation, and the dew-point to the 90 per cent. point in the A.S.T.M. distillation is

$$T_{E.A.D.} = \frac{2}{3} T_{A.S.T.M.} + \frac{2}{3}\left(39 - 10\sqrt{S}\right) + 51{\cdot}7 - 43 \log R \quad . \quad (21)$$

These equations allow the computation of equilibrium air distillation curves from A.S.T.M. curves with reasonable accuracy. At low percentages evaporated the accuracy is not so good as that obtained at higher percentages but is sufficient for all practical purposes. Equilibrium air distillation curves computed by Brown's methods from continuous equilibrium vaporization data are, however, much nearer to the true values.

It is thus possible to obtain data concerning volatility from A.S.T.M. distillation curves, consequently such curves have assumed a new importance and it has been found possible to relate them with various phases of engine performance. This would not have been possible had it not been for the above work of Bridgeman and of Brown.

Volatility Requirements for Easy Starting of Automobiles

709. One of the most important characteristics of a fuel is its ability to enable the engine on which it is to be used to be started. Automobile drivers readily recognize the differences in the effect which different fuels have on the ease of starting and not infrequently judge the relative qualities of fuels entirely on this basis. A motor fuel that does not permit easy starting in cold weather is a nuisance to the motorist and it is necessary for producers to supply fuels which do not suffer from this defect.

The subject of easy starting and the fuel qualities that determine it has been studied in detail in America by the Co-operative Fuel Research Committee and also by Professor Brown on behalf of the Natural Gasoline Association of America. In 1925, Eisinger[15] described the test procedure used in the work conducted by the former body. The engine used was a four cylinder truck engine of 4·75 inch bore and 6 inch stroke and the carburettor was replaced by a single jet mounted in a vertical pipe about 10 inches long. This pipe was connected to the inlet manifold, a flat plate orifice was employed as a throttle and, in some cases, another orifice at the lower end of the pipe acted as a choke.

In conducting the tests, the engine was driven at constant speed by a dynamometer, usually at 200 r.p.m., with the fuel supply cut off. When engine conditions had become constant, the fuel was turned on and the time required to produce an audible explosion was recorded, the fuel was then shut off immediately and the total amount used in starting the engine was determined.

No practical difference in starting time was observed whether one or all of the four sparking plugs (one in each cylinder) were connected to the ignition coil. This clearly indicated that the distribution of fuel between the various cylinders, under starting conditions, is extremely uniform, as would be the case if only that portion of the fuel supplied to the engine which was actually vaporized was effective in starting the engine. This conclusion was verified by F. C. Mock in the discussion following the presentation of Eisinger's report, who stated that a collector jar, placed between the carburettor and the engine manifold to collect all the unvaporized fuel, made no perceptible difference in starting a cold engine at low cranking speeds.

In the following year (1926), Eisinger reported data obtained in starting tests at a speed of 100 R.P.M., and showed that the same number of revolutions of the engine were required for starting as in the previous tests at 200 R.P.M. This is a further verification of the conclusion that starting depends entirely upon that part of the fuel which is vaporized under starting conditions. It also indicates that the dilution of the fuel-air mixture supplied by the carburettor, due to the fact that

the manifold contains only air at the beginning of the starting period, is an important factor in determining the number of revolutions required to obtain an explosion. Since this dilution decreases with succeeding revolutions of the engine, it is to be expected that the number of revolutions required to obtain an explosive mixture in the cylinder would be independent of cranking speed, provided the same air-fuel ratio is supplied at the lower end of the manifold in each test.

710. The vaporization of fuel in the carburettor and manifold of an engine during this cranking period has been identified by Cragoe and Eisinger[16] as "engine distillation." This is not a simple equilibrium distillation, it does not take place at atmospheric pressure nor necessarily at atmospheric temperature. Due to the choke and the throttle, the absolute pressure in the manifold during the cranking period may be considerably less than atmospheric. This tends to cause more of the fuel to vaporize than would be the case in an equilibrium air distillation. The latent heat of the fuel has the reverse effect because this lowers the temperature of the mixture and tends to reduce the amount of fuel vaporized. Furthermore, the short time interval for the completion of engine distillation prevents the attainment of equilibrium conditions. If, however, one assumes that the decreased pressure in the manifold tends to compensate for the reduced temperature due to the latent heat of vaporization and also for the short time interval, the resultant mixture obtained in the equilibrium air distillation may be regarded as the ideal attainable in engine distillation only in infinite time. Thus the efficiency of the engine distillation may be defined as the ratio of the resultant air-fuel ratio obtained in the equilibrium air distillation to that obtained in the engine distillation. This efficiency depends only to a slight degree upon such factors as temperature, fuel, mixture ratio supplied and cranking speed, but depends almost entirely upon the number of engine revolutions.

On this basis, the air-vapour mixture obtained in the engine distillation is related to that obtained in the equilibrium air distillation by a factor representing the time lag in the former distillation

$$R_E = R_{E.A.D.}\, e^{-K/t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where R = resultant air-vapour mixture obtained in engine distillation,
$R_{E.A.D.}$ = resultant air-vapour mixture obtained in equilibrium air distillation,
e = the base of Napierian logarithms,
K = a constant,
t = time.

This equation may be written as follows, since the number of engine revolutions, rather than time, is the factor controlling the lag,

$$\log\left(\frac{R_{E\,A.D.}}{R_E}\right) = \frac{C}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

in which C = another constant (differing from K),
N = number of engine revolutions.

Since R_E represents the air-vapour mixture required to obtain an explosion, this factor may be regarded as constant for all fuels and engines. Therefore, a plot of the logarithm of $R_{E\,A.D.}$, the resultant air-vapour mixture under equilibrium conditions, against the reciprocal of N should be a straight line.

From data obtained in a four cylinder truck engine and checked by tests on a six cylinder passenger car engine, Cragoe and Eisinger concluded that about 10 revolutions of the engine were required to obtain an explosive mixture in the cylinders, when a mixture was supplied at the lower end of the manifold which would give a resultant air-vapour mixture of 12 to 1 under equilibrium conditions. Their experimental data may be represented by the equation

$$\log R_{E.A.D.} = 1{\cdot}301 - \frac{2}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

with an accuracy of $\pm$ 25 per cent. This equation corresponds to a 20 to 1 air-vapour mixture required in the cylinders for starting.

711. In May, 1930, Brown[9] reported the results of similar investigations over a wider temperature range using a small four cylinder passenger car engine driven by an electric starter supplied from the same battery as was used for ignition and with the standard carburettor. The equipment employed is shewn in Figure 186.

The starting switch was connected with a solenoid, which automatically started the stop watch as soon as the starter button was depressed and stopped the stop watch as soon as the starter button was released. The revolution counter, driven directly by the engine, was read at the beginning of each test and carefully observed by the tester who recorded the reading the instant the first explosion was obtained and the starter button released. In this way the time taken to obtain the first explosion was automatically recorded by the stop watch, and the revolutions of the engine were read from the revolution counter. In order to determine the air-fuel ratio supplied by the carburettor, the rate of air flow was measured by an orifice meter placed before two 5 gallon tanks in the air line to the carburettor and the fuel used was recorded by measurement on the fuel burettes.

In starting a series of tests, the carburettor was carefully wiped dry and the engine cranked for about 100 revolutions with no fuel in the carburettor to ensure that the tests would not be influenced by the fuel

used previously. All tests were made at a fixed throttle opening of about a quarter open. The stop watch was set to zero, the reading on the revolution counter recorded and room temperature and barometer readings taken. The starter button was then depressed, automatically closing the ignition switch and starting the stop watch. The revolution counter was carefully observed in order to obtain the reading when the first explosion was obtained at which instant the starter button was also released. In order to obtain temperatures below that of the laboratory, the engine was placed in a room cooled by direct expansion of ammonia.

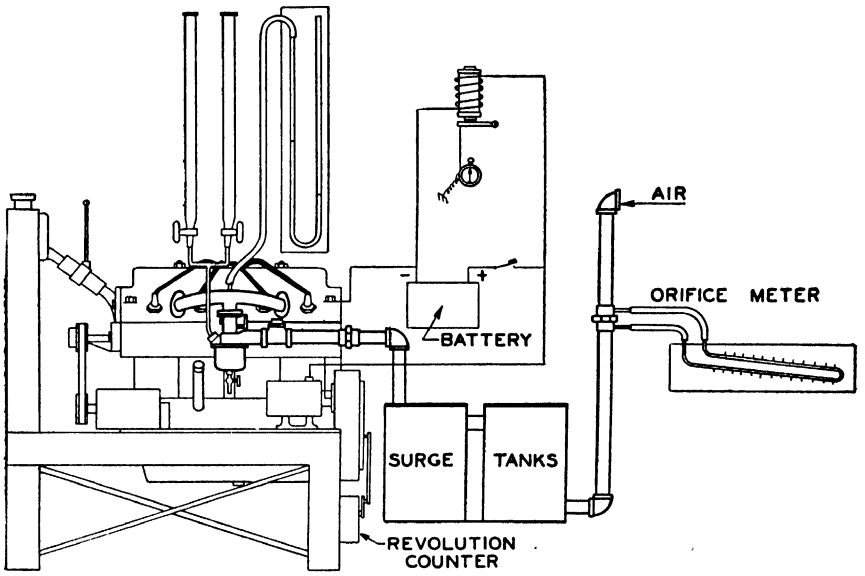


FIG. 186.—APPARATUS USED BY GRANGER BROWN FOR THE DETERMINATION OF STARTING PROPERTIES OF MOTOR FUELS.

At the lower temperatures, it was found necessary to dilute the lubricating oil with at least 25 to 30 per cent. of motor fuel in order to make cranking possible. This effect of lubricating oils upon the cold starting properties of engines is dealt with later. A further point is that the capacity of the storage battery approaches zero at about −40°F. and many of the tests were made possible only by using a battery taken from a warm room.

The results obtained by Brown confirmed to a large extent those obtained by previous investigators. Thus, although starting was found to be far more difficult at low cranking speeds, such as 20 r.p.m., than at the higher speeds, such as 140 r.p.m., when the air-fuel ratio supplied by the carburettor was computed for these different conditions, it was found that the same number of engine revolutions were required for a given air-fuel ratio at the carburettor regardless of cranking speed.

It was also found that the plot of resultant air-fuel ratio obtained under equilibrium conditions against the reciprocal of engine revolutions was a straight line, as shown by Cragoe and Eisinger. Figure 187 shows the results obtained by Brown on a wide range of fuels and also the straight line relationship deduced by Cragoe and Eisinger.

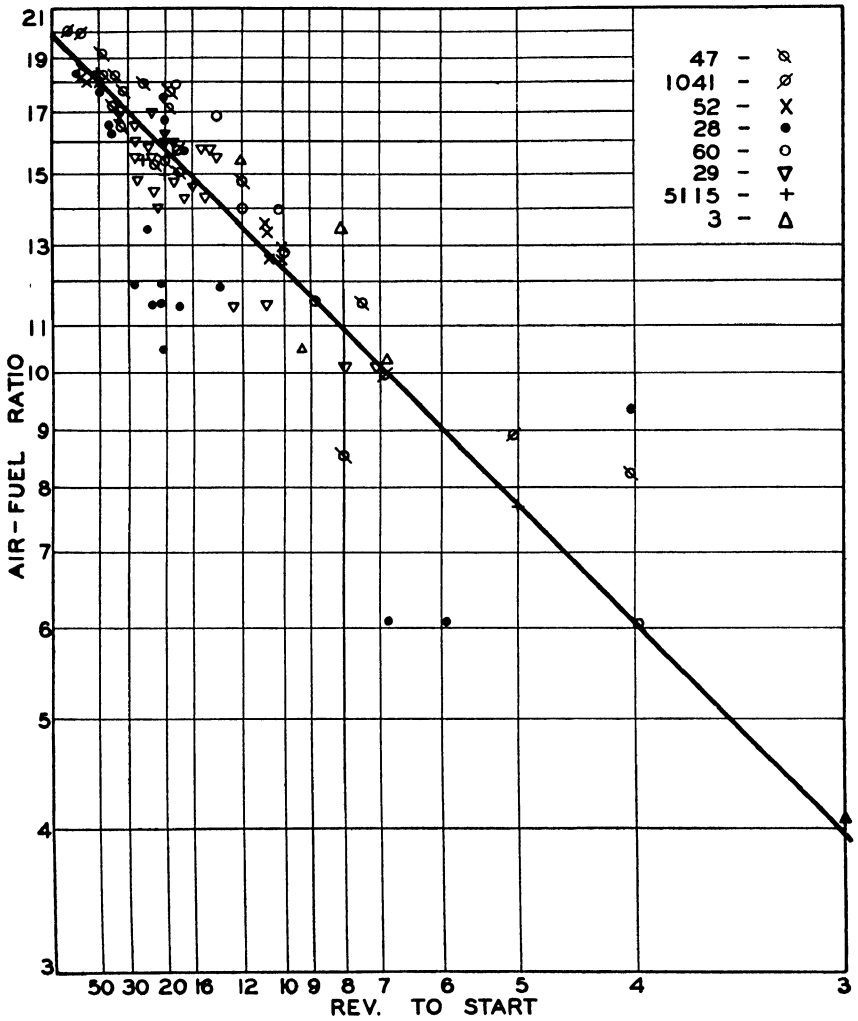


FIG. 187.—THE RELATIONSHIP BETWEEN AIR-FUEL RATIO AND MOTOR FUEL STARTING PROPERTIES. (GRANGER BROWN.)

712. The starting properties of any fuel are intimately connected with its A.S.T.M. front end distillation characteristics and although the equilibrium volatility of a fuel can only be predicted with very moderate accuracy from the lower end of the A.S.T.M. curve, this accuracy is more

than sufficient because starting tests are only consistent to within ± 20 per cent.

Eisinger and Cragoe suggested that any fuel having a 5 per cent. point on the A.S.T.M. curve at or below 119°F. (48·3°C.) should start a car engine with a 1 to 1 air-fuel ratio at a temperature of — 40°F.

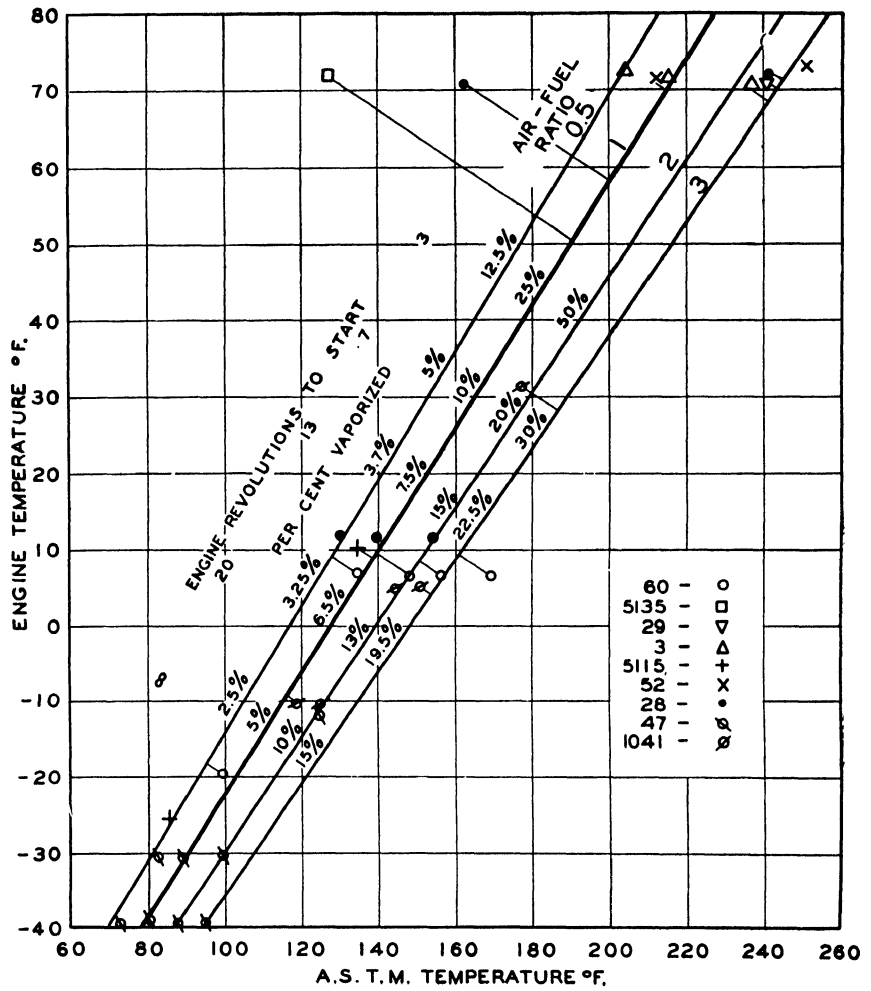


FIG. 188.—GRAPHS SHEWING THE INTER-DEPENDENCE OF ENGINE TEMPERATURES AND A.S.T.M. DISTILLATION TEMPERATURES FOR EASY STARTING. (GRANGER BROWN.)

(—40°C.). Brown considers that this is rather optimistic and has quoted the case of some fuels satisfying this distillation requirement which would not start an engine at higher temperatures or with richer air-fuel mixtures.

By use of the equation

$$\frac{T_{A.S.T.M.}}{T_{E.A.D.}} = 1{\cdot}372 - 0{\cdot}000045\,(P\text{-}50)^2 + 0{\cdot}005\,(R\text{-}16) \quad . \quad . \quad (25)$$

in which R = resultant air-vapour mixture, and the relation

$$\log_{10} R_{E.A.D} = 1{\cdot}301 - \frac{2}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

it is possible to estimate with sufficient accuracy for all practical purposes the ease of starting at various temperatures with any specified air-fuel ratio provided only the A.S.T.M. distillation characteristics of the fuel are known.

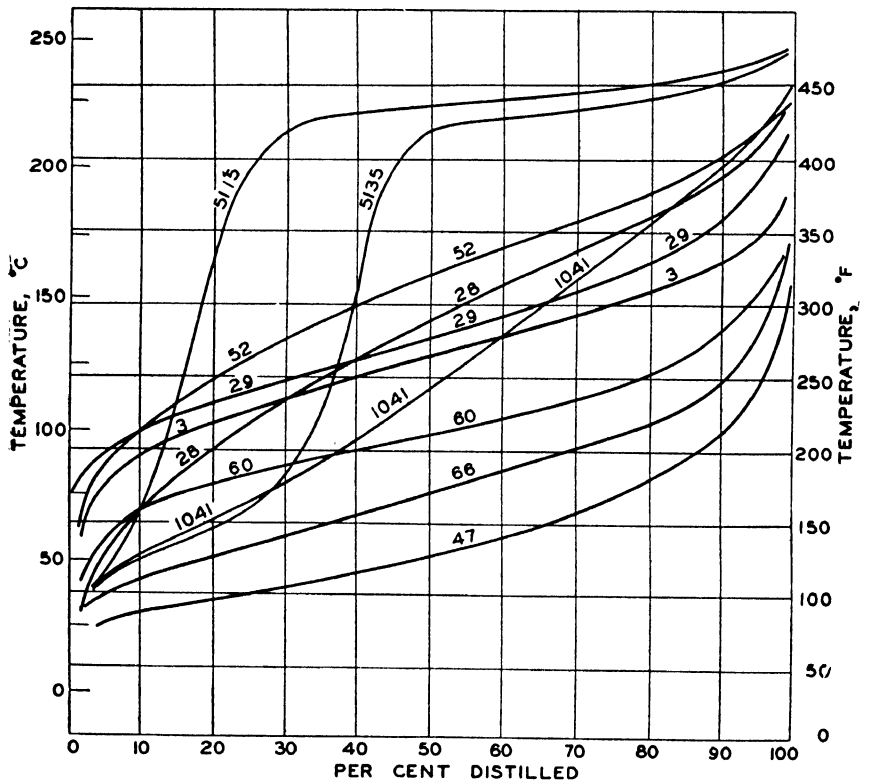


Fig. 189.—A.S.T.M. Distillation Curves of Motor Fuels Used by Granger Brown in Starting Tests.

713. Computations based on these relationships for a 1 to 1 air-fuel ratio and deduced by Brown are shown in Table 157. If the resultant air-vapour mixture of 20, requiring approximately an infinite number of revolutions for starting, be disregarded as impractical and only those

mixtures which enable an engine to be started in 20 revolutions or less be considered, and averaged, as is done in the table, the A.S.T.M. temperature may be used with an error of less than ± 4°F. to indicate all practical degrees of ease of starting. For example, at a temperature of 32°F., the percentage vaporized in the A.S.T.M. distillation at 168°F. may be used to indicate the ease of starting. If 6·5 per cent. is distilled at 168°F., the engine may be started in 20 revolutions; 7·5 per cent. distilled indicates that the engine may be started in 13 revolutions, 13 per cent. distilled corresponds to 7 revolutions and 25 per cent. to 0 revolutions, provided that in each case a 1 to 1 air-fuel ratio is supplied to the carburettor. Similar considerations for other air-fuel ratios

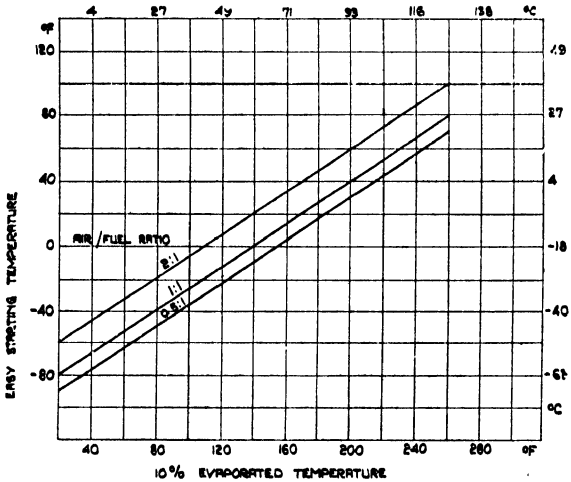


FIG. 190.—THE MAXIMUM TEMPERATURES OF THE 10 PER. CENT. A.S.T.M. DISTILLATION POINT REQUIRED FOR STARTING AT VARIOUS ENGINE TEMPERATURES AND RESULTANT AIR-FUEL RATIOS. (EDGAR, HILL & BOYD.)

indicate a similar constancy of temperature on the A.S.T.M. curve corresponding to particular engine temperatures. These temperatures are plotted for convenience in Figure 188, and for purposes of comparison, actual experimental data with the fuels whose A.S.T.M. curves are shown in Figure 189, are also plotted.

Similar information is given in Figure 190, which is due to Edgar, Hill and Boyd,[32] and which is based on the work of the Co-operative Fuel Research Committee. In this graph, are given the maximum 10 per cent. A.S.T.M. temperatures at which easy starting can be obtained with a carburettor supplying air-vapour mixtures of 0·5 to 1, 1 to 1, and 2 to 1. Thus, with a carburettor supplying a 1 to 1 mixture and at an atmospheric temperature of + 10°F., the motor fuel used must have its 10 per cent. point at least as low as 156°F., to ensure easy starting.

TABLE 157.

RELATION BETWEEN ENGINE AND A.S.T.M. TEMPERATURES FOR A 1 : 1 AIR-FUEL RATIO IN STARTING TESTS. (BROWN.)

Per Cent. Vaporised	Resultant Air-Vapour Ratio	Number of Engine Revolutions to start	$\frac{T_{A.S.T.M.}}{T_{E.A.D.}}$	Engine Temperature							
				30°C. 86°F.	20°C. 68°F.	10°C. 50°F.	0°C. 32°F.	−10°C. 14°F.	−20°C. −4°F.	−30°C. −22°F.	−40°C. −40°F.
				Corresponding A.S.T.M. Distillation Temperatures							
5	20	—	1·301	252°F.	228°F.	205°F.	181°F.	158°F.	135°F.	111°F.	88°F.
6·5	15·4	20	1·284	240	216	193	171	147	125	102	79
7·5	13·3	13	1·2774	237	214	192	169	145	122	99	77
10·0	10	7	1·27	232	209	187	164	141	119	95	74
20·0	4	3	1·284	240	216	193	171	177	125	102	79
Average of last four lines				237	213	191	145	145	122	99	77

714. The Starting Properties of Benzoles and Benzole-Petrol Blends.—The relationships found to exist between the starting properties of fuels and their A.S.T.M. distillation data, just discussed, are limited to motor fuels of purely petroleum origin and do not apply, with reasonable accuracy, to benzoles and benzole-petrol blends. This has been recently shown by Hoffert and Claxton[17] in the results of an extensive study of the ease of starting obtainable with these latter fuels. Previous to this work, there had been considerable differences of opinion regarding the relative ease of starting with benzole or benzole-blends and petrols.

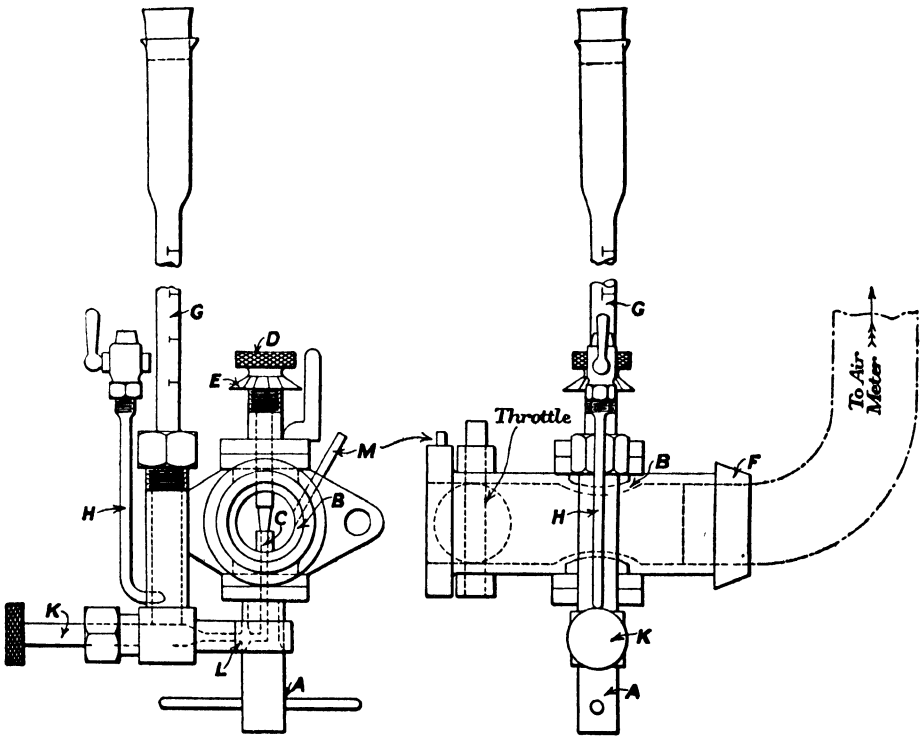


FIG. 191.—SECTION OF CARBURETTOR USED IN STARTING TESTS BY HOFFERT AND CLAXTON.
(*Courtesy of Editor, "Engineering."*)

Hoffert and Claxton used a Morris-Cowley 11·9 h.p. car engine motored at a constant speed by an electric motor. The carburettor, of special design, was clamped directly on to the side of the cylinder block and the induction manifold was inside the cylinder jacket, being warmed, when the engine was running, by the jacket cooling water.

The carburettor itself was as shown in Figure 191, and provided a constant rate of fuel feed by the employment of the principle of Marriot's bottle. During a test the calibrated and graduated burette G was closed

at the top by a cork and, as the fuel was drawn from the jet by the engine, air entered the burette from a side tube and jet (H), thus maintaining a pressure equal to that of the atmosphere at this point.

Some of the results obtained by Hoffert and Claxton are reproduced in Figure 192. These refer to various fuels, the distillation curves of which are reproduced in Figure 193. It is clear from these results that if a very rich mixture (low air-fuel ratio) can be provided by the carburettor, there is very little difference in the ease of starting on any of the fuels.

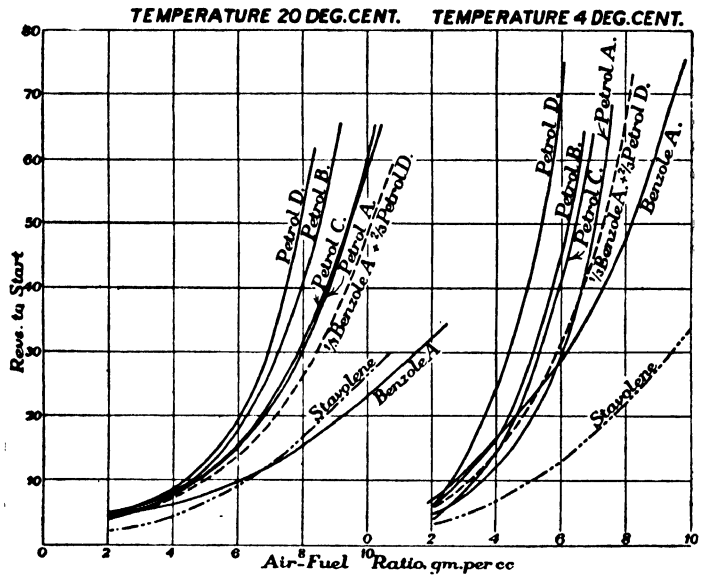


FIG. 192.—GRAPH SHEWING THE STARTING PROPERTIES OF VARIOUS FUELS.
(Courtesy of Editor, "Engineering.")

It is only when relatively weaker mixtures are supplied at the carburettor that differences in the ease of starting become apparent. At 20°C., the benzole gave much easier starting then the petrols that were examined, and it was only when the temperature approached 0°C., that starting on the benzole became slightly more difficult than on petrols A and C at low air-fuel ratios. Another interesting point is that at all temperatures between 20°C. and 0°C., the range of air-fuel ratios at which starting was possible was greater with the benzole and benzole mixtures than with the petrols.

The conclusions arrived at by Hoffert and Claxton are as follows :—

(1) Benzole gives easier starting than petrols, at temperatures between 10°C. and 20°C. The ease of starting on benzole, however, decreases with reduction in temperature more rapidly than is the case with petrol, and at temperatures below 0°C., starting

on benzole becomes appreciably more difficult than on good quality petrols (as marketed in the United Kingdom).

(2) Blends of benzole and petrol at temperatures between 10°C. and 20°C. give an ease of starting intermediate between those given by the benzole and the petrol. At temperatures of 0°C. to 10°C., however, certain blends of benzole and petrol give easier starting than either the benzole or the petrol.

(3) Benzole and benzole-petrol blends give a wider range of mixture strengths at which starting is possible than petrols.

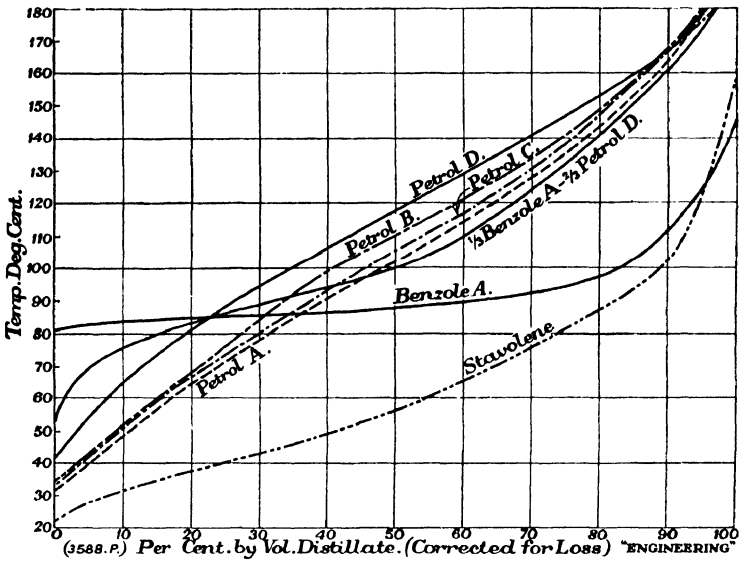


FIG. 193.—DISTILLATION CURVES OF FUELS USED BY HOFFERT AND CLAXTON.
(*Courtesy of Editor, "Engineering."*)

(4) Even when a petrol of poor starting quality is used, blends with benzole give an ease of starting at 0°C. to 20°C. that compares favourably with the case of starting on the best competing spirits (on the British market).

(5) From the point of view of ease of starting, the proportion of benzene in a benzole blended with a given petrol should be kept as high as possible.

(6) Although certain relationships between the ease of starting on motor fuels and their distillation characteristics have been proposed (such as those of Bridgeman and of Brown), such relationships do not permit the ease of starting on blended motor fuels such as are marketed in Great Britain, to be predicted.

715. Effects of Other Variables on Engine Starting Properties.

—The various relations deduced, showing the interdependence of fuel distillation characteristics and engine starting properties, assume constant mechanical conditions and, moreover, it has been regarded that starting is possible if the engine could be made to fire in any number of revolutions up to an infinite number. It is, however, very questionable if it is actually possible to start an engine in cold weather if over 20 revolutions are required. By that time the capacity of the battery, limited by the low temperature, may have been completely exhausted and what may be regarded as theoretically possible starting becomes an actual impossibility. Furthermore, most carburettors deliver a leaner mixture when the engine is cranked at low speeds than at higher speeds with the same choke setting. The viscosity of the engine lubricating oil is also a very definite limitation to cranking speeds and the number of revolutions obtainable at low temperatures. Thus, Brown (*loc. cit.*) has stated that " data obtained after leaving battery and motor (engine) in the cold room at a temperature of −20°F., for eight or more hours indicate that the maximum speed at which the motor can be cranked with a fully charged battery is reduced from 160 to less than 60 r.p.m., even with oil containing dilution in excess of fifty per cent."

The cold starting of automobile engines with particular regard to the lubricating oil viscosity limiting engine cranking speeds at low temperatures has been studied by Blackwood and Rickles,[18] in the laboratories of the Standard Oil Development Company. These workers conducted tests to determine under what conditions they could (*a*) secure a cranking speed to start the engine and keep it running, (*b*) not start the car at all due to low cranking speed, and (*c*) develop various situations to bring about the different starting difficulties with a cold engine. They realized as a result of these tests that the two factors of fuel and lubricant were inseparable, particularly when the electric starter itself established conditions unique for each car. Thus, they often found, under a given set of conditions, the engine fired on the first attempt to start it, kicked the starter out of gear and immediately stopped ; and no matter how many more attempts were made, this cycle repeated itself. Yet a matter of two or three more revolutions per minute completely prevented this occurrence. This showed that the viscosity of the lubricant employed was too high for the particular combination of fuel and electric starter employed. Further possible causes of difficulty in starting were found to be (*a*) carburettor floats sticking at low temperatures, (*b*) some types of ignition equipment are not particularly efficient at low engine speeds and (*c*) dirty sparking plugs.

Blackwood and Rickles put forward, as a result of their work, a suggestion that car manufacturers and electric starter manufacturers strive to produce a unit which will crank the engine at 35 r.p.m. or faster under the worst conditions which are anticipated.

Various aspects of the low temperature starting of automobile engines have also been considered by Kent,[19] of the Chrysler Corporation, Detroit.

It is evident, therefore, that care must be exercised in estimating the starting properties of an engine from a consideration of the distillation properties of the fuel used. The question of battery capacity and efficiency of the electric starter must also be taken into account, together with that of lubricating oil viscosity. The various relationships between starting properties and fuel volatility can only be used when the engine conditions specified are satisfied, that is, the carburettor must be capable of giving the resultant air-fuel ratio used in computing the relationships and an adequate cranking speed must be employed.

The Effect of Fuel Volatility upon Engine Performance under Normal Driving Conditions

716. After an engine has been started by obtaining a series of explosions with the aid of the choke or air control to give a rich mixture, the fuel employed must have such characteristics that the engine can be kept running and made to deliver power. The choke or air control (sometimes referred to as the " strangler ") is designed primarily as an aid to starting and should not be employed for actual driving. Its constant use, necessary with fuels of low volatility at the low temperatures existing in the manifold when the engine is first started, results in excessive crank-case dilution, in carbon formation and in the fouling of sparking plugs.

The period immediately following the actual starting is generally referred to as the " warming-up period." During this time, conditions are not constant, so that in actual tests it is found extremely difficult to reproduce the same warming up conditions for different fuels. During this period, liquid fuel begins to distribute along the walls of the manifold due to the dragging action of the air-vapour mixture passing through it. When driving at a constant speed along a level road, the velocity of this air vapour mixture is fairly constant and the liquid deposited on the walls of the manifold at the carburettor end reaches the engine cylinders at about the same rate as it is supplied by the carburettor : i.e., under these conditions, the air-fuel ratio supplied to the cylinders is practically the same as that supplied by the carburettor. During periods of acceleration, however, the amount of fuel delivered to the cylinders immediately after the throttle is suddenly opened is considerably less than that passing from the carburettor into the inlet end of the manifold. The vaporized fuel carried in the air stream reaches the cylinder almost as soon as does the latter, but the liquid fuel flowing along the walls of the manifold moves much more slowly and does not

reach the cylinders until some time later (about four seconds). For this reason, during the period immediately after the throttle is opened, the cylinders receive all the air passing through the carburettor, all the vaporized fuel, but only that part of the liquid fuel which is being distributed along the walls of the manifold before the throttle is opened.

These conditions have been considered by the manufacturers of carburettors and the modern carburettor is equipped with accelerating devices so that an extra charge of fuel is injected into the manifold whenever the throttle is suddenly opened. This, in effect, is equivalent to supplying a richer mixture for a few moments after opening the throttle.

If the carburettor is adjusted to deliver an air-fuel ratio of 12 to 1 under steady driving conditions, arrangements are provided to deliver the equivalent of a 6 to 1 air-fuel ratio immediately after the throttle is opened at low speeds. Other carburettors may be more effective in enriching the mixture at higher speeds than at extremely low speeds. But in practically all cases this characteristic is found to a greater or lesser extent.

As a result of the partial precipitation of fuel on the walls of the manifold, the mixture reaching the cylinders immediately after the throttle is opened contains, in all cases, less fuel than the mixture metered by the carburettor. When the air flow through the manifold is at a relatively high rate, part of the liquid fuel may reach the cylinders in the form of a mist almost immediately after the throttle is opened. But when the velocity of the mixture through the manifold is low, as when an attempt is made to accelerate the engine from low speed, the air stream may not carry much suspended liquid, and the mixture reaching the cylinders may be so lean in fuel that it will not fire.

717. It will be evident, from these considerations, that the demands for easy acceleration must be given careful consideration by both producers of motor fuels and automobile manufacturers. Much research work on this subject has been carried out in America. About May 1st, 1920, the Society of Automobile Engineers Committee on the Utilization of Present Fuels in Present Engines requested the U.S. Bureau of Standards to undertake research in connection with a "more miles per gallon" movement initiated by that committee. The programme as outlined included measurement of engine performance under conditions of both steady running and acceleration. In making tests incidental to this work, a method for measuring acceleration was devised by James, Dickinson and Sparrow.[20] This consisted essentially of operating an engine at light load and low speed, suddenly opening the throttle fully, and noting the successive readings of a chronometric tachometer until a certain predetermined higher speed was reached.

Readings were taken also with a chronograph which recorded time and engine revolutions. Results were expressed in the form of speed time curves. With the organization of the Co-operative Fuel Research programme in the summer of 1922 came further work on acceleration, with special reference to the effect of fuel volatility, at the U.S. Bureau of Standards. This work was first carried out on the road, using two automobiles of different makes, but such a procedure was not found to be entirely satisfactory.[21, 22] Laboratory tests did, however, show decided differences in acceleration between fuels of different volatility but nearly the same initial boiling point.

718. In 1927, Eisinger[23] made a general study of engine acceleration using a chronometric tachometer and in the course of his work demonstrated the difference in behaviour of various fuels, but up to this time no great progress had been made. However, in May, 1927, Brown[12] described the results of tests carried out on various fuels, which suggested the following conclusions :—

(1) The A.S.T.M. distillation end-point has a noticeable effect on acceleration. Although a low end-point may tend to shorten the warming up period, it also tends to cause lack of power and poor acceleration after the engine is thoroughly warmed up, particularly if the intake manifold is supplied with a large amount of exhaust heat.

(2) The ease of keeping an engine running during the warming up period depends somewhat upon the same fuel volatility characteristics as determine the ease of starting; the difference lies in the fact that the manifold and carburettor are not at any constant temperature, but are warming up, and the fuel-air ratio is less, particularly if the choke is used for starting. This means that a greater percentage of fuel must be vaporized to form an explosive mixture after the engine has been started. Although five per cent. of fuel vaporized will enable an engine to be started without serious difficulty, at least 30—40 per cent. of the fuel must be vaporized to obtain reasonable performance under driving conditions.

(3) A broad range of composition, represented by a low initial point and fairly straight distillation curve to a moderately high end-point, is highly desirable to give the best general performance over a wide range of temperatures, such as exist in all engines having effectively heated intake manifolds.

More recent work by Brown, which is described later, fully supports these conclusions.

In September, 1928, Brooks[24] described a new method of measuring

engine acceleration adopted at the U.S. Bureau of Standards. This was a displacement-time method, consisting of driving a paper tape at a speed proportional to the engine speed and discharging a spark through the tape at equal time intervals. A displacement-time record was thus obtained, the second differentiation of which gave the acceleration. This method has proved to be very satisfactory. An electrically operated tuning fork is used to obtain the constant time intervals. Results[25] obtained using this method of measurement indicated that with the intake manifold at a temperature of 10°C. (50°F.), three fuels gave increasing acceleration in the inverse order of their A.S.T.M.-50 per cent. points, while with the manifold at 32°C. (90°F.), the same fuels gave increasing acceleration in the direct order of their 50 per cent. points. These results indicated the great importance of manifold temperature.

719. At a somewhat later date, Brooks and Bruce[26] described the results of tests carried out on nine different engines under various conditions on a range of fuels. These investigators used a method of presenting their results in which " relative fuel volatilities " were employed. One fuel was selected as a reference fuel and its volatility at all temperatures was taken as unity. Relative fuel volatilities were then obtained by dividing the absolute temperatures for various percentages distilled on the A.S.T.M. curve for the reference fuel by the corresponding temperatures for the other fuels. A further method of expressing the relative volatility was adopted, in which this was defined as the effective air-fuel ratio supplied by the carburettor divided by the effective air-fuel ratio entering the cylinders at the same instant. The effective air-fuel ratio was found by comparing the observed acceleration at a speed of 50 r.p.m. above the initial speed, with a contour chart derived from brake torque versus mixture ratio tests at various constant speeds. Since acceleration at any instant is proportional to available brake torque, the effective air-fuel ratio found is that mixture, which, if vaporized and distributed as under constant speed operating conditions, would give brake torque sufficient to produce the desired acceleration. In order to eliminate the effect of differences in supplied air-fuel ratio, speed, etc., results were expressed as effectiveness of the fuel relative to one fuel chosen as a reference, just as were the relative volatilities.

A degree of similarity between these two sets of curves was obvious for a range of different fuels and a correlation suggested itself. This was inquired into and as a result the following empirical rule for finding the relative effectiveness of fuels for acceleration at any given manifold temperature was evolved.

" Multiply the manifold absolute temperature by 1·2. Convert this into units of ordinary temperature (°F. or °C.). From the A.S.T.M.

curves, select one fuel which approximates U.S. Motor Gasoline as the reference fuel and note its per cent. evaporated at the temperature found above. Then the arrangement of the other fuels at this per cent. evaporated indicates their relative effectiveness for acceleration at the manifold temperature in question, those having higher A.S.T.M. temperatures being poorer in this respect, and conversely. Further, a quantitative relation between any pair of fuels may be roughly ascertained by a comparison of their distillation absolute temperatures."

Thus, taking a manifold temperature of 50°C.,

$$50°C. = 323° \text{ Absolute.}$$
$$323 \times 1{\cdot}2 = 387{\cdot}6 = 114{\cdot}6°C = \text{approx. } 115°C.$$

The distillation temperature at which comparison between fuels is made is, therefore, in this case, 115°C. Assume a reference fuel of 34 per cent. evaporated at this temperature and assume three fuels whose 34 per cent. evaporated temperatures are, respectively :—

(*a*) 115°C. = 388° Absolute.
(*b*) 101°C. = 374° Absolute.
(*c*) 92°C. = 365° Absolute.

Then, at a manifold temperature of 50°C., fuel (*c*) will give the best acceleration and fuel (*a*) the worst. Roughly, the relative effectiveness will be

Fuel (*a*) 388 ÷ 388 = 100.
Fuel (*b*) 388 ÷ 374 = 104.
Fuel (*c*) 388 ÷ 365 = 106.

As a corollary to this general relationship, it is obvious that no one point on the distillation curve can be selected as representing the probable acceleration performance of a fuel; rather, it is dependent on practically the entire distillation curve.

720. The Work of G. Granger Brown on Acceleration.—Brown[9] has used a rather different nomenclature in his work on acceleration and has used the term "effective volatility," which he has defined as the quotient obtained by dividing the air-fuel ratio supplied at the carburettor by the air-fuel ratio burned in the cylinders immediately after the throttle is opened in an acceleration engine test. This is equivalent to the term "relative volatility," used by Brooks and Bruce.

The apparatus used by Brown in his acceleration engine tests is of interest, and is, in many respects, similar to that used by Brooks and Bruce. The engine was a six cylinder valve-in-head water cooled model, of $3\frac{1}{2}$ in. bore and $4\frac{3}{4}$ in. stroke. It was directly coupled to a dynamometer which was used to supply a resistance comparable to the rolling

and wind resistance of the automobile for which the engine was designed. Mounted on the shaft of the dynamometer was a steel disc, of such dimensions and weight that its moment of inertia added to that of the rotor of the dynamometer equalled the moment of inertia of the car when in high gear.[27] By these means the actual driving load of the engine under road conditions was closely approximated. The disc and rotor furnished the inertia and the electric load represented, approximately, the wind and rolling resistance.

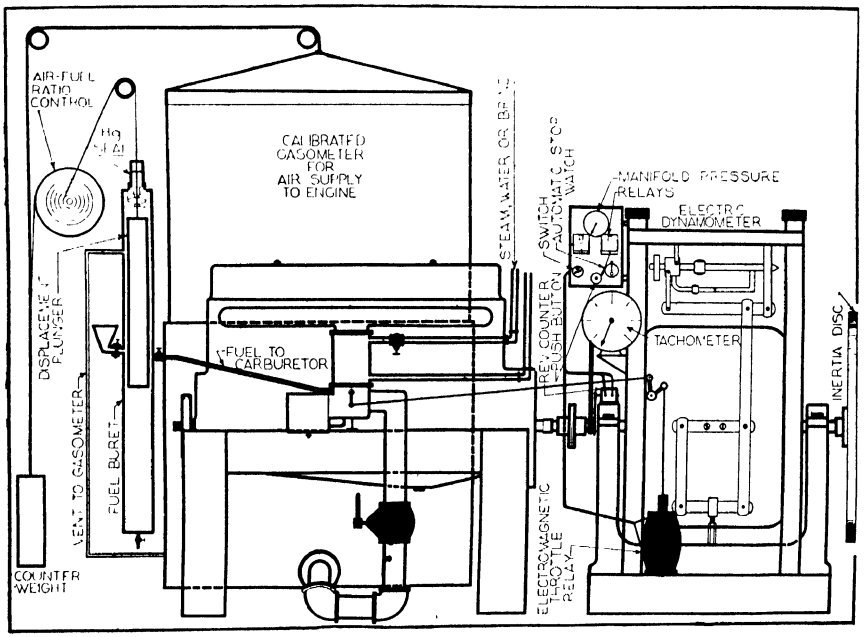


FIG. 194.—APPARATUS USED BY GRANGER BROWN IN MAKING ACCELERATION TESTS ON MOTOR FUELS.

Apparatus for Control of Air-fuel Ratio.—The fuel-air ratio supplied by most commercial carburettors changes with change in engine speed, consequently it is almost impossible to determine accurately the air-fuel ratio supplied by such a carburettor during acceleration tests. For this reason, Brown used special equipment devised to supply a constant predetermined air-fuel ratio. Air was supplied to the carburettor through a pipe fitted with two quick opening gate valves in such a manner that air could be taken directly from the atmosphere, or from a calibrated gas holder of about 50 cu. ft. capacity. When the engine was taking air from the gas holder, the latter raised a counterweight, as shown in Figure 194. This, in turn, allowed the air-fuel ratio drum to rotate in a clockwise direction, letting the steel plunger fall inside the fuel burette, which had been previously filled

with fuel. As the plunger fell, the displaced fuel was supplied to

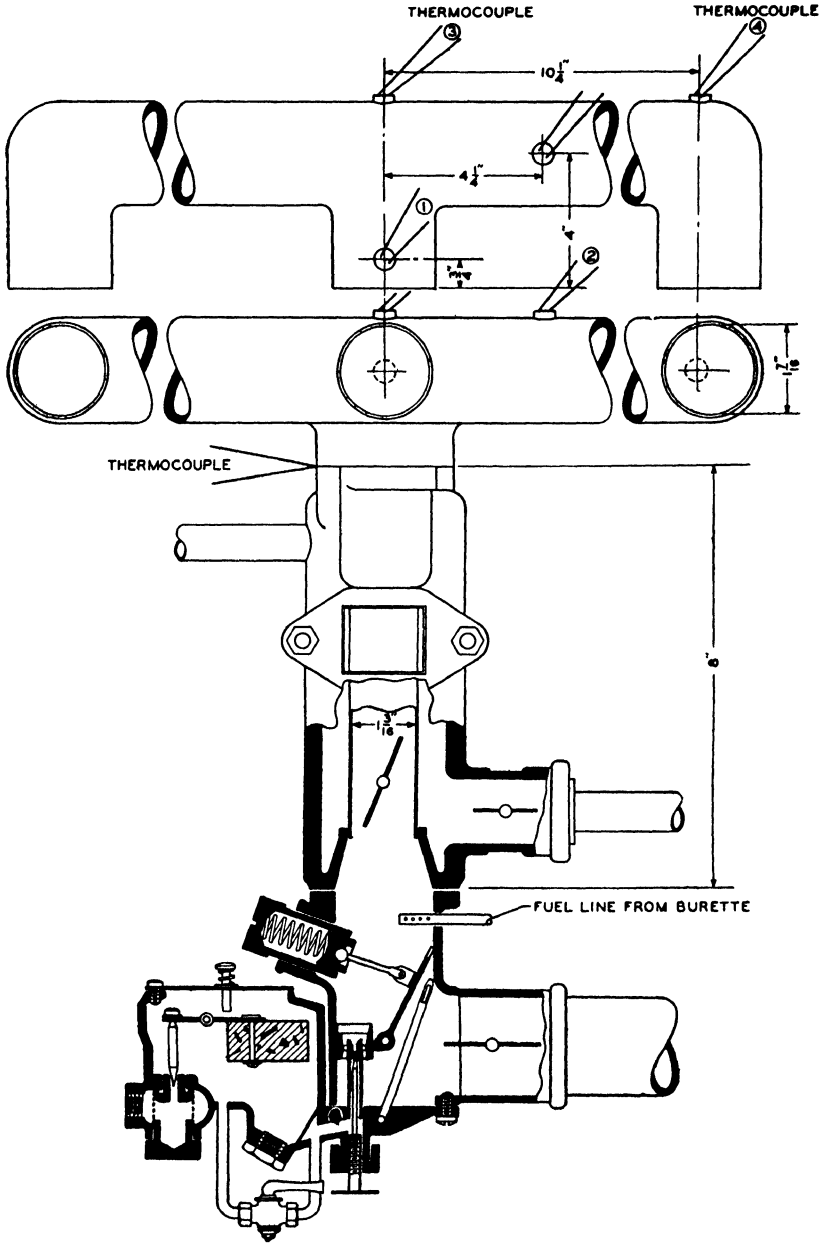


FIG. 195.—INTAKE MANIFOLD AND CARBURETTOR USED BY GRANGER BROWN IN ACCELERATION TESTS

the carburettor through a small auxiliary jet placed about an inch

above the regular jet in the carburettor. The air-fuel control drum was made of a number of concentric pulleys of different diameters. The rate at which fuel was supplied to the carburettor with any two of these pulleys in use varied directly with the rate at which air was used from the tank. The air-fuel ratio therefore remained constant, regardless of the speed of the motor. Different air-fuel ratios were obtained

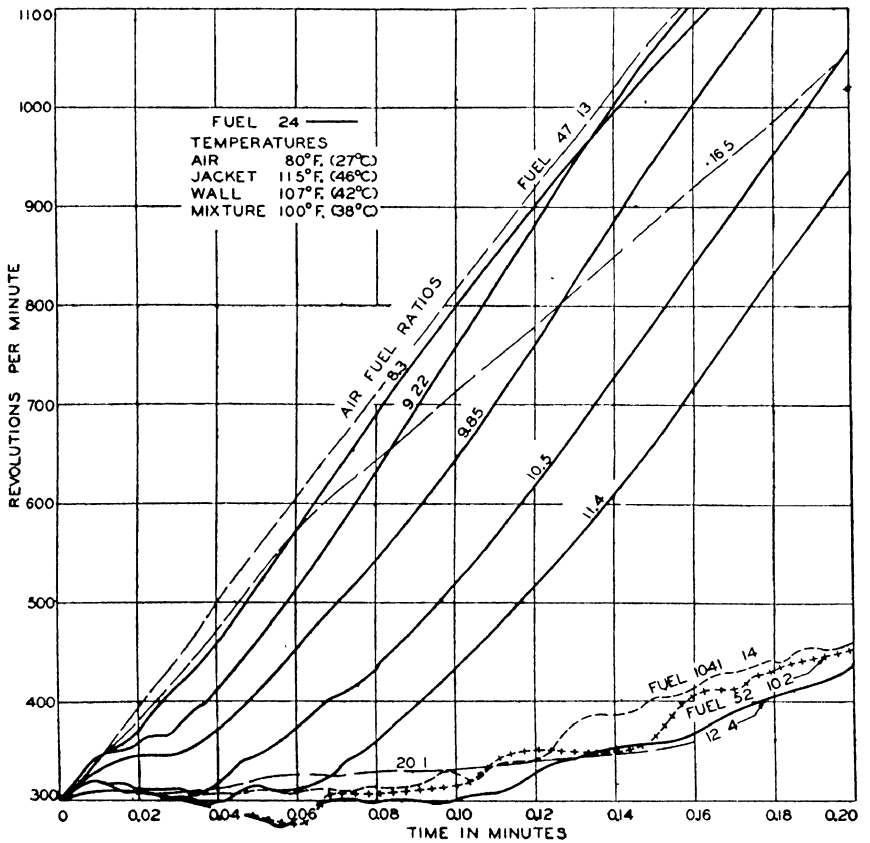


FIG. 196.—TYPICAL MOTOR FUEL ACCELERATION CURVES. (GRANGER BROWN.)

by changing to smaller or larger pulleys on the drum. This equipment gave a precision in predetermining and controlling the air-fuel ratios unattainable with any commercial carburettor. The apparatus was so arranged that the operator could, in a few seconds, shift the fuel feed from the carburettor bowl to the fuel burette, and the air supply from the atmosphere to the gas holder, by operating two cocks on the carburettor and two quick opening valves in the air line.

Intake Manifold and Carburettor.—The intake manifold was of

the straight " T " type with an exhaust heated hot spot on the vertical riser from the carburettor as shown in Figure 195. The exhaust gas connection to the heater was replaced by pipe connections, so that the

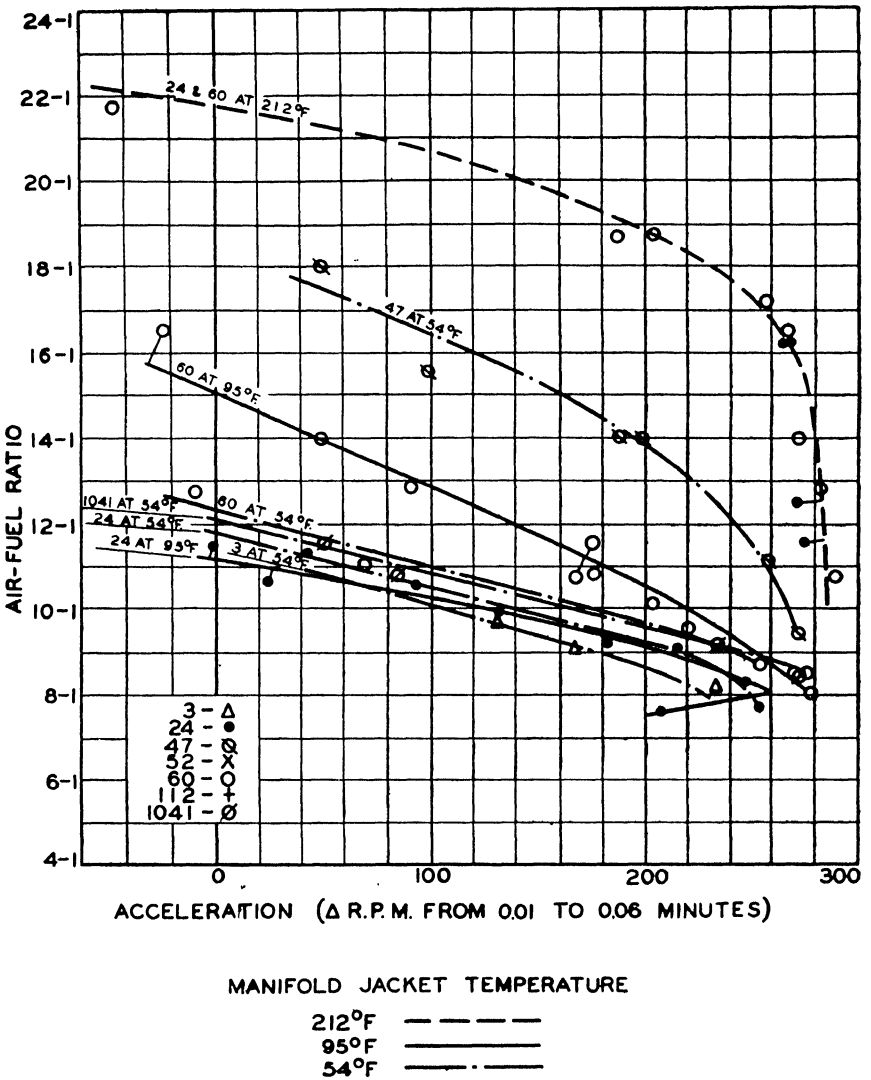


FIG. 197.—CURVES SHEWING THE RELATIONSHIP BETWEEN AIR-FUEL RATIO AND ACCELERATION PROPERTIES. (GRANGER BROWN.)

manifold could be heated with steam and cooled with water or ammonia. Temperature measurements were made with thermocouples.

In order to avoid, as far as possible, any human error, the actual acceleration tests were started and stopped by a number of relays con-

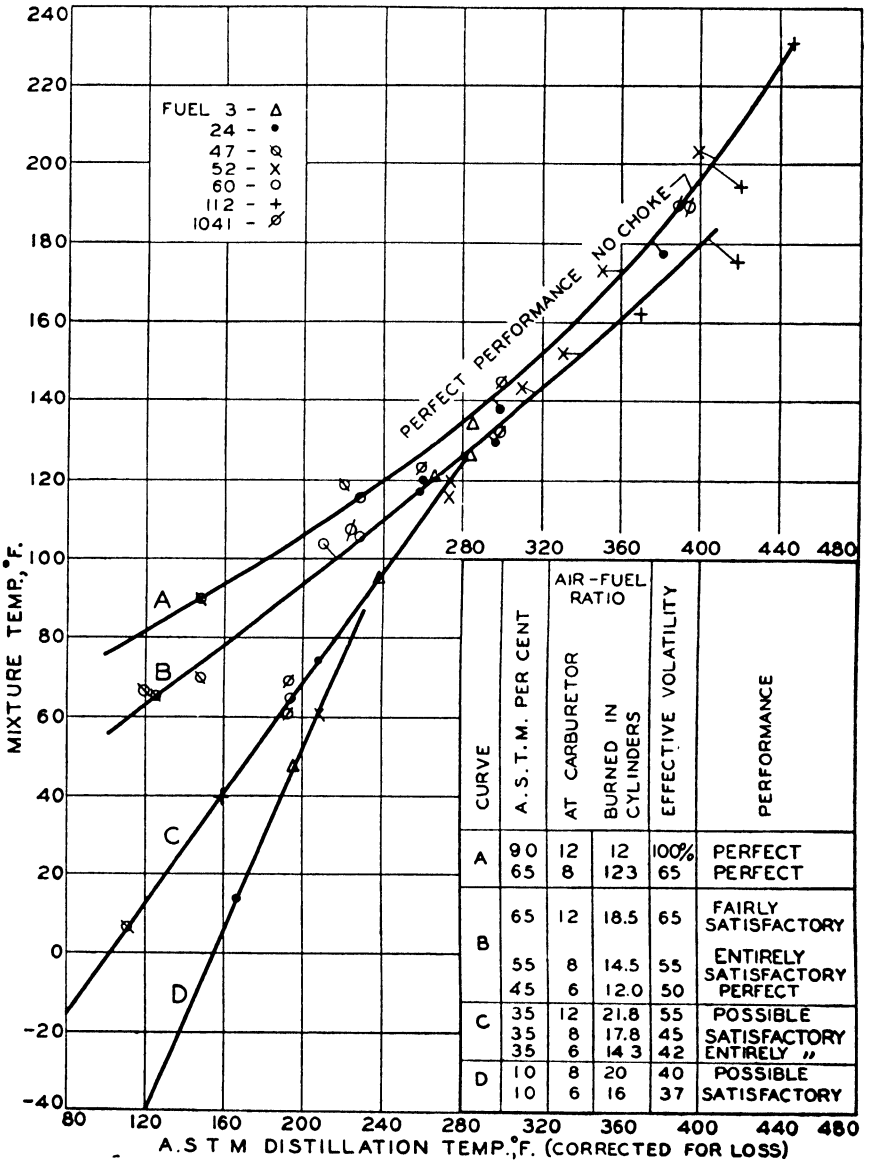
nected in series and operated by a single contact. The time speed record required was obtained by taking a motion picture record of the tachometer with a constant speed camera.

721. Results Obtained.—The fuels used in Brown's investigations covered the entire range of U.S. commercial motor fuels and had A.S.T.M. distillation curves as shown in Figure 189 (Page 244). As a quantitative measure of acceleration, the increase in r.p.m. in the time interval between 0·01 minutes and 0·06 minutes after the throttle was opened, was taken and termed "acceleration." Some typical acceleration curves are reproduced in Figure 196, in which the dashed lines refer to Fuel No. 47, which has complete effective volatility at the indicated temperatures and air-fuel ratios. It will be noticed that the 8·3 ratio curve for Fuel 24 runs approximately parallel to the 16·5 ratio curve of Fuel No. 47, from 0·01 to 0·06 minutes, indicating the same air-fuel ratio burnt in the cylinders or an effective volatility of Fuel 24 under these conditions of 8·1 /16·5 or 49 per cent. At 0·06 minutes, the curves cross, due to conditions not attributable to fuel characteristics. Effective volatilities were generally determined in this way, i.e., by dividing the air-fuel ratio supplied by the air-fuel ratio of a fuel with complete effective volatility required to give the same acceleration under similar conditions.

Typical results showing the relation between acceleration and the air-fuel ratio supplied at the carburettor for various fuels at different manifold jacket temperatures are shown in Figure 197.

Brown has prepared as a convenient summary of the approximate relation between A.S.T.M. distillation data and effective volatility, as indicating the character of engine performance at various mixture temperatures, the curves shown in Figure 198. Various considerations lead to the conclusion that the 65 per cent. point on the A.S.T.M. distillation may be related to the mixture temperature required to give fairly satisfactory performance with a carburettor delivering a constant air-fuel ratio of about 12, or practically perfect acceleration performance if the carburettor is supplied with an accelerating device which enriches the mixture to about 8 to 1 air-fuel ratio during the early stages of acceleration, or is adjusted to give a rich mixture when idling. Perfect performance with a constant mixture ratio of 12 to 1 demands complete effective volatility as indicated by a relationship between the A.S.T.M. 90 per cent. point and mixture temperature. Similarly, the 55 per cent. point should indicate the mixture temperature below which acceleration is almost impossible without the use of the choke, if the carburettor supplies a constant air-fuel ratio of 12, and the mixture temperature required for satisfactory acceleration with carburettors equipped with adequate accelerating devices.

In Figure 198, the mixture temperature corresponding to 100 per cent. effective volatility is plotted as a function of the 90 per cent.



CURVE	A.S.T.M. PER CENT	AIR-FUEL RATIO AT CARBURETOR	AIR-FUEL RATIO BURNED IN CYLINDERS	EFFECTIVE VOLATILITY	PERFORMANCE
A	90	12	12	100%	PERFECT
	65	8	123	65	PERFECT
B	65	12	18.5	65	FAIRLY SATISFACTORY
	55	8	14.5	55	ENTIRELY SATISFACTORY
	45	6	12.0	50	PERFECT
C	35	12	21.8	55	POSSIBLE
	35	8	17.8	45	SATISFACTORY
	35	6	14.3	42	ENTIRELY "
D	10	8	20	40	POSSIBLE
	10	6	16	37	SATISFACTORY

FIG. 198.—CURVES SHEWING THE RELATIONSHIP BETWEEN A.S.T.M. DISTILLATION DATA AND EFFECTIVE VOLATILITY. (GRANGER BROWN.)

A.S.T.M. temperature for various fuels. (Curve A). The same curve was also found to represent the relationship between the mixture temperature for 65 per cent. effective volatility in an air-fuel ratio of

8 and the 65 per cent. A.S.T.M. point. Curve B gives the corresponding relation for 65 per cent. in a 12 to 1 ratio and 55 per cent. in an 8 to 1 ratio.

722. As a result of extensive laboratory tests, supplemented by many road tests, the following conclusions were drawn.

(1) That part of the A.S.T.M. distillation curve from 65 to 100 per cent. is of little or no practical importance in determining effective volatility in modern automobile engines, provided the 90 per cent. point is not so high as to prevent efficient combustion of the fuel under the conditions of test, nor so low as to supply a practically dry mixture when used in cars equipped with heated manifolds and effective accelerating devices.

(2) The first 35 to 40 per cent. of the A.S.T.M. distillation curve is the controlling factor in determining fairly satisfactory performance without use of the choke, or entirely satisfactory performance with use of the choke, during the warming up period, provided the conditions stated above concerning the 90 per cent. point are fulfilled.

(3) At least 10 per cent. must be distilled on the A.S.T.M. distillation at the corresponding temperature in Figure 198, if the engine is to be operated in a manner at all satisfactory, even with excessively rich mixtures as brought about by use of the choke with a properly adjusted carburettor. It is possible to operate an engine with the choke on any fuel that will start the cold engine in ten revolutions.

Different metering characteristics possessed by different types of commercial carburettors will modify these conclusions only in degree. Low 90 per cent. points are required for satisfactory performance of aero-engines and other engines in special service where maximum power and freedom from knocking are best obtained with cold mixtures and extremely volatile fuels.

Vapour Lock

723. In the previous sections of this chapter the practical advantages to be obtained in the use of fuels having low 10, 35 and 65 per cent. points on the A.S.T.M. distillation curve have been indicated. There is, however, a practical limit to the richness of the fuel-air ratio which it is feasible to supply to an engine under starting conditions; this limit determining the temperature below which starting will not be easy with a given fuel. If starting at lower temperatures is desired, a more volatile fuel is obviously needed but, on the other hand, the more volatile a fuel, the greater will be its tendency to boil in the fuel feed

system as the engine warms up. If the fuel boils, then interruptions of fuel flow due to vapour lock may be expected. These two effects, ability to start an engine and the ability to keep an engine running when warmed up, impose limits on the practical operating range of fuel temperatures in the fuel feed system. This practical range is about 60°C. for most automobiles.

The property of a petrol which determines both the starting ability and the tendency to boil is its 10 per cent. point on the A.S.T.M. curve. A fuel having a 10 per cent. point of 60°C. permits an engine in good mechanical condition to be started fairly easily down to temperatures of −18°C. (0°F.), but such a fuel would boil if heated above its 10 per cent. point (60°C.)[28]

Some fuels containing undesirable amounts of propane may cause vapour lock at temperatures 10°C. below the 10 per cent. point, and some poorly designed fuel systems may also result in interruption of flow at temperatures below the 10 per cent. point, due to the trapping of gases which come out of solution. As shown in Chapter XVIII, in the case of aeroplanes the temperature at which vapour lock may occur becomes lower as the altitude increases, due to decrease in atmospheric pressure, and an allowance must be made for a lowering below the 10 per cent. point of about 2°F. for every 1,000 feet above sea level. Thus, for an aeroplane with a ceiling of 20,000 feet, the practical operating range of fuel temperatures is reduced to about 100°F.

During the middle part of 1930, Bridgeman and Aldrich[28] tentatively reached the following conclusions with respect to vapour lock.

(1) It is undesirable to use a fuel which has a much lower 10 per cent. point than that required for easy starting at the lowest temperature likely to be encountered. This may make it desirable to use different grades of fuel for different types of operating conditions.

(2) The temperature of the liquid fuel in the fuel lines should not exceed its 10 per cent. point. Fuel lines should be so designed and installed that they will meet this requirement with a reasonable margin of safety for variations in existing fuels.

(3) The presence of more than small amounts of propane in motor fuels is undesirable from the point of view of vapour lock. If fuels containing propane are likely to be used, a liberal margin of safety below the 10 per cent. point should be allowed in fixing the maximum operating fuel temperature which is permissible.

724. Analysis of the Vapour-Lock Problem.—Vapour lock may occur when the sum of the pressures exerted by the liquid hydrocarbons, the dissolved gaseous hydrocarbons, dissolved air and water exceeds the external pressure at any point in the fuel system. At any given tem-

perature, lowering the external pressure favours the formation of vapour, as in the case of suction lifts from the fuel pump, etc., whereas an increase in pressure retards vapour formation, as in the delivery sides of fuel pumps and gravity feeds, etc. Vapour lock cannot possibly occur at any point in the fuel feed line if the total vapour pressure of the fuel flowing through the feed line is less than the total external pressure exerted upon it, and vice versa.

Work on the vapour lock problem, conducted in America, has been logically divided into a study of the following three separate phases.

(1) A study of the vapour pressures of motor fuels as a function of temperature, including the effect of dissolved gases and dissolved water.
(2) Determination of the conditions under which vapour lock actually occurs in typical fuel feed systems.
(3) Measurement of the temperatures existing in representative fuel feed systems under various conditions of operation.

The results of work conducted on the first phase of the general problem have been reported by Bridgeman and Aldrich[28] and by Brown,[9] each of whom has tackled the problem by determining the vapour pressures of motor fuels after the removal of dissolved gases, at various temperatures, followed by a study of the effect of dissolved gases, etc., on the gas-free vapour pressure.

Bridgeman and Aldrich found that the following relationship existed between the vapour pressure and the bubble point.

$$\log \frac{p}{760} = A\left[1 - \left(\frac{T_n}{T}\right)\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where p = vapour pressure in mms. of mercury at the absolute temperature T,
A = constant for each motor fuel,
T_n = normal bubble point in ° absolute.

From this relationship and data obtained on a wide range of different fuels, they found that

$$A = 3{\cdot}41 + 3{\cdot}8 \times 10^{-3} T_{10 \text{ per cent.}} - 0{\cdot}6 \sqrt{S} \quad . \quad . \quad . \quad (28)$$

in which S = slope of the A.S.T.M. curve at the 10 per cent. point expressed in terms of °C., per unit per cent. evaporated, and $T_{10 \text{ per cent.}}$ is expressed in terms of absolute °C.

These relationships enabled them to calculate the gas-free vapour pressures of motor fuels from A.S.T.M. distillation curves with an accuracy claimed to be within 0·18 pounds per square inch. Such vapour pressure measurements were made with a very small bubble of

vapour in each case, but the effects of variations in the variable $\frac{V}{L}$, where V and L are the volumes of vapour and liquid respectively, were found to be conveniently given by the equation

$$\triangle p = -0{\cdot}025 \frac{V}{L} p_o \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where $\triangle p$ = difference between p_o and the pressure when the ratio of vapour to liquid volume is $\frac{V}{L}$.

and p_o = vapour pressure with an extremely small bubble.

General expressions for the solubility of air and propane in various motor fuels were also deduced.

725. During 1930, Bridgeman and White[29] compared the predicted conditions for vapour lock as given above with the conditions actually found to interrupt fuel flow in two types of aeroplane fuel feed systems. The vapour locking temperature, i.e., the temperature at which the vapour pressure of the gas-free fuel becomes equal to the external pressure on the fuel, was found to be given by the equation

$$t = \frac{\triangle t_{10 \text{ per cent.}} + 273{\cdot}1 \log\left(\frac{p}{760}\right)}{A - \log\left(\frac{p}{760}\right)} \quad . \quad . \quad . \quad (30)$$

in which $A = 4{\cdot}45 + 3{\cdot}8 \times 10^{-3} T_{10 \text{ per cent.}} - 0{\cdot}6 \sqrt{S}$ . . . (31)

t = vapour locking temperature in °C.

p = pressure on the fuel in the feed line in mms. of mercury.

For most motor fuels A has an average value of about 4·0.

In gravity feed fuel systems, the most important factor tending to cause vapour lock is a constriction in the fuel line, such as the metering orifice. Other details of construction such as the arrangement of T connections, size of tubing, syphons, etc., may have an important effect in determining vapour lock, but, in general, troubles from these causes can be eliminated by changes in the arrangement of the fuel system. But some kind of a jet or metering orifice is essential in any carburetting system and cannot well be eliminated. The rate of flow of a motor fuel through such an orifice increases very slowly as the temperature is slightly raised, but when the temperature is raised beyond a certain point, the rate of flow is decreased considerably, due to the formation of vapour. The temperature at which this marked decrease of flow is observed is given by equation (30) with very reasonable accuracy, as shown in the

data of Table 158. It will be noticed that there is good agreement between the predicted values and the temperatures at which the rate of fuel flow is decreased by 10 per cent., particularly at an atmospheric pressure of 760 mms. A variation in fuel feed of this amount is within the normal fluctuations of mixture ratio and does not seriously effect engine operation. However, only a very slight increase in temperature is required to reduce the rate of fuel flow by 50 per cent., which would certainly cause engine stoppage.

726. In December, 1931, Bridgeman and White[30] presented the results obtained in a survey of fuel line temperatures obtained in American automobiles. Road tests were made on a large number of new cars operated under various specified conditions and fuel temperatures were measured in each case at several points in the fuel-feed system. These investigators concluded that, for most of the cars examined, trouble from vapour lock would result in hot weather from the use of fuels having a Reid vapour pressure in excess of 7 pounds per square inch at 100°F. The production of such a product not only makes it difficult to meet the requirements necessary for easy starting during some seasons of the year but, in addition, materially curtails the available supply of suitable fuel. Therefore there is ample justification for the elimination of vapour lock by the use of well designed fuel systems. Some car manufacturers have already taken steps to re-design fuel systems and others will undoubtedly do so in the near future.

Vapour lock may normally be completely avoided by the observation of a few simple rules. Of these, perhaps the most important is to employ fuels free from propane or as free from this " wild " constituent as possible, as already explained in Chapter IV (Volume I). The fuel should also be kept as cool as possible in its passage from the fuel tank to the carburettor. Direct radiation of heat from the engine or exhaust manifold to the fuel feed lines and the carburettor itself should be avoided and long suction lifts to fuel pumps eliminated as much as possible.

727. Relation between Reid Vapour Pressure and Vapour Locking Temperature.—The workers at the U.S. Bureau of Standards have shown that the Reid vapour pressure at 100°F. is related to the vapour locking temperature by the equation

$$t = 259 - 140 \log Pr \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

in which t = vapour locking temperature °F.,

Pr = Reid vapour pressure at 100°F. in lbs. per square inch.

This equation applies specifically to vapour lock during engine operation at sea level and involves two assumptions ; namely, that the fuel has a

TABLE 158.—TEMPERATURE FLOW DATA ON MOTOR FUELS CONTAINING NO PROPANE. (BRIDGEMAN AND WHITE.)

Fuel	Pressure 760 mm. (Sea Level)					Pressure 570 mms. (8,000 ft. altitude)					Pressure 380 mms. (18,000 ft. altitude)				
	Predicted Vapour Locking Temp. °C.	Temperatures Corresponding to Various Percentage Decreases in Rate of Flow				Predicted Vapour Locking Temp. °C.	Temperatures Corresponding to Various Percentage Decreases in Rate of Flow				Predicted Vapour Locking Temp. °C.	Temperatures Corresponding to Various Percentage Decreases in Rates of Flow			
		10%	15%	20%	50%		10%	15%	20%	50%		10%	15%	20%	50%
1	45	44·5	45	46	48·5	36	35	36	37·5	39	23·5	22	24·5	25·5	29
2	43	42	43	43·5	47	34	34	35	36·5	39	21·5	22	25	25	29
3	71	71	72	72·5	75·5	61·5	61·5	62·5	64	67	49	49	50·5	51·5	54·5
4	69	65·5	67	68	71	59	56	57·5	59	62	47	40	43	45	50
5	57	55·5	56·5	57·5	61·5	47	45	47	49	52	34	34	36·5	38	41·5
6	60	59	60	60·5	64	50	49·5	50·5	52	54·5	36	35	38	39	43
7	64	64	65	68	70	53·5	50	51	54	58	40	35	38·5	40	47
8	66	62·5	64	65·5	70	56	55·5	56·5	58	61	42	39	41·5	43	48
9	67	66	67·5	69	73	56·5	55	56·5	58·5	62	43	41	44	45	50
10	49	48	49	49·5	52	39·5	38·5	40	41·5	43·5	27	27	29	30·5	34
11	53	53·5	54·5	55	58	43	44	46	48	50	30	30	34	36	41
12	27	25·5	26·5	27	28·5	—	—	—	—	—	—	—	—	—	—
13	47	46	47	48	52	37	37	39	41	44	24	23	26	27	33
14	37	38	39	40	43	27	28	29·5	31·5	35	15	14	17	18·5	24

conventional distillation curve and that equal volumes of vapour and liquid can be handled by the fuel feed system before vapour lock occurs. The equation is not applicable to benzole or alcohol blends or fuels containing an abnormal amount of light constituents, but has been corroborated by Burk.[31] It constitutes the most useful method for determining vapour lock temperatures as it involves only one vapour pressure measurement. On the other hand, it must be remembered that a fuel which will operate with entire freedom from vapour lock in one car may give much trouble in another. It is, therefore, impossible to specify definitely the *maximum* vapour pressure which a fuel should possess,

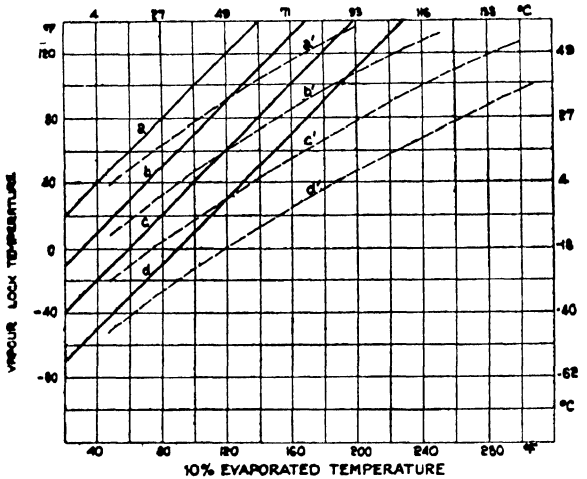


FIG. 199.—CURVES SHEWING THE VAPOUR LOCKING PROPERTIES OF MOTOR FUELS. (EDGAR, HILL & BOYD.)

without reference to the characteristics of actual automobile fuel systems, because the temperature which the fuel reaches in the fuel system is determined by the conditions of operation such as speed, load, etc., and by such equipment factors as thermostats, radiator shutters, etc. Moreover, the properties of the fuel in the fuel system may not always be identical with those of the fuel as supplied to the fuel tank. A certain amount of evaporation of light ends (stripping) may occur in the fuel tank, in the vacuum tank and in the carburettor bowl itself, so that it is possible for it to be heated somewhat above the temperature at which 10 per cent. of the original fuel evaporates without vapour lock occurring.

If we take atmospheric temperatures as ordinates and 10 per cent. temperatures as abscissae, we can obtain, for a series of given automobiles, curves representing the *minimum* 10 per cent., temperatures

which the fuel must possess in order to avoid vapour lock. These curves would approach as the ideal a curve in which the fuel does not rise above atmospheric temperature and the ordinates and abscissae would then be equal. Similar curves could be drawn with maximum vapour pressures as ordinates. The position of the curves and their exact form would vary with the design factors of the fuel feed system and sufficient data are not available at present to construct accurate graphs, but the curves for different automobiles would have the general nature of the solid lines drawn in Figure 199, where curve (*a*) represents the ideal curve mentioned above and curves (*b*), (*c*) and (*d*) represent

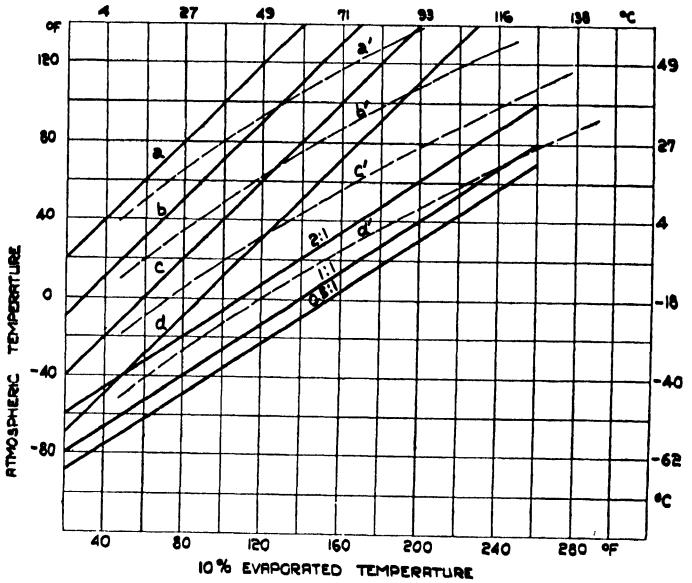


FIG. 200.—GRAPH SHEWING MAXIMUM AND MINIMUM 10 PER. CENT. DISTILLATION POINTS OF MOTOR FUELS. (EDGAR, HILL AND BOYD.)

increasingly badly designed fuel systems in which the fuel is heated 30°F., 60°F. and 90°F., respectively, above atmospheric temperature. The dotted curves *a'*, *b'*, *c'* and *d'* are corresponding curves showing the approximate effect of 2 per cent. propane on these relationships.[32]

In Figure 200, the date of Figure 199 and Figure 190 are combined, from which it is clear that a fuel which will give both satisfactory starting and freedom from vapour lock in a given car must have its temperature for 10 per cent. evaporated lying to the left of the curve for starting and to the right of the curve for vapour lock. Several important conclusions for both the automotive engineer and the oil refiner may be drawn from these curves. In the first place, it is evident that the area between the curves, which determines the permissible range of 10 per cent. points for satisfactory operation, is de-

termined by the propane content of the fuel and the design of the fuel system. For fuel systems approaching the ideal and for fuels free from the deleterious propane, the range is extremely wide even at low atmospheric temperatures. The range narrows as the fuel system becomes poorer, and at low temperatures with a very badly designed fuel system, the vapour lock and starting curves may cross and a condition in which vapour lock will occur with any fuel on which the engine will start, will result.

728. As a convenient relation to indicate probable freedom from vapour lock on modern automotive equipment, Brown[9] has advanced the equation

$$\text{Minimum A.S.T.M. 10 per cent. temperature} = 100 + \tfrac{1}{2}(\text{Average Atmospheric Temperature °F.}) \quad . \quad (33)$$

which gives the minimum 10 per cent. temperature (corrected for loss) allowable.

A more reliable relationship deduced by the same investigator is :—

$$\frac{100 - \frac{1}{2}(\text{Av. Atm. Temp. °F.}) + 460}{140} = 5{\cdot}167 - \log P \quad . \quad (34)$$

$$\text{where } \log_{10} P = 1{\cdot}167 - \frac{\text{Av. Atm. Temp. °F}}{280} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

and P = Reid vapour pressure of dry fuel at 100°F. (atmospheric pressure assumed to be 14·7 lbs. per square inch).

It is clearly desirable, from the viewpoint of the oil refiner and the general public, that as large a fraction as possible of the products of the refinery shall be available for automotive use, since this involves economy of manufacture and conservation of natural resources. It is also just as clearly desirable from the standpoint of the automobile manufacturer that his product shall operate satisfactorily on as wide a range of fuels as possible. The oil refiner may contribute his part to increasing the permissible range by eliminating propane from motor fuel and should, of course, provide a fuel whose 10 per cent. points will lie between such limits as may be satisfactory in a reasonably well designed fuel system. The automobile manufacturer may contribute his part by studying the temperatures reached in his fuel systems and keeping them as low as possible by appropriate details of location, insulation, etc.

Crank-Case Dilution

729. While it is generally agreed that a motor fuel does not need to be completely vaporized in the induction system in order to function efficiently, it has nevertheless been demonstrated that the temperature

of complete vaporization, or dew-point, of air-fuel-vapour mixtures is the controlling factor in determining the amount of fuel which finds its way into the lubricating oil in the crank case under given weather and engine conditions. This dilution of the crank case oil does not occur to an extent sufficient appreciably to affect fuel consumption, but under winter conditions, it may thin out the lubricant so badly as to give excessive lubricating oil consumption and even cause wear or injury to the engine. The tendency to cause dilution constitutes the most important present limitation on the upper boiling range of a motor fuel. It is also true that if there is too much higher boiling material in the fuel its distribution characteristics are likely to be inferior, causing both a loss of power and diminished economy, but few commercial motor fuels of to-day, either in this country or in America, have enough high boiling constituents appreciably to effect the mileage they will give under ordinary operating conditions. Thus, while the volatility of the higher portion of a motor fuel must be reasonably good, it is distinctly less important than that of the lighter portions for the reasons already discussed.

To avoid crank case dilution, the dew-point of the air-fuel mixture leaving the carburettor must be kept as low as possible by a suitable limitation of the 90 per cent. point of the fuel, but there is no justification for reducing the latter lower than 210°C. Fuels of lower 90 per cent. points may give dry air-fuel mixtures entering the cylinders and actually give a loss of power on this account, but fuels of higher 90 per cent. points may cause a certain amount of crank case dilution.

It must not be inferred, however, that the quality of the fuel used is the only factor determining crank case dilution, because the design, construction and condition of the engine are also of considerable importance, as is also the question of crank case temperature. Furthermore, the dilution is not solely caused by the heavy ends of unburnt fuel but is partly accounted for by the cracking or thermal decomposition of the lubricating oil in the hotter parts of the engine.[33] The warmer the crank case, the smaller the dilution that is obtained, because equilibrium is eventually established (after about 4,000 miles running) in the crank case. At higher temperatures, the diluent is evaporated from the crank case oil. A further point to be remembered is that most of the crank case dilution that occurs is caused in starting the engine, when the jacket cooling water is cold and when extensive use of the choke is made to obtain easy starting. Under these conditions only a small amount of the fuel delivered by the carburettor is vaporized and the remainder leaks past the piston rings into the crank case oil. If the use of the choke during starting is limited to the bare minimum, no trouble from crank case dilution will be experienced with present day fuels.

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CHAPTER XVI

KNOCK RATINGS

736. Introduction.—The existence of knocking in internal combustion engines under certain conditions has been known for many years, but the importance of knocking was not fully realized until about ten years ago; even to-day little is known regarding the exact mechanism of the phenomenon. A vast amount of work has centred on this subject and much is known concerning the effects of knocking, its prevention and the factors influencing it, but real progress is hindered by the lack of fundamental data.

In previous chapters, it has been shown that of all the factors limiting engine efficiency, knocking is by far the most important. This was first shewn by H. R. Ricardo about ten years ago and at about the same time T. Midgley and T. A. Boyd in America demonstrated that the phenomenon as it existed in ordinary petrol engines could be eliminated by the addition of minute amounts of tetra-ethyl lead (a so-called "anti-knock" agent) to the fuel. Immediately after these investigators had completed their original researches, the Asiatic Petroleum Company, who had financed the work of Ricardo, and the General Motors Corporation, who instigated the work of Midgley and Boyd, began to turn this work to practical value. The former Company, fortunate in having at its disposal valuable supplies of motor fuels of high anti-knock fuel, began to blend their products in such a way as to give the motorist freedom from knocking and advertised the subject accordingly. The General Motors Corporation commercialized the discovery of the anti-knock properties of tetra-ethyl lead by forming a new company, the Ethyl Gasoline Corporation, to place it on the market. Both ventures were highly successful, although tetra-ethyl lead met with some opposition in its infancy, due to its poisonous properties.

Immediately afterwards, the subject of knocking quickly assumed general importance and refiners and blenders were not slow to appreciate the new yardstick by which their products were being judged. The successful research carried out by the General Motors Corporation encouraged many others to investigate the same field and very soon numerous patents began to appear claiming anti-knock properties for numerous compounds and motor fuel compositions. It is a remarkable fact, however, that no new compound has ever been discovered having

greater anti-knock properties than tetra-ethyl lead and other similar lead compounds, although ten years have elapsed since this brilliant achievement.

With the development of anti-knock motor fuels, numerous methods of measuring knocking were devised. For the most part, companies chose to work independently in this field and very soon there were in existence many different types of test engines and test methods which could not well be correlated. In 1928, interested groups in America saw the need for co-operation in methods of measuring the anti-knock properties of fuels and expression of results. Previously, in 1922, it had been realized that improvement in engine performance was inseparably connected with fuel quality and a Co-operative Fuel Research Committee, representing the American Petroleum Institute, the Automobile Chamber of Commerce and the Society of Automitive Engineers, was set up to investigate problems common to the two industries. In 1928, this committee turned its attention to knock ratings and their measurement and began an ambitious research programme. The work done under these auspices has now led to the almost universal adoption of a standard test engine and procedure for knock rating measurements. To-day the subject of knock ratings is tremendously important to all those concerned with motor fuels, and the octane number scale of anti-knock measurement now finds its place in nearly all motor fuel specifications.

It is the purpose of this Chapter to deal somewhat briefly with the general subject of knocking, to indicate some of the phenomena associated with it, to indicate the methods of knock measurement now employed and to describe the anti-knock properties of typical "dopes" and fuels. To deal adequately with the subject in a book of this size devoted to the subject of motor fuels generally is, of course, not possible.

The Chemical and Physical Aspects of Knocking

737. The noise to which the name "knock" has been applied is like that produced by a sharp ringing blow upon the metal of the engine cylinder. Formerly it was supposed actually to be due to some such mechanical cause which might be derived, it was supposed, from a looseness between moving parts. Experiment soon demonstrated that this view was untenable and it is now believed that the noise is due to a wave of high pressure gas striking the inner side of the combustion chamber walls. It is known that in certain combustion mixtures, such as electrolytic gas (composed of hydrogen and oxygen), under certain conditions a pressure wave of extremely high velocity is set up some time after ignition, the so-called "detonation wave."

The phenomena of engine knock is sometimes referred to as

" detonation," but in this book the latter term is not used because there is evidence to show that if detonation, as experienced in electrolytic gas, occurred in the same way in a petrol engine, the engine would not survive the first occurrence. Knocking may be a mild form of detonation, but for the sake of clarity the terms should not be used interchangeably.

It is essential, at the outset, to appreciate the difference between " pre-ignition " and knocking. In the normal petrol engine, combustion is initiated by an electric spark timed to occur at a definite instant towards the end of the compression stroke. The correct timing varies according to the engine speed and certain other factors, but ignition should never commence before the passage of the spark. If this does happen, on account of overheated spark plug points, or scraps of stray incandescent carbon, then " pre-ignition " is occurring, a state of affairs which soon causes violent knocking and the development of excessive pressure before the end of the compression, which soon causes the engine to come to a standstill. Knocking, however, is something that happens after the passage of the spark, while the combustion is proceeding, and if it is not too violent, it may persist for long periods without doing the engine any harm. On the other hand, heavy knocking soon leads to overheating and may develop into pre-ignition. Nevertheless, pre-ignition and knocking are quite separate phenomena. Knocking follows, while pre-ignition precedes, the ignition spark.

It is now well known that different fuels vary markedly in the extent to which they are prone to knocking, straight chain paraffins boiling above about 80°C. being bad offenders in this respect, while the aromatic hydrocarbons cannot be made to knock, even at very high engine compression ratios. Generally, straight run spirits have lower knock ratings than cracked spirits from the same crude oil, while among cracked spirits, those produced under high temperature-vapour phase conditions have better knock resisting properties than those produced at lower temperatures.

738. The Effect of Engine Design on Knocking.—The compression ratio of an engine is all important in its effect upon the knocking properties of internal combustion engine fuels, and it is when the compression ratio is raised from a low value, at which low thermal efficiencies are obtained, that trouble due to knocking is encountered. This fact originally led Ricardo to a method of measuring the knocking properties of fuels in which the compression ratio of an engine operating under standardized conditions was gradually raised to the point at which the power output was a maximum, the well known " Highest Useful Compression Ratio " (H.U.C.R.). With a given fuel, however, the H.U.C.R. varies to a marked extent from engine to engine and upon

change in engine conditions, a state of affairs which suggests that engine design has an appreciable influence upon the degree of knocking which occurs. It should also be noted that, in general, any alteration in engine design or conditions of operation which involves an increase in temperature of the fuel-air mixture before combustion, increases the tendency of a fuel to knock.

A consideration of the engine factors having an effect upon the phenomena known as knocking is an aid to the understanding of its mechanism. Of these factors, the most important are as follows :—

(*a*) The absolute distance from the sparking plug points to the most remote corner of the combustion chamber. In other words, the smaller and the more compact the combustion chamber and the more central the position of the sparking plug, the less the tendency to knock of any given fuel.

(*b*) The degree and nature of the movement of the combustible mixture in the combustion chamber at the time of ignition. The greater the turbulence and the more chaotic the movement of the gases, the less the tendency to knock.

(*c*) The temperature and pressure of the gases at the time of ignition. At any given compression ratio, the temperature at the end of compression depends upon the amount of heat received by the charge before and during its entry to the cylinder.

(*d*) The temperature of the hot surfaces within the combustion space, such as the head of the exhaust valve, which, by giving rise to a certain amount of pre-oxidation of the fuel during the suction and compression strokes, will increase the temperature of the charge before ignition.

As indicating the very wide difference in the compression which can be used in different engines on the same fuel, the following tests on Ricardo " E.35 " and " E.5 " variable compression engines may be quoted.[1] These engines are described later (see paragraphs 751 and 752). In the former engine (8 in. bore by 4·5 in. stroke), in which ignition is by two synchronized sparks occurring at diametrically opposite sides of the combustion chamber, the distance between the two sparking plugs being 5 in. exactly, the H.U.C.R. of a given fuel was 5·3. In the smaller " E.5 " engine, (bore 2·75 in., stroke 3·25 in.), fitted with a single sleeve valve and central sparking plug, the H.U.C.R. of the same fuel was 6·8. Here the difference in favour of the latter engine is attributed primarily to the smaller cylinder and, therefore, reduced length of flame travel, and to the absence of hot exhaust valve heads. In a " T " headed engine of 4·375 in. bore and 6 in. stroke, fitted with a sparking plug directly over the inlet valve, the same fuel knocked heavily at a compression ratio of 3 : 1.

Ricardo has also quoted figures to show the effect of cylinder size, apart from differences in general design, upon the H.U.C.R. of a fuel. These are as follows :—

Diameter of cylinder (in.)	2·75	3·5	5·5	9·5
H.U.C.R.	7·9	7·5	6·2	5·4

and refer to an 80/20 petrol-benzole mixture in experimental single sleeve-valve engines of practically the same stroke-bore ratio and as similar as possible in every other respect. In each engine the maximum length of flame travel was approximately 25 per cent. greater than the cylinder radius.

With a compact combustion chamber there is less danger of any unburnt portion of the gas becoming stagnant and, therefore, unable to give up its heat at a greater rate than it is generated by compression, due to the burning portion of the charge. With the exception of sleeve valve engines, it is usually impracticable to place the sparking plug in the centre of the combustion space. If the gases must be ignited from one side of the combustion space, the sparking plug should be placed on the hottest side, that is to say, on the side nearest the exhaust valve, so that the unburnt gases are compressed against the coolest surfaces and can, therefore, get rid of their heat more rapidly.

739. The greater the turbulence within the cylinder, the lower will be the tendency for any fuel to knock, since turbulence tends to spread and distribute the flame uniformly throughout the charge and so reduces the dangers of portions of it being entrapped and overheated. From the point of view of knocking, the worst possible condition is reached when the exhaust valve is fitted in a pocket in which the mixture may become more or less stagnant, and the spark plug fitted at the opposite side of the combustion chamber. In such a design, which is not often found nowadays, though it was common a few years ago, a portion of the charge will be trapped in a position ideal for knocking, where the bulk of the surface to which it can impart its heat is made up of the hot exhaust valve head.

It is now common knowledge that the tendency to knock of any fuel is greater at low engine speeds than at high speeds. This might be expected, for the lower the speed the lower the degree of turbulence. As the speed is reduced, not only is the velocity of entrance of the fuel charge reduced in the same proportion, but the time during which turbulence may die down is correspondingly prolonged. Engines used for measuring knocking and which are described later usually operate at low speeds (600—900 r.p.m.) in order to accentuate the knocking properties of fuels and so make measurement easier. The influence of turbulence of different types upon the H.U.C.R. of a typical motor

fuel in the Ricardo E.5 variable compression engine has recently been discussed by T. F. Hurley and R. Cook.[2] With a powerful uni-directional swirl, the H.U.C.R. was increased by more than two whole ratios over the H.U.C.R. obtained with eddying indiscriminate turbulence, but this gave decided running roughness and caused overheating of the spark plug points, which often led to pre-ignition.

The influence of cylinder design on knocking has been studied by G. B. Maxwell and R. V. Wheeler in researches carried out on the flame characteristics of knocking and non-knocking fuels.[3] In general, their conclusions agree with those given above. Recent combustion chamber research has been described by H. S. Glyde[4] and by Ricardo.[5]

740. Conditions Existing in Explosions Under Knocking and Non-Knocking Conditions.—During recent years much research has been carried out on flames and explosions, a large proportion of which has had for its object the study of knocking in internal combustion engines.

In 1928, Maxwell and Wheeler[6] described experiments which they conducted in small stainless steel explosion vessels and in which they were able to obtain photographs of the inflammation of pentane-air, benzene-air and other combustible mixtures. The explosion vessels used were of 6 inches internal diameter, one end plate carried a centrally disposed sparking plug and the other an optical pressure indicator. In the cylinder wall there was a slot, $\frac{3}{8}$ inch wide, extending from within 1 inch of the ignition end to the other end (14 inches long), fitted with a plate glass window $\frac{1}{2}$ inch thick. Photographs of the explosion flame as it passed this window were obtained on sensitized paper attached to a rapidly revolving drum. A continuous record of pressure development was also obtained. Typical photographs are shown in Figures 201 and 202, the former referring to a 3·7 per cent. by volume mixture of pentane in air and the latter to a 3·5 per cent. by volume mixture of benzene in air. The flame can be considered as moving from the bottom to the top of the paper which itself is moving from left to right. Opposite to the first photograph, a diagram of the window in the cylinder through which the flame was photographed, is indicated, strengthening bands which obscure the window at two points being shown in white.

The records of the tuning fork (the intervals between each were 1/100th sec.) appear below the flame photograph and also the pressure record. Two horizontal lines are shown on each photograph to mark the boundaries of the window, while from the point marking the time of ignition, a perpendicular has been drawn to the base line of the pressure record. The results obtained indicated that when " maximum power " mixtures of pentane and air were ignited, under the conditions of the

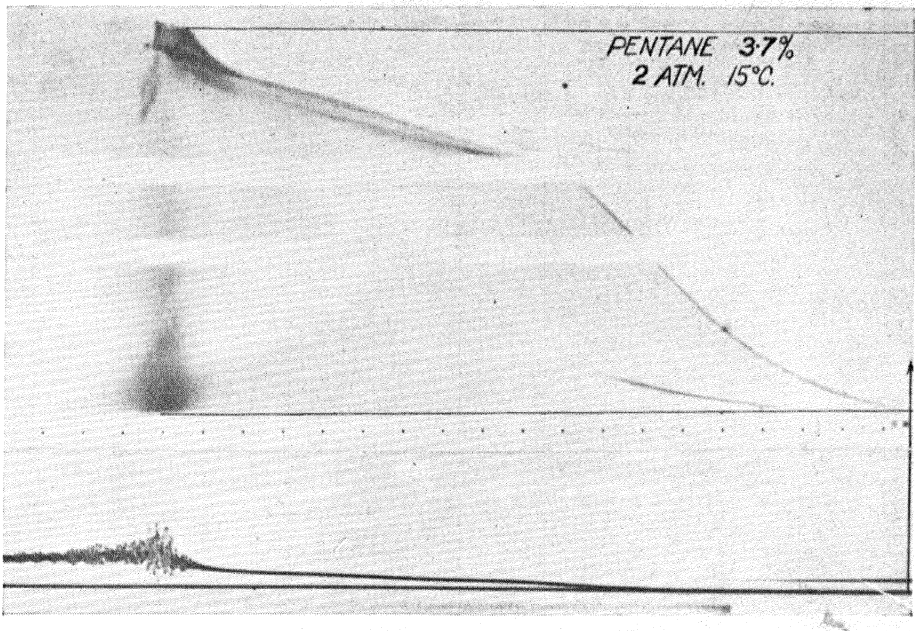


FIG. 201.—PHOTOGRAPH OF PENTANE-AIR EXPLOSION (MAXWELL & WHEELER).
(Courtesy, The Institution of Petroleum Technologists.)

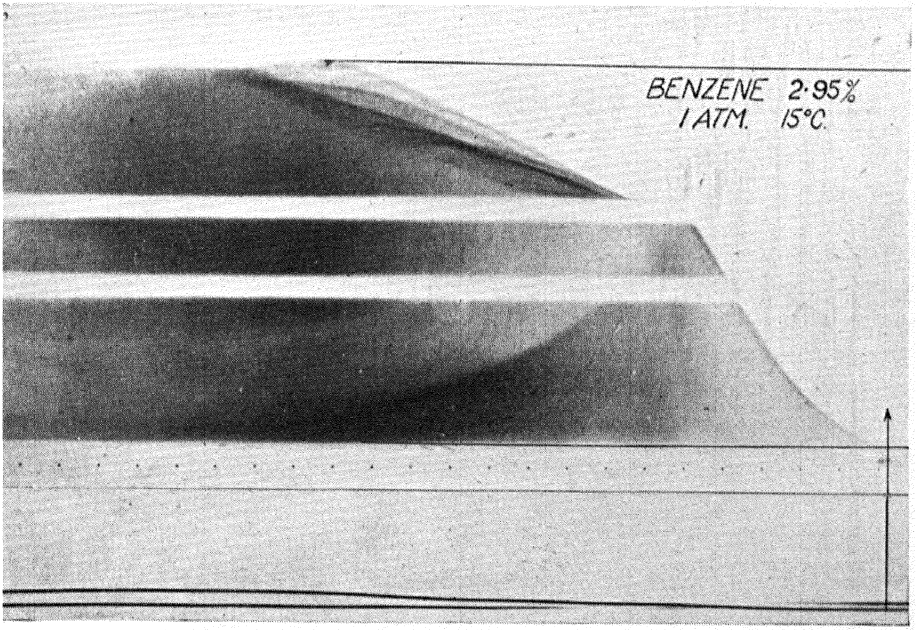


FIG. 202.—PHOTOGRAPH OF BENZENE-AIR EXPLOSION (MAXWELL & WHEELER).
(Courtesy, The Institution of Petroleum Technologists.)

[Facing page 280

experiments, a flame passed through the charge with an accelerating speed until it reached a point slightly beyond the mid-point of the cylinder. Here the flame was checked and travelled at a slower and nearly uniform rate until it reached the end plate. Beyond the point of check, the shape of the flame altered, the records showing a luminous " skirt " behind the flame front. The flame photographs also showed a faint glow from the end products up to the moment when the speed of the flames was checked, dying slowly away towards the ignition point. A more actinic after-glow begins slightly before, or simultaneously with, the arrival of the flame front at the end of the cylinder.

Using weak mixtures of pentane and air, the pressure records showed an even rise of pressure up to a maximum, which was obtained at the moment when the flame skirt reached the end of the cylinder. No sound was heard during the explosion of these mixtures.

When a rather richer mixture was used, containing 3·5 per cent., or slightly more, pentane by volume (11 to 1 air-pentane by weight), a new feature appeared in the photograph (see Figure 201). There was, as before, a check in the progress of the flame (with a simultaneous change in its character) slightly beyond the mid-point of the cylinder, followed by a slower, more uniform movement. This slower speed of flame did not, however, continue throughout the remainder of its travel but rapid vibrations, with an abrupt acceleration in the mean speed, occurred shortly before the end of the cylinder was reached. No after glow was apparent in the products of combustion behind the flame-front until this rapidly vibrating flame reached the end-point. At that moment, a faint glow travelled at an exceedingly high speed throughout the cylinder. A mild " ping " accompanied these explosions.

The mixture of benzene and air which, on explosion, produces both the highest and the most rapid development of pressure, was found to contain 3·0 per cent. benzene by volume (or about 10 to 1 air/benzene by weight). The mean rates of development of pressure and of travel of flame in this mixture were somewhat higher than the corresponding values for the " maximum power " mixture of pentane and air, though the values for the pressures developed were about the same. Fig. 202 is typical of the explosion of benzene-air mixtures at 2 atmospheres initial pressure, under which conditions the difference in behaviour of pentane and benzene is most marked. Whereas at this pressure the explosion of the pentane-air mixture produced a sharp " ping," with rapid oscillations of pressure, that of the benzene-air mixture was quite inaudible. The after glow in the benzene-air mixture was highly actinic and was almost continuous behind the flame front.

These experiments revealed the following differences between a knocking and a non-knocking explosion. In the former, such as those of pentane-air mixtures at high initial pressures, a delay occurred in the

completion of the combustion process initiated in or just behind the flame front. It would seem as though some additional impetus were required to cause the completion of the reactions. When this impetus is given, for example, by the production of a shock wave when the accelerating, vibrating flame is arrested at the end of the cylinder, the combustion is completed almost instantaneously throughout the cylinder, with a consequent rapid rise in pressure. In a non-knocking explosion, such as that of benzene-air mixtures, there is no delay in the completion of the combustion reactions, but they are continuous (and long continued) behind the flame front. The type of " after-burning " is similar to that recorded for mixtures of carbon monoxide and air.[7]

741. In further experiments, described at a later date, Maxwell and Wheeler examined the flame characteristics of a wider variety of fuels under various conditions and also studied the effect of pro-knocks and anti-knocks.[8] The previous observations were confirmed and it was found that non-knocking explosions, such as those of benzene-air mixtures and paraffin-air mixtures containing tetra-ethyl lead, exhibited the after-burning phenomena. Pro-knock substances such as ethyl ether and amyl nitrite produced marked reduction in the amount of after-burning behind the flame front and a correspondingly more intense glow at the moment the audible knock occurred. From these experiments, it appeared that for a knocking explosion to occur in a closed vessel, two conditions are necessary: (1) the shape and size of the vessel, the nature and strength of the mixture and the magnitude and rate of heat liberation in the burning gases must be such that a stationary wave can be set up in the column of gases before the initial flame has travelled throughout the vessel: (2) the nature of the fuel and its concentration in the mixture must be such that there is sufficient residual energy available to maintain a shock wave when the flame, accelerated by the stationary wave, is arrested by the wall of the vessel. On these assumptions, the effect of the addition to pentane of traces of " anti-knocks," such as tetra-ethyl lead, which renders the combustion continuous behind the flame front, is understandable. Fuels like benzene and carbon disulphide, which themselves burn continuously during explosion, act in a similar manner to tetra-ethyl lead, but less effectively.

It is of interest to compare these experiments conducted in stationary bombs with photographic experiments on flames as they exist in engine cylinders. Glyde[9] used a stroboscopic device for viewing the explosions in a side valve engine fitted with Ricardo turbulent heads at various positions across the cylinder head and measured the velocity of flame propagation. He found that as the flame front passed from the sparking plug, its velocity was at first relatively slow, the velocity then rapidly

increased to its maximum value and finally decreased rapidly as the wall of the combustion chamber was reached. The velocity with which the flame spread from the nucleus was nearly proportional to the rate of pressure rise and not dependent in its early stages on the mixture strength. The results obtained by Glyde agree well with those of Maxwell and Wheeler, in so far as they can be co-ordinated, allowing for the necessary difference in absolute values between the high rates of flame velocity and pressure rise in the engine, and the relatively low rates in the bomb experiments.

742. In 1931, Withrow and Boyd[10] made photographic studies of the flames occurring in internal combustion engines under knocking and non-knocking conditions with different fuels. These investigators reached the following conclusions :—

(1) Starting at the sparking plug, a flame of narrow combustion zone moves progressively through the charge. Oxidation of the fuel is apparently complete within this narrow zone of combustion, but the products of combustion to the rear of the flame front continue to emit light for some time.

(2) During non-knocking combustion, the time required for the average flame to travel across the combustion space (under the conditions employed) was about 40 degrees of crank angle.

(3) A knocking explosion differs from one in which knock does not occur only in the way the last portion of the charge burns. Whereas in a non-knocking explosion the flame continues to move at a comparatively constant velocity near to the end of the combustion space, in a knocking explosion the latter portion of the charge inflames at a much higher rate than normal. This rate is often so high that at the instant of knock the flame appears simultaneously throughout the whole of the portion of the charge still remaining to be burned.

(4) The extremely high rate of inflammation in that portion of the charge which burns at the instant of knock is apparently due to *auto-ignition* occurring within it. This may be caused by temperature induced within that part of the charge by adiabatic compression.

(5) The violence of the knock is determined by how large a proportion of the charge is involved in the spontaneous inflammation, or the amount of it remaining to be burned at the instant knock occurs.

(6) The very rapid, and often substantially instantaneous, inflammation that occurs within the portion of the charge which burns at the instant of knock is accompanied simultaneously by a very

rapid rise in cylinder pressure. The magnitude of this pressure rise increases with the intensity of the knock.

(7) The one effect upon combustion of the presence of tetra-ethyl lead in a gasoline is to prevent the extremely rapid inflammation of the latter portion of the charge, and the accompanying pressure rise, which is the knock. Lead-tetra-ethyl has no effect upon the velocity or the character of the flame prior to the time at which knock would have occurred in its absence.

It will be evident from these conclusions that there are several points common to the work of Withrow and Boyd and Maxwell and Wheeler, but the latter investigators did not express the opinion that auto-ignition of part of the charge was responsible for the knock, but held that the formation of a stationary wave before the charge had been fully burned was probably responsible.

Schnauffer[11] has reached conclusions similar to those of Withrow and Boyd and considers that when a true knock occurs, a portion of the unburnt charge ahead of the advancing flame front ignites simultaneously throughout its mass, thus leading to sudden large increases in temperature and pressure.

Further support to this view is given by Withrow, Lovell and Boyd[12] who used a special sampling valve to take gas samples from the combustion space over short intervals of the cycle and concluded that the phenomena known as knocking occurs in that part of the charge which burns last and that there is a more rapid spread of combustion in the last portion of the charge than in non-knocking explosions.

743. The Spontaneous Ignition Theory of Knocking.—These researches, and many others which have led to the same conclusions, have resulted in wide acceptance of the theory put forward by Ricardo in 1921, to explain the knocking properties of various fuels—the so-called Spontaneous Ignition Theory.

According to this theory, the knocking properties of a fuel are determined by the temperature at which it will ignite on compression by the travelling wave front. The theory therefore implies a tendency to knock proportional to the spontaneous ignition temperature of the fuel. When the behaviour of an engine in practice is considered, the Spontaneous Ignition Theory accounts for most of the facts. Thus, knocking occurs more readily in large than in small cylinders because the surface-volume ratio and, therefore, the cooling, is less; more readily with paraffinic than with aromatic hydrocarbons, since the ignition temperatures of the former are lower; more readily with paraffins of high molecular weight than with the lower paraffins for the same reason and also because the flame temperature increases with the molecular weight.

It is when the effect of dopes is considered that the most trouble is experienced in reconciling facts with theory. Anti-knock dopes are found to increase the spontaneous ignition temperatures of knocking fuels, and this agrees with the theory, but the latter does not explain how the dopes are effective in bringing this about. A combination of the "spontaneous ignition" and "peroxide" theories of knocking could, however, probably meet the known facts.

744. Spontaneous Ignition Temperatures.—The spontaneous ignition temperatures of liquid fuels have been studied by numerous investigators during the past twenty years, mainly in connection with the anti-knock properties of petrol engine and diesel engine fuels. These investigators have used such a large variety of methods and apparatus that the work done has not so much established definite ignition temperatures for various substances as indicated the complexity and magnitude of the variables involved.

The "spontaneous ignition temperature" of a substance is the temperature at which that substance, under certain specified conditions, takes fire or explodes spontaneously, without the application of a spark or flame. Various methods have been employed to determine this property, but in the more commonly known procedures, a small drop of the fuel is allowed to fall into a heated pot through which a stream of air or oxygen is passed. The lowest temperature at which the drop of fuel ignites is taken as the spontaneous ignition temperature (S.I.T.). Other investigators have used methods involving adiabatic compression of fuel-air mixtures, static determinations in bombs and flow-through experiments in heated tubes. These need not be described in detail here, as a full bibliography is given at the end of this Chapter. Descriptions of a heated pot or "crucible" method of S.I.T. determination and another method specially intended for diesel oils are given in Chapter XIX.

The present state of knowledge with regard to spontaneous ignition temperatures, in so far as they are of interest in consideration of motor fuel quality, may be briefly summarized as follows :—

(1) In general, hydrocarbons and motor fuels of high anti-knock properties have higher S.I.T.'s than those of low knock ratings.
(2) Anti-knock dopes, such as tetra-ethyl lead and iron carbonyl, raise the S.I.T.'s of hydrocarbons to which they are added, while pro-knock dopes lower the S.I.T.'s.
(3) The S.I.T.'s of the normal paraffin hydrocarbons decrease with increasing molecular weight, and are much lower than those of aromatic hydrocarbons and alcohols.

(4) It is possible, by S.I.T. determinations, to differentiate with reasonable accuracy between a good motor fuel and a bad fuel, but the methods of test usually employed are not sufficiently sensitive to differentiate between fuels having anti-knock values not widely different.

(5) S.I.T. determinations should not be used as criteria of anti-knock quality, since actual engine tests are much more accurate and reliable. Considerable care is needed in the interpretation of S.I.T. results.

745. The Detonation Theory of Knocking.—Berthelot[13] and Le Chatelier[14] discovered that, under certain circumstances, a detonation wave is set up during the combustion of gases or vapours. Immediately after ignition, the flame travels for some distance at a normal rate and then suddenly assumes a great velocity. Various investigators have suggested that these pressure waves are related to engine knock, but the hypothesis that a true detonation wave is set up, due to ignition of the unburnt charge immediately ahead of the flame front, does not appear to agree with experimental evidence. Although it is possible that the initial acceleration of the flame may be sufficiently great to develop a detonation wave in certain instances, experiments in closed vessels under conditions comparable to those existing in an engine cylinder do not show flame speeds and accelerations comparable to those of mixtures known to give detonation waves. The argument that turbulence may accelerate the flame sufficiently to set up a detonation wave is opposed by the fact that knocking is intensified at low speeds.

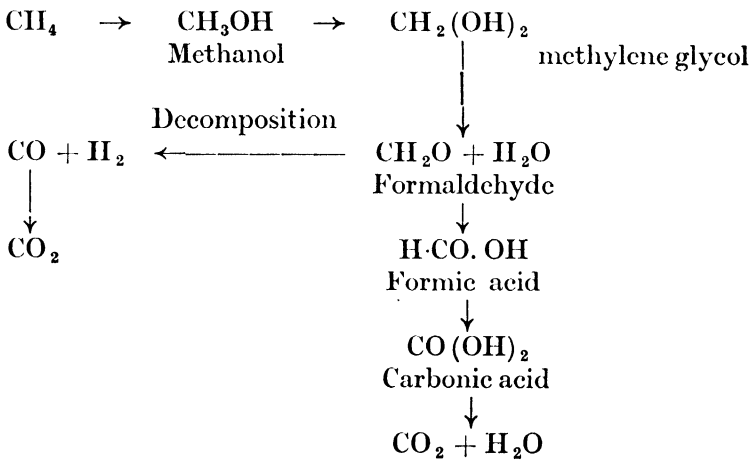
The rate of rise of pressure in a progressive homogeneous reaction cannot be the sole factor determining the tendency of a fuel to knock. Brown and Watkins[15] determined the rate of pressure rise in a number of such reactions and came to the following conclusions :

The rate of pressure rise (1) increases with the molecular weight of the normal paraffin hydrocarbons, (2) varies inversely with the number of methyl groups attached to an aromatic nucleus, (3) is approximately the same for benzene and *n*-octane, toluene and *n*-heptane, xylene and *n*-hexane, (4) is about the same for the higher alcohols as for the corresponding paraffin hydrocarbons, (5) is very rapid for ethyl ether. From a study of the effect of initial temperature on the rate of rise of pressure, Brown, Leslie and Hunn[16] arrived at the same conclusions. Fenning's[17] results, showing that the rate of flame propagation is greater in benzene-air than in hexane- or gasoline-air mixtures, also supports the contention that tendency to knock cannot be measured by flame speeds.

746. The "Nuclear Drop" Theory of Callendar.—From a consideration of the temperature-entropy diagrams of the saturated vapours

of fuels, Callendar[18] was led to propose that nuclear drops of the higher boiling constituents of the fuel might be present in an engine cylinder at the moment of ignition of the fuel-air mixture. It was suggested that these nuclei would be easily ignitable since the higher members of a hydrocarbon are more easily ignited and would thus become foci for the ignition of the unburned charge. An objection to this theory is that it is based on data referring to the saturated vapours of the fuels and not to dilute air-vapour mixtures. The presence of liquid fuel drops in the dilute air-fuel mixtures drawn through the carburettor and hot intake manifold, and mixed with the hot residual gases in the cylinder is doubtful. Also, many very volatile fuels, such as ether, knock easily, while others of very low volatility have very high anti-knock values. The theory does not account for the fact that some gaseous fuels knock fairly easily.

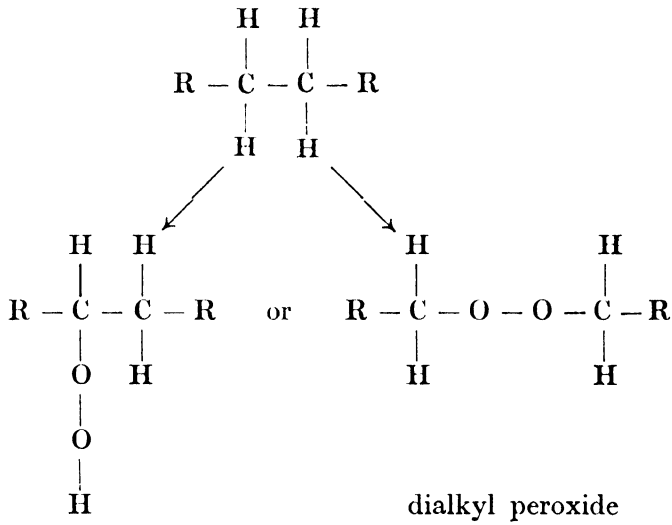
747. The Peroxide Theory of Knocking.—The combustion of a hydrocarbon, leading to the ultimate formation of oxides of carbon and water, involves the formation of various intermediate reaction products containing oxygen, and of the theories advanced to show the course of the combustion (or oxidation) process, two are of outstanding importance. One of these is the well known "Hydroxylation" theory, developed by Professor W. A. Bone and his co-workers.[19] In this, the mechanism postulated involves the successive formation of hydroxyl compounds, which may add oxygen to form additional hydroxyl groups or which may lose water and decompose. In this way, methane, to take the simplest example, would first form methanol, and then methylene glycol, which would be decomposed to formaldehyde and water. Formaldehyde would be oxidized to formic acid or decomposed to carbon monoxide and hydrogen. Thus :—



This theory has met with some criticism because products such as mono-

and di-hydroxy derivatives of the hydrocarbons, which are essential to the theory, have not been found experimentally except under special conditions where other factors are involved. An aldehyde and water (and peroxides) are usually the first products observed. The explanation offered by Bone and his co-workers for the non-appearance of mono-hydroxy products in actual experiments at low pressures is that the alcohols undergo such rapid oxidation or decomposition that their presence in the product could not be expected. This is not, however, in accord with the results of other workers who have found that in the case of paraffins higher than ethane, the alcohols are more difficult to oxidize than the corresponding normal paraffins or aldehydes.

The other theory developed to show the mechanism of combustion processes is that known as the "Peroxidation" theory, in which it is postulated that the first product in the oxidation of a hydrocarbon is a peroxide, formed by direct chemical union of the hydrocarbon with one molecule of oxygen, e.g.,



alkyl hydrogen peroxide dialkyl peroxide

748. The peroxide theory has developed largely from work in the liquid phase or at low temperatures conducted primarily in attempts to solve some of the questions regarding knocking phenomena. The following observations have been made as a result of experiment.

(1) Hydrocarbons begin to oxidize in the presence of air at comparatively low temperatures. Thus, in the case of a 10 per cent. mixture of hexane in air, traces of oxidation products of the hydrocarbon, namely, water, aldehydes and carbon dioxide have been obtained at 325°C. ("Temperature of Initial Combustion" or T.I.C.).[20]

(2) The T.I.C. of the paraffin hydrocarbons decreases with increasing molecular weight in the same way as the S.I.T., and as a broad general rule fuels of high anti-knock value have higher T.I.C.'s than those of low knock rating.[20, 21, 22]

(3) In low temperature oxidation experiments, such as those used in T.I.C. determinations, certain fuels give measurable amounts of compounds containing very reactive oxygen which have chemical properties the same as those of known unstable oganic peroxides. Knocking fuels give these substances much more readily than non-knocking fuels or fuels of high knock rating.[23, 24]

(4) These peroxide-like compounds have been found to be formed during the compression stroke in engine operation under temperature and pressure conditions necessary for knocking.[25, 20]

(5) Organic peroxides have pronounced pro-knock action when added to motor fuels, the more unstable peroxides such as acetyl di-peroxide having a more pronounced effect than comparatively stable peroxides such as benzoyl peroxide. Many peroxides are explosive when heated suddenly.[20]

(6) When tetra-ethyl lead is added to a fuel, the amount of peroxides formed in low temperature oxidation experiments or during the compression stroke in engine operation is much reduced. Pro-knock substances such as ether and amyl nitrite have the reverse effect.[20, 26]

It will thus be seen that the phenomena of knocking is closely connected with that of oxidation and particularly closely linked up with peroxide formation. In consequence, the peroxide theory of knocking, which postulates that knocking is caused by the sudden decomposition of peroxides formed from easily oxidized hydrocarbons during the early stages of the engine cycle is now widely accepted.

749. Of particular interest is the work of Pope, Dykstra and Edgar,[26] who found a remarkable relationship between the ease of oxidation of a series of isomeric octanes and their knock ratings, those most susceptible to oxidation having the lower knock ratings and vice versa. The addition of tetra-ethyl lead to these hydrocarbons had a marked effect in reducing the extent of oxidation under a given set of conditions.

The peroxide theory of knocking is, however, not universally accepted. Thus, Brunner[27] has suggested that although peroxides may be formed in the oxidation of hexane, these may be formed from an unsaturated body resulting from the dehydrogenation of hexane, as well as from hexane directly. Experimental work by Berl, Heise and Winnacker[28] has led to the same conclusion.

The peroxide theory has been further criticized by Lewis, who claims

that Callendar's evidence for peroxide formation is inconclusive since it might have indicated hydrogen peroxide or peroxides resulting from unsaturated hydrocarbons which were first formed. Hydrogen peroxide has been found in the flames from coal gas and hydrogen.[29] Lewis postulated the dehydrogenation of the paraffin, the hydrogen liberated forming water and the unsaturated compounds forming aldehydes and peroxides. The pressure changes occurring during the oxidation of carefully purified amylene in bulbs, the temperature of which was slowly raised, were recorded as functions of the temperature. These curves showed three sections : (*a*) a region deviating but slightly from the normal vapour pressure curve, (*b*) a gradual drop in pressure to a minimum point indicating slow reaction with a decrease in the number of molecules, (*c*) a sharp rise in pressure due to the decomposition of the products formed in (*b*), followed by nearly normal gas pressure. Analyses made during the first period gave positive evidence of reaction with formation of aldehydes and carbon oxides. The presence of 0·5 per cent. of lead tetra-ethyl resulted in a linear relation between pressure and temperature and permitted only slow oxidation as evidenced by the presence of oxidation products.

The common peroxide theory of knocking does not explain the fact that unsaturated hydrocarbons, e.g., pentene, hexene, etc., have greater resistance to knocking than the corresponding paraffin hydrocarbons, even though they form peroxides and oxidize more rapidly than the latter. Lewis suggests that the unsaturated hydrocarbons are effective as anti-knock agents in that (*a*) they have a smaller hydrogen content and are less likely to be dehydrogenated, i.e., they act partly as diluents, and (*b*) they may enter into combination with the hydrogen evolved from the paraffins, by increasing the active mass of unsaturated hydrocarbons. Thus, in the reaction

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2,$$

the olefines produced are reinforced by the unsaturated hydrocarbons present and also even by the aromatics, and this tends to reverse the reaction with a decrease in the active mass of hydrogen. This may be an explanation but it does not appear to carry conviction. In the absence of any other more likely explanation, the fact that the olefines have higher knock ratings than the corresponding paraffins is a point against the acceptance of the peroxide theory.

750. Oxidants and Anti-Oxidants.—The mechanism of autoxidation advanced by Moureau and Dufraisse[30] is similar in many respects to the peroxide theory. According to this, the combination of an active molecule of oxygen with a hydrocarbon gives a peroxide molecule of high activity which is unstable. This may break down to give oxy-

genated products. When the peroxide concentration reaches a critical value, chain reaction ensues, causing excitation and combination of molecules coming into contact with these active reaction centres. The mechanism of autoxidation is outside the scope of this book and for further information the reader is referred to well known works on the subject.[31]

Knock-Rating Engines

751. The knocking properties of motor fuels are determined by tests on various engines, operating under such conditions of speed and load, etc., etc., that small changes in knock intensity may easily be measured. It is usual for such tests to be made on engines specially designed for this work, usually of the single cylinder type, because multi-cylinder engines used primarily for power generation or vehicle propulsion are not sufficiently flexible, and are not convenient in operation.

Ricardo Variable Compression Testing Engines.—There are two Ricardo variable compression testing engines,

(*a*) Type E.35, Poppet valve, 2 litre capacity,
(*b*) Type E.5, Sleeve valve, 350 ccs. capacity.

both of which are designed for general research work on petrol engines and fuels.

*Type E.*35.—This engine was designed and used in Ricardo's celebrated researches for the Asiatic Petroleum Company which began in August, 1919. It is essentially a high duty engine, capable of running at fairly high speeds and has an exceptionally high power output and thermal efficiency.

The engine is a single cylinder water-cooled unit of 4·5 inches bore and 8 inches stroke. Two inlet and three exhaust valves are carried in the cylinder head and are operated through rockers from an overhead camshaft, the camshaft being driven through the medium of bevel gears and a telescopic vertical shaft. The cylinder is cast integrally with its water jacket, the outside of which is machined and ground, and slides up and down in a massive guide which is fixed to the crank case. The compression ratio is thus variable over the range 3·7 to 7·5.

The very light aluminium alloy piston is of the slipper type, all superfluous bearing surface being cut away in order to reduce friction.

Arrangements are provided for measuring the amount of fuel feed and cooling water. Swinging field dynamometers are fitted as standard.

752. *Type E.*5.—This engine has a cylinder bore of $2\frac{7}{8}$ inches and a stroke of $3\frac{1}{4}$ inches. The valve gear is of the Burt and McCollum single-

sleeve type. The variation in volume of the combustion chamber is obtained by raising or lowering the cylinder crown, in contradistinction to the practice of moving the whole cylinder adopted in the E.35 engine. The employment of Burt sleeve valve gear enables a cone-shaped combustion space, with a central sparking plug, to be utilized. This type of chamber is entirely free from pockets, and is almost ideal on thermodynamic grounds, as turbulence is well maintained and detonation reduced to a minimum. The compression ratio is variable over the range 5 to 10·75.

The only method available for the determination of knock ratings on either of these two engines is that involving the measurement of Highest Useful Compression Ratios. No arrangements are available for the use of a bouncing pin mechanism. Consequently, these two engines, though of great value for general research on fuels and engines, are now very little used for knock rating determinations. They are of interest in this connection mainly in the historical sense.

753. The Ethyl Gasoline "Series 30" Engine.—The Ethyl Gasoline Corporation produces for its laboratories and also for its customers a type of knock testing engine known as the "Series 30" or "S.30," which has been developed from the older "Delco" lighting set engine.

This engine, a photograph of which is reproduced in Figure 203, has a bore of $2\frac{1}{2}$ inches and a stroke of $4\frac{5}{8}$ inches, and is coupled by two V belts to a synchronous motor. This arrangement ensures that the speed of the engine is always constant independent of the output and avoids the use of a hand operated speed control. The engine has overhead valves, one inlet and one exhaust, and an evaporative cooling system. Cooling liquid is pumped through the jacket spaces at a high enough rate to prevent the formation of stagnant portions and vapour from the cooling medium is condensed in a reflux condenser and returned to the system. For jacket temperatures up to 212°F. (100°C.) water is used, but for temperatures higher than this, ethylene glycol is necessary. A single sparking plug is used for ignition and this is supplied by a spark coil. A neon-tube indicator is fitted to the crankshaft so that the ignition timing can be read when the engine is running. Splash lubrication is provided and the piston is of aluminium alloy. No inlet air heater is provided and the fuel is fed to the carburettor from one or two bowls which are mounted on screw racks so that the fuel head on the jet can be adjusted to give any necessary air-fuel ratio.

The engine is not of variable compression, but the compression ratio can be altered when the engine is at rest by inserting or removing shims from the joint between the cylinder and the crank case. The maximum ratio available is approximately 7·5 to 1. Intensity of knock

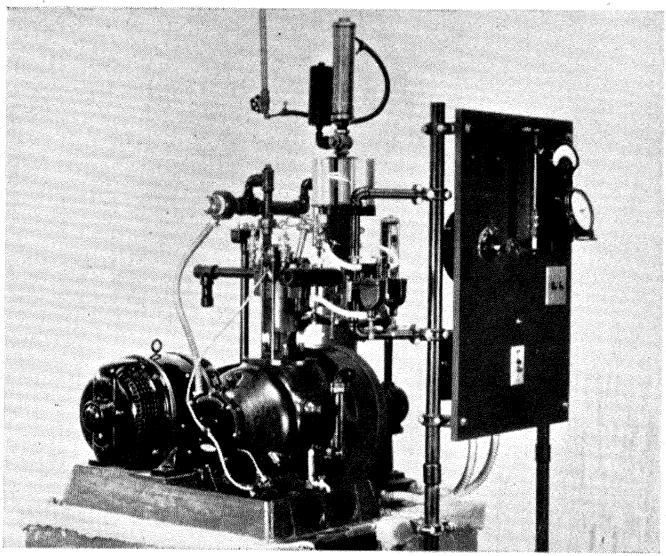


FIG. 203.—THE ETHYL GASOLINE SERIES 30 KNOCK TESTING ENGINE.
(Courtesy, Ethyl Gasoline Corporation.)

[*Facing page* 292

is varied by alteration of the throttle valve on which a fine adjustment is fitted.

Knock ratings are measured by the use of the bouncing pin indicator in conjunction with the usual gas burette or a "knock-meter." This is an instrument which consists of a millivoltmeter calibrated in arbitrary divisions connected electrically to a sensitive thermocouple placed in very close contact with a small coil of resistance wire through which the bouncing pin current is made to flow. When this current flows, the coil of wire gets warm and the temperature of the couple is recorded on the meter scale. Thus the meter responds to any change in knock intensity. In use, the knockmeter has an advantage over the gas burette in that knock measurements are made much more quickly, and because adjustment of the fuel feed for maximum degree of knock (see later) is made much more simply. There is, naturally, a small time lag before the meter responds to a slight change in knock intensity, but this has been found to be no disadvantage. The gas burette is now rarely used.

The engine conditions usually employed for tests on ordinary motor fuels and aviation spirits are as follows.

TABLE 159.

	Ordinary Motor Fuels.	Aviation Spirits	Standard Conditions Specified by U.S. Naval Dept. for Aviation Spirits
Speed	600 r.p.m.	600 r.p.m.	900 r.p.m.
Spark Advance	22°B.T.D.C.	22°B.T.D.C.	16–18°B.T.D.C.
Cooling Water	212°F.	300°F.	375 ± 9°F.
Compression Pressure	195 ± 5 lbs.	195 ± 5 lbs.	220–240 lbs.
Bouncing Pin Gap	0·01″–0·025″	—	—
Spark Plug	Champion C–7	Champion A1–64	Hornet BG–1XB or BG–4B or BG–4B1
Breaker Points Gap	0·018″	—	—
Lubricating Oil (Saybolt viscosity at 210°F.)	62 secs.	120 secs.	100–120 secs.
Quantity of Lubricating Oil	800 ccs.	800 ccs.	800 ccs.
Valve Timing (with 0·002″ clearance between rockers and valve stems).	—	—	Inlet opens 20 ± 5°A.T.D.C. Closes 10 ± 5°A.B.C. Exhaust opens 55 ± 5°B.B.C. Closes 10 ± 5°A.T.D.C.

754. The Armstrong Whitworth Variable Compression Knock-Testing Engine.—This fuel testing engine was developed from a

standard " B " type Armstrong Whitworth engine in collaboration with the Research Department of the Anglo Persian Oil Company.

A general view of the set is shown in Figure 204. The cylinder bore is $2\frac{7}{8}$ inches and the piston stroke is $3\frac{1}{2}$ inches, giving a capacity of 22·72 cubic inches or 372·5 ccs. The cylinder is cast in one piece with the crankcase, and the cylinder bore is finished by grinding. The valves, of which there are two, one inlet and one exhaust, are of the side by side type and are well cooled, the guides passing through the water cooling space. The joint between the cylinder head, which is detachable, and the cylinder is made with a special metal jointing material only 0·01 inches thick, ensuring an absence of any appreciable variation in the thickness of the joint on successive assemblies. The piston is of cast iron and is fitted with three gas rings at the top and a scraper ring in the skirt. The connecting rod is an H-section steel stamping and the crankshaft is also a steel stamping, made in one piece, with the exception of the balance weight which is bolted on. The bearings are of ample proportions throughout, the gudgeon pin bearing is bronze-bushed and the big end and main bearings are lined with white metal.

Splash lubrication is employed and the oil capacity is small to ensure that a steady temperature is reached in a short time.

The construction of the cylinder head is shown in the accompanying Figure 205. It will be seen that the main casting is cored out at the base for the water jacket space, and terminates at the top in a vertical cylinder, threaded on the outside. The corresponding nut is in the form of a handwheel, to which is secured a central sleeve. This sleeve extends through a hole in the head casting to the combustion space, and carries a bouncing pin mechanism. The joint between the sleeve and the cylinder head is made with a gland of the usual type near the middle, and a set of rings at the bottom. It is evident that, by turning the handwheel, the sleeve is raised or lowered, thus altering the volume of the combustion space and so altering the compression ratio. The compression ratio can be varied through the range 4·0 to 8·0.

It would appear, at first sight, that the cylindrical pocket formed when the sleeve is raised would lead to imperfect ignition of the mixture, but it is stated that, in practice, it is effectively scavenged.

The bouncing pin mechanism is, of course, very similar to that used on other knock-testing engines. Diaphragms of tempered steel, 0·0145 inches in thickness and 0·53 inches in diameter are employed.

The fuel feed system takes the form of a four way change over supply with rustless steel needle control valves fitted with drain cocks and waste pipes for clearing the pipe lines from air locks. The cover of each fuel chamber is sealed, after filling, by closing inlet and vent cocks, the only inlet for air then being through head equalizing pipes, which have openings close to the bottoms of the fuel chambers. The fuel flows

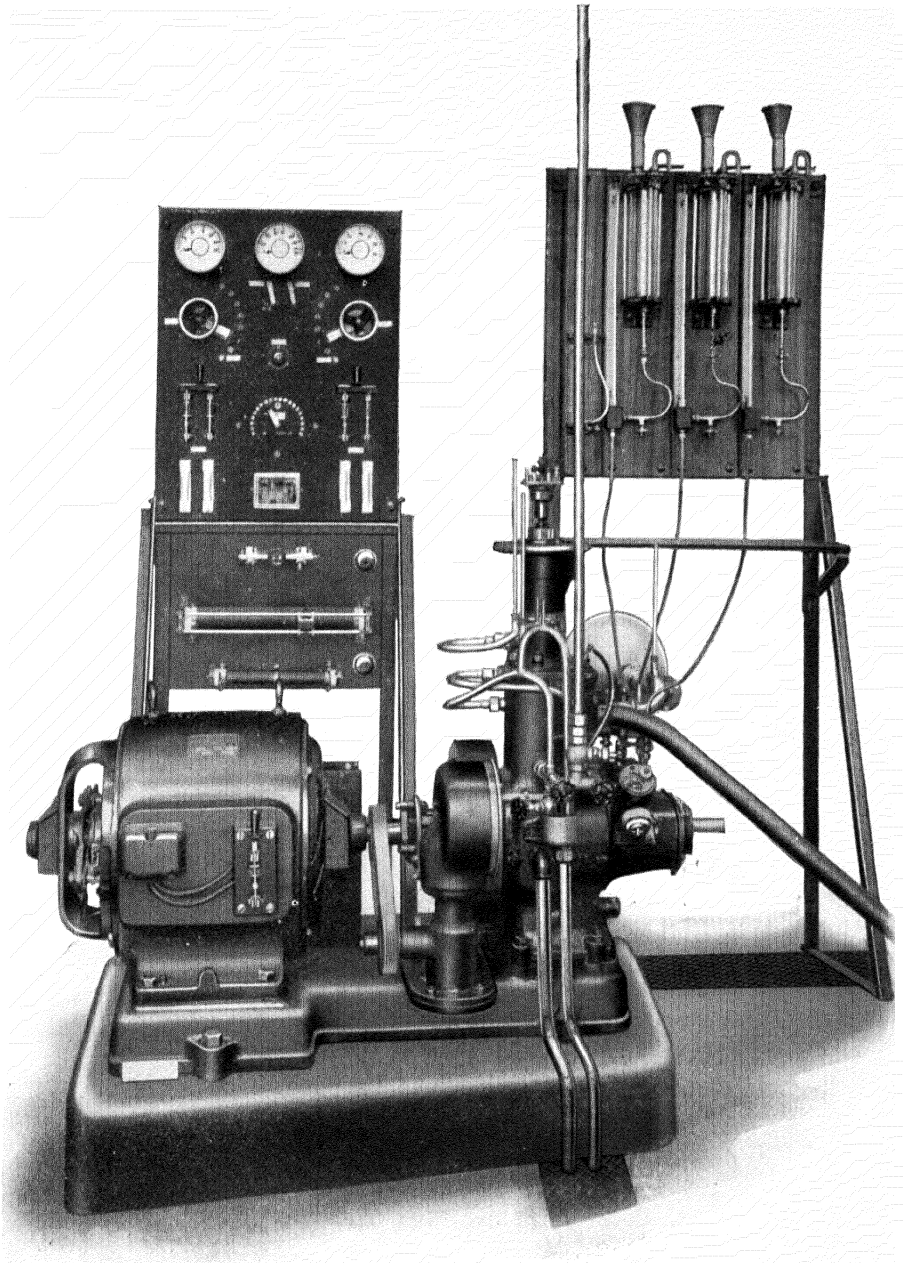


FIG. 201. -THE ARMSTRONG-WHITWORTH VARIABLE COMPRESSION KNOCK TESTING ENGINE.
(Courtesy, Sir W. G. Armstrong-Whitworth, Ltd.)

[*Facing page* 294

downwards through a measuring nozzle into the carburettor feed pipe, and upwards into a gauge glass, the level in the glass indicating the rate of fuel flow to the carburettor.

The air inlet to the carburettor is fitted with an electric heating element by means of which the air can be raised to any desired temperature.

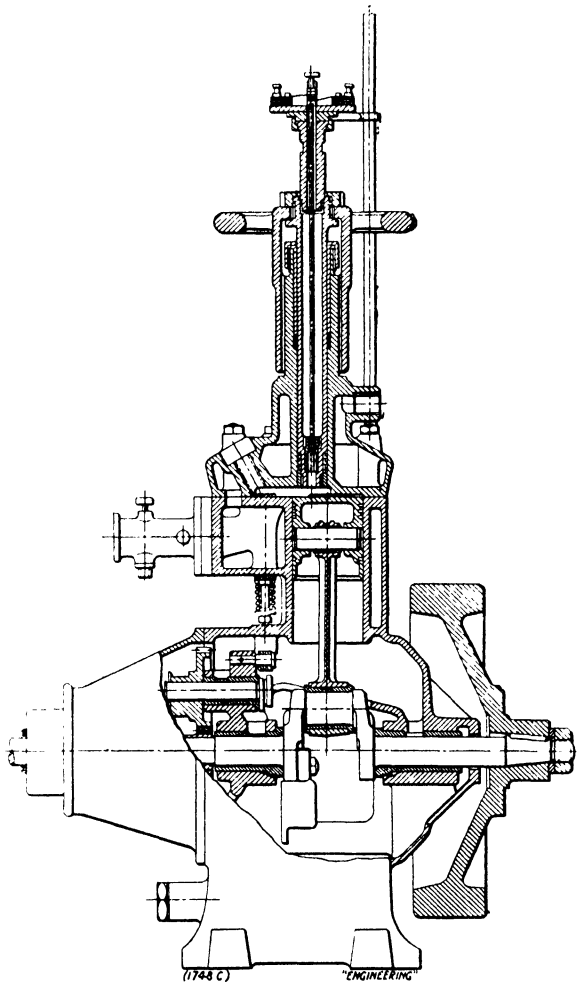


FIG. 205.—SECTION OF THE ARMSTRONG-WHITWORTH VARIABLE COMPRESSION KNOCK TESTING ENGINE.
(Courtesy, Sir W. G. Armstrong-Whitworth, Ltd.)

The water cooling system is divided, so that the water in the head and cylinder jackets may be at different temperatures if desired. Evaporative cooling systems may also be employed.

The operating conditions normally used in tests on petrols in the Armstrong Whitworth engine are as follows :—

Speed, 750 r.p.m.
Inlet air temperature, 120°F. (48·9°C.).
Cooling water exit temperature, 120°F. (48·9°C.)
Ignition, 12°B.T.D.C.
Valve Timing :

Inlet opens, 8°—10° after top centre.
Inlet closes, 17°—15° after bottom centre.
Exhaust opens, 37°—35° before bottom centre.
Exhaust closes, 7°—5° after top centre.

755. The C.F.R. Knock-Testing Engine.—As already mentioned, a move was made in America in 1928 to standardize methods of knock-rating measurement, because results obtained by different observers on different engines could rarely be reduced to a common scale. Wide discrepancies were often observed and it was recognized that the adoption of a standard test equipment and a standard method of test was necessary.

The first step made was the production of a test engine, and the requirements decided upon to be met were as follows :—

(1) That the equipment be universal, permitting testing as a fixed compression ell-head engine, or as an overhead-valve variable compression engine ; that it be suitable for the throttle method, or the spark method of test ; that it be adapted for a bouncing pin indicator or a listening post ; that the engine operate with a uniform jacket temperature ; and that it have convenient connections for accessory drives, thermometers, etc.
(2) That the engine be unusually rugged and free from the weaknesses and unreliability of conventional designs.
(3) That the design be such that the cost would be low enough to permit general use of the engine throughout the industry.

By the end of 1929, engines had been built embodying these requirements and tests on them had been carried out in various laboratories in America. The design of these engines, which were the first C.F.R. engines, has been described in detail by H. L. Horning.[32]

756. The unit decided upon was a single cylinder engine, of $3\frac{1}{4}$ inches bore and $4\frac{1}{2}$ inches stroke, with a swept volume of 37·4 cubic inches, fitted with a variable compression head, but also provided with a range of fixed compression ell-shaped heads. The piston was of cast iron so as to permit accurate close fitting in the cylinder, made long in the skirt to give great bearing area and prevent tilting with resulting ring leakage. Four compression rings and one oil ring were fitted. The

tendency for an iron piston to run at a considerably higher temperature than aluminium alloy pistons was largely offset by the unusually high metal thicknesses employed. The bearing construction also gave a very rigid structure, which is a great advantage in prolonging the life of the engine. The cylinder barrel extended down into the crankcase, this construction permitting a higher and stiffer crankcase.

The engine was designed so that it could be converted from a fixed compression ell-head engine to an overhead-valve variable compression engine merely by changing the two cylinder assemblies. This process did not disturb the valve timing or camshaft drive in any way, because, as shown in Figure 209 the fulcrum of the valve rocker arms is carried at the mid-point of a lever, one end of which is fixed to the crankcase, and the other end moves with the cylinder. The rocker arm fulcrum, therefore moves half the distance the cylinder moves, which is the amount necessary to keep the clearance constant.

As a visual means of indicating the spark timing the neon tube indicator as fitted to the Ethyl Gasoline S. 30 engine was incorporated.

An electric hot plate was attached to the bottom of the lubricating oil pan to promote rapid warming of the oil at the start of a day's run. Lubrication was by pressure feed from a gear pump through drilled passages in the crankcase walls, crankshaft and connecting rod to all bearings, constant pressure being maintained by means of a spring loaded relief valve. Timing gears were lubricated by a stream of oil directed at the point of mesh. In a single cylinder engine, some difficulty is often experienced due to the breathing action in the crankcase discharging oil at all openings. To counteract this, the C.F.R. engine crankcase was operated at a partial vacuum by means of a check valve in the oil filler cap. In addition to the use of conventional oil slings where shafts leave the crankcase, felt packing was provided at each of these openings.

The engine was cooled by circulating steam, obtained from the cooling water, and coil ignition was employed. The carburettor first adopted was a modification of that used on the Ethyl Gasoline S. 30 engine, a plate orifice jet being fitted to obtain a uniform air-fuel ratio over a fair range of loads.

As a means of measuring knock ratings, a bouncing pin indicator was provided and also a listening post for the audible determination of H.U.C.R.'s. In the latter, ear pieces were used with double branches, one leading to a listening post in the cylinder and the other to a standard "knock producer," a mechanism which dropped a steel ball from a given height on to a sound box cover. This method was, however, abandoned later in favour of the bouncing pin.

In a variable compression knock-testing engine, the question of spark timing is of some importance. The C.F.R. committee decided that the latter should be adjusted to its optimum setting for each compression

ratio, and fitted the engine with a link arrangement to make this adjustment automatically when the position of the cylinder head is altered.

The work done by the C.F.R. committee on this engine during 1930 was reported by T. A. Boyd at the end of that year at the Eleventh Annual Meeting of the American Petroleum Institute.[33] Members of the Committee worked on the engine for some considerable time and made various suggestions regarding suitable modifications in design which they considered desirable. Fortunately these modifications were only concerned with comparatively minor details of engine construction. The carburettor system was found not to be completely successful and the development of a suitable carburation system was delegated to a sub-committee with special capabilities in that field.

The question of reference scales of anti-knock quality was settled by the adoption of normal-heptane and iso-octane as primary standards (see paragraph 779) and by the adoption of octane numbers as indices of knock quality. *Octane number was defined as the percentage of iso-octane by volume in a mixture of iso-octane and normal heptane required to match the anti-knock value of any given fuel.* This scale was very quickly adopted throughout the petroleum industry, even before the C.F.R. engine was standardized.

Much work was also carried out to determine the effect of the outstanding variables that may influence the measurement of knocking. The results of this are described later.

757. By the end of the following year (1931), sufficient development work had been done to allow the publication of a tentative recommended practice for making knock rating tests.[34] Evaporative cooling was decided upon as the method of maintaining engine temperatures constant and, as a result of much experimental work, it was agreed that the engine should be of the variable compression type, so that the fixed compression heads originally provided became redundant. Carburation difficulties were overcome by the work of the special sub-committee appointed to study this subject, who designed a new carburettor on the lines suggested by E. M. Dodds and F. H. Garner of the Anglo American Oil Company in England. This carburettor is shown attached to the engine in Figure 207. The fuel jet is of fixed size and the metering of the fuel is accomplished by means of a stream of secondary air passing over the jet. Variations in mixture ratio are obtained not by adjusting the size of the fuel jet, but by varying the supply of secondary air. Four or two fuel bowls are provided, according to choice. The intake to the engine is down-draft.[35]

As a power absorbing medium, a slotted-rotor type induction motor, connected to the engine by means of V-type belts, was selected because it performs three functions. The first is to start the engine, the second

is to absorb the output of the engine and the third is automatically to hold the engine speed constant at 600 r.p.m. The latter is of particular value on account of the importance of constancy of speed in knock testing and because of the desirability to relieve the operator of the burden of ensuring it. To furnish direct current for the ignition system (if battery type ignition is used) and also for the bouncing pin circuit, a small 100 v. generator of 0·22 kilowatt nominal capacity was used, mounted directly above the induction motor and driven by a V-belt from a pulley on the induction motor shaft.

The engine conditions for knock rating determinations were tentatively standardized as follows :—

Engine Speed, 600 r.p.m.
Jacket Temperature, 212°F. (100°C.)— boiling water.
Spark Advance—That for maximum power, automatically adjusted.
Mixture Ratio—That for maximum knock (see later).

758. Correlation with Road Test Results.—Immediately following the development of a common apparatus and method for the determination of knock ratings, the Detonation Sub-Committee was instructed by the Co-operative Fuel Research Committee to undertake a comprehensive study to determine whether knock ratings determined in this way agreed with actual road performance. This work was carried out during 1932 and has been fully described.[36, 37]

Results were first of all received from various laboratories which indicated that in some cars fuels were rated the same as in the C.F.R. engine, under the tentatively standardized conditions, but that in other cars discrepancies between road ratings and laboratory ratings were observed. This led to a series of co-operative road tests to compare the car ratings of a number of selected fuels with conventional C.F.R. ratings and to investigations in the laboratory to evaluate the effects on the ratings of various types of fuels of changes in the conditions of test on the C.F.R. engine. In the first series of tests, covering a range of six fuels of different types, and 13 different cars, it was found that two fuels showed behaviour in the cars which was in fair agreement with their respective ratings by the C.F.R. procedure, but that four of the fuels knocked worse in cars than in the laboratory engine by the equivalent of from 5 to 7 octane numbers.

In August, 1932, very comprehensive road tests were conducted at Uniontown, using fifteen cars and eleven different fuels. The general procedure was to match the fuel under test with a mixture of reference fuels, "C.6" and "A.2,"* the comparison being based upon knock intensity as judged by car. The matching was carried out so that the

* These fuels are described later. See paragraph 780.

test fuel fell between a reference fuel mixture of higher anti-knock value and a reference fuel of lower anti-knock value than that of the fuel to be rated, the mixtures of reference fuels not differing in composition by more than 20 per cent. of " C.6 " in " A.2," or the equivalent of about 5 octane numbers. Ratings were made at intervals of 5 miles per hour, usually beginning at speeds between 10 and 15 m.p.h. and extending up to the speed at which knocking disappeared. The results of these road tests showed a greater degree of reproducibility than might well have been expected, but it was found, however, that some cars rated the same fuel differently and the same car in some cases rated one fuel differently at different speeds.

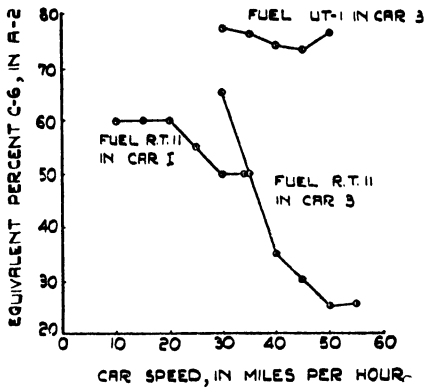


FIG. 206.—COMPARISON OF LABORATORY KNOCK RATINGS WITH ROAD TEST RATINGS.
(Courtesy, Waukesha Motor Co.)

The results obtained on two particular fuels in two different cars and reproduced in Figure 206 illustrate this. In one car (No. 1), a certain fuel (No. RT 11) knocked from 10 to 34 m.p.h., the knock disappearing at 34 m.p.h. In another car (No. 3), which was of different make and fitted with automatic ignition advance, the fuel knock was first evident at 30 m.p.h., and disappeared at 54 m.p.h. In the first car, the rating of this fuel was 60 per cent. " C.6 " in " A.2 " (apparent octane number 65) from 10 to 20 m.p.h., and at the knock disappearing point, (34 m.p.h.), 50 per cent. " C.6 " in " A.2 " (apparent octane number 62·5), the total spread being only 10 per cent. " C.6," or about 2·5 octane numbers. In the second car (No. 3), however, the rating of this same fuel was 65 per cent. " C.6 " in " A.2 " (apparent octane number 67) at 30 m.p.h. ; 35 per cent. " C.6 " in " A.2 " (apparent octane number 58) at 40 m.p.h. ; and 25 per cent. " C.6 " in " A.2 " (apparent octane number 56) at the speed at which knock disappeared (54 m.p.h.). Thus, the rating of this one fuel in one car varied anywhere between 25 per cent. and 65 per cent. of " C.6 " in " A.2," (i.e., between 56 and 67 octane number) and in the other car anywhere between 50 and 60 per cent. " C.6 " in

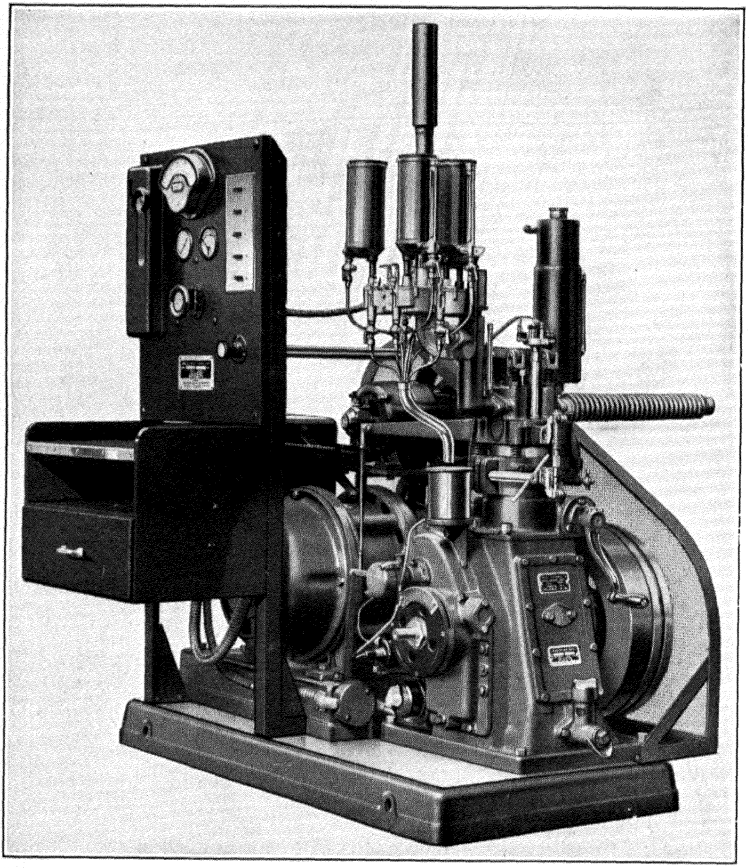


FIG. 207.—THE C.F.R–A.S.T.M. STANDARD KNOCK TESTING ENGINE.
(*Courtesy, Waukesha Motor Co.*)

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"A.2" (62·5 to 65 octane number), depending upon the speed at which the rating was made. Figure 206 also shows that another fuel (No. UT-1) gave practically the same rating at all speeds between 30 and 50 m.p.h.

Because of such apparent discrepancies, it was decided to rate the fuels in road tests according to their maximum degree of audible knock, irrespective of speed, in terms of blends of reference fuels. This method of rating is not free from objections, but in view of the great difficulties in making accurate road tests of this nature, it is acceptable in the absence of a better procedure.

759. The C.F.R. "Motor Method."—Having completed these road tests and obtained the road ratings of fifteen fuels covering a wide range, it was found that the latter did not agree with the knock ratings as determined on the C.F.R. engine according to the adopted procedure. Consequently experiments were carried out in order to determine what modifications to the C.F.R. procedure were necessary to make the test engine results agree with the road ratings. These experiments need not be considered in detail, but the result of this work was that a new C.F.R. engine test procedure was recommended called the "C.F.R. Motor Method" to take the place of the older method which now became known as the "C.F.R. Research Method." The new method gave satisfactory correlation with road results (see Table 160), and involved the following operating conditions.

Speed, 900 r.p.m.
Spark timing, 26° B.T.D.C., at a compression ratio of 5 to 1 and following the existing timing mechanism at other compression ratios, becoming 22° at 6 to 1 and 19° at 7 to 1.
Jacket Temperature, 96—102°C. (205—215°F.)
Mixture Temperature, 300°F. ± 2°F. (149°C. ± 1°C.)

Various modifications to the engine were necessary to obtain these new operating conditions. These were as follows:—

(1) The provision of an electric heater in the air intake system between the carburettor and the intake port.
(2) The use of a shrouded inlet valve.
(3) An improved vapour condenser and the elimination of the jacket cooling liquid circulating pump.

The new C.F.R. "Motor Method" has not met with unanimous approval in the United States, but it has been standardized and accepted by the American Society of Testing Materials as a tentative method.[38] Similarly, it has been accepted by the Institution of Petroleum Technologists in England.

TABLE 160.—SUMMARY OF RATINGS ON FUELS IN UNIONTOWN TESTS.
(Road ratings are average results.)

C.F.R. Research Method			Road Ratings		C.F.R. Motor Method	
Fuel Number	Reference Fuel C.6 in Reference Fuel A.2 Per cent.	Equivalent Octane Number	Reference Fuel C.6 in Reference Fuel A.2 Per cent.	Equivalent Octane Number	Reference Fuel C.6 in Reference Fuel A.2 Per cent.	Equivalent Octane Number
RT-9	95	76	77	70	74	70
RT-10	111	80	75	70	74	70
RT-11	66	67	54	64	55	64
RT-12	68	68	49	62	50	62
UT-1	82	72	63	66	64	67
UT-2	1	50	4	50	6	50
UT-3	56	64	53	63	53	63
UT-4	61	66	55	64	54	64
UT-5	75	70	63	66	61	66
UT-6	110	80	100	77	101	77
UT-7	69	68	56	64	58	65
UT-8	82	72	70	68	70	68
UT-9	76	70	67	68	68	68
UT-10	103	77	90	74	87	73
UT-11	111	80	96	75	89	74

The "Motor Method" is not meant to be a rigid standard, but will be changed in details as circumstances demand and as new cars find their way on to the road.* It will always be attempted to make the knock method give the same results as actual road tests. Criticism may be levelled against the method in that it does not correlate so satisfactorily with English cars as with American cars and that the method rates benzole blends and alcohol blends lower, relative to straight run and cracked fuels, than it should in the light of actual road tests. On the other hand, a standardized method of test that gives satisfactory results with most fuels is much preferable to a host of different methods, all of which give different results and which cannot be correlated with each other. As a knock-testing engine, the C.F.R. machine is very satisfactory and very flexible, and if the operating conditions are occasionally adjusted to correlate with road tests on a very wide range of fuels and cars, it will serve its purpose admirably.

A photograph of the C.F.R. knock-testing outfit is reproduced in Figure 207 and sectional views of the engine are shown in Figures 208 and 209. These are self explanatory. The inlet mixture heater and condenser are shown in Figure 210.

* During 1934, a further test programme has been completed at Uniontown (*Nat. Petr. News* 1934, **26**, (33), 5-8.

760. Operation of the C.F.R. Engine.—In addition to the operating conditions already given for the Motor Method, the following must also be observed.

Oil pressure, 20—30 lbs. per square inch under operating conditions.

Valve clearances, intake 0·008 inches, cold; exhaust 0·010 inches, cold.

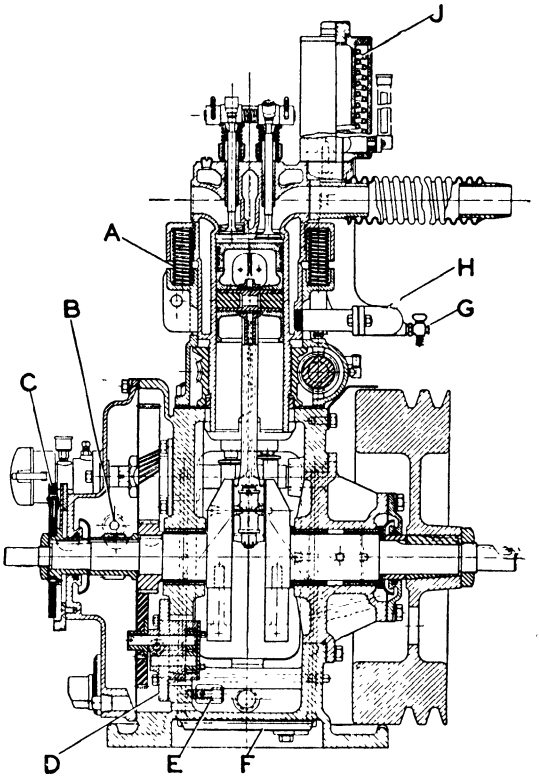


FIG. 208.—SECTIONAL VIEW OF C.F.R.-A.S.T.M. ENGINE.
(*Courtesy, Waukesha Motor Co.*)

Breaker point clearance, battery system 0·015 inches; magneto 0·020 inches.

Spark plug, equivalent to Champion No. 8; gap setting 0·025 inches.

Throttle opening, All tests to be conducted with the throttle opening at the point of maximum volumetric efficiency, approximately 90 on the throttle scale.

Carburettor adjustment, That for maximum knock, see later (paragraph 771).

Exhaust Pipe, this should be made from $1\frac{1}{4}$ in. pipe having a maximum of two ells with a total length not to exceed 20 feet. The

use of a short straight-through muffler of $1\frac{1}{4}$ in. diameter is permissible.

Bouncing pin assembly, gap setting 0·003 inches to 0·005 inches.

Before conducting knock rating tests, the engine should be run for about an hour so that temperature conditions may become steady at the values indicated above. Tests are then made according to the usual blend matching technique using either the gas evolution cell or the knock meter. The knock intensity used in C.F.R. engine tests is that obtained with a mixture of 65 parts iso-octane and 35 parts normal

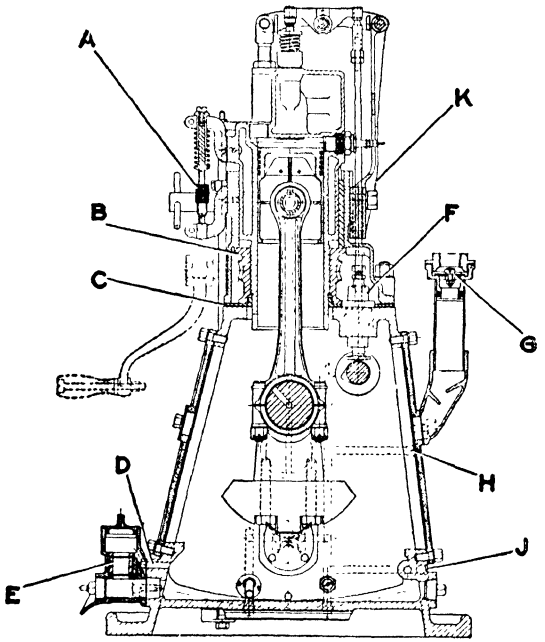


FIG. 209.—SECTIONAL VIEW OF C.F.R.-A.S.T.M. ENGINE.
(*Courtesy, Waukesha Motor Co.*)

heptane at a compression ratio one unit higher than that giving first audible knock. Full details regarding the operation of the C.F.R. engine are given in A.S.T.M. Tentative Standard, D 357—33T and in the handbooks issued by the manufacturers, The Waukesha Motor Company, Waukesha, Wisconsin, U.S.A.

The development of the C.F.R. engine has recently been described in detail by Boyd and Veal.[39]

761. The Knock Ratings of Aviation Fuels on the C.F.R. Engine.—The C.F.R. "Motor Method" is only intended for the testing of motor spirits and it is not applicable to aviation spirits. However, the question of aviation spirits is no less important and work has been

carried out in England by a small sub-committee of the Institution of Petroleum Technologists to evolve a suitable method of test which would correlate with known results on air cooled and water cooled aero-engines, both normally aspirated and supercharged.[40] A series of nine different fuels, ranging from 70 to 80 octane number, and composed mainly of straight run spirits and blends of straight run spirits with solvent naphtha and benzole (none contained tetra-ethyl lead or cracked spirit), were examined for knocking properties in various aero-engine cylinders and also in the C.F.R. engine under various operating conditions. In

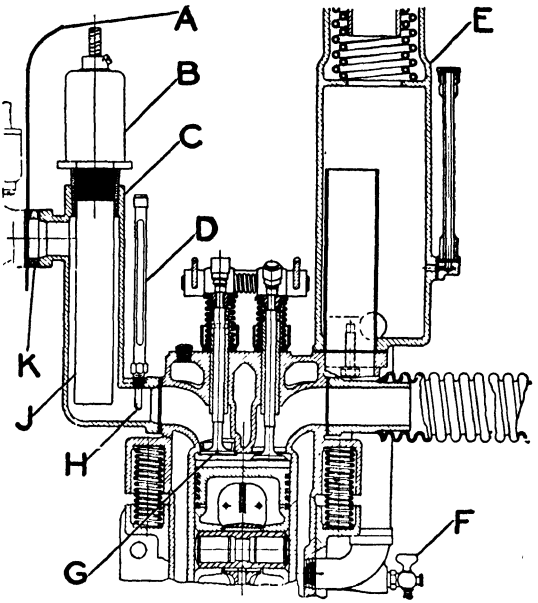


FIG. 210.—SECTION OF MIXTURE HEATER AND CONDENSER OF C.F.R.-A.S.T.M. ENGINE.
(*Courtesy, Waukesha Motor Co.*)

each case, results were expressed in equivalent T.E.L. reference fuel (B-2) blends and in octane numbers.

The results of the aero-engine tests fall into two categories, the one containing water cooled cylinder results and normally aspirated and air cooled cylinder results, while in the second category are the results in a supercharged air cooled cylinder and an air cooled cylinder of compression ratio 7·5.

It was concluded that the C.F.R. is the most suitable test engine for aviation fuels and that good correlation with the results obtained on the aero-engine cylinders can be achieved without going above 900 r.p.m. or 212°F. jacket temperature. For the aero-engine results in the first category given above, the best correlation was given by the C.F.R. engine with a mixture temperature of 100°F. For the second category, a

mixture temperature of 260°F. gave the better correlation. It was concluded, therefore, that the use of the C.F.R. engine at a speed of 900 r.p.m., with a jacket temperature of 212°F. and mixture temperature of 260°F., should afford a satisfactory means of rating aircraft fuels such as those examined.

It may be asked how it happens that the conditions found appropriate for automobile engines can be too severe for an air cooled engine under supercharged conditions, so that it is desirable to lower the mixture temperature in the test engine from 300° to 260°F. In so far as any useful comparison can be made between engines so widely different in type, it may be remarked that when a road vehicle is pulling at low speed on full throttle, the conditions are not only severe by reason of the low speed, but that in many types there is also provision for a large amount of mixture heating which may very well exceed even the heating provided by a supercharger on an aero-engine.

In America it has been found that a modified C.F.R. engine of $2\frac{5}{8}$ inches bore operating at 1,200 r.p.m. with a jacket temperature of 330°F. and a spark advance of 30°, gives reasonable correlation with aero-engines used by the U.S. Air Corps.[41] These conditions have, therefore, been standardized in the latest Air Corps specification for Fighting Aviation Spirit—Anti-Knock Grade (No. Y-3557-F), (see Chapter XV, paragraph 840). A temperature plug is used to measure the knock, as described later.

762. Comparison of Results obtained on Different Test Engines.—Knock ratings determined on one engine under a given set of conditions are very rarely the same as those obtained on another engine of different make and may differ by as much as 10 octane numbers or more. This is one of the main reasons why the Co-operative Fuel Research Committee in America decided to standardize a suitable engine.

Under certain conditions, various engines can be made to give substantially the same results. Thus, Barton, Sprake and Stansfield[42] have described tests carried out on Ethyl Gasoline, Armstrong Whitworth and Ricardo E. 35 engines, with English market fuels, which gave results varying by not more than $\pm$ 2·5 per cent. of benzene in heptane. The fuels tested covered a very narrow range, however, from 57 to 67 per cent. benzene in heptane, equivalent to a range of only about 5 octane numbers. On a wider range of fuels, these three engines no longer give the same results. Generally, the Ethyl Gasoline engine gives results 3—5 octane numbers lower than the Armstrong Whitworth engine.

A further comparison between the results obtained on different types of engines has been made by Swanson,[43] who has found dis-

crepancies of as much as 8 octane numbers between engines of similar design operating at the same temperature. Generally, results obtained on different models of the same make of engine do not vary by more than ± 1·0 octane numbers in normal cases. In extreme cases, the results may vary to an extent of ± 3 octane numbers.

Methods Employed for the Determination of Knock Ratings

763. In any considerations of the knock ratings of motor fuels, distinction must always be made between absolute knock ratings and relative knock ratings. In the latter category, results can only be interpreted correctly by a consideration of the absolute values of the standards with which the knock ratings of samples being examined are compared. This is extremely important when comparing the knock ratings of fuels of different composition, e.g., benzole blends and blends containing tetra-ethyl lead under different engine conditions.

Absolute knock ratings are now little used because of the difficulty in obtaining repeatable results, and fuels are rated in anti-knock value by comparing their knocking properties with those of standard fuels. There are occasions, however, when absolute knock rating scales are of importance in clearing up apparent discrepancies between results.

764. H.U.C.R. Determinations.—The method of measuring knocking developed by Ricardo, involving the determination of the engine compression ratio at which a standard intensity of knocking is produced, is an absolute method, but is absolute with respect to one engine only. It does not allow direct translation of results on one engine to those obtained on another engine, even of the same make.

This method, the so called Audible method of H.U.C.R. (Highest Useful Compression Ratio) determination is operated as follows :—

Standard engine conditions are adopted, generally those conducive to knocking, and maintained constant. The cylinder head is then lowered, to increase the compression ratio, until audible knocking is obtained. The first indication of the phenomena is somewhat irregular and spasmodic and is disregarded. A further small downward movement of the cylinder head causes the characteristic metallic clang to become more frequent and regular. At this second, and well defined, stage of knocking, the value of the compression ratio is noted and recorded. This procedure is repeated, using different rates of fuel flow and the values of compression ratio obtained plotted against the rate of fuel feed. The minimum value of the compression ratio, as shown by the curve, is recorded as the H.U.C.R. of the fuel under examination.

The power output of an engine at the H.U.C.R., determined in this way, is a maximum; that is, any further increase in compression ratio

produces heavier knocking and the power output no longer increases. This facilitates the observation.

Owing to the variations which occur from day to day in barometric and temperature conditions, the observed H.U.C.R. does not remain constant for any one fuel and should be corrected. This is often done by checking the H.U.C.R. of a reference fuel and adding the difference between the observed H.U.C.R. of this fuel and its arbitrarily chosen H.U.C.R. to the observed value of the fuel under test. The value so obtained is then referred to as the " corrected H.U.C.R."

With a trained operator, repeat tests of " observed H.U.C.R." often check to within 0·03 of a compression ratio. This corresponds, on the Ricardo E.35 engine at 1,500 r.p.m. and at full throttle, with a jacket temperature of 55°C., to an accuracy of about 0·6 per cent. benzene in a mixture of 60 per cent. benzene with 40 per cent. heptane by volume.

The uncertainties associated with the audibility method of H.U.C.R. determinations may be avoided by the use of a bouncing pin mechanism and a heavily damped millammeter, in the manner suggested by Stansfield and Thole.[44] The compression ratio is adjusted so that the ammeter reading is about 80 millamperes on the sample under test and is then readjusted to give the same reading on a standard reference fuel. This avoids the aural detection of H.U.C.R. and gives very good accuracy.

As shown earlier in this Chapter, the H.U.C.R. values assigned to fuels in one engine are not the same as those determined in an engine of different design running under different conditions. Thus, a fuel may knock heavily in one engine at 5 to 1 compression ratio, yet give perfectly smooth operation in another at a compression ratio of 7 to 1. For this reason, among others, the audibility method of H.U.C.R. determinations is very little used. On the other hand, the effects of engine design and operating conditions are eliminated to an appreciable extent if results are expressed, not in terms of absolute compression ratios, but in terms of H.U.C.R. difference from that of a standard fuel.[45] Thus, if a standard fuel has an H.U.C.R. of say 5·0 and a fuel under test an H.U.C.R. of 5·5, the difference 0·5 is sometimes referred to as the " engine test " of the sample.

765. The Expression of Results in Terms of Equivalent Blends of Standard Fuels.—In order to make the results of knock rating tests almost independent of engine design and more readily understood, Midgley and Boyd[46] proposed in 1922 that such results be expressed in terms of blends of standard fuels, e.g., a fuel would be stated to be equivalent to say x per cent. of aniline in fuel A, or equivalent to say y per cent. of benzole in fuel B. The advantages of this method of

expressing results were soon recognized, and knock ratings are now invariably reported in this manner.

This method was soon adopted for use in conjunction with the H.U.C.R. technique. The H.U.C.R.'s of blends of a pair of fuels, usually benzole and a straight run spirit of poor anti-knock value, were determined and recorded in the forms of graphs. When a sample of spirit was examined for anti-knock value, it was reported as, say, "x" per cent. benzole in standard spirit, this being the mixture having the same H.U.C.R. as the sample under test. Thus came into use such terms as "benzole equivalent," "tetra-ethyl lead equivalent," etc. It should be noted, however, that unless the information is required for some specific purpose, fuels should never be rated by determining how much anti-knock material must be added to them to bring them up to a common standard, or by determining how much pro-knock material must be added to them to lower their value to that of a low standard. The reason for this is the same in both cases. It is because cases are common in which two fuels, of the same knock rating (H.U.C.R. or "benzole equivalent"), require the addition of different amounts of anti-knock or pro-knock material to make them equal to a fixed high or low standard. Such anomalies, and they are very frequent, prevent the adoption of these two kinds of scales, even though it is often a matter of importance to known how much tetra-ethyl-lead must be added to a certain spirit to raise its knock rating to a given standard.

One may say, therefore, that when determining the knock rating of a spirit this should always be measured using the spirit itself unblended with any other material. On occasions this is not possible, as when testing materials of high anti-knock value which cannot be made to knock, e.g., benzoles. These materials are not used as automobile fuels in the undiluted state and therefore it is permissible to examine them in the form of dilute solutions in low grade spirits. It should also be noted that the anti-knock effect of a substance is not linear with its concentration in any but the most rare cases and often varies to a very marked extent with change in concentration. Therefore extrapolation of knock rating curves is often a matter of considerable doubt.

766. The Use of the Bouncing Pin Mechanism in Knock Rating Determinations.—The bouncing pin mechanism was invented by Midgeley for the measurement of knocking in the well known researches which he and Boyd carried out in a search for anti-knock materials, and during which the amazing efficacy of tetra-ethyl lead was discovered.

In its original form, the apparatus consisted of an opening in the head of the engine combustion chamber into which was screwed a long cylinder fitted with a piston, the under side of which was flush with the

inner surface of the cylinder head and which was held down by a powerful spring. On the upper side of the piston there rested, merely by gravity, a heavy steel pin, and immediately above the top of the pin was mounted a pair of contact points connected in series with a source of current, a filament lamp and an electrolytic cell containing dilute sulphuric acid. During normal combustion in the cylinder head of the engine, the pressure of the spring was so adjusted that the piston moved up and down only a very small distance (a few thousandths of an inch). When the explosion was a knocking one, the sudden production of a high pressure caused a greater movement of the piston and the bouncing pin was lifted clear, thus closing the electrical circuit described. In the course of a short time interval, a considerable amount of gas collected in the cell, and the lamp glowed almost continually. Midgeley assumed that the volume of gas collected in a given number of engine revolutions was proportional to the "amount of knocking produced by the fuel."

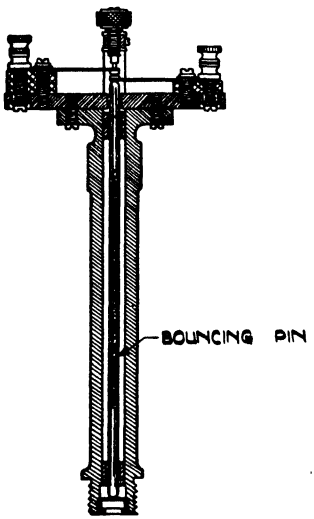


FIG. 211.—THE BOUNCING PIN MECHANISM OF C.F.R. ENGINE.

At a later date, the piston originally used in the instrument was replaced by a thin steel diaphragm. This construction is still used.

767. The bouncing pin element now used with the C.F.R. engine is shown in Figure 211. The pin is a steel rod, about 0·215 inches diameter and seven inches long and the upper end is made non-conductive with a piece of insulating material. The diaphragm is made of alloy steel of very high elastic limit and is 0·545 inches diameter and 0·015 inches thick. Just above the pin are two leaf springs, the lower one resting lightly on the top of the pin and each bearing at its inner end a tungsten contact point, these points being separated by an adjustable gap which is set at 0·003 to 0·055 inches. The upper leaf spring is held down at its inner end by a plunger, which is free to move upward against a light coil spring, carried in a screw member that serves the purpose of adjusting the gap between the contact points carried at the tips of the leaf springs.

Care must be exercised in using the bouncing pin apparatus as a method of measuring knock; it cannot be adapted indiscriminately to any cylinder. In engines such as the Ethyl Gasoline "S. 30", the Armstrong and the C.F.R., however, it is eminently satisfactory. Its sensitivity is very good and repeat experiments do not vary by more

than about 0·5 per cent. of benzole in a reference fuel. The knock intensity at which bouncing pin determinations are made should be considerably heavier than that adopted for H.U.C.R. audibility tests and it is usual to standardize this knock intensity as has been done in the case of the C.F.R. engine (see paragraph 760).

Using a bouncing pin, the knock rating of a given fuel is determined in the following way. The engine compression ratio range is first of all calibrated in terms of a suitable pair of reference fuels, say pure benzene and a low grade straight run spirit, by the usual H.U.C.R. method. Then the spirit sample to be tested is examined for H.U.C.R. and its equivalent benzene-straight run spirit blend determined. Suppose this is 40 per cent. benzene and 60 per cent. straight run spirit. Two blends of these reference fuels are then made up, one having a slightly lower knock rating than the sample under test and the other having a slightly higher knock rating. In the case under consideration, these would contain 37·5 and 42·5 per cent. benzene, respectively. Little accuracy is lost, however, if interpolation between fuels differing by as much as 5 octane numbers (e.g., about 10 per cent. of benzole) is attempted.[47] These two blends and the sample under test are then placed in three of the bowls attached to the engine carburettor. The engine is then run on each fuel in turn, and measurements of the amounts of gas collected in one minute runs on each fuel are determined, sufficient time being allowed to lapse before taking a reading after changing from one fuel to another. The carburettor adjustment must be separately adjusted on each fuel to give the maximum degree of knock. Let us now assume that the following amounts of gas have been collected in one-minute readings on the three fuels mentioned above and that these amounts have been checked two or three times.

Gas Evolution per 1 Minute Reading.

Fuel under Test.	37·5% Benzene in Straight Run Spirit.	42·5% Benzene in Straight Run Spirit.
0·40 ccs.	0·50 ccs.	0·35 ccs.

The equivalent benzene-straight run spirit blend of the sample under test is then calculated by interpolation and is, obviously, equal to

$$37{\cdot}5 + \left(\frac{5}{{\cdot}50 - {\cdot}35} \times ({\cdot}50 - {\cdot}40)\right)$$

$= 40{\cdot}8$ per cent. benzene in straight run spirit.

The bouncing pin method of knock rating determinations is, essentially, one of matching blends in this manner. When the Knockmeter is employed similar interpolation is adopted.

The following terms are often applied to indicate the efficiency of the bouncing pin mechanism.

The Sensitivity is the difference in average readings obtained on two fuels differing by 0·5 octane number.

The Stability is the average difference between consecutive readings.

The Stability Factor is the product of the greatest difference by the stability.

The Pin Factor is then defined as the ratio of the sensitivity to the stability factor. This may be greatly changed by very small changes in the adjustment of the pin.

Occasionally it is found that the bouncing pin gas evolutions or Knockmeter readings tend to drift in one direction. This is nearly always due to the engine not operating under steady temperature conditions and may be corrected accordingly.

A recent improvement on the gas evolution cell is the "knock meter," which has already been described in this Chapter under the Ethyl Gasoline S. 30 engine. It has been proved so satisfactory in use that it has now largely replaced the gas cell. Its chief advantage is that it enables knock rating determinations to be conducted more quickly. A further point in its favour is that it gives a visual indication of the degree of knocking occurring at any instant.

The bouncing pin mechanism can only be used satisfactorily at engine speeds up to about 1,000 r.p.m. At higher speeds it loses sensitivity to a very marked extent.

768. Electric Audibility Methods of Measuring Knock Ratings.—In 1931, Huff, Sabina and Hill[48] conducted a research to determine whether one of two fuels that cause incipient knocking under identical conditions may not possibly cause knocking of a violent character before the other, and it was considered advisable to use some other method of measuring knocking than the bouncing pin because motorists use sound as a criterion of knock. They therefore developed a device in which the knocking sound was received by a microphone, the resulting currents amplified by a thermionic valve amplifier and passed on to a filtering circuit (to eliminate unwanted frequencies) and a highly damped milliammeter. Using such an arrangement, they showed that the intensity of knock at which measurements are made does not effect fuel knock ratings if a fuel matching method is employed and demonstrated the workability of this "audiometer" method of determining knock ratings.

Somewhat later, in June, 1932, Stansfield and Carpenter made various improvements in this method and described an instrument called the "Strobophonometer," for the analysis and measurement of sounds or vibrations emanating from any source in cycles.[49] This

instrument applies to sound from an engine or other machine, a principle analogous to that of the stroboscope, that is to say, it selects, on a time basis, some part of a recurrent noise to be investigated. The relative intensity of this noise is indicated on a meter as in the former apparatus. The length of the listening period in degrees of cycle, and the phasing of this period round the cycle, can readily be adjusted when necessary and the use of a relatively short listening period makes external noises unimportant. Thus, it is possible, with the Strobophonometer, to select the period during the engine cycle over which the noise of knock occurs and so eliminate most other engine noises. This gives the instrument extremely good sensitivity.

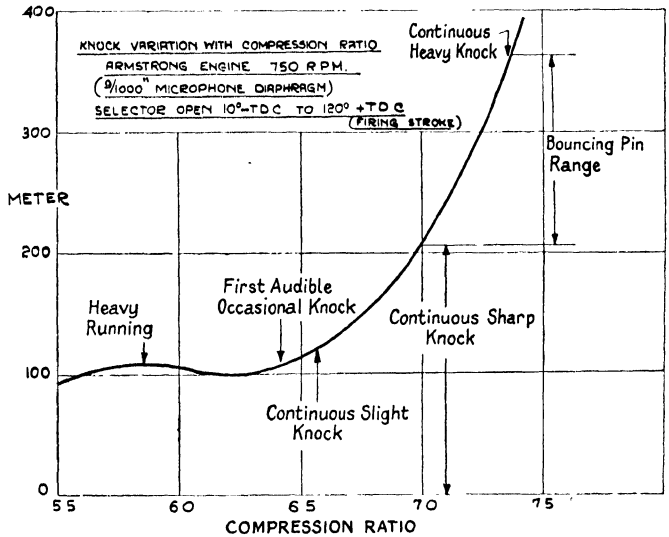


FIG. 212.—CURVE SHEWING THE EFFECT OF COMPRESSION RATIO UPON STROBOPHONOMETER READINGS. (STANSFIELD AND CARPENTER).
(Courtesy, The Institution of Petroleum Technologists.)

The curve given in Figure 212 refers to a test made with an Armstrong engine running on a spirit which allowed smooth operation at a compression ratio of 5·5 to 1. Starting from this ratio, the compression was increased and Strobophonometer meter readings taken at every increment of 0·1 ratio. It will be noticed that the noise first increases slightly with heavy running. After this stage, there is a slight drop in noise but still no audible knock. The drop may be due to the shape of the combustion chamber of this particular engine, which is altered in form with increase in ratio, by reducing the length of the pocket of small bore. Following the heavy running period, the meter reading begins to rise sharply, and the first faintly audible and intermittent knock commences. The meter reading has risen about 20 per cent. above the smooth running level by the time the knock is continuous but slight, and

at this intensity it is possible to distinguish easily between fuels of different anti-knock value. This is not possible with the bouncing pin. By the time the bouncing pin electrolytic cell gives 0·2 ml. of gas per minute, the meter scale reading has increased more than 100 per cent. from smooth running. The range of meter readings covering the usual bouncing pin range of knock is shown on the diagram, and much heavier intensities can be explored if desired, up to the point where pre-ignition may damage the engine.

So far no differences of importance have been detected between fuel knock ratings by means of this instrument and those taken with a bouncing pin on the same engine, neither has any difference been noted between results taken with very light, average or heavy knock, provided that pre-ignition is not present.

The Strobophonometer also lends itself to the measurement of fuel knock ratings in multicylinder engines and Stansfield and Carpenter quote a case of an aero-engine running at 2,100 r.p.m., with a noise level so high that shouting was inaudible in the engine house. In this case, a difference of 6 octane numbers between two fuels gave about 10 per cent. change in meter reading, although the knock was too light to be audible. At 2,000 r.p.m., it just became audible on the poorer fuel and the difference in meter readings between the two fuels was about 20 per cent. A further point of interest is that the microphone used in conjunction with the Strobophone can be so adjusted as to give a uniform response over a wide range of frequencies or to give a sharp cut-off at any desired frequency. This facilitates the selection of the noise of knock and improves the sensitivity of the instrument.

Such electric audibility methods have many other applications in engine and fuel research.

769. Temperature Methods of Measuring Knock Ratings.—Failure of an aircraft engine as a result of the use of a fuel of insufficient anti-knock value is nearly always the result of overheating of the cylinder unit. Generally speaking, fuels have a heating effect in this way in inverse proportion to their anti-knock value, but this is not always the case, benzole blends causing more over-heating than tetra-ethyl lead blends or straight spirits of the same anti-knock value under non-knocking or knocking conditions. In 1929, it was pointed out by S. D. Heron[50] of the Material Division of the Air Corps of the United States Army that a temperature method of rating fuels for aircraft use may prove to be more desirable than one depending on the intensity of knock, because the temperatures reached in relatively large air cooled engines under full throttle conditions may be as high as 200°F. below the plastic point of the pistol alloys employed.

The U.S. Army specification for Anti-Knock Fighting Grade Aviation

spirit, dated October 18th, 1932 (No. Y-3557-F.—see Chapter XVIII, paragraph 840), embodied such a method for rating fuels. The Ethyl Gasoline S. 30 engine was specified as standard, operating at 900 r.p.m. and 180—200°C., but with a thermo-couple plug instead of a bouncing pin. The thermo-couple was connected to a millivoltmeter for temperature measurements, capable of detecting a temperature change of 1°C.

Knock was then measured in terms of the recorded temperatures, the fuel giving the higher temperature being considered as of the lower anti-knock value and vice versa. The fuel feed for maximum knock was determined by temperature measurements in a manner analogous to that in bouncing pin operation and the intensity of knock was standardized at that giving a cylinder head temperature between 320 and 340°C.

770. Time Lag in Knock Rating Measurements.—In making anti-knock determinations by the direct matching of fuels, it is some-

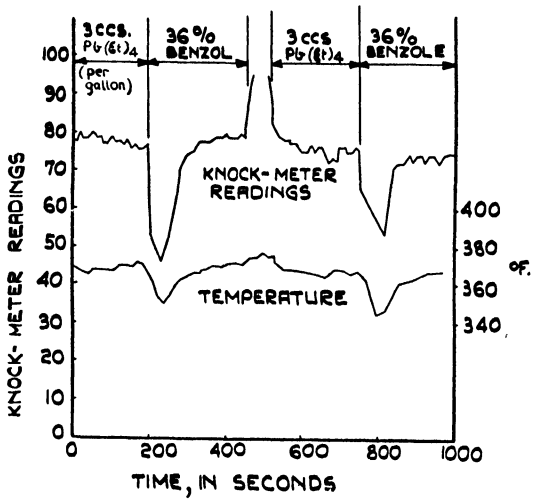


FIG. 213.—TYPICAL BOUNCING PIN RESULTS OBTAINED IN CHANGING OVER FROM ONE FUEL TO ANOTHER. (MAC COULL)

times observed that the knock instantly disappears when the carburettor is switched from one fuel to the other, even though the two fuels may be of equal anti-knock value. Sometimes the knock increases in intensity when the change over is made. This phenomenon, which is called *Time Lag*, is especially noticeable when matching fuels differing widely in composition, such as a benzole blend and a spirit containing tetra-ethyl lead, and has been studied by Neil MacCoull.[51]

Typical results obtained are reproduced in Figure 213, in which knock meter readings at 10 second intervals obtained in changing over from a Pennsylvanian gasoline containing 3 ml. of tetra-ethyl lead per

U.S. gallon to a blend of 36 per cent. benzole in the same spirit are plotted against time intervals. The variation of the individual readings from smooth lines indicates a characteristic of the bouncing pin readings. Since the mean value of the knock meter readings finally reached the same value after the change over that it had before, the two fuels are considered to be of equal anti-knock value.

The point of principal interest in such curves is the observation that from 100 to 200 seconds may be required after the change over before the knock resumes its normal value. Sometimes it is found that readings taken in less than 7 minutes are considerably in error. Even greater time lag is sometimes observed, but none has been noticed when changing from one leaded fuel to another. It is of interest to note that the piston temperature follows the change in knock meter ratings when changing from one fuel to another.

The reason for this time lag has not yet been definitely found, but it is believed to be due to differences in fuel volatility, leaded fuels containing more anti-knock material in their heavy fractions and benzole blends in their light fractions. Time lag is reduced when perfectly dry fuel-air mixtures are supplied to the engine cylinder.

The Effect of Engine Conditions upon Knock Ratings.

771. It has already been mentioned that knock ratings determined under one set of engine conditions are rarely the same under different conditions and that octane numbers determined on different engines show very wide variations. The reasons for these changes are to be found in considerations of the effect of various engine variables upon the relative knock ratings of fuels.

The difference between " absolute " knock ratings and relative knock ratings has already been stressed and it should be observed that the octane number scale is a relative scale only. That is, if under one set of conditions the octane number of a spirit is say, 50, and under other conditions it is, say, 60, the anti-knock properties of the spirit may have been increased by the change in conditions or the anti-knock properties of the octane-heptane blend may have decreased, that of the spirit remaining substantially constant. Another possibility is that both fuels change in absolute knock rating, though to different extents. The use of sub-standard fuels introduces further complications.

The Effect of Carburettor Setting on Relative Knock Ratings. —The importance of fuel-air ratio, or carburettor setting, upon the relative knock ratings of various fuels was first reported by Campbell, Lovell and Boyd in 1929.[52] The same workers have made a more detailed investigation into this phenomenon at a later date.[53]

Figure 214 is a reproduction of some results obtained by these in-

vestigators and is a plot of the results of a test comparing a spirit containing 1·1 mls. T.E.L. per U.S. gallon with four different concentrations of benzole in the same spirit. The bouncing pin readings plotted on the vertical axis indicate the relative intensity of knock for each fuel at the carburettor settings plotted on the horizontal axis. Thus, the spirit containing T.E.L. had its maximum tendency to knock at a carburettor setting corresponding to a mixture ratio of 14·1. If the mixture ratio were made either richer or leaner, the bouncing pin readings fell off, showing a decrease in intensity of knock.

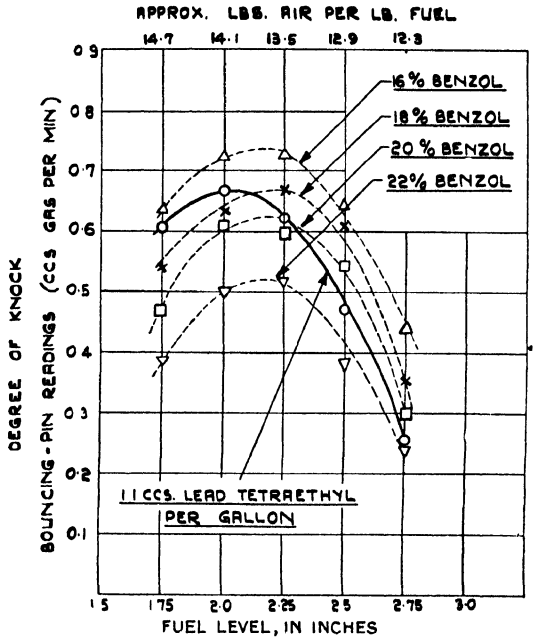


FIG. 214.—CURVES SHEWING THE EFFECT OF FUEL-AIR RATIO UPON RELATIVE KNOCK RATINGS

This diagram shows how the change in intensity of knock is not uniform for the two fuels as the carburettor setting is changed. This leads to two important generalizations. The first is that two fuels may knock alike at one carburettor setting and yet knock differently at some other carburettor setting. For example, referring to Figure 214, at the setting corresponding to a mixture ratio of 13·9, the 18 per cent. benzole blend knocked to the same extent as the spirit containing 1·1 mls. of T.E.L. But at richer mixtures this benzole blend knocked more than the same spirit and at leaner mixtures the benzole blend knocked less.

The second important generalization is that when comparisons are made between two fuels at independent carburettor settings for each fuel, the fuels may or may not knock alike according to the relative mixture

ratios. Thus, referring again to Figure 214, it may be seen that if comparison between the spirit containing T.E.L. and the benzole blends be made at a mixture ratio of 13·0 for the former and at a mixture ratio of 13·6 for the latter, it will be found that the leaded spirit knocks to the same extent as the 22 per cent. benzole blend. But, if both carburettor settings are adjusted to give mixture strengths of 13·6, then the leaded spirit knocks to the same extent as a 19 per cent. benzole blend. In other words, the apparent benzole equivalent of T.E.L. in motor spirit depends upon the carburettor setting at which the comparison is made.

The effect of mixture strength upon the relative knock ratings of T.E.L. blends and benzole blends increases as the spark timing is advanced. Similar effects are observed in the comparison of other types of fuel, e.g., octane-heptane blends, etc., etc.

In view of the marked effect of carburettor setting in this way, the question has naturally been asked what setting shall be used in making knock rating determinations. Campbell, Lovell and Boyd recommended in 1929 that such measurements be made using the mixture strength giving the maximum degree of knock for each individual fuel. This mixture ratio is well defined and can readily be found by making use of the same instrumentation as is employed for making the knock determination itself. This mixture ratio is a practical one because it lies within the range of ordinary engine operation.

This recommendation has now been universally adopted and when two fuels are compared for knock ratings, each fuel is separately adjusted to the mixture strength giving the maximum degree of knock. The knock rating is then made at these two mixture strengths.

772. The Effect of Ignition Timing.—A few years ago a common method of determining knock ratings was the measurement of ignition advance required to give a predetermined intensity of knock at a fixed compression ratio, or else the matching of fuels to give the same intensity of knock at a selected ignition advance. This procedure was used satisfactorily for some time, but gradually various discrepancies were observed. This led to a critical examination of the method. Stansfield and Thole[44] compared various fuels with benzene blends in Persian straight run spirit in an Armstrong engine and found that nearly all of these depreciated in knock rating relative to the benzene blends as the ignition advance was increased from 0° to 20° B.T.D.C. Alcohol blends relatively improved with retardation of the ignition, as also did vapour phase cracked spirit blends, but spirits containing T.E.L. became relatively lower in value.

Using a standard C.F.R. engine, operating at 600 r.p.m. and 212°F. jacket temperature, Campbell, Lovell and Boyd (loc. cit.) found variations in spark advance to be rather more important. For instance,

they found that in the case of a certain blend of 40 per cent. benzene in a petroleum spirit, the equivalent T.E.L. blend changed from 3·4 mls. T.E.L. to over 7·0 mls. as the ignition was advanced from 7° to 42° before top-dead-centre. For spark timings earlier than that for maximum power (in this case, 20°), the effect of spark timing on the comparison between fuels containing T.E.L. and those containing benzene was more pronounced than at spark timings after that for maximum power.

Spark timing was found to have a similar effect upon the relative knock ratings of benzene-heptane and iso-octane-heptane blends and upon the relative knock ratings of straight run gasoline and each of these two types of blends.

Because of these variations, Campbell, Lovell and Boyd recommended that all knock ratings be determined at the spark advance for maximum power. This setting is not materially affected by ordinary changes in fuel composition at compression ratios below the knocking point. This procedure is now followed in the standardized C.F.R. operating technique. The spark timing is automatically adjusted for changes in compression ratio.

773. The Effect of Knock Intensity.—In knock rating determinations it is usual to standardize the knock intensity at which measurements are made. This is particularly so in cases where the bouncing pin is used, because the latter requires a fairly high knock intensity for satisfactory operation. Apart from this, however, the knock ratings of most fuels are not appreciably altered by variations in knock intensity. Two fuels equal at one degree of knock are generally equal at either heavier or lighter knock. This has been demonstrated by Huff, Sabina and Hill (loc. cit.) and by Stansfield and Carpenter (loc. cit.) in work on audiometric methods of knock measurement (see paragraph 768).

774. The Effect of Air Humidity and Barometric Pressure.—Work conducted by Brooks, White and Allen[54] and by Brooks, White and Rogers[55] at the Bureau of Standards in connection with the Cooperative Fuel Research programme, included a study of the effect of air humidity upon the benzole and tetra-ethyl lead equivalents of various fuels. The effects of barometric pressure and air temperature were also studied.

The apparatus used in this work consisted of a standard C.F.R. engine operating at 600 r.p.m. and 212°F. jacket temperature. The air supply to the carburettor was conditioned by passage through a vertical tube, the temperature being controlled by passing steam or water of suitable temperature through copper spirals and the humidity was controlled by a jet of dry steam. The air was then passed over baffles to ensure homogeneity. Temperature and humidity were measured by

continuously passing part of the air supply over wet and dry bulb thermometers graduated at 0·2°C. and 0·1°C., respectively. This air sample was then rejected, as its humidity had been altered materially during passage over the wet bulb.

The lead equivalents of the fuels examined decreased with increasing humidity, the ratio of the lead equivalents at air humidities of 10 mms. Hg. and 40 mms. Hg. appeared to have a constant value of 1·325. The benzole equivalents of the fuels at different air humidities did not often vary by an amount greater than the experimental error.

Later work by Brooks, White and Rodgers (loc. cit.), in which octane numbers were determined directly by comparison, indicated that the octane numbers of Texas spirit-Californian Aviation spirit blends varied to a noticeable degree with change in humidity (2—6 octane numbers for a change of humidity from 6 to 45 mms. Hg.), but that other blends were not effected to an extent outside that of experimental error.

It should be noted, however, that the humidity variations mentioned above are very large and not likely to be encountered in practice in this country.

The effect of barometric pressure on relative knock ratings is very small and is inconsiderable over the pressure range 720—800 mms.

775. The Effect of Lubricating Oil in Knock Rating Measurements.—The effect of lubricating oil in the combustion chamber on the knock ratings of fuels has been considered in England by King and Moss[56] of the Air Ministry, and in America by Stacey.[57] This subject is important because a certain amount of lubricating oil always finds its way into the combustion space via the cylinder walls and piston rings and also because a present tendency is to add a small amount of lubricating oil to the fuel used in high duty engines to help lubricate valve stems.

In their work, King and Moss used five typical lubricating oils, a Russian oil (naphthene base), a Venezuelan oil (asphaltic base), a light and heavy distillate from Pennsylvanian oil (paraffin base) and a refined residual oil from the same crude. The fuels used were aviation spirit plus benzole or T.E.L. and a series of blends made up with varying amounts of paraffins, naphthenes and aromatics. A Ricardo E. 35 engine was used, running at 900 r.p.m., and knock ratings were measured by H.U.C.R. determinations.

It was found, at normal induction temperatures, that T.E.L. blends suffer a deterioration in anti-knock value when lubricating oils are added to them, asphaltic base oils having the greatest and paraffinic residual oils the least effect. Vegetable oils, such as rape or castor, have no such deleterious effect. Thus, a petrol had an H.U.C.R. of 4·5 and the addi-

tion of 12 mls. T.E.L. per Imperial gallon raised this to 6·0. The addition of 12 per cent. of an asphaltic base lubricating oil to this blend reduced the H.U.C.R. to 5·25 and the addition of the same amount of a Pennsylvanian lubricating oil reduced the H.U.C.R. to 5·95 only. At induction temperatures of 40°C. and above, all the lubricating oils became deleterious to the same extent, including the vegetable oils. Blended fuels containing no tetra-ethyl lead are also deteriorated in knock rating in the presence of lubricating oils, but naphthenic spirits are less affected than aromatic spirits.

The work of Stacey did not include such high lubricating oil concentrations. The effect of such oils was determined in two ways, (*a*) by adding lubricating oil to the fuel and (*b*) by using loose fitting pistons to allow lubricating oil to pass from the crankcase into the combustion chamber. The effect of possible differences in piston temperature due to differential rates of heat transfer between the piston and the cylinder wall was eliminated by changing the temperature of the oil in the sump. In this work an Ethyl Gasoline S. 30 engine was used, operating at 212°F. jacket temperature, 600 r.p.m. and inlet air temperature 85°F.

The results obtained, using two lubricating oils of the same viscosity at 210°F. (62 sec. Saybolt), one from Pennsylvania crude and the other from Coastal crude, indicated that, under conditions of low oil consumption (approximately 0·5 per cent. of the fuel consumption), obtained by using a close fitting piston and two oil rings, no relative change in octane rating was obtained between the two oils. On the other hand, a difference in lubricating oil temperature of 75°F. (from 110°—185°F.) may cause an error of ± 1 octane number.

All knock-testing engines should be designed and run with the oil consumption at the minimum for safety and good lubrication. This improves the accuracy of the results, decreases the carbon formed in the combustion space and results in steadier running of the engine. The oil temperature should be kept constant and as low as possible consistent with good lubrication. Increase in oil consumption, from 0·5 to 2·0 per cent. of the fuel consumption, usually causes a decrease in knock rating of 1 octane number and often causes irregular running.

776. The Effect of Engine Temperatures Upon Knock Ratings.—Of all the engine variables having an effect upon the relative knock ratings of various fuels, engine temperature is, perhaps, the most important. This variable largely accounts for the large differences in results obtained on different engines.

The marked effect of cylinder temperature in this direction was observed by S. D. Heron in 1928, and the use of a 300°F. jacket temperature, obtained by circulative-evaporative cooling with a suitable ethylene glycol-water mixture, on a Series 30 Ethyl Gasoline engine, was

specified for the rating of aircraft fuels in U.S. Army Specification, Y-3557-A.

One of the most noticeable effects of engine temperature is that, relative to benzole blends, the knock ratings of tetra-ethyl lead blends increase with rise in temperature. On an absolute knock rating scale (e.g., one of H.U.C.R.'s), the anti-knock effect of T.E.L. decreases with rise in temperature, but to a less extent than that of benzole or octane. Towards the end of 1929, E. Bartholemew, of the Ethyl Gasoline Corporation, published a curve showing the amount of T.E.L. in an aviation spirit required to equal the anti-knock value of a blend of 60 parts Mid-Continent gasoline and 40 parts benzole. This is reproduced in Figure 215. A year later, R. Stansfield and F. B. Thole[44] of the Anglo Persian Oil Company, confirmed these results on a wide range of benzole blends and leaded fuels, but showed, for the first time, that the effect was a purely relative one as mentioned above.

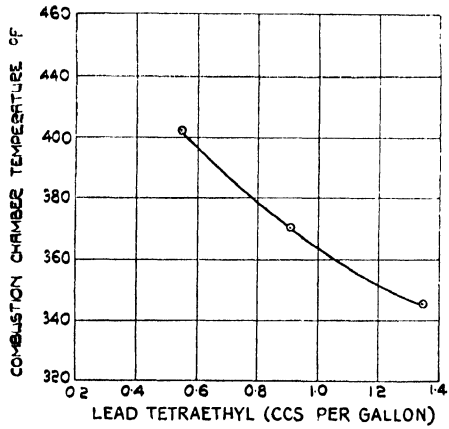


Fig. 215.

The effects of jacket and cylinder head temperatures upon the relative knock ratings of benzole blends and fuels containing T.E.L. have been studied in detail by Edgar in tests on a C.F.R. engine[58] and on a S. 30 engine,[59] whose original papers should be consulted for complete information.

777. Garner and Dodds[60] have recently published the results of experiments in three different engines which are of much interest in showing the large effects of temperature upon knock ratings in general. These investigators found that in a water cooled engine fitted with solid steel valves, T.E.L.-benzole equivalents are comparatively little influenced by variation in jacket temperature, the values at 100°C. and 150°C. only varying by an amount slightly greater than the experi-

mental error. With a water cooled engine fitted with liquid cooled valves, the differences were much more marked and at 50°C., a mixture of 75 parts benzole and 100 parts gasoline required about one third more T.E.L. in the standard fuel to give a spirit of equal anti-knock value, than did a similarly proportioned benzole-gasoline blend under the same conditions in the solid valve engine. With an air cooled engine, the amount of T.E.L. required to equal a benzole mixture in anti-knock value was, in general, less than that in either of the other two engines. In the air cooled engine, between 50° and 100°C. jacket temperature, there was a marked improvement in the relative anti-knock value of T.E.L. as compared with benzole. This improvement continued at higher temperatures, but was much less marked over the range 100° to 150°C. At still higher temperatures, however (300° to 400°C.), the relative improvement in anti-knock value again occurred to a very marked extent. At an engine temperature of 50°C. approximately 5 mls. T.E.L. per gallon was equivalent to 80 parts of benzole added to 100 parts of standard gasoline, but at a temperature of 400°C., the same relative anti-knock value was obtained with only 1·2 mls. of T.E.L.

The figures quoted in Table 161 were obtained by Garner and Dodds in three different engines and refer to the amounts of T.E.L. (mls. per Imperial gallon) and benzole (parts per 100 parts) required to be added to a reference fuel to equal the knock ratings of each of five typical English motor fuels, A, B. etc., E. being highly cracked. All the figures refer to a jacket temperature of 100°C., and show the extreme importance of standardized conditions in knock rating tests.

Tests were also carried out to determine the effect of exhaust valve temperature and it was found that, even among fuels of equal anti-knock value, exhaust valve temperatures varied considerably under heavy knocking conditions. In general, these were higher with benzole blends and cracked spirits than with T.E.L. blends.

Using oil jet cooling for the piston in an engine fitted with cooled valves resulted in a much higher knock rating of cracked fuels relative to T.E.L. blends. The importance of engine temperature upon relative knock ratings is also evident in the work of the C.F.R. Committee on the correlation of tests results with road tests, which has already been described. Here it was found that the use of a high *mixture* temperature was required to reduce test engine octane numbers to the same values as those obtained in road tests.

Blends of *n*-heptane and *iso*-octane now used as knock rating standards suffer comparatively little change in anti-knock value as engine temperatures are raised. Most commercial fuels, therefore, are found to have lower octane numbers at high engine temperatures than at low temperatures. In general, in the S. 30 engine the fall in octane numbers of various fuels, when increasing the jacket temperature

TABLE 161.—AMOUNTS OF T.E.L. AND BENZOLE IN A REFERENCE FUEL EQUIVALENT TO TYPICAL BRITISH PETROLS IN THREE DIFFERENT ENGINES AT JACKET TEMPERATURES OF 100°C. (GARNER & DODDS.)

Petrol	Air-Cooled Engines		Water-Cooled Engines			
			Solid Valves		Cooled Valves	
	T.E.L. mls. per Imperial Gallon	Benzole. Parts per 100 parts of Reference Fuel	T.E.L. mls. per Imperial Gallon	Benzole. Parts per 100 parts of Reference Fuel	T.E.L. mls. per Imperial Gallon	Benzole. Parts per 100 parts of Reference Fuel
A.	0·6	11	0·5	10·0	0·6	12
B.	1·0	19	1·05	20·5	1·25	25
C.	1·4	27	1·2	24·5	1·5	29
D.	1·75	33	1·5	29·0	1·75	33
E.	4·15	78	2·6	49·5	3·7	63

from 150°C. to 190°C., is much larger than the fall from 100° to 150°C. Blends of pure benzene with a reference fuel of low octane number may decrease in octane number from 8 to 9 units on an increase in jacket temperature from 150° to 190°C. The conditions in the S. 30 engine at 900 r.p.m. and 190°C. are more severe than the C.F.R. conditions of the Motor method, and rather lower octane number ratings are obtained.[61]

STANDARD FUELS IN KNOCK RATING MEASUREMENTS

778. When comparison methods began to be employed in knock rating measurements it became necessary to employ some kind of calibrated reference standard. Usually a laboratory would set aside a supply of some stable spirit, either of very poor or very good anti-knock quality. The rating of a sample was then determined by the amount of some anti-knocking compound required in the standard or in the sample to obtain a match.

Numerous scales came into existence. Some laboratories reported their results in terms of the amount of aniline, tetra-ethyl lead, benzole, toluole, xylidine or iron carbonyl required in a reference fuel to match the sample or vice versa. Many used benzole and reported the data as "benzole equivalents," no mention being made of the nature of the benzole or of the reference fuel. Consequently, a sample that was rated as having a "50 per cent. benzole equivalent" might well have a 30 or a 70 per cent. equivalent in some other laboratory where an entirely different reference fuel was in use.

The experiences of the Standard Oil Development Co., in this field, are probably typical.[62] This Company found it necessary at the begin-

ning of their knock-testing work to devise a method of measurement, to prepare a reference fuel and to set a scale for the expression of results. Knock-ratings were determined by finding the proportion of benzole required in the reference fuel to match the sample under test. The standard fuel, of poor anti-knock quality, was a straight run naphtha from Mid-Continent crude. A knock rating scale was adopted which consisted of ten units (0 to 10) and covered the range of the then existing commercial fuels. A rating of 10 was arbitrarily assigned to this reference fuel and one of 0 to a 50/50 blend with motor benzole. Intermediate points were specified in terms of the two, in such a manner that a difference of one unit would result approximately in the same change of knock intensity at all parts of the scale. From time to time, it was necessary to prepare new batches of reference fuel. This was done by using straight run spirit from the same crude and duplicating as nearly as possible the distillation curve and anti-knock quality of previous batches.

This procedure was subject to error in several respects. First, a spirit is composed of a large number of hydrocarbons and there is no known method of making certain that successive batches are of the same composition. The anti-knock quality required was obtained either by altering the distillation curve or by blending with some other suitable straight run gasoline. An exact match was dependent on the accuracy of the test method. There is a cumulative error in the rating of a standard fuel, though it may be obviated to some extent by checking against retained samples of previous batches, but until comparatively recently, no pure compounds of anti-knock quality suitable for primary standards were available for definitely determining whether or not the retained samples still possessed their original anti-knock value.

779. Primary Reference Standards.—During 1930, the Cooperative Fuel Research Committee in America recognized the confusion that existed due to the use of so many different knock rating scales and adopted the use of mixtures of *n*-heptane and *iso*-octane (2-2-4 trimethyl pentane) as primary standards, as originally recommended by Edgar in 1927.[63] Of these, normal heptane occurs in a reasonable degree of purity in the pine oil, Pinus Sabiniana, and *iso*-octane can be produced synthetically from tertiary butyl alcohol. The chief advantage of pure hydrocarbon standards is that they can easily be reproduced at any time and do not deteriorate on storage. Normal heptane has a very low anti-knock value and *iso*-octane has anti-knock properties better than any motor fuel commercially available in quantity. It is thus possible by blending the two in suitable proportions to match the anti-knock value of any spirit. Results are expressed in terms of octane numbers, as already defined (see paragraph 756).

The physical properties of these two hydrocarbons are very similar, thus :—

	N-Heptane.	*Iso-Octane.*
B.P. 760 mms.	98·4°C.	99·3°C.
Specific Gravity, $\frac{20}{20}$ °C. ..	0·6847	0·6914
Viscosity at 18·5°C.	0·00427	0·00543
Refractive Index at 20°C. ..	1·3874	1·3921
Air-Fuel Ratio for complete combustion		

and it follows from this that the fuel-air ratios obtained with various mixtures of heptane and octane will not be materially altered by variation in the proportions of the two constituents. With benzene-heptane blends, of course, considerable variation is obtained.

The chief advantages of *iso*-octane over benzene or toluene as a high anti-knock standard are held to be as follows :—

(1) Octane blends show a smaller drop in knock rating with increase in cylinder temperature than is the case with blends of benzene or toluene.
(2) The knock ratings of mixtures rich in benzene increases much more rapidly than that of the corresponding octane mixtures, hence experimental errors due to inaccuracy of blending become more serious in the case of benzene mixtures at high concentration.
(3) Fuels containing high proportions of benzene are more liable to give pre-ignition and overheating of the cylinder head than octane mixtures.

780. Secondary Reference Fuels.—Octane-heptane blends are now almost universally used as primary knock rating standards, but both heptane and *iso*-octane are very expensive and cost about £5 per U.S. gallon in this country. Therefore the need for secondary reference fuels has arisen, which may be calibrated directly against octane-heptane mixtures and used for routine tests.

At the beginning of 1931, the Standard Oil Development Company released their specially prepared secondary reference fuels (or sub-standard fuels) for use in the industry generally, with the full approval of the C.F.R. Committee. The first two fuels issued were known as A-2 and B-2. Both were straight run products, A-2 being a blend of 83 per cent. Mid-Continent and 17 per cent. Colombia naphthas, while B-2 was made from a California crude. To eliminate the disadvantages of small and frequently prepared batches, A-2 and B-2 were made in

quantities estimated to last for two or three years. These secondary standards were then calibrated against octane numbers. At that time, the calibration curves were made for the Ethyl Gasoline Corporation S. 30 engine, running at 600 r.p.m. and at a jacket temperature of 212°F. Later, similar curves were made for the C.F.R. engine by the "Research Method," and still later by the "Motor Method." When these fuels were prepared, the general practice was to use an anti-knock substance such as benzene or tetra-ethyl lead in reference standards to cover the range of commercial fuels. The advent of high octane number cracked, hydrogenated and aviation fuels soon called for another secondary standard above the range covered by the fuel B-2. It was also found that there were advantages in using two widely separated secondary fuels for as much of the octane number range as possible. These two factors led to the production of a high octane number reference fuel, which became known as C-6, a stabilized Smackover casing-head spirit.

TABLE 162.—PROPERTIES OF SECONDARY REFERENCE FUELS PREPARED BY THE STANDARD OIL DEVELOPMENT COMPANY.

Fuel	A–2	A–3	B–2	C–6
Octane Number				
C.F.R. Motor Method ..	48·4	44·2	68·0	76·0
C.F.R. Research Method ..	48·4	—	68·0	76·2
S. 30, 212°F., 600 r.p.m. ..	50·0	—	67·6	76·6
Gravity, A.P.I.	60·3	62·8	55·6	67·3
Colour, Saybolt	+ 30	+ 25	+ 30	+ 25
Sulphur, Per Cent.	0·025	0·057	0,024	0·017
Doctor Test	Passes	Passes	Passes	Passes
Acid Heat Valve, °F.	1	4	2	2
Reid Vapour Pressure, lbs. ..	5·5	3·9	5·6	6·4
Copper Dish Gum, mgs. ..	6·0	4·1	5·5	2·3
Air Jet Gum, mgs.	1·4	0·1	0·2	0·5
Aniline Point, °F.	131	138	74	127
Corrosion at 122°F.	Passes	Passes	Passes	Passes
Initial Boiling Point, °F. ..	115	133	111	122
End Point, °F.	389	361	359	316
90% Distillate at, °F.	343	307	332	248
Recovery, Per Cent.	98	98	99	98
Loss, Per cent.	1·0	1·0	0·5	1·0
% at 122°F. (50°C.)	—	—	0·5	—
140°F. (60°C.)	0·5	—	2·0	4·0
158°F. (70°C.)	4·0	2·0	6·0	19·0
176°F. (80°C.)	8·0	5·5	10·5	40·0
212°F. (100°C.)	25·0	22·0	23·0	75·0
248°F. (120°C.)	46·5	50·5	43·0	90·0
284°F. (140°C.)	68·0	80·0	67·5	94·5
356°F. (180°C.)	93·5	98·0	98·0	—

The supply of fuel A-2 has now been exhausted and has been replaced by a fuel A-3, prepared from Pennsylvanian crude. New fuels, C-7 and C-8, have also been prepared to replace C-6, the stocks of which have rapidly been reduced. C-7 has an octane number of about 76 by the C.F.R. Motor Method. A-3 has an octane number of approximately 44. The properties of these fuels are detailed in Table 162.

These fuels have fulfilled a long felt want. The volatility of C-6 is, however, rather high, and is not suitable for use in hot climates.

Other secondary standards may be used equally well. Usually blends of benzene with a well stabilised straight run spirit of low anti-knock value are quite satisfactory. Care should be taken that the spirit is free from olefines and of good stability, so that it will not deteriorate in knock rating on storage. Its volatility should be low so as to minimize the possibility of evaporation losses and consequent change of anti-knock value on storage.

Metallic Anti-Knock Dopes

781. Tetra-Ethyl Lead.

Historical Development.—Tetra-ethyl-lead ($Pb\ (Et)_4$), the most effective anti-knock dope known, was discovered in 1921 in America by T. Midgley, Junior, and T. A. Boyd, in the Research Laboratories of the General Motors Corporation. Mr. C. F. Kettering of the same Company had developed a lighting plant for use on farms, on boats and in other places where ordinary electric power was not available. Petrol had been used as fuel in all the experimental work but due to the objections of the underwriters to the storage of the petrol required to operate the engines, attempts were made to substitute kerosene for the petrol previously used. Immediately the knocking properties of the kerosene were observed and it was realized that unless this could be prevented the compression ratio of the engine must be reduced and a certain amount of power output sacrificed. At this point Mr. C. F. Kettering outlined the problem to the above-named gentlemen, and suggested a line of research. This was carried out and the result was the discovery of the extreme efficacy of tetra-ethyl lead. In 1921, appeared the first English patent covering the use of such organo-metallic dopes as knock suppressors. This was E.P., 196,237 of June 23rd, taken out by Midgley and the General Motors Corporation.

Very little time elapsed before "Ethyl Gasoline," i.e., petrol containing tetra-ethyl lead, was made available to the American public. On February 1st, 1923, it was introduced by the newly formed "Ethyl Gasoline Corporation." The original method of supply was by means of a small gas-tight container with pump called an "Ethylizer," which

delivered a measured amount of " ethyl fluid " (containing the tetra-ethyl lead) into the fuel tank.

Following the introduction of Ethyl petrol in America, the first warning as to the poisonous character of tetra-ethyl lead was issued in England in the form of an Editorial article in " The Chemist and Druggist " for February 2nd, 1924. In 1925, the first propaganda began against the use of Ethyl petrol in America and on May 5th of the same year the Ethyl Gasoline Corporation voluntarily abandoned the sale of the spirit despite the fact that 300 million gallons had been used without any sign of lead poisoning among its users. During the same month, a committee was appointed by the United States Public Health Service to enquire into " the health hazards involved in the retail distribution and general use of tetra-ethyl lead in motor fuel."

The report of this committee appeared dated January 17th, 1926, and it concluded that " there are no grounds for prohibiting the use of Ethyl gasoline of the composition specified (1 in 1,300 parts by volume) as a motor fuel, provided that its distribution and use are controlled by proper regulations." In April, 1926, regulations to be adopted for the manufacture of tetra-ethyl lead and its blending with motor fuel were published. These required chemical workers and blenders to undergo periodic examination, blending to be carried out only in tank car lots and containers to be labelled " Ethyl Gasoline containing tetra-ethyl lead. To be used for motor fuel only."

As a direct outcome of this report, the sale of Ethyl gasoline was resumed in the United States on June 1st, 1926.

In January, 1928, the Anglo American Oil Company introduced Pratts' " Ethyl petrol " in England after the conclusion of an agreement with the Ethyl Gasoline Corporation. Immediately the question of a possible hazard to health was raised. A well known newspaper conducted an enquiry into the question and on February 29th it was announced in the House of Lords that an Inter-departmental Committee, consisting of representatives of the Ministry of Health, the Home Office and the Medical Research Council, would be appointed to consider the poison hazard. This committee presented an interim report on July 16th, 1928, in which they concluded that although there was no evidence to show that the use of ethyl petrol as a motor fuel involved more dangers to health than the use of ordinary petrol, the observance of the regulations suggested by the United States Committee was desirable. The latter consisted of warnings that ethyl petrol should only be used as a motor fuel and not for cooking and cleaning purposes, the labelling of cans and pumps and the use of a distinctive red dye in the fuel itself.

The final report of this committee was presented February 10th, 1930, and in it the same conclusions were arrived at.

782. The Use of Tetra-Ethyl Lead in Motor Fuels.—The successful development of tetra-ethyl lead as an anti-knock agent in marketed motor fuels was the result of much careful research. It was soon noticed that this substance had a deleterious effect upon the combustion chambers, pistons and valves of engines in which it was used, due to the accumulation of metallic lead. Consequently, steps were taken in an attempt to overcome this disadvantage. It was then found that if certain halogen compounds were added to fuels containing tetra-ethyl lead, lead halides were formed as the end products in the combustion. These were found to be non-fluxing and did not attack the engine. The patent[64] disclosing this discovery mentions the use of carbon tetrachloride, bromine, chlorine and iodine compounds in this connection. At a later date, it was found that the addition of a lubricant for the valve stems and piston rings was an advantage and such compounds as monochlor naphthalene were suggested for this purpose.[65] This compound is also known as "Halowax-oil." The mixture of tetra-ethyl lead, halogen compound (ethylene dibromide is now used) and lubricant is termed "Ethyl Fluid" and is dyed red with Sudan IV dye. When ethyl fluid was first introduced into this country, it had the following approximate composition.

Tetra-ethyl lead	54·6 % volume.
Ethylene dibromide	36·4 % ,,
Monochlor naphthalene ..	9·0 % ,,
Sudan IV dye	0·01% ,,

The main disadvantage of motor fuels containing tetra-ethyl lead is the fouling of the engines with lead deposits which occasionally results. The type of deposit (when not obscured with carbonized oil) varies with combustion conditions, being grey and fluffy during light load conditions under which imperfect combustion conditions obtain. It has been stated that metallic lead is present at this stage and that contamination of the lubricating oil with lead occurs. At cruising speeds, most of the lead is blown out of the exhaust as yellow lead bromide, as intended by the inclusion of ethylene dibromide in "Ethyl fluid." On heavy loads the deposits remaining in the engine become browner in colour. It is quite conceivable that lead products ranging from metallic lead to lead bromide, lead sulphate and the higher lead oxides are formed, according to the conditions of combustion, such as temperature and mixture strength, sulphur content of the fuel, etc. The production of lead deposits in the combustion chamber is, however, not of serious dimensions. A much more important occurrence is the corrosion of exhaust valves, their seats and guides, which may be noticeable in certain engines. A combination of good design and material will overcome any such

troubles and, in any case, these will never be so bad as the damage done by operating under knocking and high temperature conditions in the cylinder. The effect of tetra-ethyl lead upon the valves and seats is largely a function of temperature and under normal working conditions, the valve should be " black," say 480°—510°C., and not exceed 595°C., under full lead conditions. Austenitic steels of various specifications have been used with success and good valve steels of the type " K.E. 965 " and " Era " are very satisfactory.

The valves should have wide seats to get rid of the heat as efficiently as possible to the cylinder head and also reduce the unit loading on the seat inserts. High nickel-chrome steels may be used with ethyl petrol with satisfaction, even on air-cooled radial engines, but cobalt-chrome steel valves are liable to attack if they are not adequately cooled. " Nitriding " is rather bad for corrosion and particularly where ethyl petrol is concerned.[66]

783. The Anti-Knock Properties of Tetra-Ethyl Lead.—When tetra-ethyl lead is added to a normal motor fuel, the anti-knock value of the latter is increased, but the increase so obtained is not directly proportional to the amount of tetra-ethyl lead added and varies with the nature of the base spirit. It is found that the anti-knock effect of tetra-ethyl lead falls off with increasing concentration in all cases and that it is possible to have two fuels of the same initial knock rating which have their knock ratings raised to different amounts on the addition of the same amount of tetra-ethyl lead. These points are shown in Figure 216.

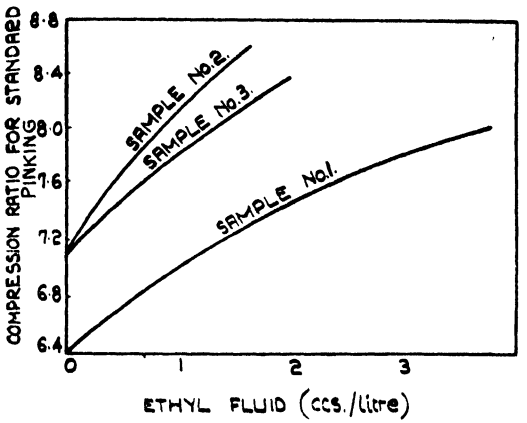


Fig. 216.—Curves shewing the Effect of Ethyl Fluid on Samples of Spirit from Different Sources.

A further important point with regard to the effectiveness of this anti-knock material is that, *relative to benzole or iso-octane*, its anti-knock effect increases with rise in engine temperature, as already shown.

Compared with other fuels, therefore, tetra-ethyl lead blends have the advantage that they are more suitable in hot running engines, for example, air cooled aero engines and motor cycle engines, etc., and any method of measuring knock ratings involving high temperature conditions is favourable to them. (Cf., the relative ratings of cracked spirits and ethyl petrols by the C.F.R. Research and Motor Methods.)

It has already been mentioned that different spirits vary in the extent to which their knock ratings are raised by a given amount of tetra-ethyl lead. This property may be termed "lead susceptibility" and is important in determining the cost of raising the anti-knock value of a spirit to a predetermined value by the addition of lead. It has been studied by Hebl and Rendel,[67] by Thole and Stansfield,[68] and by Hebl, Rendel and Garton.[69] The first named investigators considered the results of H.U.C.R. tests in a Ricardo E.35 engine and came to the conclusion that the improvement in H.U.C.R. was some exponential function of the concentration of tetra-ethyl lead and might be expressed by the relation.

$$I = SN^K$$

where I is the increase in H.U.C.R.

S is a measure of the steepness of the curve relating H.U.C.R. with concentration of tetra-ethyl lead, and expresses the effectiveness of the latter in raising the H.U.C.R. or the "lead susceptibility" of the fuel.

N represents the number of millilitres of tetra-ethyl lead added to 1 U.S. gallon of fuel.

K is a constant which represents the curvature of the line.

This equation may be written in the form

$$K = \frac{\log I - \log S}{\log N}$$

from which the value of K may be determined. Hebl and Rendel found that for some 60 or 70 different gasolines the value of K was substantially constant at 0·75, and that, consequently

$$S = \frac{1}{N^{0.75}}$$

The value of S varied considerably, spirits of high H.U.C.R. tending to have higher lead susceptibilities than those of low H.U.C.R. There are, however, many exceptions to this generalization, as shown in the following table.

TABLE 163.—H.U.C.R.S AND LEAD SUSCEPTIBILITIES OF GASOLINES FROM DIFFERENT CRUDES. (HEBL AND RENDEL.)

Source of Crude	H.U.C.R.	Lead Susceptibility (S)
California	5·40	0·54
Mid-Continent	4·99	0·40
West Texas	5·17	0·36
Dubbs cracked gasoline from mixed Mid-Continent and West Texas crudes ..	5·61	0·35
Burma	5·59	0·34
Persia	4·80	0·29
Roumania	4·91	0·22

Experimental work also showed that there was a relation between fuel volatility, H.U.C.R. and lead susceptibility, the more volatile spirits requiring less tetra-ethyl lead to reach a given anti-knock value, which fact was not wholly accounted for by their higher H.U.C.R. By expressing fuel volatility in terms of dew points (see Chapter XV), it was found that in the case of straight run gasolines from any one crude, the H.U.C.R. and lead susceptibilities were inverse functions of the dew point. Cracked spirits were found, in general, to have lower lead susceptibilities than straight run spirits but, of course, to have higher H.U.C.R.s.

With regard to the use of cracked stock for reducing the amount of tetra-ethyl lead required to meet a given H.U.C.R. specification, it is found, in general, that unless this material has an exceptionally high H.U.C.R., it has to be used in fairly large proportions to be very effective, because of its influence in lowering the lead susceptibility.

The following apparent anomaly mentioned by Hebl and Rendel is interesting. A particular gasoline of H.U.C.R. 5·0 was blended with 1·0 ml. tetra-ethyl lead per gallon, which raised the H.U.C.R. to 5·4. When this blend was mixed in equal proportions with an undoped straight run gasoline of H.U.C.R. 5·4, the resulting material had an H.U.C.R. of over 5·4. This effect was due to the fact that the effectiveness of tetra-ethyl lead is not linear with concentration so that the 0·5 ml. of tetra-ethyl lead per gallon in the final mixture produced an increase in H.U.C.R. which was more than half as great as that produced by the 1·0 ml. per gallon in the first spirit. This kind of anomaly is emphasized if the lead susceptibility of the gasoline of higher H.U.C.R. is greater than that of the gasoline to be doped.

784. A short time after the publication of the above results of Hebl and Rendel, Thole and Stansfield (loc. cit.) showed that while the nature of K (as defined above) may be constant for fuels tested in the E. 35 engine, it varies over a wide series of tests in the Armstrong

engine, and quoted the case of three different spirits for which the value of K was 0·888, 0·529 and 0·710 respectively. They also stated that tests made in the Armstrong engine with Persian spirit blends showed that the effect of volatility upon lead susceptibility was exactly the reverse of that stated by Hebl and Rendel, and that this result was independent of the engine used, because tests on C.F.R. and S.30 engines verified those made on the Armstrong engine. The results of Hebl and Rendel do not, therefore, apply to all fuels.

During the early part of 1933, Hebl, Rendel and Garton [69] extended their previous work on lead susceptibility in terms of H.U.C.R.'s to embrace the newly standardized method of reporting anti-knock values in terms of octane numbers, as determined on the C.F.R. engine, at jacket temperatures of 212°F. (100°C.) and 300°F. (148·9°C.), and gave several blending charts for determining the amount of tetra-ethyl lead required to obtain various octane numbers. Reference should be made to the literature cited for further details.

One important point was observed, however, which is worthy of note. In the case of certain West Texas gasolines, severe acid treatment may leave certain compounds in the spirit which render the first few millilitres of tetra-ethyl lead practically ineffective, after which the effect of further lead addition is normal. This " lag " in the effectiveness of tetra-ethyl lead is reduced by redistillation of the spirit and is believed to be due to the presence of certain sulphur compounds, possibly di-sulphides. It is only observed in rare cases.

The lead susceptibilities of various pure hydrocarbons have been reported by Garner and Evans,[70] who, as a result of tests carried out on 20 per cent. blends of various hydrocarbons in A-2 reference fuel, concluded that there is a definite rise in the lead susceptibility in all series as the length of the paraffin chain increases and as the octane number falls. The increasing order of lead susceptibility was found to be aromatics, cyclohexanes, cyclopentanes and, most responsive of all, α-olefines.

785. The Manufacture of Tetra-Ethyl Lead.—The manufacture of tetra-ethyl lead is effected on a large scale by the interaction of metallic lead (in the form of an alloy with metallic sodium) and an alkyl halide. Various modifications of this procedure have been proposed.[71] The consumption of metallic lead for the manufacture of tetra-ethyl lead in the United States has been as follows :—[72]

1927. 1,300,300 lbs.
1928. 2,700,000 lbs.
1929. 5,000,000 lbs. (estimated).

786. Iron and Nickel Carbonyls.—Although they are effective

anti-knock agents, second only in effectiveness to tetra-ethyl lead, iron and nickel carbonyls have not been developed for this purpose to the same state of perfection as T.E.L. In Germany iron carbonyl has been marketed in the motor fuel "Motyl," but not to any great extent because of the deposit of iron oxide which it leaves on sparking plugs and valve stems. Nickel carbonyl is susceptible to traces of moisture[73] and is about half as effective as tetra-ethyl lead in raising the knock rating of a given fuel. The use of iron carbonyl has been covered by various patents[74] and its manufacture by the interaction of carbon monoxide or gases rich in carbon monoxide with reduced metallic iron at elevated pressures and temperatures has been similarly protected.[75]

It has been stated that the decomposition of iron carbonyl by light can be retarded or even avoided by the addition of colouring matters, such as soluble azo dyes, oil brown and iron compounds of acetyl acetone, etc., etc.,[76] or amines.

787. Other Metallic Anti-Knock Dopes.—Of the very many other anti-knock dopes proposed, none has been used to any great extent and it is highly probable that none has been developed beyond the experimental stage.

The petrol soluble compounds of iron have been mentioned, e.g., the iron acetyl acetonates,[77] organic ferro- and ferri-cyanides,[78] ferric compounds of oxymethylene camphor[79] and ferric compounds of β diketones.[80] Similarly, copper compound[81] and the alkali metals[82] are the subject of numerous patents.

The Knock Ratings of Pure Hydrocarbons *

788. As already mentioned, the various classes of hydrocarbons differ widely in the extent to which they exhibit anti-knock or pro-knock properties. This was first made evident by the celebrated work of Ricardo,[83] who showed that of the various types of hydrocarbons, the aromatics withstood detonation to the greatest extent and the straight chain paraffins the least. The results obtained in this investigation are shown in Table 164.

Ricardo found that in the case of ethyl alcohol, acetone, toluene and xylene, it was impossible to induce detonation under any circumstances. When benzene and certain other fuels were tested in the variable compression engine and attempts were made to induce knocking by raising the compression, occasional pre-ignition occurred when the compression ratio exceeded 7 to 1, these pre-ignitions being denoted by a dull thud and an immediate drop in speed and power.

* Since this section was written further information on the Knock Ratings of pure hydrocarbons, both in solution in standard spirit and also in the undiluted state, has been published by Lovell, Campbell and Boyd. (Ind. Eng. Chem., 1934, 26, 475 and 1105.]

Ricardo also found that some naphthenes, methanol and methylated spirit exhibited the same phenomenon. This was, however, probably more a function of engine design than a property of the fuels.

TABLE 164.

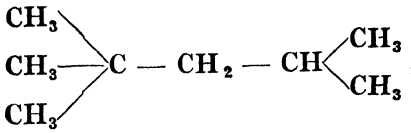
	Variable Compression Engine			Super Charged Engine
	H.U.C.R.	Compression Pressure Pounds per Square Inch	Toluene Value	Toluene Value
Hexane (80%)	5·1	113·5	8·0	7·0
Heptane (97%)	3·75	72·0	— 37·0	—
Benzene (Pure)	6·9*	179·0*	(67)	(66)
Toluene (99%)	> 7·0	> 183·0	100·0	100·0
Xylene (91%)	> 7·0	> 183·0	(35)	(83)
Cyclohexane (93%)	5·9*	140·5*	35·0	38·0
Methyl Cyclohexane (80%) ..	5·8	136·5	31·5	28·0
Dimethyl Cyclohexane (60%) ..	4·9	107·0	1·5	2·5

To indicate the relative anti-knock values of petroleum motor spirits, Ricardo made use of so called " toluene values," on which scale toluene itself had a toluene value of 100 and a standard petrol of very low H.U.C.R. had a value of 0. Pure normal heptane had a toluene value of −37.

In April, 1926, Egloff and Morrell[84] deduced from these results, by chemical analysis of a large number of motor fuels, that the relative effectiveness of aromatics, naphthenes and unsaturated hydrocarbons in suppressing tendency to knock was in the ratio of 20 : 5 : 4, i.e., the aromatics being five times more effective than olefines and four times more effective than naphthenes. However, these workers admitted that such a relationship was extremely limited in its application because Ricardo did no work with perfectly pure hydrocarbons and because no allowance was made for the probability of different members of the same hydrocarbon class having different anti-knock values.

In August, 1926, Graham Edgar of the Ethyl Gasoline Corporation presented a paper to the Division of Petroleum Chemistry at the 72nd meeting of the American Chemical Society, Philadelphia, Pennsylvania, in which he showed, for the first time, that certain paraffin hydrocarbons have valuable anti-knock properties and quoted the case of 2·4·4 trimethyl pentane

* Denotes pre-ignition before audible detonation.
( ) Denotes extrapolated values from blends of the hydrocarbon with an aromatic-free spirit of which the H.U.C.R. was 4·85 and the toluene value 0.


, a branched chain octane,

which has anti-knock properties roughly equivalent to those of benzole.[85]

In the early part of 1927, Egloff and Morrell re-examined their values for the relative efficiencies of various hydrocarbons in suppressing knocking, and after a series of actual engine tests found a lack of correlation between the toluene values or "aromatic equivalents" as determined by the engine tests and chemical analyses. They quoted the above work of Edgar as one of the possible reasons for this non-agreement.[86] The comparison of motor fuels by analytical and engine tests was also carried out by Stevens and Marley,[87] who concluded that the only accurate method of determining anti-knock value was by engine tests and found that 1 per cent. of toluene added to a fuel suppressed detonation to the same extent as the addition of 2 per cent. of hexylene or 2 per cent. of methyl cyclohexane. These figures do not, of course, agree with those of Egloff and Morrell and, moreover, do not take into account the effect of cyclopentane naphthene hydrocarbons.

Rather earlier, in November, 1925, Callendar, King and Simms[88] described the results of anti-knock tests on various hydrocarbons and other substances. These are mentioned later.

By about 1928, when the general anti-knock properties of various hydrocarbons had begun to be appreciated, many researches were in progress in attempts to obtain more detailed information on specialized aspects of this general subject. The results of this work may best be described by considering the various classes of hydrocarbons separately.

789. Paraffin Hydrocarbons.—Our present knowledge of the knock ratings of paraffin hydrocarbons is largely due to the work of Lovell, Campbell and Boyd,[89] who have examined many of these substances, of both straight and branched chain structure. The anti-knock scale adopted was not a particularly happy one, but sufficed to show the effect of chemical structure very clearly. 1-molar solutions of the various hydrocarbons in a reference gasoline were employed and the anti-knock value of the blends determined in terms of equivalent aniline-reference gasoline mixtures. In the case of those hydrocarbons which had lower knock ratings than the reference gasoline, the knock rating was determined by measuring the amount of aniline which had to be added to the hydrocarbon blend to restore its knock rating to that of the reference gasoline. This scale may be illustrated by the following examples:—

The aniline equivalent of 2·2·4 trimethyl pentane (molecular weight, 114) was found to be 16. This means that 114 grams of the hydrocarbon

made up to a litre with reference gasoline are equivalent in knock rating to a solution containing aniline to the extent of 16/100 × 93 grams per litre (molecular weight of aniline = 93). Similarly, the aniline equivalent of *n*-heptane (molecular weight 100) was found to be −14. This means that 100 grams of the heptane and 14/100 × 93 grams of aniline made up to a litre with reference gasoline has the same knock rating as the undiluted reference gasoline itself.

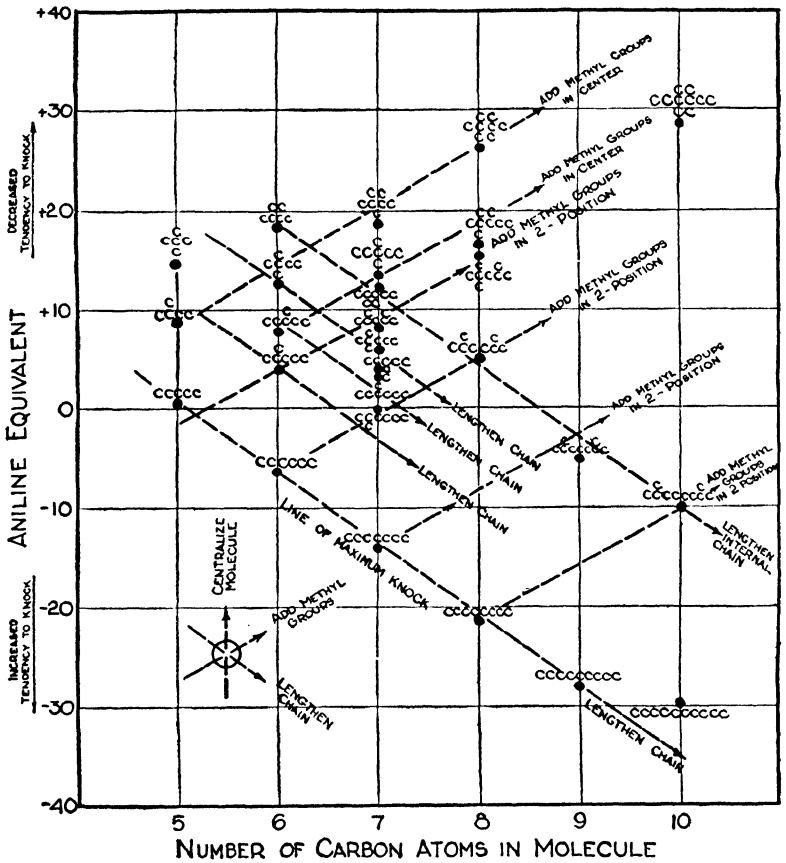


FIG. 217.—THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND ANTI-KNOCK CHARACTERISTICS OF PARAFFIN HYDROCARBONS. (LOVELL, CAMPBELL & BOYD.)
(*Courtesy of Editor, "Industrial and Engineering Chemistry."*)

The results obtained in this study are reproduced in Table 165 and Figure 217, and in order to convey some conception of the magnitude of the scale of knock rating employed, the following figures are of interest.

(1) Normal Heptane	Aniline equivalent, −14.
	H.U.C.R. (undiluted), 2·75.
(2) 2·4·4 Trimethyl Pentane	Aniline equivalent, +16.
	H.U.C.R. (undiluted), 6·9.
(3) Benzene	Aniline equivalent, +10.

TABLE 165.—KNOCK RATINGS OF PARAFFIN HYDROCARBONS.
(LOVELL, CAMPBELL AND BOYD.)

Hydrocarbon	Aniline Equivalent	Hydrocarbon	Aniline Equivalent
n-Pentane	1	3·3-Dimethyl pentane	13
2-Methyl butane	9	2·2·3-Trimethyl butane	19
2·2-Dimethyl propane	15	3-Ethyl pentane	4
n-Hexane	— 6	*n*-Octane	— 21
2-Methyl pentane	4	2·5-Dimethyl hexane	5
3-Methyl pentane	8	2·2·4-Trimethyl pentane	16
2·2-Dimethyl butane	13	2·2·3-Trimethyl pentane	17
2·3-Dimethyl butane	19	2·2·3·3-Tetramethyl butane	26
n-Heptane	— 14	*n*-Nonane	— 28
2-Methyl hexane	0	2·6-Dimethyl heptane	— 6
3-Methyl hexane	3	*n*-Decane	— 30
2·2-Dimethyl pentane	8	2·7-Dimethyl octane	— 10
2·3-Dimethyl pentane	12	3·3·4·4-Tetramethyl hexane	29
2·4—Dimethyl pentane	8		

The results obtained show a number of interesting relationships.

(1) For the normal paraffin hydrocarbons, there appears to be a regular increase in tendency to knock with increase in the length of the hydrocarbon chain in the molecule, or with the molecular weight.

A somewhat similar phenomenon of an increased tendency to knock with increased length of the carbon chain is observed in the series 2-methyl-butane, 2-methyl-pentane and 2-methyl-hexane. This is indicated by the appropriate dotted line in Figure 217. An entirely analogous behaviour is observed in the series of 3-methyl pentane and 3-methyl hexane and also for 2·2-dimethyl-butane and 2·2-dimethyl pentane. It appears that, for similar structures, an increase in the length of an unbranched carbon chain increases the tendency to knock.

(2) The branched chain paraffin hydrocarbons have higher knock ratings than their straight chain homologues.

(3) In all the series considered, the introduction of methyl groups in a basic chain progressively increases the anti-knock properties by substantiating a constant amount per methyl group.

(4) For a given molecular size, as the " centralization of the molecule" is increased, the aniline equivalent increases, i.e., the tendency to knock decreases. It is difficult to define this concept of centralization except, in a general way, as a more compact space arrangement of the structural formula of the molecule. This relationship appears to be universal.

With regard to the octane numbers of paraffin hydrocarbons, a few figures have been published, but these do not always agree among themselves. The following values were obtained in the laboratories of the Anglo Persian Oil Company and reported by Thorneycroft and Ferguson,[90]

	Octane Number. Ricardo E. 5 Engine.
n-Pentane ..	66
n-Hexane ..	45
n-Heptane ..	0
n-Octane ..	−32
n-Nonane ..	−44 (Interpolated)
n-Decane ..	−53

whereas Oberfell[91] has given the following figures :—

	Octane Number.
Iso-butane ..	100
n-Butane ..	90
Mixed Butanes ..	93
Iso-Pentane ..	91
n-Pentane ..	64
Mixed Pentanes ..	74
n-Hexane ..	35 (Estimated)
Mixed Hexanes ..	63
n-Heptane ..	0
Mixed Heptanes ..	65

790. A recent paper by Garner, Evans, Sprake and Broom[92] details and critically examines the data available for the knock ratings of paraffin and other hydrocarbons and converts the " aniline equivalent " results of Campbell, Lovell and Boyd into " blending octane numbers." The latter are calculated by the equation

$$O_B = VO_H + (100 - V)\, O_R$$

where V = % by volume of pure hydrocarbon in a blend with a reference fuel.
O_H = Blending octane number of pure hydrocarbon.
O_R = Octane number of reference fuel.
O_B = Octane number of the blend.

It should be noted that the " blending octane number " of a hydrocarbon deduced in this way is not the same as its actual octane number determined by direct test in an undiluted state, because the anti-knock effect of pure hydrocarbons is not linear with concentration. The blending octane number of a hydrocarbon is, however, of importance in indicating the extent to which the hydrocarbon is effective from the anti-knock standpoint when in dilute concentrations (i.e. up to about 20% by volume). A comparison between blending octane numbers and actual octane numbers indicates that the blending octane numbers of

aromatic hydrocarbons are lower and those of olefine hydrocarbons higher than the actual octane numbers. For paraffin and naphthene hydrocarbons the blending octane numbers are approximately the same as the actual octane numbers. The results of Garner, Evans, Sprake and Broom for paraffin hydrocarbons are reproduced in Table 166.

TABLE 166.—GENERAL COMPARISON OF BLENDING OCTANE NUMBERS DEDUCED FROM VARIOUS SOURCES, FOR PURE HYDROCARBONS, WHEN TESTED IN APPROXIMATELY 20% BY VOLUME CONCENTRATION IN REFERENCE FUELS OF APPROXIMATELY 50 OCTANE NUMBER AT 212°F. JACKET TEMPERATURE.

Hydrocarbon	Lovell, Campbell and Boyd	Ratings on Delco and S.30 engines	
		at 212°F.	at 300°F.
PARAFFINS.			
n-Pentane	60	70	57·5
2-Methyl butane	92	94·5	82·5
2·2-Dimethyl propane	116	—	—
n-Hexane	29	26·5	23·5
2-Methyl pentane	69	—	—
3-Methyl pentane	84	—	—
2·2-Dimethyl butane	101	—	—
2·3-Dimethyl butane	124	—	—
n-Heptane	0	0	0
2-Methyl hexane	55	—	—
3-Methyl hexane	65	—	—
2·2-Dimethyl pentane	80	—	—
2·3-Dimethyl pentane	94	—	—
2·4-Dimethyl pentane	80	—	—
3·3-Dimethyl pentane	98	—	—
2·2·3-Trimethyl butane	116	—	—
3-Ethyl pentane	68	—	—
n-Octane	— 19	— 20	— 13
2·5-Dimethyl hexane	69	—	—
2·2·4-Trimethyl pentane	100	100	100
2·2·3-Trimethyl pentane	105	—	—
2·2·3·3-Tetramethyl butane	130	—	—
n-Nonane	— 34	—	—
2·6-Dimethyl heptane	36	—	—
n-Decane	— 32	—	—
2·7-Dimethyl octane	25	—	—
3·3·4·4-Tetramethyl hexane	124	—	—

791. Unsaturated Hydrocarbons.—In the early part of 1929, the authors published[93] some preliminary knock rating values for unsaturated hydrocarbons obtained on a Delco engine running at 500 r.p.m. and a jacket temperature of 180°F. Each of the hydrocarbons examined

was tested in the form of a 20 per cent. volume solution in a standard spirit. The results obtained were as follows :—

	Equivalent Blends in Base Spirit	
	Tetra-Ethyl Lead. Ccs./Gallon	% Benzole
20% Cyclohexane	1·0	10·5
20% Benzene	2·1	19·2
20% Toluene	2·75	—
20% Pentene-2	3·5	22·2
20% Trimethyl Ethylene	4·5	31·2
20% Diamylene	6·0	37·6
20% Di-isobutylene	6·6	40·0
20% Cyclohexene	2·4	21·0

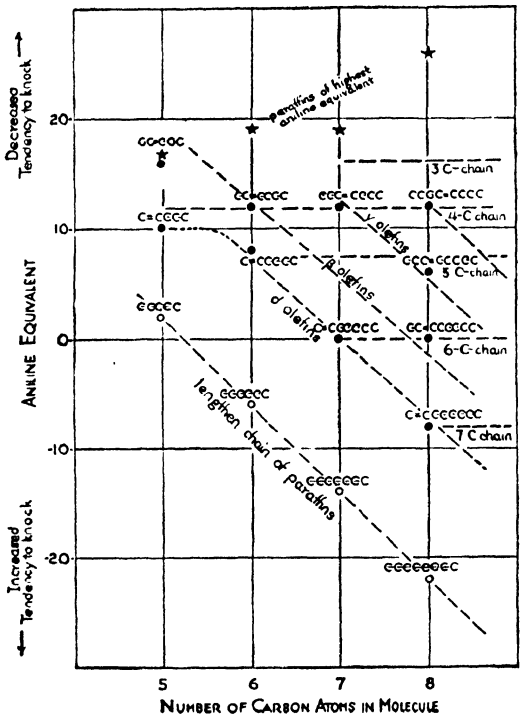


FIG. 218.—GRAPH SHEWING RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND ANTI-KNOCK CHARACTERISTICS OF OLEFINE HYDROCARBONS. (LOVELL, CAMPBELL & BOYD.)
(Courtesy, Editor, Industrial and Engineering Chemistry.)

and show that these substances have very valuable anti-knock properties. The high value of "diamylene" was questioned by Birch and Stansfield,[94] who maintained that, in all cases, the olefine polymers have lower knock ratings than the parent hydrocarbons and that trimethyl

ethylene has a higher knock rating than diamylene. Other figures for the knock rating of diamylene have not yet been published, so that it is not possible to say whether the statement of Birch and Stansfield is correct, but it would appear from the results of Lovell, Campbell and Boyd,[95] (see later), in which data are given for some hydrocarbons that may be regarded as olefine polymers, that their generalization with regard to polymerization always lowering knock ratings is not true in all cases. Again, Hoffman, Lang, Berlin and Schmidt[96] have shown that cyclopentadiene has a lower knock rating than its dimer.

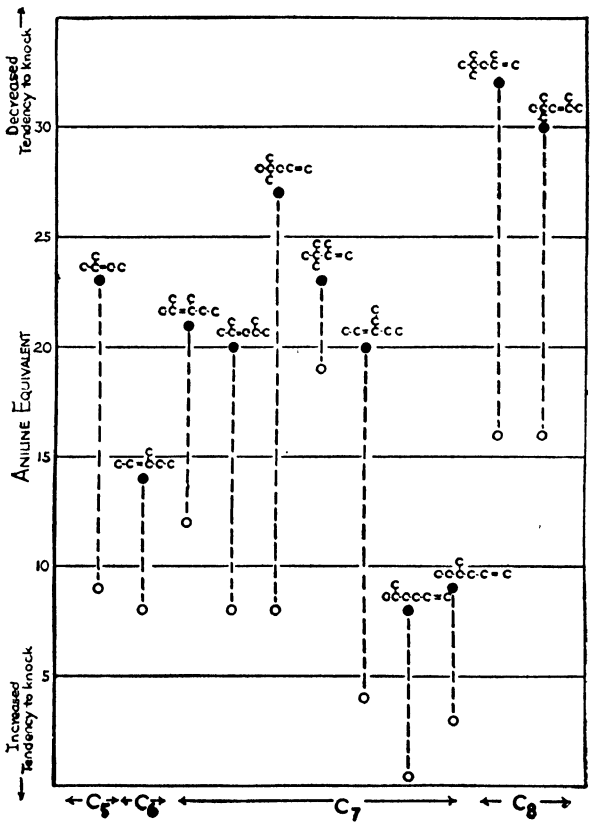
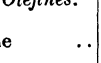
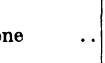
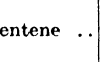
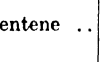
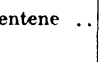
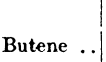
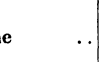
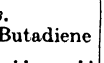


FIG. 219.—GRAPH SHEWING ANTI-KNOCK RATINGS OF BRANCHED CHAIN OLEFINES. (LOVELL, CAMPBELL & BOYD.)
(Courtesy, Editor, Industrial and Engineering Chemistry.)

The figures obtained by Campbell, Lovell and Boyd are of especial interest and are reproduced in Table 167 and Figures 218 and 219.

The scale of anti-knock quality adopted was the same as that used by the same workers in their similar study of paraffin hydrocarbons which has already been described, but Table 167 gives blending octane numbers

TABLE 167.—KNOCK RATINGS OF OLEFINE HYDROCARBONS.
(LOVELL, CAMPBELL AND BOYD.)

Hydrocarbon	Formula	Blending Octane Number	Blending Octane Number of Corresponding Paraffin	Increase in Blending Octane Number due to Unsaturation
Straight Chain Hydrocarbons.				
1-Pentene	c = c-c-c-c	98·5	60	38·5
2-Pentene	c-c = c-c-c	125	60	65
1-Hexene	c = c-c-c-c-c	85	29	56
2-Hexene	c-c = c-c-c-c	100	29	71
1-Heptene	c = c-c-c-c-c-c	55	0	55
3-Heptene	c-c-c = c-c-c-c	95	0	95
1-Octene	c = c-c-c-c-c-c-c	25	— 19	44
2-Octene	c-c = c-c-c-c-c-c	55	— 19	74
3-Octene	c-c-c = c-c-c-c-c	73	— 19	92
4-Octene	c-c-c-c = c-c-c-c	91	— 19	110
Branched Chain Olefines.				
2-Methyl 2-Butene ..		157	92	65
3-Methyl 2-Pentene ..		109	84	25
2·3-Dimethyl 2-Pentene ..		127	94	33
2·4-Dimethyl 2-Pentene ..		122	80	44
2·2-Dimethyl 4-Pentene ..		147	80	67
2·2·3-Trimethyl 3-Butene ..		132	116	16
3-Ethyl 2-Pentene ..		124	68	56
2-Methyl 5-Hexene ..		83	55	28
3-Methyl 5-Hexene ..		86	65	21
2·2·4-Trimethyl 4-Pentene		150	100	50
2·2·4-Trimethyl 3-Pentane		144	100	44
Diolefines.				
2·3-Dimethyl 1·3-Butadiene		212	124	88
1·5-Hexadiene	c =c-c-c-c = c	79	29	50
2·4-Hexadiene	c-c = c-c = c-c	174	29	145
3-Ethyl 1·3-Pentadiene ..		140	68	72

calculated by Garner and his co-workers.[92] It will be observed that the knock ratings of the olefines are greater than those of the corresponding paraffins, but that the increase in knock rating, due to the presence of a double bond in the molecule, is not constant. This varies with the molecular weight of the hydrocarbon and with the position of the double bond within the molecule. The same general relationships between molecular structure and knock rating do, however, apply equally well in the case of both classes of hydrocarbons. With regard to diolefines, it will be observed that 2·4 hexadiene, with more centralized double bonds, has a much higher knock rating than 1·5 hexadiene which contains a greater length of unbroken and unbranched carbon chain.

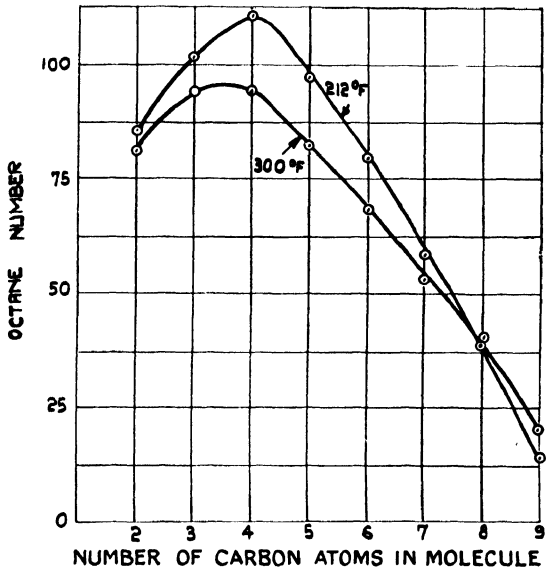


FIG. 220.—GRAPH SHEWING KNOCK RATINGS OF THE α OLEFINES. (GARNER, WILKINSON AND NASH.)

The knock ratings of the α-olefines have been reported by Garner, Wilkinson and Nash,[97] in a study embracing 9 hydrocarbons from ethylene to α-nonene. These were examined in the form of 20 per cent. solutions in a standard spirit in an Ethyl Gasoline S.30 engine, at jacket temperatures of 212°F. and 300°F., and the blending octane numbers of the undiluted hydrocarbons calculated as shewn above.

The results obtained are reproduced in Table 168 and Figure 220, and show that increase in molecular weight from α-butene to α-nonene is accompanied by a decrease in knock rating, but that from ethylene to butene the reverse is the case. This is the first series of hydrocarbons

examined in this way that has embraced nine consecutive members of analogous structure.

TABLE 168.—BLENDING OCTANE NUMBERS OF OLEFINES.
(GARNER, WILKINSON AND NASH.)

Hydrocarbon	Octane Numbers of 20% Blends in Standard Spirit		Calculated Blending Octane Numbers of Pure Hydrocarbons	
	212°F.	300°F.	212°F.	300°F.
Ethylene	58·9	54·9	85·5	82·5
Propylene	61·6	57·2	102·0	94·5
α-Butene	64·4	57·4	111·5	95·0
α-Pentene	61·4	34·2	98·5	82·0
α-Hexene	56·3	52·0	80·0	68·5
α-Heptene	53·5	49·6	59·5	54·5
α-Octene	50·0	47·0	38·5	39·5
α-Nonene	44·0	40·0	15·0	20·0

792. The Aromatic Hydrocarbons.—Although values for the more common aromatic hydrocarbons, such as toluene and benzene, had been reported from time to time previously, the first published results of a systematic study of the knock ratings of a series of aromatic hydrocarbons were those of Howes and Nash.[98] In this investigation, the hydrocarbons were made up into 20 per cent. blends with a Californian straight run spirit, and knock ratings determined in a standard Delco engine operating at 500 r.p.m., and with a jacket temperature of 140°F. The results obtained, which are detailed below, showed that toluene had a better knock rating than benzene and the three xylenes were more effective than toluene. Of the xylenes, *p*-xylene was found to be the most effective and *o*-xylene the least. In general, the para-disubstituted benzenes were found to be the best anti-knock agents, e.g., *p*-cymene, *p*-xylene and *p*-tertiary butyl toluene. Tertiary groupings appeared to have a better effect than secondary groupings, e.g., tertiary butyl benzene was more effective than secondary butyl benzene. Of the hydrocarbons examined, only one was found to have a lower anti-knock value than benzene, namely, secondary butyl benzene.

This work was later extended by Garner and Evans,[99] who used a different reference fuel (A-2) and who used an Ethyl Gasoline S. 30 engine, operated at 600 r.p.m., and at jacket temperatures of 212°F. and 300°F. Both investigations were, however, carried out in the laboratories of the Anglo American Oil Company, and it was found possible to convert the results obtained in the first investigation so as to compare with the later results. Table 169 details the results of Garner and Evans, and also gives those of Howes and Nash, suitably corrected for

the change in engine and reference fuels. The two sets of results agree fairly well. Of the various classes of hydrocarbons, Garner and Evans found that the aromatics depreciated in knock rating to by far the greatest extent when the engine temperature was raised.

As early as 1925, Callendar, King and Simms[88] stated that additions of 5 per cent. by volume of aromatic hydrocarbons to a fuel of H.U.C.R. 4·9 (Ricardo E. 35 engine) produced the following increases of H.U.C.R.

Benzene ..	1%
Toluene ..	2%
o-Xylene ..	0·6%
Pseudo Cumene	−0·4%

The decrease of H.U.C.R. for pseudo cumene does not appear to be a very accurate result because other investigators have always found aromatic hydrocarbons to have very high knock ratings.

TABLE 169.—THE KNOCK RATINGS OF AROMATIC HYDROCARBONS. (GARNER AND EVANS.)

Hydrocarbon	212°F. Jacket Temperature		300°F Jacket Temperature	
	Octane Number of 20% Blend	Calculated Blending Octane Number of Pure Hydrocarbon	Octane Number of 20% Blend.	Calculated Blending Octane Number of Pure Hydrocarbon
Benzene	60·2	101·0	55·2	88·0
Toluene	62·6	113·0	58·0	102·0
Ethyl benzene	64·1	120·5	60·0	112·0
Mixed xylenes	62·5	112·5	56·1	92·5
n-Propyl benzene ..	64·0	120·0	60·0	112·0
Mesitylene	66·2	131·0	64·4	134·0
n-Butyl benzene ..	62·1	110·5	58·0	102·0
Results of Howes and Nash.				
Benzene	59·2	96·0	—	—
Toluene	61·3	106·5	—	—
Ethyl benzene	64·6	123·0	—	—
o-Xylene	62·8	114·0	—	—
m-Xylene	65·1	125·5	—	—
p-Xylene	65·6	128·0	—	—
Iso-Propyl benzene ..	60·9	104·5	—	—
p-Cymene	65·6	128·0	—	—
Sec. Butyl benzene ..	58·2	91·0	—	—
Tert. Butyl benzene ..	62·8	114·0	—	—
Tert. Amyl benzene ..	62·8	114·0	—	—
p-Tert. Butyl toluene	64·6	123·0	—	—

793. Naphthene Hydrocarbons.—Comprehensive studies of the knock ratings of naphthene hydrocarbons have been conducted by Garner and Evans[99] and by Lovell, Campbell and Boyd,[100] whose results are reproduced in Table 170. In the cases of both the cyclohexane and cyclopentane series, there is a consistent fall in anti-knock value as the series is ascended. Cyclohexane differs very little in 20 per cent. concentration from pure benzene in the same concentration, although pure cyclohexane can readily be made to knock when undiluted, whereas benzene can be subjected to a compression ratio of 15 : 1 without knocking occurring. In general, the more centralized the molecule the greater the knock rating. The effect of engine temperature is interesting: 1·3 dimethyl cyclopentane is very little affected, despite the fact that it is spontaneously oxidized in air, *iso*-amyl acetate and methyl *iso*-amyl acetone being formed through peroxidation.[101] 1·3-Dimethyl cyclohexane has a higher value at 300°F. than at 212°F., but the 1·2- and 1·4-hydrocarbons are similar to the lower cyclohexane hydrocarbons. In general, however, it may be stated that the *relative* order of the knock ratings of the various hydrocarbons is the same at 300°F. as at 212°F.

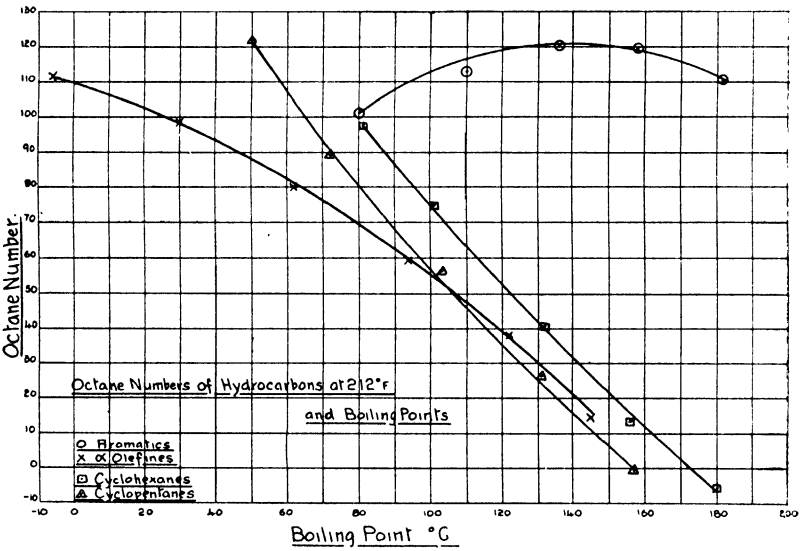


FIG. 221.—RESULTS BY GARNER AND EVANS.
(Courtesy of the Institution of Petroleum Technologists.)

Figure 221 shows the relationship existing between the boiling points of various classes of hydrocarbons and their extrapolated or "blending" octane numbers (not actual octane numbers). At a boiling point of 80°C., the ascending order in knock rating is α olefine, cyclopentane, cyclohexane, aromatic; at 100°C., it is the same, and at 150°C., the olefine and cyclopentane are approximately equal, but the difference

TABLE 170.—KNOCK RATINGS OF NAPHTHENE HYDROCARBONS (BLENDING OCTANE NUMBERS).

Hydrocarbon	Lovell, Campbell and Boyd	Garner and Evans Ratings on Delco and S.30 engines	
		at 212°F	at 300°F
NAPHTHENES.			
Five carbon atom ring.			
Cyclopentane ..	125	122	114
Methyl-cyclopentane	71·5	89	84
1.3-Dimethyl-cyclopentane	51	85	87
Ethyl-cyclopentane ..	58·5	57	57
1.3-Methyl-ethyl-cyclopentane	44	—	—
n-Propyl-cyclopentane	15·5	27	32
1.3-Methyl-*n*-propyl-cyclopentane	31	—	—
n-Butyl-cyclopentane	−11	0	9·5
1.3-Methyl-*n*-butyl-cyclopentane	−4	—	—
n-Amyl-cyclopentane	−18·5	—	—
1.3-Methyl-*n*-amyl-cyclopentane	−8·5	—	—
1.3-Methyl-iso-amyl-cyclopentane	0	—	—
Six carbon atom ring.			
Cyclohexane	85·5	97·5	84
Methyl-cyclohexane	74	75	65·5
1.2-Dimethyl-cyclohexane	75	81	71
1.3-Dimethyl-cyclohexane	68	68·5	69·5
1.4-Dimethyl-cyclohexane	75	73·5	62·5
1.3.5-Trimethyl-cyclohexane	61	—	—
Ethyl-cyclohexane ..	44	41	35·5
1.2-Methyl-ethyl-cyclohexane	55	—	—
1.3-Methyl-ethyl-cyclohexane	34	—	—
1.4-Methyl-ethyl-cyclohexane	27	—	—
1.3-Diethyl-cyclohexane	12·5	—	—
1.4-Diethyl-cyclohexane	12·5	—	—
n-Propyl-cyclohexane	19·5	14	15
Iso-propyl-cyclohexane	55	—	—
1.2-Methyl-*n*-propyl-cyclohexane	37	—	—
1.3-Methyl-*n*-propyl-cyclohexane	22	—	—
1.4-Methyl-*n*-propyl-cyclohexane	20	—	—
1.4-Methyl-iso-propyl-cyclohexane	57·5	—	—
n-Butyl-cyclohexane	2·5	−5	−2
Iso-Butyl-cyclohexane	35	—	—
sec-Butyl-cyclohexane	45	—	—
tert-Butyl-cyclohexane	98·5	—	—
1.2-Methyl-*n*-butyl-cyclohexane	6	—	—
1.3-Methyl-*n*-butyl-cyclohexane	−5	—	—
1.4-Methyl-*n*-butyl-cyclohexane	−5	—	—
1.3-Methyl-iso-butyl-cyclohexane	40·5	—	—
n-Amyl-cyclohexane	−7·5	—	—
iso-Amyl-cyclohexane	13·5	—	—
tert-Amyl-cyclohexane	70	—	—
1.2-Methyl-*n*-amyl-cyclohexane	7·5	—	—
Dicyclohexane ..	−7·5	—	—
Seven carbon atom ring.			
Cycloheptane ..	26·5	—	—
UNSATURATED NAPHTHENES.			
Five carbon atom ring.			
Cyclopentene ..	139·5	—	—
1-Methyl-cyclopentene	143	—	—
1-Ethyl-cyclopentene	101·5	—	—
1-*n*-propyl-cyclopentene	96	—	—
1-*n*-Butyl-cyclopentene	82	—	—
1-*n*-Amyl-cyclopentene	63	—	—
Six carbon atom ring.			
Cyclohexene	101·5	—	—
1-Methyl-cyclohexene	132·5	—	—
1.2-Di-methyl-cyclohexene	121	—	—
2.4-Di-methyl-cyclohexene	120	—	—
1-Ethyl-cyclohexene	100	—	—
1-Methyl-2-ethyl-cyclohexene	132·5	—	—
2-Ethyl-4-methyl-cyclohexene	116·5	—	—
1-Ethyl-4-methyl-cyclohexene	109·5	—	—
1-Methyl-2-*n*-propyl-cyclohexene	105	—	—
2-*n* Propyl-4-methyl-cyclohexene	105	—	—
1-*n*-Propyl-4-methyl cyclohexene	88	—	—
1-*n*-Butyl-cyclohexene	63	—	—
1-Methyl-2-*n*-butyl-cyclohexene	88	—	—
2-*n*-Butyl-4-methyl-cyclohexene	88	—	—
1-*n*-Butyl-4-methyl-cyclohexene	72·5	—	—
1-*n*-Amyl-cyclohexene	57·5	—	—
1-Isoamylcyclohexene	45	—	—
1-Methyl-2-*n*-amylcyclohexene	81	—	—
Cyclohexyl-cyclohexene	68·5	—	—
ACETYLENES.			
Seven carbon atom ring.			
*Heptine-1	—	79·5	—

* Bowen, Nash and Garner.[99a]

between these hydrocarbons and the aromatic hydrocarbons is very great. The curves shown in this Figure only apply to the hydrocarbons in which normal alkyl radicles have been substituted, as the results for the various di- and iso-substituted benzene, cyclohexane and cyclopentane hydrocarbons do not fall on smooth curves.

It will be evident from the above data, that although our knowledge of the knock ratings of pure hydrocarbons is rapidly expanding, it is impossible to forecast the knock ratings of a fuel by chemical analysis. Different hydrocarbons of the same class vary enormously in knock rating and, at present, it has not been found possible to correlate knock ratings with chemical constitution. The aromatic hydrocarbons appear to be exceptional in that they have very high knock ratings even among their higher members. The lower aliphatic alcohols, however, namely, methanol and ethyl alcohol, have higher knock ratings than the best of the aromatic hydrocarbons, a fact used to great advantage in the production of fuels for racing engines.

The Knock Ratings of Various Non-Metallic Organic Compounds

794. It has been known for some time that among various organic compounds certain groupings are generally anti-knock in effect and other certain groupings are generally associated with pro-knock action. Thus, aromatic and aliphatic amines, phenols and alcohols are generally anti-knock, while ethers, alkyl nitrites and nitrates and aldehydes are generally pro-knock.

When compared with tetra-ethyl lead, however, such anti-knock compounds as these are relatively ineffective though they may be up to 15 times as efficient as benzene (on a volume basis). The relative efficiencies of tetra-ethyl lead and other metallic-organic compounds, benzole, xylidine and ethyl iodide as anti-knock agents are evident from the following figures.[102]

TABLE 171

Compound	% Volume in Kerosene Requied to Produce a Given Suppression of Knocking	Approximate number of moles of Theoretical Fuel-Air mixture in which 1 mol. Exerts Effect on Knocking of a Given magnitude
Benzene	25·0	150
Ethyl Iodide	1·6	2,150
Xylidine	2·0	2,600
Tetra-Ethyl Tin	1·2	7,100
Tetra-Ethyl Selenium	0·4	11,750
Tetra-Ethyl Tellurium	0·1	50,000
Tetra-Ethyl Lead	0·04	215,000

The aromatic amines are, as a class, anti-knock in character and some members of this series are about ten to fifteen times as effective as benzene in suppressing knocking when in very dilute concentrations. The effect of chemical constitution is here very noticeable; aniline, $C_6H_5NH_2$, is quite effective as an anti-knock agent, but if one hydrogen atom in the NH_2 group is replaced by one ethyl (C_2H_5) group to give monoethyl aniline, the anti-knock property is reduced by about 50 per cent., and if both hydrogen atoms are replaced by ethyl groups, giving diethyl aniline, the anti-knock property is practically reduced to zero. With methyl group substitutions, it is found that monoethyl aniline is rather more effective as an anti-knock agent than aniline itself, but that dimethyl aniline has extremely slight anti-knock effect.

Among the toluidines, the meta isomer is slightly more effective than the other two and the same is found to be the case among the xylidines. The relative effects of some aromatic amines and benzene in suppressing knocking are shown in Figure 222.

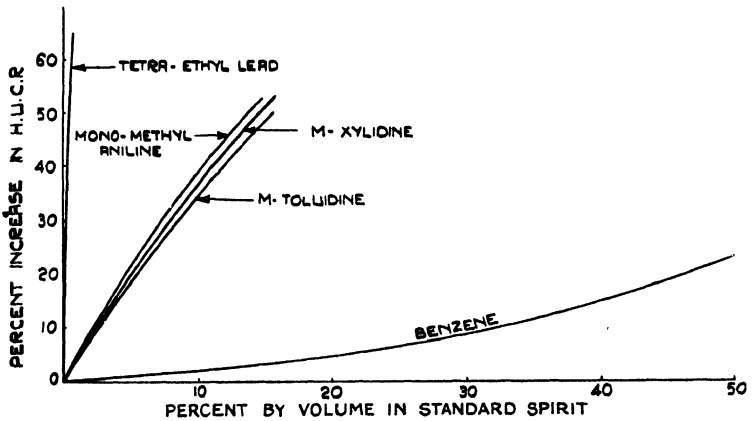


FIG. 222.—THE RELATIVE ANTI-KNOCK EFFICIENCIES OF VARIOUS SUBSTANCES. (FROM DATA OF CALLENDAR, KING AND MOSS.)

The phenols have a definite anti-knock effect and the lower members of the series in concentrations of 1—3 per cent. by volume are about 3—5 times as good as benzene. The cyclic alcohols or completely hydrogenated phenols, such as cyclohexanol, are about equivalent to benzene in anti-knock effect in very small concentrations.

With regard to the aliphatic alcohols, the anti-knock values of methanol and ethyl alcohol are discussed at length in Chapter IX (Volume I), where it is shown that in concentrations up to about 20—30 per cent., these alcohols are approximately equal in anti-knock value and have a benzole equivalent of 1·8—2·0. Little information is available regarding the anti-knock values of higher aliphatic alcohols, but there are indications that the longer the open carbon chain in the molecule, the

lower the knock rating of the alcohol. Isopropyl alcohol is approximately equivalent to 1·5 times the quantity of benzole in concentrations up to about 40 per cent.

As already indicated, ethers are, as a class, pro-knock in effect and resemble aldehydes, alkyl nitrates and nitrites in this respect. However, no figures are available which allow any quantitative conclusions to be drawn.

The use of various organic compounds as anti-knock agents has been proposed in numerous patents, a very small selection of which are as follows :—

E.P., 246,094. Riedel, Akt. Ges., January 19, 1925. Cyclohexanol and hydrogenated phenols.

E.P., 277,326. Avenarices, September 7, 1926. Carboxylic acids of high molecular weight.

E.P., 301,076. Wernicke and Beyer, November 5, 1927. *p*-Dioxybenzene.

E.P., 253,131. Petroleum Chemical Corporation, June 4, 1925. Polymers of pentenes, butenes or hexenes.

U.S.P., 1,645,109. Marley and Gruse (Gulf Refining Co.), October 11, 1927. Alkoxy derivatives of aromatic hydrocarbons carrying an amino group in the ortho, para, or meta position (preferably para), such as phenetidin (the ethyl ether of *p*-amino phenol) or anisidin (the methyl ether of para amino phenol).

E.P., 303,505. Carbide and Carbon Chemicals Corporation, January 6, 1928. Alkyl substituted benzenes, the alkyl group containing two or more carbon atoms (e.g., ethyl benzene, propyl benzene, etc.).

E.P., 311,115. Schanzer. Hydroquinone.

E.P., 323,463. S. Coffey and I.C.I. Ltd. Aryl ethanes, etc.

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CHAPTER XVII

MOTOR FUEL SPECIFICATIONS AND PROPERTIES OF MOTOR FUELS MARKETED IN DIFFERENT COUNTRIES

801. Introduction.—Wherever motor fuels are sold in appreciable quantities, their qualities are controlled by various specifications. In the absence of Government specifications, the marketing companies decide upon the properties of fuels to be distributed, which are usually rather more than adequate to meet the requirements, and where independent specifications exist the fuel properties are, if necessary, adjusted to fall in with these requirements. The case of Great Britain is noteworthy in this connection, for here, although no up-to-date fuel specifications exist, the quality of motor spirits marketed is adequate for all demands made upon it. It is the purpose of this Chapter to outline the gasoline specifications in operation in different countries and to indicate the properties of fuels marketed.

United States of America

802. Development of Motor Fuel Specifications since 1915.—The United States of America is the home of the petroleum industry and it is here that nearly all improvements in petroleum technology and improvements in the quality of products originate. Motor fuels are sold in the United States of America on a specification basis and from time to time the U.S. Government issue specifications to which all products supplied to Government departments must comply. These specifications are accepted by the country at large. In addition, individual States have their own specifications.

In the very early days of the American Industry petroleum spirits were graded almost entirely on specific gravity considerations, and regulations controlling the quality of gasoline adopted by several state and municipal bodies between 1912 and 1918 specified either a maximum permissible specific gravity, or a minimum Baumé gravity. Somewhat unusual requirements were also included; for instance, a Colorado requirement of this date was that the spirit should not contain more than 5 per cent. of solid matter! At this time less than half a dozen States made any reference in their specifications to a distillation test.

In 1915, the United States Bureau of Mines reported[1] on the quality of 52 samples of motor fuel sold in various parts of America. In 1917,

a paper was read before the Western Union Jobbers' Association at St. Louis, on March 21st, by A. A. Ashworth calling attention to the distillation test, and the American Society of Testing Materials Year Book of 1915 suggested the distillation method then in use for the examination of turpentine products as suitable for the testing of motor fuels.

803. On July 31st, 1918, President Wilson issued an order to the U.S. Fuel Administrator to prepare standard specifications for petroleum and its products to be used for purchasing such materials by the U.S. government. As a result of this order, uniformity in testing methods and specifications was initiated. This work was begun by the Federal Specifications Committee in consultation with technical experts and an advisory board composed of representatives from the industry, trade associations and technical societies. In October, 1918, the U.S. Fuel Administrator, Oil Division, issued the Report of the Committee on Standardization of Petroleum Products, Bulletin 1. It contained specifications for aviation gasoline (export, domestic and fighting grades) and motor gasoline. At the same time, the methods to be adopted in making the necessary tests were described in the U.S. Bureau of Mines Technical paper 166. These were described in greater detail than had hitherto been attempted and included a standard distillation test. Thus came into use the well known New Navy specifications which contained a distillation test and a general statement covering quality.

On November 8th, 1921, there was formed the Inter-departmental Petroleum Specifications Committee under the authority of the Bureau of the Budget, as an agency of the Federal Specifications Board, and between October 2nd, 1918 and 1924 the specifications governing general fuel quality were changed five times and colour and corrosion tests requirements were added. On March 18th, 1924, the term New Navy gasoline was changed to U.S. Motor gasoline.

In December, 1920, Bulletin No. 191 of the United States Bureau of Mines by Hill and Dean was published, and consisted of a survey of the quality of motor fuels marketed in America in 1917 and in 1919, made with the principal purpose "of obtaining information regarding the grades and varieties of fuels on the market so that intelligent and practical specifications could be written for government purchases." The results of this survey are of interest.

Of the samples of marketed fuels examined in 1917, practically all of them were found to be of water white colour, but in 1919, a high percentage of the samples were reported as "slightly yellow" or "yellowish" and very few were of water white colour. It was, however, realized that such a change was not in itself a deterioration in quality. The odour of spirits marketed in 1919 was also inferior to that of spirits sold in 1917. Such changes were due to the increasing

use of cracked spirit and the adoption of less drastic refining methods. With regard to the Doctor Test, 85 per cent. of the samples examined in 1917 passed the test, but only 71 per cent. in 1919. During the same period, Baumé gravities were lowered on an average by 2 to 3 degrees, a change caused, to the greater part, by a rise in end points.

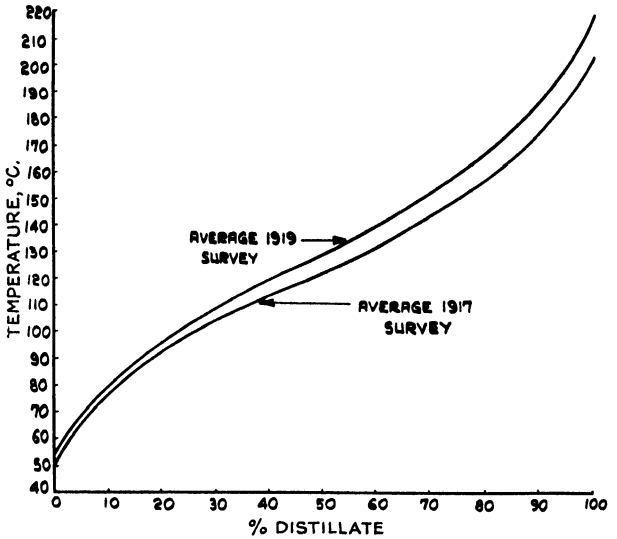


FIG. 223.—AVERAGE DISTILLATION CURVES OF MOTOR SPIRITS SOLD IN U.S.A. 1917 AND 1919 (REPRODUCED BY PERMISSION FROM U.S. BUREAU OF MINES, *Bulletin* 191, 1920).

Figure 223 shows curves representing average distillation figures for all the samples examined in the two years in question. The curves practically coincide up to the 20 per cent. point, showing that the percentage of relatively volatile constituents remained constant over the period, probably due to an increase in the use of casinghead spirit. Above the 20 per cent. point, the curves diverge and show that the 50 per cent. point was 7°C. higher in 1919, the 90 per cent. point 15°C. higher and the end point 16°C. higher.

One important point emerged from the 1919 survey. Of the total number of samples examined, only 26·9 per cent. satisfied all the requirements of the distillation test embodied in the specification of October, 1928. This is shown in the following figures.

Specification mark	Initial Point	20 per cent.	45 per cent.	90 per cent.	End Point
Maximum distillation temperature required °C.	60	105	135	180	220
Maximum distillation temperature required °F.	140	221	275	356	428
Percentages of samples satisfying requirement	81·7	89·0	89·7	37·2	50·1

Percentage of samples satisfying all requirements = 26·9.

It is evident that the 90 per cent. point was the most difficult to meet and the 20 per cent. and 45 per cent. points the least stringent. As a result of this, the U.S. government specification was amended. The end point was raised from 220°C. maximum to 225°C. maximum, the 90 per cent. distillate requirement was raised from 180°C. to 190°C., and the 45 per cent. distillate requirement was replaced by a clause demanding 50 per cent. distillate at a temperature not above 140°C. A study of the distillation analyses of the various samples examined in the 1919 survey showed that about 46 per cent. would satisfy this specification, as against only 27 per cent. satisfying the October, 1918 specification.

The retail prices of motor fuels sold in various American cities in 1917 and 1919 are given in Table 172.

TABLE 172.—RETAIL PRICES OF MOTOR GASOLINE IN AMERICA, 1917 AND 1919. (U.S. BUREAU OF MINES, BULLETIN 191.)

State	City	Retail Price. Cents per gallon		State	City	Retail Price. Cents per gallon	
		1917	1919			1917	1919
Alabama ..	Birmingham	26	25·5	Montana ..	Butte ..	30	—
California ..	San Francisco	20	20·5	Do. ..	Missoula ..	—	29
Colorado ..	Denver ..	25	28	New York ..	Buffalo ..	25	26
Illinois ..	Chicago ..	21	23	Ohio ..	Cleveland ..	24	25·5
Kentucky ..	Louisville ..	24	25·5	Oklahoma ..	Tulsa ..	24	22·5
Louisiana ..	New Orleans	22	23	Pennsylvania	Pittsburgh ..	25	27
Maine ..	Portland ..	26	27·5	Tennessee ..	Nashville ..	23	—
Massachusetts	Boston ..	25	27·5	Do. ..	Chattanooga	—	24
Michigan ..	Detroit ..	20	23·7	Texas ..	Dallas ..	22	24·5
Missouri ..	St. Louis ..	18·4	22·4	Do. ..	Houston ..	22	24·5
Do. ..	Kansas City	18·3	22·3	Utah ..	Salt Lake City	28	27

804. Between October 2nd, 1918 and March, 1924, the specifications for U.S. motor gasoline were changed five times, as shown in Table 173. In December, 1920, a clause was introduced into the specification requiring gasoline to be of water white colour. In March, 1922, this requirement was modified and a colour of at least 16 Saybolt substituted, and at the same time a corrosion test was introduced. This consisted of heating the spirit with a cleaned copper strip for 3 hours at 122°F. (50°C.), when no discoloration of the latter was allowed. The specification was made more stringent in October, 1922, by the lowering of the maximum permissible initial boiling point from 60°C. to 55°C., and again in March, 1924 by the imposition of a total sulphur limit of 1·0 per cent.;

TABLE 173.—UNITED STATES GOVERNMENT SPECIFICATIONS FOR MOTOR GASOLINE, 1918-1927

	Date of Specification	October 2nd, 1918	November 25th, 1919	December 29th, 1920	March 1st, 1922	October 21st, 1922	March 18th, 1924
1.	Distillation						
	Initial Boiling Point °C.	60°C. (max.)	60°C. (max.)	60°C. (max.)	60°C. (max.)	55°C. (max.)	55°C. (max.)
	20% distillate at ..	105°C. (max.)	105°C. (max.)	105°C. (max.)	105°C. (max.)	105°C. (max.)	105°C. (max.)
	45% distillate at ..	135°C. (max.)	not specified	not specified	not specified	not specified	not specified
	50% distillate at ..	not specified	140°C. (max.)	140°C. (max.)	140°C. (max.)	140°C. (max.)	140°C. (max.)
	90% distillate at ..	180°C. (max.)	190°C. (max.)	190°C. (max.)	190°C. (max.)	200°C. (max.)	200°C. (max.)
	End Point °C. ..	220°C. (max.)	225°C. (max.)	225°C. (max.)	225°C. (max.)	225°C. (max.)	225°C. (max.)
	Total distillate ..	95% (min.)	95% (min.)	95% (min.)	95% (min.)	95% (min.)	95% (min.)
2.	Colour	Not specified	Not specified	Water white	16 Saybolt (min.)	16 Saybolt (min.)	16 Saybolt (min.)
3.	Sulphur content ..	Not specified	Not specified	Not specified	Not specified	Not specified	0·1% (max.)
4.	Corrosion test .. .. Copper strip test 3 hours at 122°F. (50°C.) ..	Not specified	Not specified	Not specified	Copper strip not to be discoloured	Copper strip not to be discoloured	Copper strip not to be discoloured
5.	Free from undissolved water and suspended matter	Not specified	Not specified	Specified	Not specified	Not specified	Not specified

but in October, 1927 the corrosion test was made rather less stringent by the allowance of " extremely slight colouration " of the copper strip.

805. New specifications which became effective on September 11th, 1929, differed in several important respects from those issued previously. For the first time specifications were issued for two different grades of motor spirit, namely, Motor Gasoline for use as a fuel for automobiles, trucks, tractors and motor boats, etc., and " Motor Fuel V," a special fuel for use in ambulances, fire engines, emergency vehicles, etc. In the case of " motor gasoline," the specification was only amended in one respect. The 20 per cent. temperature requirement was eliminated and in its place substituted a requirement for 10 per cent. distillate to be obtained at a distillation temperature of not more than 80°C. and not lower than 50°C. The added requirement was made that for each 1 per cent. distillation loss less than 4 per cent. the minimum 10 per cent. temperature was lowered 3°C.

The new Motor Fuel V specification was naturally more stringent than that of motor gasoline. Both are given in full in Table 174.

TABLE 174.

UNITED STATES GOVERNMENT SPECIFICATIONS, SEPTEMBER 11TH, 1929

U.S. MOTOR GASOLINE.

1. Free from water and suspended matter.
2. *Corrosion Test.* Copper strip, 3 hours at 122°F. (50°C.), not to show more than extremely slight discoloration.
3. *Distillation.*
   - (*a*) 10% distillate - - 80°C. (max.)—50°C. (min.). For each 1% distillation loss less than 4 per cent., the minimum 10% temperature to be lowered 3°C.
   - (*b*) 50% distillate - - 140°C. (max.).
   - (*c*) 90% distillate - - 200°C. (max.).
   - (*d*) End point - - - 225°C. (max.).
   - (*e*) Total distillate - - 95% (min.).
4. Total Sulphur - - - - - - 0·1% (max.).

MOTOR FUEL V.

1. Free from water and suspended matter.
2. *Corrosion test.* Same as for motor gasoline.
3. *Distillation.*
   - (*a*) 10% distillate - - 65°C. (max.)—50°C. (min.). For each 1% distillation loss less than 4%, the minimum 10% temperature to be lowered 3°C.
   - (*b*) 50% distillate - - 125°C. (max.).
   - (*c*) 90% distillate - - 18[illegible]°C. (max.).
   - (*d*) End point - - - 205°C. (max.).
   - (*e*) Total distillate - - 95% (min.).
4. Total Sulphur - - - - - - 0·1% (max.).

806. The specifications were next amended on July 21st, 1931, when those detailed below came into force. These specifications were still in force in May, 1933.

MOTOR FUEL V, SPECIFICATION V.V. M-571, JULY 21ST, 1931

(*a*) *Corrosion.* Copper strip test—not more than extremely slight corrosion after 3 hours at 122°F.

(*b*) *Sulphur.* Not more than 0·10%.

(*c*) *Vapour Pressure* (*Reid*). Maximum 10 lbs. at 100°F.

(*d*) *Distillation.* 10% evaporated* (min.) at 158°F. (70°C.).
50% ,, (min.) at 257°F. (125°C.).
90% ,, (min.) at 356°F. (180°C.).
Residue 2% maximum.

U.S. GOVERNMENT MOTOR GASOLINE, V.V. G 101, JULY 21ST, 1931

(*a*) *Corrosion.* Same as Motor Fuel V. above.

(*b*) *Sulphur.* Same as Motor Fuel V. above.

(*c*) *Vapour Pressure* (*Reid*). Maximum 12 lbs. at 100°F.

"The government reserves the right to reject material (*a*) in those localities where the normal mean temperature during the month of January is greater than 27°F. (−2·8°C.), if the vapour pressure at 100°F. is above 10 lbs. per square inch : (*b*) during the months of June, July, August and September if the vapour pressure at 100°F. exceeds 8 lbs. per square inch."

(*d*) *Distillation.*

Not less than 10 per cent. evaporated at 167°F. (75°C.).
,, ,, ,, 50 ,, ,, ,, ,, 284°F. (140°C.)
,, ,, ,, 90 ,, ,, ,, ,, 392°F. (200°C.).
Residue 2 per cent. maximum.

807. Other American Specifications.—The United States Army and Navy Departments issue their own specifications to which suppliers of all grades of motor spirit must comply. Details of the Navy specifications from October 1st, 1913, to the present date, are given in Table 175, from which it will be evident that these follow, in the main, the U.S. Government Federal Specifications. Thus Specification No. 7G2a is the same, in essentials, as the Federal Specification VV-M-571 for Motor Fuel V. It is of interest to note that the specification 8G1a, drafted October 1st, 1913, contains a clause prohibiting the use of Natural Gasoline, no doubt due to the fact that this product was then in considerable disfavour because it often contained varying amounts of

* Per cent. evaporated = per cent. distillate plus distillation loss.

TABLE 175.—GASOLINE SPECIFICATION OF THE UNITED STATES NAVY DEPARTMENT

Number of Specification	8G1a.	8G1b.	8G1c.	8G1d.
Date of Specification	October 1st, 1913	September 1st, 1917	July 1st, 1919	February 1st, 1921
1. General Clauses Governing Quality.	High grade, refined and free from water and all impurities.			High grade, refined from undissolved and suspended
	No natural gasolines will be accepted, nor will they be mixed with any gasoline submitted for acceptance.	—	—	—
	5 mls. of the sample when poured over a sheet of white paper shall evaporate completely without leaving a stain.		—	—
2. Distillation. Initial Boiling Point	130°F. / 54·5°C. } min.	140°F. / 60°C. } max.	140°F. / 60°C. } max.	140°F. / 60°C. } max.
20% distillate at ..	—	221°F. / 105°C. } max.	221°F. / 105°C. } max.	221°F. / 105°C. } max.
45% distillate at ..	—	275°F. / 135°C. } max.	275°F. / 135°C. } max.	—
50% distillate at ..	275°F. / 135°C. } max.	—	—	284°F. / 140°C. } max.
90% distillate at ..	—	356°F. / 180°C. } max.	356°F. / 180°C. } max.	374°F. / 190°C. } max.
95% distillate at ..	340°F. / 171·1°C. } max.	—	—	—
End Point	360°F. / 182·2°C. } max.	428°F. / 220°C. } max.	428°F. / 220°C. } max.	437°F. / 225°C. } max.
Total distillate %	95% minimum.	95% minimum.	95% minimum.	95% minimum.
3. Colour	—	—	—	—
4. Corrosion	—	—	—	—
5. Sulphur content ..	—	—	—	—
6. Vapour pressure ..	—	At 100°F. (37·8°C.) must not exceed 10 lbs. per sq. inch. (Test method according to "Regulations for transportation of explosives, etc." Interstate Commerce Commission, Paragraph 1824—K, Feb. 5th, 1916.)		—

* Provided that for each per cent. distillation loss less than 4% the minimum 10% temperature requirement shall be lowered 3°C. (5·4°F.).

(REPRODUCED BY THE PERMISSION OF THE NAVY DEPARTMENT, WASHINGTON)

7G1.	7G1a.	7G1b.	7G1c.	7G2.	7G2a. (Motor Fuel V)
October 2nd, 1922	July 2nd, 1923	December 1st, 1924	June 1st, 1928	February 1st, 1930	March 1st, 1933
fined and free solved water matter.	—	—	—	Free from water and suspended matter.	
—	—	—	—	—	—
—	—	—	—	—	—
140°F. 60°C. } max.	131°F. 55°C. } max.	131°F. 55°C. } max.	131°F. 55°C. } max.	* 10% distillate at	
221°F. 105°C. } max.	221°F. 105°C. } max.	221°F. 105°C. } max.	221°F. 105°C. } max.	176°F. 80°C. } max.	†10% at 158°F. 70°C. } max.
—	—	—	—	140°F. 60°C. } min.	
284°F. 140°C. } max.	284°F. 140°C. } max.	284°F. 140°C. } max.	284°F. 140°C. } max.	284°F. 140°C. } max.	257°F. 125°C. } max.
374°F. 190°C. } max.	392°F. 200°C. } max.	392°F. 200°C. } max.	392°F. 200°C. } max.	392°F. 200°C. } max.	356°F. 180°C. } max.
—	—	—	—	—	—
437°F. 225°C. } max.	437°F. 225°C. } max.	437°F. 225°C. } max.	437°F. 225°C. } max.	437°F. 225°C. } max.	—
95% minimum	95% minimum	95% minimum	95% minimum	95% minimum	Residue 2% max.
Shall be practically water white.	Shall be not darker than 16 Saybolt.		—	—	—
A clean copper strip shall not be discoloured when submerged in the gasoline for 3 hours, at 122°F. (50°C.).				A clean copper strip not to shew more than extremely slight corrosion for 3 hours at 122°F. (50°C.).	
—	—	0·1% (max.)	0·1% (max.)	0·1% (max.)	0·1% (max.)
—	—	—	—	—	10 lbs./sq. inch maximum at 100°F. (37·8°C.) Reid apparatus.

† In this specification, the temperatures refer to percentage evaporated and not to percentage distillate (% evaporated = % distillate + distillation loss).

low grade high boiling distillates added by unscrupulous blenders. Its quality was, of course, improved later, but some time elapsed before natural gasoline was looked upon as a high grade product.

Another point of interest is that as early as 1917, the U.S. Navy Department Motor Gasoline Specification contained a maximum vapour pressure clause. This was retained until February 1st, 1921, but was then deleted and did not appear again until March 1st, 1933, when the Reid vapour pressure apparatus had become standardized.

808. Quality of Motor Spirits Sold in the United States of America, 1920-1932.—Detailed information regarding the quality of the motor fuels sold in America is made available by the published results of the Semi-Annual Surveys conducted by the United States Bureau of Mines. These surveys are very thoroughly carried out and cover the whole country. They are made semi-annually so as to give information regarding the relative properties of summer and winter grade spirits. In August, 1930, the usefulness of the surveys was increased by the separate classification of different types of fuels, such as "competitive price spirits," benzole blends, ethyl gasolines, etc., etc., instead of grouping all fuels together as in previous surveys.

The average properties of all motor fuels sold in America during the years 1920 to 1930, as indicated by these surveys, are shown in the accompanying tables, from which the improvements made in quality are evident, as are the differences existing between winter and summer grades. For the purpose of these surveys, fuels sold in America are divided into two classes :—

(1) "*Competitive price*" *spirits*, which includes those fuels that are sold at the generally recognized local base price or at any lower price.
(2) *Premium price spirits*, those that are sold at higher prices than the generally recognized base price. These include ethyl gasoline, benzole blends, "high test" spirits and those fuels that owe their superior anti-knock value to the process of manufacture rather than to the addition of other material such as benzole or tetra-ethyl-lead.

The term "high test" is generally applied to motor fuels that are more volatile than the regular competitive price spirits and which may have higher knock ratings.

The average properties of competitive price and premium price motor fuels examined from August, 1930 to August, 1931, are detailed in Table 178, from which it will be observed that :—

(1) The premium priced fuels offer advantages over the competitive

TABLE 176.—AVERAGE PROPERTIES OF MOTOR FUELS SOLD IN THE UNITED STATES OF AMERICA, 1920–1929 (SUMMER SEASONS)

	Specific Gravity	Gravity °A.P.I.	Initial Boiling Point		10 per cent. Distillate		20 per cent. Distillate		50 per cent. Distillate		90 per cent. Distillate		End Point		Average Boiling Point		Per Cent. Recovery (Total Distillate)
			°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	
July, 1920	0·749	57·4	130	54·4	182	83·3	208	98·7	268	131·1	388	197·8	466	241·1	277	136·1	96·7
„ 1921	0·747	57·9	125	51·7	177	80·6	202	94·4	262	127·8	377	191·7	433	222·8	270	132·2	96·7
„ 1922	0·752	56·8	121	49·4	176	80·0	208	98·7	270	132·2	375	190·6	429	220·6	273	133·9	96·8
„ 1923	0·751	56·9	125	51·7	179	81·7	206	96·7	269	131·7	382	194·4	436	224·4	273	133·9	96·8
„ 1924	0·751	56·9	107	41·7	167	75·0	200	93·3	271	132·8	390	198·9	431	221·7	275	135·0	96·0
„ 1925	0·754	56·2	108	42·2	169	76·1	204	95·6	275	135·0	387	197·2	427	219·4	275	135·0	96·2
„ 1926	0·750	57·2	100	37·8	162	72·2	194	90·0	266	130·0	382	194·4	421	216·1	267	130·6	96·7
„ 1927	0·748	57·7	102	38·9	159	70·6	193	89·4	267	130·6	381	193·9	417	213·9	267	130·6	96·4
„ 1928	0·748	57·7	100	37·8	156	68·9	190	87·8	265	129·4	380	193·3	413	211·7	265	129·4	96·1
„ 1929	0·748	57·7	102	38·9	155	68·3	187	86·1	263	128·3	378	192·2	410	210·0	264	128·9	96·1
August, 1930	0·746	58·2	99	37·2	149	65·0	182	83·3	260	126·7	366	185·6	403	206·1	257	125·0	97·3

Reprinted from U.S. Bureau of Mines Report of Investigations 3129, August, 1931.

TABLE 177.—AVERAGE PROPERTIES OF MOTOR FUELS SOLD IN THE UNITED STATES OF AMERICA, 1920–1931 (WINTER SEASON)

	Specific Gravity	Gravity °A.P.I.	Initial Boiling Point		10 per cent. Distillate		20 per cent. Distillate		50 per cent. Distillate		90 per cent. Distillate		End Point		Average Boiling Point		Per Cent. Recovery (Total Distillate)
			°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	
January, 1920	0·748	57·7	119	48·3	172	77·8	200	93·3	259	126·1	369	187·2	427	219·4	264	128·9	96·6
,, 1921	0·744	58·7	113	45·0	168	75·0	197	91·7	261	127·2	377	191·7	431	221·7	264	128·9	95·9
,, 1922	0·745	58·4	102	38·9	168	75·0	200	93·3	267	130·6	377	191·7	430	221·1	268	131·1	96·0
,, 1923	0·744	58·8	107	41·7	167	74·4	201	93·9	267	130·6	375	190·6	427	219·4	268	131·1	96·0
,, 1924	0·748	57·7	96	35·6	164	73·3	196	91·1	267	130·6	383	195·0	431	221·7	268	131·1	96·2
,, 1925	0·746	58·2	95	35·0	161	71·7	195	90·6	266	130·0	382	194·4	425	218·3	267	130·6	96·2
,, 1926	0·747	57·9	93	33·9	155	68·3	189	87·2	264	128·9	380	193·3	423	217·2	264	128·9	96·3
,, 1927	0·748	57·7	92	33·3	149	65·0	185	85·0	264	128·9	383	195·0	421	216·1	264	128·9	96·5
,, 1928	0·747	57·9	90	32·2	146	63·3	181	82·8	261	127·2	378	192·2	416	213·3	260	126·7	96·5
,, 1929	0·746	58·2	87	30·6	143	61·7	179	81·7	263	128·3	380	193·3	414	212·2	260	126·7	96·1
,, 1930	0·741	59·5	93	33·9	139	59·4	174	78·9	256	124·4	371	188·3	406	207·8	254	123·3	96·6
March, 1931	0·740	59·7	91	32·8	139	59·4	172	77·8	254	123·3	366	185·6	401	205·0	252	122·2	96·6

Reprinted from U.S. Bureau of Mines Report of Investigations 3129, August, 1931.

priced fuels with respect to their higher volatilities, higher vapour pressures and higher knock ratings. They offer no advantages with respect to sulphur content or gum content.

(2) American motor fuels have very low gum contents.

(3) There is a very noticeable difference between the vapour pressures of gasolines sold in winter and those sold in summer.

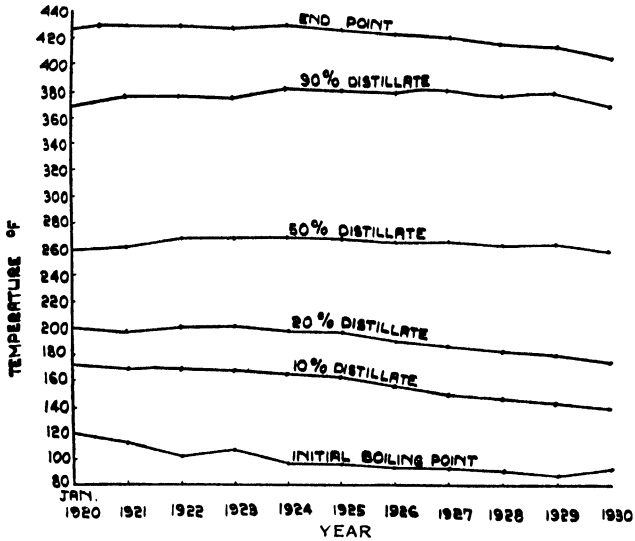


FIG. 224.—GRAPH SHEWING CHANGE IN VOLATILITY CHARACTERISTICS OF U.S. WINTER GRADE MOTOR FUELS, 1920–30, FROM FIGURES OF U.S. BUREAU OF MINES, SEMI-ANNUAL SURVEYS.

The knock ratings of American Motor Fuels are of especial interest. In March, 1931, the octane numbers of all grades were approximately 3 units higher than those of spirits marketed in August, 1930, but the August, 1931, survey showed a decline of between 1 and 2 units. Approximately 85 per cent. of the competitive priced fuels sold are in the range 55 to 69 octane number, and 86·5 per cent. of the premium priced fuels within the range 70 to 84 octane number. These figures compare favourably with 66 octane number for English No. 3 grade spirits and 70 octane number for English No. 1 grade spirits.

809. Results of Other Surveys.—From time to time the results of investigations carried out by independent companies regarding the quality of motor fuels have been published.

Trimble[2] has presented the results of knock rating surveys carried out by the Phillips Petroleum Company in 1930 and 1929. The samples obtained in these surveys were secured monthly from filling stations in approximately 70 cities located in 19 States east of the Rocky Mountains,

TABLE 178.—AVERAGE PROPERTIES OF AMERICAN MOTOR FUELS 1930-1931

	August, 1930.			March, 1931.			August, 1931.		
	All Fuels	Competitive Price	Premium Price	All Fuels	Competitive Price	Premium Price	All Fuels	Competitive Price	Premium Price
1. Specific gravity	0·746	0·746	0·746	0·740	0·738	0·743	—	—	—
2. Gravity °A.P.I.	58·2	56·9	58·2	59·7	60·2	58·9	—	—	—
3. Initial boiling point °F. ..	99	98	99	91	90	92	—	—	—
10% evaporated at °F. ..	149	141	139	139	130	133	—	—	—
20% distillate at °F... ..	182	187	176	172	173	170	—	—	—
50% „ „	260	266	243	254	258	245	—	—	—
90% „ „	366	380	338	366	371	355	—	—	—
End point	403	414	380	401	404	395	—	—	—
% Recovery	97·3	97·0	97·4	96·6	96·2	97·1	—	—	—
4. Sulphur.									
0·1% or less	85·6%	84·5%	87·5%	85·8%	83·9%	89·3%	87·6	86·4	90·8
0·08% or less	73·8%	74·2%	73·1%	66·6%	67·5%	64·6%	74·9	75·1	74·4
0·06% or less	54·4%	53·6%	54·8%	53·1%	54·0%	51·3%	59·9	61·1	57·1
5. Steam oven gum test, mgs./100 mls.									
1 mg. or less	18·1%	20·1%	14·4%						
2 or 3 mgs.	38·6%	38·7%	38·5%						
4 or 5 mgs.	17·1%	20·1%	11·5%	92·3 per cent. of all fuels had a gum content less than 5 mgs. per 100 ccs.			90·9 per cent. of all fuels had a gum content of less than 5 mgs. per 100 mls.		
6 or 7 mgs.	10·4%	8·8%	13·4%						
8 to 10 mgs.	6·7%	5·1%	8·6%						
11 to 15 mgs.	6·7%	5·1%	10·6%						
16 to 20 mgs.	1·7%	1·0%	2·9%						
Above 20 mgs.	0·7%	1·0%	—						
6. Colour.									
Lighter than 10 Saybolt ..	—	—	—	—	66·7%	6·6%	—	60·6%	—
Darker than 10 Saybolt ..	—	—	—	—	10·1%	1·0%	—	13·1%	—
Artificially coloured ..	—	23·7%	84·6%	—	23·2%	92·4%	—	26·2%	98·0%
7. Doctor test.									
% Samples positive ..	—	4·4%	7·7%	—	—	—	—	4·5%	3·0%
8. Corrosion test.									
% Samples corrosive ..	—	—	—	nil	nil	nil	0·6 per cent. of all fuels.		
9. Vapour pressures at 37·8°C. (100°F) 8·0 lbs. per square inch or less	80·9%	78·9%	84·6%	28·5%	22·2%	40·0%	68·0%	64·2%	76·5%
8·1 lbs.—10 lbs.	19·1%	21·1%	15·4%	51·6%	55·1%	45·7%	31·7%	35·3%	23·5%
More than 10 lbs.	—	—	—	19·9%	22·7%	14·3%	0·3%	0·5%	—
10. Knock Ratings. (C.F.R. Research Method).									
Average octane number ..	—	59	74	—	62·5	77	65	60·8	75·6
Octane number range ..	—	51–58	65–80	—	—	—	—	—	—
Octane number 40–44 ..	—	—	—	0·6%	1·0%	—	—	—	—
45–49 ..	—	—	—	1·3%	1·9%	—	1·6%	2·2%	—
50–54 ..	—	—	—	6·1%	8·7%	1·0%	7·5%	10·8%	—
55–59 ..	—	—	—	11·6%	17·4%	—	17·9%	25·6%	—
60–64 ..	—	—	—	22·4%	32·4%	2·8%	25·4%	35·0%	3·1%
65–69 ..	—	—	—	17·3%	22·7%	6·7%	17·9%	22·4%	7·3%
70–74 ..	—	—	—	15·1%	14·5%	16·2%	11·6%	4·0%	29·2%
75–79 ..	—	—	—	15·7%	1·4%	43·8%	10·6%	—	35·4%
80–84 ..	—	—	—	5·4%	—	16·2%	6·6%	—	21·9%
85–89 ..	—	—	—	4·5%	—	13·3%	0·9%	—	3·1%

and the numbers of samples taken of the various brands were made approximately proportional to their relative sales volumes. The results of this survey are reproduced in Figure 225, and may be summarized as follows :

	1929	1930
Ethyl Gasolines—		
Percentage above 74 octane number	40	70
Premium Non-Ethyl Gasolines—		
Percentage above 70 octane number	24	49
Standard Price Gasolines—		
Percentage above 60 octane number	14	47
,, ,, 58 ,, ,,	26	55
,, ,, 54 ,, ,,	62	79

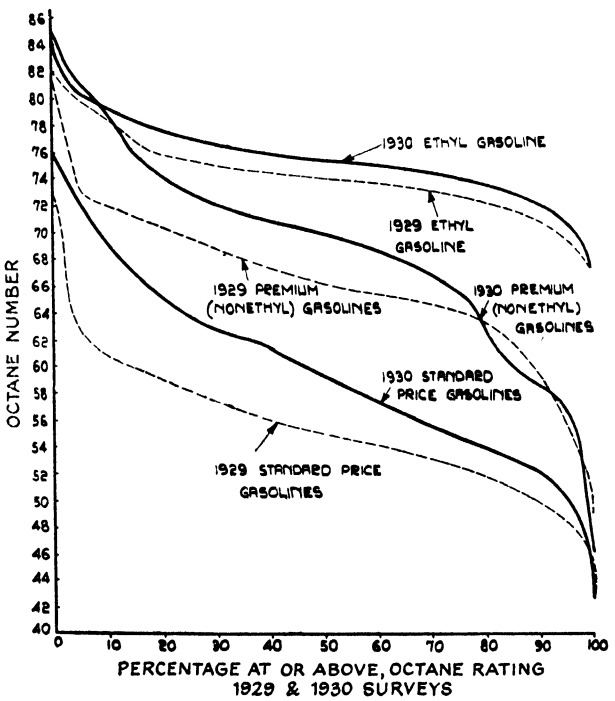


FIG. 225.—THE RESULTS OF THE PHILLIPS PETROLEUM COMPANY'S SURVEY OF AMERICAN MOTOR FUELS, 1929 AND 1930. (TRIMBLE.)

These knock ratings were determined on Ethyl Gasoline S. 30 and C.F.R. engines operating under the following conditions. Values on the two engines agreed to within one octane number.

	C.F.R. Engine	Ethyl Gasoline S.30 Engine
Oil temperature °F.	160°F.	—
Cooling medium (exit from head) ..	212°F.	212°F.
Cooling medium (inlet to cylinder) ..	165–175°F.	212°F.
Mixture temperature	120°F.	—
Air to carburettor	—	120°F.
Spark advance	20°	21°

Haslam and Bauer[3] have estimated (March, 1931) the sales of gasolines of different knock ratings in the United States of America to be as follows :—

Sales Per Cent.	*Octane Number.*
6	Below 43
10	43—47
62	57—66
6	66—73
10	73 (Ethyl Standard at time of estimate).
6	Above 73

The properties of motor fuels marketed in Cleveland, Chicago, Fort Worth and Kansas City during 1933 are revealed in the results of a Survey undertaken by The Oil and Gas Journal.* The average Octane Number (C.F.R., M.M.) of regular grades was 69, of premium grades 75, and third grades 53. Vapour Pressures by the standard Reid method averaged 9·5 lbs., 8·8 lbs., and 8·4 lbs. for these three grades respectively.

TABLE 179.—PROPERTIES OF U.S. THIRD GRADE GASOLINES

	January 1st, 1932	January 1st, 1933
Octane Number	51	53
Initial Point °F.	102	96
10 per cent.	152	148
20 per cent.	193	181
50 per cent.	276	264
90 per cent.	380	368
End Point °F.	426	426
Recovery per cent.	97·3	97·3
Reid Vapour Pressure, lbs. per square inch at 100°F. (37·8°C.)	6·5	7·6

* W. T. Ziegenhain, Oil & Gas J., 1933, 32, (31), 8.

Third Grade Gasolines.—In the United States there are considerable sales of so called " Third grade gasolines " which are inferior to the regular grades in both knock rating and volatility and which are retailed at lower prices. The quality of these spirits is shown in the above figures of Ziegenhain.[4]

Benzole Blends in U.S.A.—The production of benzole in the United States of America during 1931 was approximately 420,000 tons, an amount equivalent to only about 1 per cent. of the country's consumption of petroleum spirit. The amount of benzole consumed as motor fuel in U.S.A. is therefore negligible in proportion to the total motor fuel consumption.

810. Ethyl Gasoline in America.—Tetra-ethyl lead is a very popular anti-knock agent in America, and Ethyl Gasoline sales are very appreciable. In 1929, 8·2 per cent. of the motor fuel sold in America contained tetra-ethyl lead. In 1930, this figure increased to 11·6 per cent. and the same figure was maintained in 1931. However, the first half of 1932 showed a decline in the output of ethyl gasoline and the quantity blended was only equivalent to 8·2 per cent. of the total motor fuel consumed. This decline was solely due to the prevailing economic conditions which compelled motorists to use cheaper fuels.

TABLE 180.—ETHYL GASOLINE OUTPUT IN U.S.A., 1929–1932

	Ethyl Gasoline Blended at Refineries					
	1932	1931	1930	1929	1928	1927
Millions of U.S. gallons	1,284	1,970	1,854	—	—	300
Per cent. of total motor fuel consumption	8·2	11·6	11·6	9·1	4·5	2·5

The anti-knock standard set by the Ethyl Gasoline Corporation was 74 octane number prior to March 1st, 1932, but on this date the standard was raised to 78 octane number. All gasoline blended with tetra-ethyl lead for sale as Ethyl gasoline must conform to the following specification drawn up by the Ethyl Gasoline Corporation.[5]

(1) *Sulphur.* Not more than 0·1 per cent.

(2) *Corrosion.* A copper strip immersed in the fuel for 3 hours at 100°C. must not show more than extremely slight corrosion.

(3) *Gum Content.* Satisfactory to the Ethyl Gasoline Corporation.

(4) *Distillation*—

(*a*) *April 1st to October 1st.*

Not less than 10% evaporated at 158°F. (70°C.).
" " " 50% " " 284°F. (140°C.).
" " " 90% " " 392°F. (200°C.).

(*b*) *October 1st to April 1st.*

Not less than 10% evaporated at 149°F. (65°C.).
„ „ „ 50% „ „ 284°F. (140°C.).
„ „ „ 90% „ „ 392°F. (200°C.).

(5) *Vapour Pressure*—

April 1st to October 1st. Maximum 8 lbs./sq. in. (Reid).
October 1st to April 1st. „ 10 lbs./sq. in. (Reid).

Ethyl gasolines in America do not contain more than 3 ccs. of tetra-ethyl lead per U.S. gallon. The minimum amount was raised on March 1st, 1932, from 0·75 ccs. to 0·9 ccs. per gallon.

Blenders are required to buy their tetra-ethyl lead from the Ethyl Gasoline Corporation at a price of 0·35 cents per c.c., and to pay a premium on gallonage at the rate of 0·425 cents per gallon.

At the beginning of 1933, the Ethyl Gasoline Corporation reached a decision to allow the use of tetra-ethyl lead in second grade motor fuels sold by those refiners and marketers already holding contracts for the sale of the usual Ethyl Gasoline as from June 1st, 1933. Under the terms of the agreement covering the use of tetra-ethyl lead in this way, the latter will cost 0·35 cents per cubic centimetre, plus a gallonage charge of 0·05 cents per gallon. The amount of tetra-ethyl lead which may be used must lie between 0·3 ccs. per gallon and 1·5 ccs. per gallon. Thus, the cost to the refiner will range between 0·155 cents and 0·565 cents per gallon. A further restriction imposed on this grade of motor fuel is that it must not exceed 70 octane number as determined by the C.F.R. motor method.[6]

811. Gasoline Taxes in America and State Inspection Laws.—With the object of obtaining revenue for the building of roads and highways, individual States in America have resorted to the taxation of motor fuels. The first State to adopt such a tax was Oregon, the law becoming effective February 25th, 1919, and by 1928, all of the States except two had levied taxes on motor fuels at rates varying from 2 to 5 cents per gallon. Regulations governing the quality and the methods of handling gasoline and other petroleum products have also been adopted by 29 States, and many of these laws antedate the adoption of gasoline taxes.

The tax rates of the various States on September 1st, 1931 are given in Table 181, reprinted from U.S. Bureau of Mines Information Circular 6576, January, 1932, in which it will be seen that the average gasoline tax is 4·06 cents per gallon. Florida has the highest tax (7 cents per gallon) and Connecticut, Missouri, New York, Rhode Island and the District of Columbia have the lowest (2 cents per gallon).

Different States have their own inspection laws, but these are even less uniform than the taxes. Several States automatically change their requirements to conform to any changes in specifications adopted by the Federal Specifications Board for Government purchases, but others have independent requirements. In 8 States all motor fuel must conform to U.S. Government specifications.

Full details regarding the State Laws at present in force are given in the above mentioned U.S. Bureau of Mines Information Circular.

TABLE 181.—GASOLINE TAXES IN AMERICAN STATES
(CENTS PER GALLON)

Alabama	5	Nebraska	4
Arizona	5	Nevada	4
Arkansas	6	New Hampshire	4
California	3	New Jersey	3
Colorado	4	New Mexico	5
Connecticut	2	New York	2
Delaware	3	North Carolina	6
Florida	7	North Dakota	3
Georgia	6	Ohio	4
Idaho	5	Oklahoma	5
Illinois	3	Oregon	4
Indiana	4	Pennsylvania	3
Iowa	3	Rhode Island	4
Kansas	3	South Carolina	6
Kentucky	5	South Dakota	6
Louisiana	5	Tennessee	2
Maine	4	Texas	4
Maryland	4	Utah	4
Massachusetts	3	Vermont	4
Michigan	3	Virginia	5
Minnesota	3	Washington	5
Mississippi	5	West Virginia	4
Missouri	2	Wisconsin	4
Montana	5	Wyoming	4
District of Columbia	2		
Average tax	4·06 cents per gallon.		

Federal Taxes.—In addition to the individual State Taxes, the U.S. Federal Government also impose a tax on all gasoline sold in the United States. This amounts to 1 cent per gallon.

As an example of how the retail price of spirit sold is made up, the following figures regarding California are of interest.

	Cents per Gallon.	*Per Cent.*
California State Tax ..	3	16·7
Federal Tax ..	1	5·6
Cost of Gasoline ..	6	33·3
Freight	2	11·1
Distribution	4	22·2
Retailers' Profit ..	2	11·1
	18	100·0

811a. Motor Fuels in Canada.—The properties of Canadian motor fuels marketed in 1933 have recently been described by Mr. D. Chantler of the Canadian Department of Mines.* The average of all samples examined was 65 Octane Number (C.F.R. Motor Method) and 6·9 lbs. Reid vapour pressure at 100°F. 66% of all samples were artificially coloured. The knock-ratings of Canadian motor fuels during 1933 were as follows :—

11·1%	75–79	Octane Number (C.F.R., M.M.)
11·1%	70–74	,, ,,
26·5%	65–69	,, ,,
31·6%	60–64	,, ,,
12·0%	55–59	,, ,,
6·0%	50–54	,, ,,
1·7%	45–49	,, ,,

The United Kingdom

812. Specifications.—The only specification governing the properties of petrols sold in Great Britain for use in road vehicles is that issued by the British Engineering Standards Association in April, 1923, (No. 121). This is, however, sadly out of date and is disregarded. It bears no relation whatever to the quality of motor fuels now sold.

The quality of motor fuels marketed in Britain is determined by the three major oil companies operating there, and, despite the lack of published specifications, they market motor fuel of extremely good quality. These three oil companies, namely, the Shell group, the Anglo Persian Oil Company and the Anglo American Oil Company, have agreements among themselves whereby the English market is divided between them on a quota basis and the properties of motor fuels sold by them are adjusted to an agreed standard.

Three grades of motor fuel are marketed. First, petrol of superior all round properties intended for use in privately owned cars and

* Universal Oil Products Library Bulletin of Abstracts, 1934, 9, (45).

TABLE 183.—PROPERTIES OF NO. 1 GRADE PETROLS MARKETED IN UNITED KINGDOM

	1931–1932					1931–1932				1927		
	(a)	(b) Winter Grade	(c) Summer Grade	(d)	(e)	(f)	(g)	(h)	(i)	(a)	(b)	(c)
Specific Gravity at 60°F.	0·736	0·732	0·743	0·735	0·735	0·740	0·743	0·735	0·749	0·727	0·742	0·734
Initial Boiling Point °C.	35°C.	32°C.	41°C.	34°C.	34°C.	34°C.	48°C.	31°C.	33°C.	47°C.	40°C.	39°C.
1% distillate at ..	37	36	49	37	38	38	52	35	—	58	50	50
2% „ „ ..	42	40	54	40	41	42	54	40	—	62	55	53
5% „ „ ..	50	47	60	50	50	50	62	48	51	67	63	60
10% „ „ ..	58	55	69	60	60	59	72	59	66	73	72	68
20% „ „ ..	72	70	82	75	77	73	83	74	84	83	87	81
30% „ „ ..	86	84	94	89	90	85	99	89	97	93	100	92
40% „ „ ..	100	98	105	102	102	98	110	104	108	101	110	102
50% „ „ ..	112	109	115	114	112	109	120	116	118	110	120	112
60% „ „ ..	123	121	126	125	120	120	130	130	130	118	131	121
70% „ „ ..	137	135	137	138	130	130	141	144	144	128	142	132
80% „ „ ..	152	149	151	153	143	143	152	160	161	139	154	144
90% „ „ ..	173	167	168	171	163	161	175	174	180	157	172	163
95% „ „ ..	187	183	180	186	177	175	187	187	190	173	191	—
F.B.P.	197	196	190	196	185	193	200	197	195	180	198	183
Recovery per cent. ..	98	97	98	97	97·5	98	98	98	97	97	—	—
Residue „ ..	1	1·1	1	1	1·0	1	1	1	—	2	—	—
Loss „ ..	1	1·9	1	2	1·5	1	1	1	—	1	—	—
Octane Number ..	72	70	70	70	77	73	67	70	75–77	56	—	—

TABLE 184.—PROPERTIES OF COMMERCIAL (No. 3) GRADE PETROLS MARKETED IN THE UNITED KINGDOM

	1931–1932				1931–1932				1927		
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(a)	(b)	(c)
Specific Gravity at 60°F.	0·740	0·737	0·737	0·749	0·742	0·755	0·740	0·745	—	0·742	0·730
Initial Boiling Point	34°C.	36°C.	35°C.	38°C.	33°C.	33°C.	35°C.	51°C.	47°C.	40°C.	46°C.
1% distillate at °C...	—	43	40	47	39	—	42	62	59	50	55
2% „ „ ..	—	48	44	50	45	—	46	66	63	55	59
5% „ „ ..	55	55	52	57	54	55	53	74	69	63	65
10% „ „ ..	64	62	64	66	66	71	62	80	76	72	72
20% „ „ ..	80	81	81	81	85	92	80	93	87	87	84
30% „ „ ..	93	95	96	96	100	107	99	103	97	100	95
40% „ „ ..	105	106	108	110	113	119	114	112	106	110	106
50% „ „ ..	117	117	119	123	124	129	126	119	116	120	116
60% „ „ ..	129	128	131	134	135	141	139	129	126	131	125
70% „ „ ..	141	139	143	145	148	155	151	139	137	142	136
80% „ „ ..	156	153	156	159	160	169	165	149	149	154	146
90% „ „ ..	172	170	177	177	175	186	184	163	167	172	163
95% „ „ ..	186	189	195	196	188	195	200	173	184	191	177
Final Boiling Point ..	199	196	205	205	198	198	206	183	193	198	186
Recovery per cent. ..	97·5	97·5	97	98·5	98	96	97·5	98	—	—	—
Residue „ ..	1·0	1·0	1	1·0	1	2	1·4	1	—	—	—
Loss „ ..	1·5	1·5	2	0·5	1	2	1·1	1	—	—	—
Octane Number ..	66	66	65	74	66	74–76	69	59	56	—	—
% Aromatics ..	—	10·4	—	—	—	—	9·5	12	—	—	—

TABLE 185.—PROPERTIES OF BENZOLE MIXTURES MARKETED IN THE UNITED KINGDOM.

	1931–1932					1927		
	(a)	(b)	(c)	(d)	(e)	(a)	(b)	(c)
Specific Gravity at 60°F. ..	0·777	0·767	0·756	0·747	0·750	0·774	0·768	0·760
Initial Boiling Point °C. ..	50°C.	43°C.	39°C.	37°C.	39°C.	53°C.	46°C.	42°C.
1% distillate at	56	50	44	42	45	66	58	53
2% „ „	60	53	48	46	49	69	63	57
5% „ „	68	61	56	53	55	73	69	65
10% „ „	74	71	66	62	65	78	75	74
20% „ „	82	82	82	76	81	85	83	87
30% „ „	88	90	93	88	96	92	91	97
40% „ „	94	97	103	99	110	98	97	105
50% „ „	100	107	113	109	123	106	104	115
60% „ „	108	117	123	120	137	117	115	127
70% „ „	120	130	135	130	151	132	129	142
80% „ „	140	145	146	143	165	150	143	158
90% „ „	160	168	162	161	184	170	161	171
95% „ „	175	180	175	175	200	187	177	195
Final Boiling Point	187	186	188	193	205	199	186	195
Recovery	98	97·5	98	97·5	97·5	—	—	—
Residue	1	1·0	1	1·3	1·0	—	—	—
Loss	1	1·5	1	1·2	1·5	—	—	—
Octane Number	69	74	72	74	70	—	—	—
% Aromatics	39	29	19	17	15	35	23	17

designated No. 1 grade; secondly, a petrol of good grade suitable for such purposes as do not demand No. 1 grade, the so called "Commercial" or No. 3 grade petrols; and thirdly, benzole mixtures, made up by the blending of benzole of British manufacture with imported petrols.

TABLE 182.—BRITISH STANDARD SPECIFICATION FOR MOTOR SPIRIT. No. 121, APRIL, 1923

1. The liquid shall consist of hydrocarbons and be free from visible impurities.
2. The range of distillation shall be
   (*a*) Initial Boiling point not above 55°C.
   (*b*) 20 per cent. distillate at not above 105°C.
   (*c*) End point not above 225°C.
3. The motor spirit shall be free from mineral acidity.

813. Quality of Motor Fuels Marketed in Great Britain.—Many changes have taken place in the British motor fuel market during the past few years, the most important of which, from the users' point of view, being the marked improvement in quality. Immediately after the late war the petrol available to the English public had an octane number of about 35, but this figure has increased at a very rapid rate, as shown in the following figures.[7]

Year of Average Sample	Octane Number. C.F.R. Engine. (Research Method)	
	No. 1 Grade Petrol	No. 3 Grade Petrol
1922	51	43
1925	55	53
1928	58	55
1931	68	61

Improvements have been made with regard to volatility. Front-end volatility has been increased to give better starting properties, mean volatilities have been increased to give better acceleration performance, and vapour lock tendencies have been obviated by scientific blending and the use of seasonal changes in motor fuel volatility. The magnitude and importance of these desirable changes has been made evident by W. A. Whatmough[8] in a series of articles recently published in *The Automobile Engineer*, from which the data collected in Tables 183, 184 and 185 have been taken.

These tables give the properties of those motor fuels most widely distributed in Great Britain over the period 1931/32, and draws comparisons with the properties of similar petrols sold in 1927. Referring to the No. 1 grade spirits, only two contain tetra-ethyl lead to improve anti-knock value, "Pratts' Ethyl" petrol being coloured red and "B.P. Plus"* a light blue. Pratts Ethyl was the first leaded petrol to appear on the English market, and made its debut in January, 1928, at a retail price of 1d. more than the normal No. 1 grades. B.P. Plus was not introduced until much later (April, 1931). In 1932, approximately 77 million gallons of gasoline containing tetra-ethyl lead were sold in England.

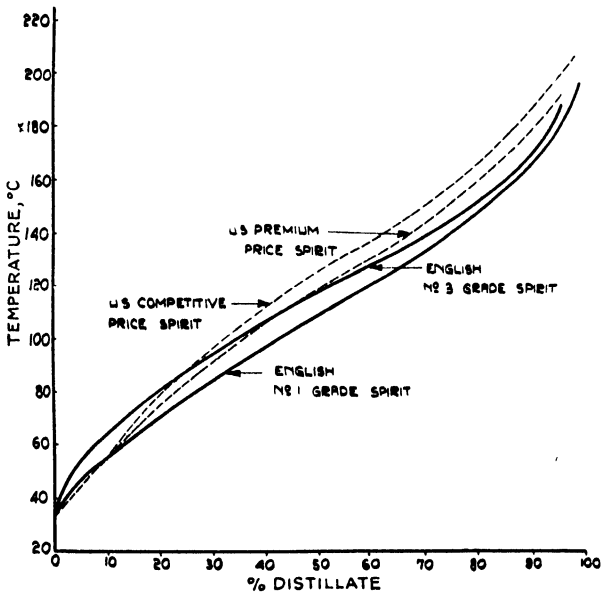


FIG. 226.—THE DISTILLATION CHARACTERISTICS OF MOTOR FUELS MARKETED IN ENGLAND AND U.S.A.

Most English spirits contain cracked spirits, both liquid-phase cracked and vapour-phase cracked products being used in the production of B.P. spirits.

The seasonal adjustment of volatility characteristics to avoid vapour locking in summer and to ensure easy starting in winter is well illustrated in the accompanying tables.

The spirits marketed by combine companies have fully adequate volatility characteristics, but others are variable in this respect.

* This petrol is now marketed as "B.P. Ethyl" and is dyed red.

The knock ratings of the No. 1 grade spirits of combine companies are stabilized at about 70 octane number, and the No. 3 spirits at about 66 octane number. These values are adequate for most of the cars and automobiles in present use. Ethyl Petrols have an octane number about 76.

Various benzole mixtures are also marketed. The most important of these is National Benzole mixture, a mixture of Persian spirit supplied from the Anglo Persian Oil Company quota and benzole produced by the National Benzole Association. This benzole mixture normally contains about 30 per cent. of added benzole and has a knock rating equal to that of No. 1 spirits. It is sold at the same price as No. 1 petrol. Other benzole mixtures contain rather less benzole. On the whole, benzole mixtures, though widely used in Great Britain, are not nearly so popular as in some parts of the Continent.

814. One of Whatmough's main conclusions is that the volatility characteristics of British and American motor spirits differ but little above 75 per cent. effective volatility, i.e., at 124°F. (51·1°C.) the effective volatility of U.S. motor gasoline is 90 per cent., as compared with 98 per cent. for a typical British petrol. On the other hand, the effective volatility of the British product with a 16 to 1 air-fuel mixture at 50°F. (10°C.) is double that of the American spirit.

It must be pointed out, however, that the figures given by Whatmough for a typical American gasoline do not agree with the latest figures published in the semi-annual surveys of the U.S. Bureau of Mines, and that the true difference existing is less than that indicated by Whatmough. Figure 226 gives curves comparing the distillation properties of English No. 1 and No. 3 spirits sold in 1931—1932, with those of typical American grades of fuel sold in March, 1931, all of winter grade volatility.

815. Two alcohol fuels are marketed in England, the properties of which are as follows :—

	(A)	(B)
Sp. Gr. at 60°F.	0·75	0·755
Initial Boiling Point°C ..	40	46
% distillate at 100°C. ..	56	51
Final Boiling Point°C. ..	195	195
Alcohol Content	16	15
Octane Number	76	76

816. Racing Fuels in Great Britain.—For racing purposes and attacks upon speed records, etc., No. 1 grade petrols have not a sufficiently high anti-knock value or mean volatility and other fuels are usually employed. For unsupercharged racing engines of fairly low compression ratios, i.e., up to about 7·0 or 7·5, 50/50 petrol benzole blends are commonly used. Higher compression ratios and the use of supercharging necessitate the use of petroleum spirits doped with tetra-ethyl lead, or alcohol fuels. Benzole is not a particularly suitable fuel for such purposes because of its tendency towards engine over-heating and because its volatility is not high enough. A noticeable development during the past two years is the growing use of methanol as a constituent of racing fuels. This is dealt with in greater detail in Chapter IX (Volume I).

Two alcohol fuels are marketed by Solvent Products Limited, a subsidiary of The Distillers Company Limited. The properties of these fuels are as follows.

	(A)	(B)
Sp. Gr. at 15/15°C.	0·828	0·822
Hydrocarbons	23%	10%
Acetone	trace	9%
98% Ethyl alcohol	77%	79%
Initial Boiling Point	68·5°C.	64°C.
95% distillate at	78°C.	78°C.

European Countries

817. The motor fuel position in Europe is much complicated by the continuously changing laws making the addition of various amounts of home produced alcohol compulsory. Political unrest aggravates the position and threats are being made in various countries to convert the importation of petroleum and its products into Government monopolies.

General Properties of the Petrols Sold in Europe as Indicated by the Properties of American Imported Fuels.—In general, three grades of motor fuel are marketed in Europe. (1) A premium fuel which may be either a benzole blend, an alcohol mixture or a high grade petroleum spirit with or without tetra-ethyl lead. (2) Standard grade spirit, comparable to English No. 1 spirit as far as volatility is concerned, and (3) a heavy grade or commercial spirit. These three grades naturally vary to some extent in different countries and are sometimes blended with benzole and/or with alcohol to meet local requirements, but the figures presented in Table 187, showing the pro-

perties of the various grades of spirit marketed by the associated companies of the Standard Oil Company of New Jersey, give a general idea of the quality of the spirits marketed in those countries where the addition of benzole or alcohol is not enforced.*

TABLE 187.—PROPERTIES OF STANDARD OIL COMPANY PETROLS IMPORTED INTO EUROPEAN COUNTRIES

	Premium Grade "Esso"	Standard Grade	Heavy Grade (Commercial Spirit)
Specific Gravity at 60°F. ..	0·745–0·770	0·725–0·735	0·740
Initial Boiling Point °C. ..	30–35	30–35	35
% at 100°C.	40–45	40	28–30
Final Boiling Point °C. ..	Below 200	Below 200	200
Octane Number	80	66	64
	This sometimes contains tetra-ethyl lead.		

818. France.—The question of motor fuel quality in France is intimately connected with the legislation compelling the addition of alcohol to imported fuels, a subject dealt with in detail in Chapter IX. "Essence Tourisme," which contains no alcohol, has volatility characteristics very much like those of an English No. 1 petrol, but its knock rating is no higher than an English No. 3 grade.

"Carburant poids lourds" is the description exclusively reserved by a Government decree dated October 26th, 1931 for petrol-alcohol mixtures containing 25—35 per cent. alcohol. Such mixtures are not popular in France, because, containing so much alcohol, they give poor performance and a rather higher consumption than normal petrols.

819. Germany.—Two grades of motor spirit are retailed in Germany. The higher quality grade is usually designated by branded names, and such advertised motor fuels are invariably blends of petroleum spirit, benzole and alcohol. The inclusion of alcohol and benzole in these motor fuels produces, as shown in Chapter IX, a peculiar type of distillation curve. The concavity of this type of curve is characteristic of azeotropic mixtures formed by such blends. Nearly 70 per cent. of a typical blended German motor fuel distils below 100°C., as compared with 40 per cent. in the case of first grade British petrol. Good grade

* The authors are indebted to D. S. Paul, Esq., of the Anglo-American Oil Company, London, for permission to publish these figures.

TABLE 188.—PROPERTIES OF MOTOR FUELS MARKETED IN FRANCE, 1931-1932

	Typical "Essence Tourisme"*	Esso	Carburant Poids Lourds	Esbol
Specific Gravity at 60°F.	0·735	0·745	0·77	0·765
Initial Boiling Point	38°C.	30	56	46
1% at	42°C.	—	17·2% at 100°C.	—
2%	45	—	—	—
5%	52	—	—	—
10%	61	—	—	—
20%	75	—	—	—
30%	88	—	—	—
40%	100	100	—	—
50%	112	—	—	—
60%	123	—	—	62% at 100°C.
70%	136	—	—	—
80%	150	83% at 150	65% at 150°C.	—
90%	170	89·2% at 160	89% at 175	93% at 150°C.
95%	185	94·12% at 75	95% at 183	160
Final Boiling Point	196	—	—	—
Octane Number ..	66	83	89 contains 25% alcohol	72 contains 30% benzole

TABLE 189.—PROPERTIES OF MOTOR FUELS MARKETED IN GERMANY, 1931-1932

	Typical German Blended Fuel.*	Typical German Commercial Fuel*	Benzole Verbandt "Aral"
Specific Gravity at 60°F. ..	0·790	0·745	0·782
Initial Boiling Point ..	48°C.	43°C.	55°C.
1% distillate at	49	46	—
2% ,, ,, ...	51	48	63
5% ,, ,, ...	53	56	65
10% ,, ,, ...	56	67	67
20% ,, ,, ...	61	84	69
30% ,, ,, ...	66	98	72
40% ,, ,, ...	72	110	76
50% ,, ,, ...	82	120	92
60% ,, ,, ...	95	130	99
70% ,, ,, ...	110	140	108
80% ,, ,, ...	130	150	124
90% ,, ,, ...	158	169	146
95% ,, ,, ...	179	182	158
Final Boiling Point	192	198	184
Octane Number	Above 75	71	98

* Whatmough (8).

German motor fuels contain 10 per cent. of alcohol and a notable proportion of benzole which accounts for their high specific gravity. In addition, they have very high anti-knock values. Benzole is freely obtainable in Germany and some 25 per cent. of the motor spirit consumed is home produced in this form.

The inclusion of alcohol in German motor fuels appears to be advantageous. The small amount of alcohol used does not interfere with carburetting characteristics and the presence of benzole obviates any tendency for separation into two layers.

820. Italy.—According to Whatmough, three grades of motor fuel are marketed in Italy, a light spirit, a heavy spirit and benzole mixtures. The properties of these fuels are detailed in the following Table.

TABLE 190.—PROPERTIES OF MOTOR FUELS MARKETED IN ITALY, 1931-1932

	Light Motor Spirit	Heavy Motor Spirit	Benzole Blend	Milano
Specific Gravity at 60°F.	0·724	0·736	0·769	0·769
Initial Boiling Point	40	40	48	—
1% distillate at ..	44	44	50	—
2% ,, ,, ..	47	47	52	—
5% ,, ,, ..	54	56	58	—
10% ,, ,, ..	63	68	66	—
20% ,, ,, ..	78	84	79	—
30% ,, ,, ..	90	97	88	—
40% ,, ,, ..	103	108	94	—
50% ,, ,, ..	114	119	100	56% at 100°C.
60% ,, ,, ..	123	128	107	—
70% ,, ,, ..	134	139	118	—
80% ,, ,, ..	147	154	132	88·5% at 150°C.
90% ,, ,, ..	166	174	166	—
95% ,, ,, ..	179	187	172	166·5
Final Boiling Point ..	190	199	185	—
Octane Number ..	56	67	—	82
				Contains 33 per cent. Benzole.

821. Denmark.—Two grades of motor spirit are marketed in Denmark, approximating to English No. 1 and No. 3 grades in all essentials except octane number. These fuels for the most part consist entirely of petroleum spirit and are unblended. An exception, however, is Esso, containing 30 per cent. benzole.

TABLE 191.—PROPERTIES OF MOTOR FUELS MARKETED IN DENMARK.

	First Grade Spirit	Second Grade Spirit	Esso
Specific Gravity at 60°F. ..	0·732	0·732	0·764
Initial Boiling Point	42	46	46
1% distillate at	45	50	—
2% ,, ,, ...	48	53	—
5% ,, ,, ...	54	61	—
10% ,, ,, ...	63	72	—
20% ,, ,, ...	78	89	—
30% ,, ,, ...	91	99	—
40% ,, ,, ...	100	110	—
50% ,, ,, ...	109	119	54% at 100°C.
60% ,, ,, ...	117	128	—
70% ,, ,, ...	127	137	—
80% ,, ,, ...	138	150	—
90% ,, ,, ...	155	166	87·6% at 150°C.
95% ,, ,, ...	172	180	168
Final Boiling Point	184	193	—
Octane Number	61	60	74

822. Belgium.—Specifications for fuels used by the Belgian Army have recently appeared, covering both aviation spirits and fuels intended for use in automobiles. The latter is as follows :—

(1) *Distillation.*

(*a*) Not more than 20 per cent. at 70°C.

(*b*) At least 60 per cent. between 70°C. and 140°C.

(*c*) Not more than 25 per cent. above 140°C.

(*d*) Recovery at 200°C. at least 95 per cent. (In the case of cracked spirits, 40 per cent. to distil between 70°C. and 140°C., not more than 40 per cent. above 140°C., and recovery at 200°C. to be at least 90 per cent.

(2) *Sulphur.*

Not more than 0·1 per cent.

823 REFERENCES

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Chapter XVIII

AVIATION FUELS

824. Introduction.—The criteria for satisfactory quality are necessarily much more stringent in the case of fuels intended for use in aero engines than in the case of ordinary automobile fuels. The first essential in all phases of aircraft operation is reliability and this makes fuel quality a matter of great importance. Furthermore it is much more important in aero practice to ensure that the fuels and engines "fit," as aircraft engines are in general very susceptible to fuel quality.

The Special Requirements of Aircraft Fuels.

825. Specific Gravity.—In aviation fuels, specific gravity has an importance out of proportion to its slight significance in the case of automobile fuels, because of considerations concerning both cruising radius and pay-load. In military and commercial aviation particularly, it is an advantage, other things being equal, to have as large a cruising radius as possible (i.e. miles per normal fuel complement). It is also of advantage to reduce the amount of fuel carried to the minimum so as to allow the transport of the maximum amount of paying load or other materials, e.g. bombs, etc., in the case of military aircraft.

The fuel factors determining cruising radius and amount of fuel carried are specific gravity and heat of combustion (calorific value). Ordinarily motor fuels are sold on a gallonage basis, but in the case of aircraft, gallonage takes second place in importance to fuel weight, and calorific value per pound is of greater importance than calorific value per gallon. Among normal petroleum spirits, a relationship exists between specific gravity and heat of combustion which is given approximately by the equation

$$Q_v = 12{,}400 - 2100d^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q_v = total heat of combustion at constant volume of motor fuel free from water, ash and sulphur.—Final products gaseous CO_2 and liquid H_2O.—Calories per gram.

d = Specific gravity at 60°/60°F.

The nett heat of combustion at constant pressure is similarly given by

$$Q_p = Q_v - \%H\,[(9 \times 585) - 220]\,0{\cdot}01 \quad . \quad . \quad . \quad . \quad (2)$$

in which the figure 9 represents the number of grams of water formed from 1 gram of hydrogen, 585 represents the latent heat of vaporization of water at 20°C. (68°F.) and the figure 220 is a small correction to take into account the change in volume from initial to final products. Average values for the percentages of hydrogen in oils of various specific gravities may be obtained from the relation

$$\%H = 26 - 15d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These equations are necessarily approximate but are correct to within about 1 per cent. in the case of normal straight-run spirits. In the case of cracked spirits and spirits containing appreciable quantities of aromatics less accurate results are obtained.[1]

It will be evident from such considerations that the heats of combustion, or calorific values per unit weight of petroleum spirits rise slightly with decrease in specific gravity, e.g.,

°A.P.I.	*Sp. gr.* 60°/60°*F.*	Q_v (*Cals./gram.*)	*BTU/gallon*
50	0·7796	11,120	130,100
60	0·7389	11,250	124,800
70	0·7022	11,360	119,800
80	0·6690	11,460	115,100
90	0·6388	11,540	110,700

but that heats of combustion per gallon fall with decrease in specific gravity. Therefore, other things being equal, a fuel of low specific gravity is preferable as an aviation fuel to a fuel of high specific gravity, because it has a higher heat of combustion per unit weight.

However, other considerations to some extent prevent the adoption of fuels of very low specific gravity. First there is the question of volatility and boiling range. This imposes a very definite lower limit to the specific gravity because of vapour lock considerations. Secondly there is the very important question of anti-knock value and probably the only way to obtain a fuel that has a high knock rating and a low specific gravity while conforming to the usual volatility standards is to dope a paraffinic straight run fuel with tetra-ethyl-lead. This necessitates the use of large quantities of the latter. Fuels which have high inherent anti-knock values have usually high specific gravities, e.g. spirits containing aromatics or naphthenes. Therefore, a compromise must be made between the beneficial effects of a low specific gravity on the one hand and the absolute necessity of a high anti-knock value on the other. It is interesting to note that the British Air Ministry Specifications D.T.D. 224 and 230 for aviation spirit impose a maximum specific gravity of 0·79 at 15°C. As a class the aromatic hydrocarbons have higher specific gravities than either paraffins and naphthenes, but

lower calorific values per pound, although they have higher calorific values per gallon.

TABLE 192

	Sp. gr. at 15°C.	Gross Calorific Value		Nett Calorific Value	
		Cals./gram	B.T.U./gallon	Cals./gram	B.T.U./gallon
Benzene ..	0·885	10,090	160,500	9,720	154,500
Toluene ..	0·871	10,160	159,500	9,740	153,000
m-Xylene ..	0·869	10,250	160,500	9,825	153,500
n-Hexane ..	0·665	11,500	137,500	10,715	128,000
n-Heptane ..	0·689	11,490	142,500	10,715	130,000
n-Octane ..	0·707	11,430	145,500	10,665	135,000
Cyclohexane	0·785	11,160	158,000	10,470	144,500

Because of these considerations, if hexane had the same anti-knock characteristics as benzene it would be more suitable as a constituent of aviation fuels than the latter.

American aviation spirit specifications include no specific gravity limitations, because when high anti-knock values are required these are obtained by the addition of tetra-ethyl-lead rather than the addition of benzole or other aromatics.

826. Volatility Requirements of Aviation Fuels.—The volatility requirements of aviation fuels are second in importance only to anti-knock value. A consideration of the conditions under which aviation fuels are required to operate is sufficient to give a full appreciation of the special qualities required.

The effect of fuel volatility upon engine performance, with regard to ease of starting, warming up, acceleration and vapour lock has already been dealt with in considerable detail in Chapter XV, and the relationships described therein with particular respect to automobile fuels apply equally well to aviation fuels.

In the United Kingdom there are two distinct classes of aviation activities. The Air Ministry and His Majesty's Services require a very high grade fuel for use in military and naval aircraft, while the Air-Line Companies and private aircraft users only require a spirit of less superior characteristics because they do not use their aircraft under such exacting conditions. Thus the latter often use blends of English No. 1 spirit and benzole, ordinary market Benzole mixtures or even ordinary No. 1 spirits with satisfaction, while the Air Ministry buys all its aviation fuel to Specifications D.T.D. 224 and 230 (see later). However, the major difference between these various grades of fuels is one of anti-knock value rather than of volatility and need not enter into the present considera-

tions. It has already been shewn in Chapter XV that different parts of the Engler distillation curve may be related to various phases of engine performance. Thus the initial part of the curve is related to starting ability and also to vapour locking tendencies; the lower middle part determines the ease of warming up after starting and the higher middle part determines acceleration characteristics. It has also been shewn that satisfactory all round engine operation is obtained by choosing a fuel having the lowest permissible front end volatility and the highest possible volatility at about the 65 per cent. distillate point. The same generalization holds for aviation spirits, but with greater stringency. Referring first of all to vapour lock properties, these are much more likely to manifest themselves in aircraft operation at elevated altitudes than at ground level. Increase in altitude brings about a reduction in atmospheric pressure and also a reduction in temperature. The atmospheric temperature normally decreases about 3·6°F. (2·0°C.) for every 1000 ft. increase in altitude, whereas the atmospheric pressure at any altitude may be calculated from the relationship[2]

$$H = 62{,}000 \log_{10} \frac{76}{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where H = altitude in feet,
and P = barometric height in centimetres of mercury.

This relationship and also that between temperature and altitude is graphed in Figure 227.

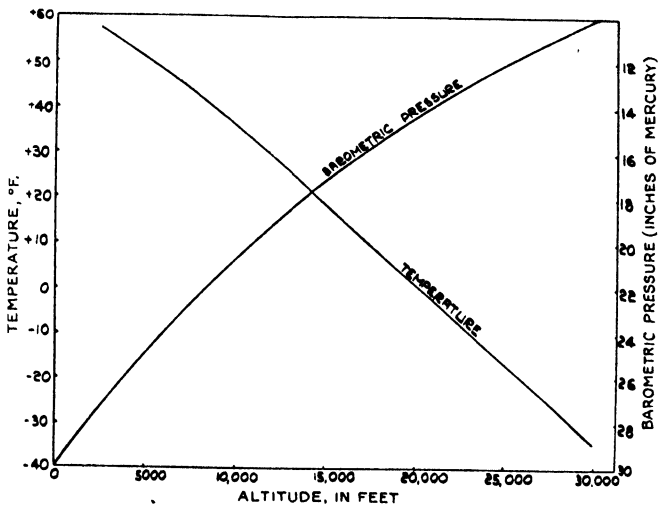


FIG. 227.—THE EFFECT OF ALTITUDE ON BAROMETRIC PRESSURE AND TEMPERATURE.

827. It has already been shewn that the vapour locking temperature

of a motor fuel is determined by its Reid vapour pressure at a temperature of 100°F. (37·78°C.) and that

$$t = 250 - 140 \log \rho_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which ρ_r = Reid vapour pressure in pounds per square inch,
and t = vapour locking temperature in °F.

This equation has been used by Bridgeman, Ross and White[3] to shew that the vapour locking temperature at any altitude is given by

$$t = 259 - 140 \log \left(\frac{\rho_r \times 14{\cdot}7}{\rho} \right) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or by

$$t = \frac{4t_{10\%} + 460 \log \left(\frac{\rho}{14{\cdot}7} \right)}{4 - \log \left(\frac{\rho}{14{\cdot}7} \right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where ρ = atmospheric pressure in pounds per square inch at the given altitude,
and $t_{10\%}$ = A.S.T.M. 10 per cent. distillation temperature in °F.

These relationships are means for predicting with reasonable accuracy the conditions of temperature and altitude under which a fuel of given properties will give trouble from vapour lock, as shewn in Figures 228 and 229. Thus a spirit having a vapour pressure of 10 pounds per square inch will cause vapour lock at 119°F. (48·3°C.) at ground level, but at an altitude of 30,000 ft. will cause vapour lock at a temperature as low as 51°F. (10·6°C.)

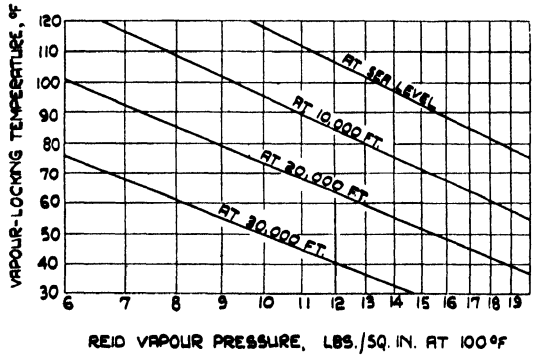


Fig. 228.—Graphs Shewing Relation between Vapour-Locking Temperature and Reid Vapour Pressure at Various Altitudes. (Bridgman, Ross and White.)

There is therefore much more opportunity for aviation fuels to give vapour lock troubles than ordinary automobile fuels, and, in general, it

may be said that three different sets of conditions may be responsible for this trouble.[3]

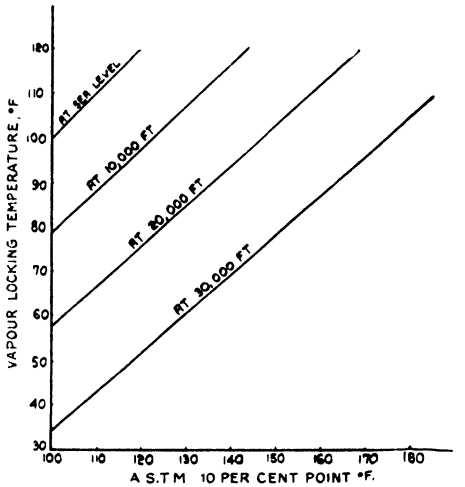


FIG. 229.—GRAPHS SHEWING RELATION BETWEEN A.S.T.M. 10 PER. CENT. POINT AND VAPOUR-LOCKING TEMPERATURE AT VARIOUS ALTITUDES. (BRIDGMAN, ROSS AND WHITE.)

(1) In hot weather, when a 'plane is standing on ground level, the fuel line leading from the fuel tank to the carburettor may reach a sufficiently high temperature partially to interrupt the flow of fuel. The flow may be enough to permit the engine to run smoothly when throttled but may be reduced sufficiently to cause a crash when the 'plane attempts to take off from the ground.

(2) If the fuel approaches, while the 'plane is on the ground, a temperature close to the vapour locking temperature, the combined effects of reduction in atmospheric pressure and heating of the fuel in the line leading to the carburettor during a rapid climb may lead to vapour lock at a moderate height. Engine stoppage under these conditions might leave some time for manœuvring to a landing field, but it is hazardous. This type of vapour lock is probably limited to gravity feed fuel systems.

(3) Vapour lock may also occur as a 'plane climbs steadily and the atmospheric pressure decreases. If the fuel in the fuel tank does not cool quickly (and it has been found not to cool so quickly as the surrounding air) an altitude will be reached at which the fuel will commence to boil. This will probably manifest itself by a loss in power and irregular running of the engine, and can ordinarily be cured by descending a few thousand feet. This type of vapour lock essentially limits the ceiling of a 'plane and may occur with either gravity or pressure feed fuel systems.

A considerable amount of work has been done in America to determine how vapour lock arising from these various causes may be prevented. As far as is known little work on this subject has been done elsewhere. The American investigations on aviation fuel vapour lock have been largely carried out by the U.S. Bureau of Standards, whose results form the basis of the present remarks.

828. Conditions Existing in an Aeroplane Fuel System During Flight.—Bridgeman and his co-workers[3] have described the results of test flights carried out with different types of American Army and Navy aeroplanes to determine fuel and fuel system temperatures during flight at different altitudes. They have shewn, as a result of these tests, that, as a 'plane leaves the ground, the temperature of the fuel in the tank is naturally the same as that of the surrounding atmosphere, while the temperature in the carburettor is about 10°F. (5·6°C.) higher due to gain of heat from the engine. As the 'plane rises the fuel temperatures in the tank and in the carburettor drop steadily, but not as rapidly as the atmospheric temperature. In one case examined at 15,500 feet, reached in about 30 minutes of climbing, the fuel temperature was about 50°F. (27·8°C.) above that of the surrounding air. As the 'plane descends, the fuel temperature rises and returns approximately to its original value as the 'plane lands again. These temperature changes are shewn in Figure 230, which refers to an observation type of U.S. Aircraft.

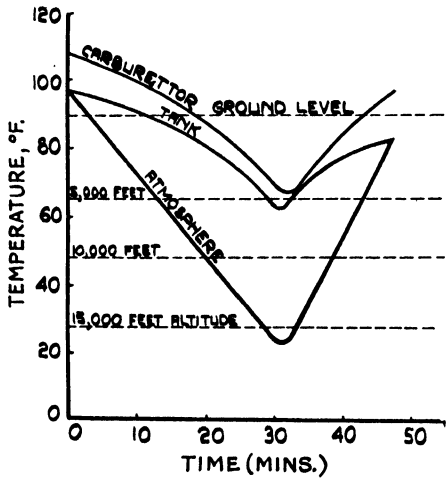


FIG. 230.—CURVES SHEWING TEMPERATURES EXISTING IN AN AEROPLANE FUEL SYSTEM DURING FLIGHT.

829. Remedies for Vapour Lock Troubles.—Vapour locking tendencies may be obviated by rigid control of fuel distillation

characteristics and/or by modifications to the engine fuel feed systems. With respect to the fuel, limits are generally imposed on the front end volatility characteristics, as in U.S. Government and British Air Ministry Aviation spirit specifications. Thus the latter specifies :—

(*a*) Distillation loss not greater than 2%.
(*b*) Reid Vapour Pressure at 100°F., 7 lbs. maximum.

whereas the latest U.S. Army Specification for fighting grade spirit requires :—

(*a*) At least 10 per cent. evaporated at 75°C.
(*b*) Vapour Pressure 7·0 lbs. maximum at 100°F. (37·8°C.).

Conditions may also be considerably improved by careful design of the fuel feed system. In pressure feed systems employing a pump, the suction lift should be reduced to the minimum possible. Thus a reduction in pump suction lift from 6 feet to 2 feet, for example, is equivalent to raising the ceiling of a 'plane many thousands of feet and materially increases the safety of operation.[4] Fuel lines should be so arranged that their temperatures are kept as low as possible.

830. Volatility Requirements of Aviation Fuels Affecting Ease of Acceleration and Manœuvrability.—In Chapter XV, the term " effective volatility " has been dealt with in detail and its significance explained. It is the term given to the quotient obtained by dividing the weight of fuel in the mixture delivered to the cylinders by the weight of fuel in the mixture supplied by the carburettor, and is of importance in determining the lag with which the engine responds to the throttle. The effective volatility required for satisfactory operation of motor fuels in ordinary automobiles has already been dealt with and need not be considered here, but it must be pointed out that military aircraft particularly must be capable of rapid climbing, turning, banking, etc., and must possess all-round manœuvrability of a very high order. It is therefore necessary for fuels intended for such aircraft to have a very high effective volatility and the aim is to secure, under all flying conditions, the same fuel-air composition fed to the cylinders as is supplied by the carburettor. This high effective volatility is also of importance in enabling an aeroplane to take off easily from the ground, as a slight increase in the number of engine revolutions caused by short time lag after opening the throttle enables the pilot to take off in less distance and to climb at a steeper angle. Both of these advantages are important when taking off from a field of limited dimensions, as is often necessary after a forced landing. In general the peculiar conditions of airplane operation call for a more volatile fuel for maximum power than is required for maximum power with automobiles. In aviation fuels

high partial volatility at low temperatures in the A.S.T.M. distillation test is of more importance than complete volatility as indicated by low end-point fuels. Therefore the temperatures at which up to about 90% is evaporated should be kept as low as possible, and it is a general rule for aviation fuels to be more volatile in the middle and upper parts of their distillation curves than automobile fuels. To meet all exigencies at least 50 per cent. should be evaporated in the A.S.T.M. distillation test at 100°C. The 90 per cent. point should also be kept low to ensure as complete vapourization as possible, although end points up to 180—190°C. do not appear to be disadvantageous. Higher end points than 190°C. are to be avoided because of dangers of crank case dilution, as already shewn in Chapter XV. High volatility in the middle portion of the boiling range is also a valuable aid in obtaining high volumetric efficiencies. To obtain perfect distribution, complete vaporization of the fuel within the manifold is essential.

831. Physical Stability at Low Temperatures.—A further important requirement that aviation spirits must meet is that they must be physically stable at low temperatures. They must not freeze or separate into two layers. They must fully retain their homogenous liquid character at temperatures as low as −50° to −70°C. This requirement prevents the adoption of alcohol blended fuels for aviation purposes and places a very definite upper limit upon the amount of benzole which may be added to the fuel to increase its anti-knock rating.

Petroleum spirits have, in general, very low freezing points. Thus Coste[5] gave, in 1927, the solidifying point of Pratts petrol as −128°C., and according to Cabot,[6] a petrol with a specific gravity of 0·698 at 22·8°C. was found to be slightly pasty at −122°C. and to resemble a viscous oil at −125°C. Another petrol with a specific gravity of 0·713 at 22·8°C. became pasty at −120°C. and at −147°C. was a horn-like solid. Of the various hydrocarbon constituents of petrols most have freezing points below −60°C., but the following are notable exceptions :

Benzene	+ 5·5°C.
p-Xylene	+ 13·2°C.
Prehnitene	− 4°C.
Cyclohexane	+ 6·5°C.

However, these hydrocarbons are present in normal petrols to such a small extent that rarely if ever is a freezing point above −50°C. encountered. Trouble due to high freezing points are only likely to be met in practice in the case of petrol-benzole blends such as are used to obtain high anti-knock values. Thus Air Ministry Specifications D.T.D. 224 and 230 impose maximum freezing points of −50°C. and −60°C. respectively

but in order to obtain the required anti-knock value it is only permissible to add aromatics. The most convenient source of aromatics is "motor benzole" which consists chiefly of benzene and which has a freezing point of −11°C. When this is blended with petroleum spirits it is generally found that 20—30 per cent. of benzole is sufficient to raise the freezing point of the blend to −50°C. As cracked spirits are not acceptable by the clauses of the Specification this addition of benzole is often not sufficient to obtain the desired anti-knock value. One method that is adopted to overcome this difficulty is to employ refined coal-tar solvent naphtha, B.P. 125°—170°C., and which consists mainly of the xylenes and higher boiling aromatics instead of benzole. These higher aromatics have a higher anti-knock value than benzole itself. On the other hand base spirits with which they are blended must be rather more volatile than those used in blending with benzole, so that the blends may meet volatility requirements.

As an anti-knock blending agent for aviation spirits toluene would appear to offer various advantages over benzene, both with respect to its slightly higher knock rating and its freedom from freezing. However, it is less volatile than benzene and is more expensive because of the demand that exists for it in the chemical and explosives industries.

Most of the fuel freezing troubles that occur in aircraft occur in the carburettor, where a large drop in temperature is brought about by the evaporation of the fuel. Often water present in the air passing through the carburettor is frozen out and accumulates in the carburettor throat.

832. General Cleanliness and Freedom from Foreign Material.—Clauses requiring freedom from undissolved water and foreign material are almost invariably included in fuel specifications but their importance is often overlooked or given less attention than it deserves.

In automobile operation, the accumulation of water and dirt on fuel line filters and the subsequent stoppage of fuel flow is a nuisance that all try to avoid, but in aircraft operation such an occurrence is dangerous and must be avoided at all costs. Therefore clauses demanding the absence of all foreign matters must be rigidly enforced.

Further trouble may be caused by the separation of dissolved water from aviation fuels at low temperatures.

833. Knock Rating Requirements of Aviation Spirits.—The desirability of high compression engines of high power output and low specific fuel consumption is nowhere so important as in aviation, and it is in this field that all the advantages of high compression engines are experienced to the greatest extent.

There is no need to consider the effect of compression ratio upon

power output and fuel consumption in any detail here, as this has already been dealt with in Chapter XIV, but it is of interest to quote various figures in this connection. In the case of a Pegasus 9 cylinder radial aero-engine, manufactured by the Bristol Aeroplane Company, England, the increase in power output obtained by the use of fuels of different octane numbers at higher compression ratios is indicated in the following table.[7]

TABLE 193.—BRISTOL "PEGASUS" AERO-ENGINE. EFFECT OF INCREASED FULL KNOCK RATINGS

Fuel Octane Number	Power Output B.H.P.	Weight* lbs./B.H.P.	Fuel Consumption	
			Pints/B.H.P./H. at Normal Power	Gallons/hr. cruising at 400 H.P.
73	600	1·7	0·58	28
84	650	1·58	0·52	25
87	670	1·54	0·49	23
100	760	1·38	0·41	20

In the case of supercharged engines, fuels of low knock rating impose a very definite limit to the degree of supercharge that may be employed. The following figures, given by Taylor[8] refer to American aero-engines and shew the brake mean effective pressures realized in supercharged engines when using fuels of various knock ratings.

Octane Number.	*B.M.E.P.*
65	130
70	142
75	153
80	165
85	177
90	188
95	200

Besides the greater power output advantage of high knock rating fuels when higher compression ratios are used, there are other great advantages. Such fuels prevent cylinder overheating and so reduce the likelihood of cylinder distortion and piston seizure and they prevent the development of excessive explosion pressures. High knock rating fuels thus make a noteworthy contribution to engine reliability. When high compression ratio engines are used with suitable fuels further advantages are lower engine and exhaust temperatures.

Aviation fuel specifications given later in this Chapter shew that the

* The weights of these engines are suitably adjusted for increased stresses.

aviation fuels now in general use in America and England have octane numbers of at least 73, while special fuels purchased by the American Army are rated as high as 92 octane number.

834. Permissible Gum Contents.—The presence of gum in aviation fuels, even in very small amounts, constitutes a potential hazard. Consequently specifications are framed so as to impose very necessary restrictions in this direction. The troubles which may be caused by excessive gum contents may be divided into two main classes, those which lead to an obstruction in fuel flow, and those which result in choked inlet manifolds and sticking inlet valves. Both kinds of troubles are serious. When stoppage of fuel flow is caused by vapour locking this can often be cured by a lowering of altitude of a few thousand feet but when fuel flow becomes prevented by gum deposition in the fuel lines, fuel filters or gauges or in the carburettor jet, the blockage is permanent until it is cleaned out. Such a blockage may easily reduce the fuel flow to such an extent that a forced landing is imperative or it may prevent fuel reaching the engine at all. Sticking inlet valves are also dangerous in aircraft operation because they immediately reduce the power output of the engine and may cause further damage. For these reasons gum cannot be tolerated in aviation fuels in anything but the smallest quantities. Some specifications merely impose a limit upon the amount of existent gum in the fuel at the time of purchase, but others demand compliance with an accelerated ageing test as well. In some specifications aviation fuels are required to be free of cracked spirit and olefines because of the ease with which some of these substances form gum (cf. British and American Aviation Fuel Specifications).

835. Sulphur Contents and Acidities.—Limits are imposed upon the sulphur contents and acidities of aviation fuels because these are considered responsible for corrosion troubles and because they are capable of reducing engine reliability. In general, however, the requirements are no more stringent than those associated with normal automobile fuels.

836. British Aviation Fuel Specifications.—In April, 1923, the British Engineering Standards Association published specifications[9] for motor spirit and aviation spirit, two grades of the latter being provided for. These specifications have not been amended since their date of issue and are consequently out-of-date. Their requirements bear no relation to the quality of aviation fuels now sold in The United Kingdom.

The two grades of aviation spirit specified are known as 720 grade and 760 grade respectively, the first having a specific gravity at 15°C. of

0·720 to 0·740 and the second a specific gravity of 0·760 to 0·790. The complete specifications are given in Table 194 and shew that, apart from specific gravity and the slightly different requirements with respect to volatility at 100°C., the major difference between the two grades is one of aromatic hydrocarbon content. The 720 grade is required to have an aromatic content of 12—25 per cent. by volume, and a toluene value of the aromatics of at least 10 per cent., whereas the 760 grade spirit must contain not less than 35 per cent. by volume of aromatics with a toluene equivalent of not less than 28 per cent. Therefore, the difference between the two grades is essentially one of anti-knock value. Toluene equivalents were specified as a means of ensuring anti-knock

TABLE 194.—BRITISH ENGINEERING STANDARDS ASSOCIATION AVIATION FUEL SPECIFICATIONS. No. 121—1923

	Aviation Spirit Grade 720	Aviation Spirit Grade 760
1. *General*	The aviation spirit shall be clear, water white, and free from all visible impurities. It shall not contain more than traces of cracked spirit.	
2. *Specific Gravity*	At 15°C. not less than 0·720 and not more than 0·740.	At 15°C. not less than 0·760 and not more than 0·79.
3. *Distillation*	Below 75°C. not less than 10% „ 100°C. „ 60% „ 140°C. „ 95%	Below 75°C. not less than 10% „ 100°C. „ 50% „ 150°C. „ 90%
4. *Residue on Evaporation*	Not more than 0·1% by weight and must be of an oily nature.	
5. *Sulphur Content*	Not more than 0·05%	Not more than 0·05%
6. *Freezing Point*	—	Below —60°C.
7. *Acidity*	Shall be free of mineral acid.	
8. *Aromatic Hydrocarbons*	Between 12–20% vol.	Not less than 35%
9. *Critical Solution Temperature in Aniline.*	—	After removal of aromatics, the residue shall have an aniline point not exceeding 55°C. If it does exceed 55°C. the % of aromatics must be increased by 1% for each 1°C. in excess of 55°C.
10. *Toluene Value of Aromatics.**	Not less than 10%.	Not less than 28%.

* Toluene value $= \frac{x}{1·5} + y + \frac{z}{1·2}$ where

x = % benzene in sample, y = % toluene in sample,
z = % xylene in sample.

quality, in the absence of standardized engine testing methods, and it is of interest to note that, in the work of The Empire Motor Fuels Committee[10] on a Ricardo E.35 engine, a toluene value of 10 per cent. corresponded to an H.U.C.R. of about 5·2 and a toluene value of 35 per cent. to an H.U.C.R. of about 5·8, a difference of approximately 0·6 in compression ratio, equivalent to an increase in brake mean effective pressure from 132 pounds to 138 pounds per square inch.

In the case of 760 grade aviation spirit, the minimum aromatic content is adjusted according to the quality of the non-aromatic portion as determined by aniline point, the higher the aniline point of this portion (i.e., the lower its knock rating) the greater the minimum allowable aromatic content. Thus in the case of the non-aromatic fraction having an aniline point of 55°C. or below, the minimum allowable aromatic content is 35 per cent., but this figure is increased by 1 per cent., for each 1°C. by which the aniline point of the non-aromatic portion exceeds 55°C. That is, if the aniline point is 65°C., the aromatic content must be at least 35 + 1 (65—55) = 45 per cent. by volume.

It will be observed that these specifications only permit the presence of traces of cracked spirit, and allow total sulphur contents of only 0·05 per cent. The 760 grade spirit must have a freezing point below —60°C., and contain not more than 0·01 per cent. of non-volatile material when heated on a boiling water bath for one hour.

837. In June, 1930, the Air Ministry issued its now well-known specification for Standard Fuel for Aircraft Engines, Number D.T.D. 134,[11] which included an engine test for anti-knock value instead of clauses requiring minimum contents of aromatics, etc. This specification is given in Table 195, and the chief points of interest concerning it are as follows :—

(1) The provision of a maximum front-end volatility limit and a minimum distillation recovery, to avoid troubles due to vapour lock, etc.

(2) A maximum specific gravity of 0·79 at 15°C., to obtain a satisfactory aircraft performance in terms of cruising radius per unit weight of fuel.

(3) The allowance of up to 0·15 per cent. of total sulphur (excluding free sulphur which must be completely absent).

(4) The specification of a minimum anti-knock value. The 50/50 Benzene-Hexane blend has an octane number of 74 when tested in an Armstrong Whitworth variable compression engine operating at 750 r.p.m., jacket temperature 50°C. and spark advance 12°.

TABLE 195.—AIR MINISTRY GENERAL SPECIFICATION NUMBER D.T.D. 134
STANDARD FUEL FOR AIRCRAFT ENGINES

June, 1930.

1. *General*	To consist of high grade petrol refined entirely from crude petroleum. Not to contain more than traces of cracked spirit. Must be clear, free from undissolved water, mineral acid and any other impurities. To obtain the required anti-knock value aromatics only may be added.
2. *Specific Gravity* ..	Not more than 0·79 at 15°C.
3. *Distillation*	Below 50°C. not more than 5%. ,, 75°C. ,, less ,, 5%. ,, 100°C. ,, ,, ,, 50%. ,, 150°C. ,, ,, ,, 90%. End Point—not above 190°C. Total distillate—at least 96 per cent.
4. *Residue on Evaporation*	Not more than 0·01 per cent. by weight after 1 hour on a boiling water bath. Residue must be of an oily nature.
5. *Sulphur Content* ..	Complete absence of free sulphur. Total sulphur not more than 0·15 per cent.
6. *Freezing Point* ..	Below—50°C.
7. *Anti-knock Value* ..	At least equal to a 50/50 mixture of Benzene and standard Hexane in a standard single cylinder engine running at 900 r.p.m. *Standard Hexane.* *Boiling Range.* At least 97% to distil between 67·5° and 69·5°C. *Density at* 15°C. Between 0·685 and 0·695. *Aniline Point.* (I.P.T. Method.) *Before Sulphonation.* Not less than 56·5°C. *After Sulphonation.* Not less than 64°C.

In October, 1933, Air Ministry Specification No. D.T.D. 134 was replaced by two new specifications D.T.D. 224 and 230, the former referring to 77 octane number fuel and the latter to 87 octane number. The main features of these specifications are shewn in Table 196.

838. Properties of Aviation Fuels Marketed in Great Britain.—All aviation fuels used by His Majesty's Services must comply to Air Ministry Specifications but the requirements for private aeroplanes and for some of the 'planes operated by Air-Line companies are not quite so stringent. In the latter cases ordinary marked grades of No. 1 spirits are often employed, while market benzole blends or blends of No. 1 Spirits with varying amounts of benzole are very popular. The major oil companies operating in the United Kingdom market aviation spirits

TABLE 196.—AIR MINISTRY AVIATION FUEL SPECIFICATIONS, OCTOBER, 1933

		D.T.D. 224	D.T.D. 230
1	Distillation Range		
	Below 75°C.	Not less than 10%	
	At 100°C.	Not less than 50%	
	At 150°C.	Not less than 90%	
	End Point	Not to exceed 180°C.	
	Distillation Loss	Not to exceed 2%	
	Total distillate	Not less than 96%	
2	Vapour Pressure (Reid) at 37·8°C. (100°F.)	7 lbs. per sq. inch maximum	
3	Specific gravity at 15°C. ..	0·79 maximum	
4	Sulphur Content	Complete absence of free sulphur when determined by the copper strip method and the total sulphur content shall not exceed 0·15% by weight.	
5	*Gum.*		
	(*a*) Existent gum	Not to exceed 10 mgm. per 100 ml. as determined by the evaporative glass dish method.	
	(*b*) Potential gum	After 50 ml. of the fuel have been incubated at 35°C. for 20 hours, the increase of gum yield over and above the existent gum as determined by the evaporative glass dish method shall not exceed 10 mgm. per 100 ml.	
6	*Anti-Knock Value.* C.F.R Motor Method, but with a mixture temperature of 260°F.	Not less than 77 octane number	Not less than 87 octane number
7	Tetra-Ethyl lead content ..	nil	Not more than 4 mls. of IT Ethyl fluid per Imperial gallon.
8	Freezing Point	Not above -50°C.	Not above -60°C.

under their respective trade names and these may be purchased in cans or sometimes from pumps at road side garages. They are not, however, distributed widely and the sales of these grades must still be very low. The properties of such aviation fuels in the Summer of 1931 were as shewn in Table 197.

839. American Aviation Fuel Specifications.—The first United States Government Specifications for aviation fuels were adopted October 2nd, 1918 and published in Bulletin No. 1 of the Committee on Standardization of Petroleum Specifications. These were modified at frequent intervals and the specifications in force at present are those

adopted October 21st, 1927. Revision of these specifications is now under consideration.

TABLE 197.—PROPERTIES OF ENGLISH MARKET AVIATION SPIRITS. (SUMMER,'1931)

		1	2	3
1	Sp. Gr. at 15°C. ..	0·723	0·737	0·715
2	Freezing Point °C. ..	Below —60°C.	Below - 60°C.	Below —60°C.
3	Elemental Sulphur ..	nil	nil	nil
4	Total Sulphur	0·01%	0·015%	0·013%
5	Corrosion Test .. .. Copper dish.	negative	negative	negative
6	Gum contents. mgs./100 mg.			
	Pyrex dish	0·6	0·4	0·4
	Copper dish	1·4	1·3	0·9
7	*I.P.T. Distillation.*			
	I.B.P. °C.	49°C.	45°C.	37°C.
	% distillate at 50°C.	nil	0·5	3·0
	75°C.	15·0	13·0	23·5
	100°C.	60·0	59·0	61·5
	150°C.	99·0	93·0	98·5
	F.B.P. °C.	150°C.	183°C.	150·5°C.
	Total Distillate	99%	99%	98·5%
8	Knock Ratings. A.W. Engine 50°C. Octane Number ..	69·0	69·4	68·0
9	% Carbon	86·40	86·2	86·1
	% Hydrogen	13·58	13·7	13·9
	H/C Ratio	1·89	1·91	1·94

Details of the various changes made are evident from Table 198. In 1924 clauses limiting the unsaturated hydrocarbon content were dropped and a sulphur limitation of 0·1 per cent. (the same as for motor fuels) imposed. Volatility requirements are still very much the same as they were in 1924.

The United States Navy Department issued its first specification for aviation fuel on September 1st, 1917, mentioning only one grade, called " Aeroplane gasoline." On July 1st, 1919, this was replaced by specifications for two grades, namely—Domestic Aviation and Export Aviation, and on February 1st, 1921, the latter was replaced by a specification for Fighting Aviation grade. The changes made in the U.S. Navy department Aviation fuel specification from 1917 to 1928 are detailed in Table 199.

Between September 23rd, 1932 and May 5th, 1933 this Department

TABLE 198.—U.S. GOVERNMENT SPECIFICATIONS FOR AVIATION FUELS

Date of Specification	October 2nd, 1918			December 29th, 1920		March 1st, 1922		October 31st, 1932		March 18th, 1924		October 21st, 1927	
	Export Grade	Fighting Grade	Domestic Grade	Fighting Grade	Domestic Grade	Fighting Grade	Domestic Grade	Fighting Grade	Domestic Grade	Fighting Grade	Domestic Grade	Fighting Grade	Domestic Grade
1. General Clauses	Free from acid, water and suspended matter.			Free from undissolved water and suspended matter.		Free from undissolved water and suspended matter.		Free from undissolved water and suspended matter.		Free from undissolved water and suspended matter.		Free from undissolved water and suspended matter.	
2. Colour ..	Water white.			Water white.		Minimum of 25 Saybolt.		Minimum of 25 Saybolt.		Minimum of 25 Saybolt.		Minimum of 25 Saybolt.	
3. Doctor Test ..	Negative.			Negative.		Negative.		Negative.		Negative.		Negative.	
4. Corrosion ..	No grey or black corrosion in a copper dish and no weighable gum.			100 mls. in a copper dish to give no grey or black corrosion and to leave no weighable deposit.		100 mls. in a copper dish to give no grey or black corrosion and to leave no weighable deposit.		100 mls. in a copper dish to give no grey or black corrosion and the deposit not to weigh more than 3 mgs.		100 mls. in a copper dish to give no grey or black corrosion and the deposit not to exceed 3 mgs.		100 mls. in a copper dish to give no grey or black corrosion and the deposit not to exceed 3 mgs.	
5. Unsaturateds	—	—	—	Not more than 1% soluble in conc. H_2SO_4.	Not more than 2% soluble in conc. H_2SO_4.	Not more than 1% soluble in conc. H_2SO_4.	Not more than 2% soluble in conc. H_2SO_4.	Not more than 1% soluble in conc. H_2SO_4	If required to be stored for more than 90 days, 2% max.	—	—	—	—
6. Acid Heat Test	—	—	—	Gasoline shall not increase in temp. more than 10°F.		—	—	—	—	—	—	—	—
7. Distillation.													
5% distillate	65°C. max.	70°C. max.	75°C. max.	65°C. max.	75°C. max.	65°C. max.	75°C. max.	65°C. max.	75°C. max.	65°C. max.	75°C. max.	65°C. max.	75°C. max.
	50°C. min.	60°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.	50°C. min.
50% „	95°C. max.	95°C. max.	105°C. max.	95°C. max.	105°C. max.	95°C. max.	105°C. max.	95°C. max.	105°C. max.	95°C. max.	105°C. max.	95°C. max.	105°C. max.
90% „	125°C. max.	112°C. max.	155°C. max.	125°C. max.	155°C. max.	125°C. max.	155°C. max.	125°C. max.	155°C. max.	125°C. max.	155°C. max.	125°C. max.	155°C. max.
96% „	150°C. max.	125°C. max.	175°C. max.	150°C. max.	175°C. max.	150°C. max.	175°C. max.	150°C. max.	175°C. max.	150°C. max.	175°C. max.	150°C. max.	175°C. max.
End Point ..	165°C. max.	140°C. max.	—	165°C. max.	190°C. max.	165°C. max.	190°C. max.	165°C. max.	190°C. max.	165°C. max.	190°C. max.	165°C. max.	190°C. max.
Total distillate	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.	96% min.
Loss	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.	2% max.
8. Acidity ..	—	—	—	Residue in flask not to shew acid reaction.		Residue in flask not to shew acid reaction.		Residue in flask not to shew acid reaction.		Residue in flask not to shew acid reaction.		Residue in flask not to shew acid reaction.	
9. Sulphur Content	—	—	—	—	—	—	—	—	—	0·1% max.	0·1% max.	0·1% max.	0·1% max.

TABLE 200.—U.S. ARMY SPECIFICATIONS FOR ANTI-KNOCK FIGHTING-GRADE AVIATION SPIRITS

		No. Y-3557-F. October 18th, 1932. 87 Octane Number.	No. Y-3557-G. April 10th, 1933. 92 Octane Number.
1	General	Only gasoline consisting of a refined fraction of crude petroleum, natural gas or a mixture thereof will be considered. Tetra-ethyl lead and/or aromatic hydrocarbons may be added as specified herein. The gasoline shall be free from water and suspended matter.	
2	Anti-Knock Value ..	Shall be not less than that of Reference Fuel C6* to which has been added 1·1 ml. T.E.L. per U.S. gallon. (S.30 engine*) 900 r.p.m. 180–200°C. jacket temp.	Shall be not less than that of Reference Fuel C6* to which has been added 2·0 ml. T.E.L. per U.S. gallon. (C.F.R. Engine.)*
3	Content of Tetra-ethyl lead	6 mls. per U.S. gallon maximum.	
4	Corrosion	100 mls. of the gasoline evaporated in a polished copper dish shall cause no grey or black corrosion.	
5	Gum Content ..	After an accelerated ageing test at 100°C. with oxygen at 100 lbs. pressure for four hours, the gum content shall not exceed 10 mgs. per 100 mls.	
6	Sulphur	0·1 per cent. maximum.	
7	Distillation		
	At 75°C. (167°F.)	Not less than 10 per cent. evaporated.	
	At 100°C. (212°F.)	,, ,, ,, 50 ,, ,, ,,	
	At 135°C. (275°F.)	,, ,, ,, 90 ,, ,, ,,	
		The sum of the individual temperatures in °C. of the 10, 50 and 90 per cent. evaporated temperatures shall not be less than 260°C.	
	Residue	2 per cent. maximum.	
8	Reid Vapour Pressure	At 100°F. (37·8°C.) 6·5 lbs. max.	At 100°F. (37·8°C.) 7 lbs. max.
9	Freezing Point ..	As indicated by initial formation of solid not higher than −60°C.	
10	Water Tolerance ..	80 mls. of the finished fuel to be shaken with 20 mls. distilled water at room temperature. After settling the volume of the aqueous layer must not increase nor decrease by more than 2 mls.	

* See Chapter XVI.

tions contain a clause eliminating fuels containing water-soluble components, e.g. alcohols. This is necessitated by the fact that water displacement storage systems are used extensively in the Air Corps activities.

The aviation fuels covered by these specifications are intended for use in hot running and high compression or supercharged engines.

841. Quality of Aviation Spirit Sold in America.—It is believed that a comparatively small percentage of the total purchases of aviation fuel in America are made according to U.S. Federal Government Specifications, as the greater part of the spirit is consumed by the Military and Naval Services and commercial air lines which have their own specifications.

Regarding the use of tetra-ethyl lead in American aviation fuels, this material was used by the U.S. Navy Department as early as 1924. At present commercial aviation spirits contain on the average, 2–2·5 mls. per U.S. gallon, the range being 0·75 to 3 mls. For military gasolines the average is 3 to 4 mls., the range being 2 to 6 mls. Outside the military services, aviation fuel of 87 and 92 octane number is in very limited use.

About eighteen months ago the general manufacture of aero engines for operation on fuel of 80 octane number, or better, was started. Most of the U.S. Air Lines are at present specifying either 80 or 83 octane number, or intend to specify this requirement for any new purchases. The minimum knock rating of American aviation gasolines is about 73 octane number.

842. Other Countries.—In Europe, benzole mixtures are used extensively as Aviation fuels by the Air line companies, particularly in Germany, Belgium and France. In France alcohol fuels containing up to 15 per cent. by volume of alcohol are used to a slight extent. No very stringent freezing point requirements are enforced and often fuels containing 50 or 60 per cent. of benzole are used, having freezing points of −10°C. or higher. In winter months, however, the benzole content of these fuels is often materially decreased.

843. Aviation Natural Gasolines.—Aviation natural gasoline is the term that is ordinarily used to denote an aviation fuel made exclusively from natural gasoline—the light hydrocarbon distillate recovered from natural gas by the methods described in Chapter IV (Volume I). This type of aviation fuel is comparatively a new product and originated only about seven or eight years ago, but it has met with not inconsiderable success, and during 1929 accounted for about 20 per cent. of the total aviation fuel sold in U.S.A. This is rather remark-

able as this type of product did not meet the U.S. Government aviation fuel specifications in force at this time with respect to front end volatility and, in the case of later specifications, with respect to vapour pressure. Aviation natural gasolines have been largely advocated by the Phillips Petroleum Company and by The Natural Gasoline Association of America.

Properties of Aviation Natural Gasolines.

(1) A.S.T.M. DISTILLATION CHARACTERISTICS.

A comparison of the A.S.T.M. distillation curves of aviation fuels meeting the various U.S. Government and U.S. Army specifications and those of typical aviation natural gasolines show that the latter have appreciably higher front end volatilities—that is, the 5 per cent. and 10 per cent. temperatures are lower. This is shewn in Figure 231, in which curve No. 1 is a typical U.S. aviation spirit and curve No. 2 is a Phillips Petroleum Company Aviation Natural gasoline as described by Oberfell, Legatski and Parker.[12]

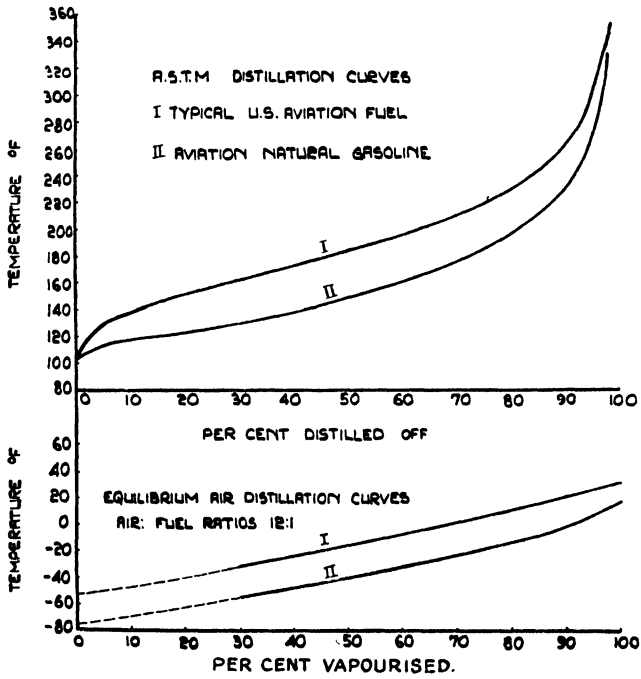


FIG. 231.

A detailed comparison of these fuels is as follows :—

TABLE 201

	Aviation Fuel.	*Aviation Natural Gasoline*
Gravity°A.P.I.	67·9	75·0
Recovery %	98·8	98·0
Residue %	0·6	0·8
Loss %	0·6	1·2
I.B.P. °F.	102	102
5% distillate °F.	128	114
10%	138	117
20%	151	122
30%	161	129
40%	172	137
50%	183	147
60%	195	160
70%	209	175
80%	228	195
90%	260	229
95%	288	266
End Point	352	329
Weight lbs. per U.S. gallon ..	5·91	5·70

TABLE 202.—COMPARISON OF THE DISTILLATION CHARACTERISTICS OF AVIATION NATURAL GASOLINES WITH THE DISTILLATION REQUIREMENTS OF U.S. GOVERNMENT AVIATION FUEL SPECIFICATIONS

		Domestic Aviation Grade		Fighting Aviation Grade		Fighting Aviation Anti-knock grade		Aviation Natural Gasoline
		Max.	Min.	Max.	Min.	Max.	Min.	
5 per cent. condensed ..	°F.	167	122	149	122	—	—	115
	°C.	75	50	65	50	—	—	41·1
10 per cent.	°F.	—	—	—	—	167	—	117
	°C.	—	—	—	—	75	—	47·2
50 per cent.	°F.	221	—	203	—	212	—	147
	°C.	105	—	95	—	100	—	63·9
90 per cent.	°F.	311	—	257	—	275	—	234
	°C.	155	—	125	—	135	—	112·2
96 per cent.	°F.	347	—	302	—	302	—	278
	°C.	175	—	150	—	150	—	136·6
Distillation loss per cent.		2·0	—	2·0	—	2·0	—	1·2
Recovery per cent. ..		—	96%	—	96%	—	96%	98%
End Point	°F.	374	—	329	—	—	—	324
	°C.	190	—	165	—	—	—	162·2

A further comparison has been made by Alden and Parker[18] who

have compared the distillation characteristics of aviation natural with U.S. Government aviation fuel specifications, as shewn in Table 202. It will be noted that, except for the initial portions of the distillation curve, aviation naturals meet the specification requirements with a wide margin to spare. The superior volatility characteristics of these fuels is perhaps better shewn by a consideration of equilibrium air distillation curves, which may be derived from A.S.T.M. distillation curves by the methods already described in Chapter XV.

Figure 231 shews such curves plotted for the two aviation fuels whose A.S.T.M. distillation curves are also plotted in the upper portion of the graph. From such curves the following figures may be taken, and shew the marked difference in the volatilities at low temperatures.

	Normal Aviation Fuel.	*Aviation Natural.*
% vaporized at −60°F.	nil	22
−40°F.	19	50
−20°F.	44	73
0°F.	69	91
+20°F.	88	100

Hydrocarbon Composition.—The marked difference between these two types of fuels is caused by their hydrocarbon compositions, which are approximately as follows :—

Composition.	*Typical Aviation Fuel.*	*Typical Aviation Natural.*
" Butanes and lighter "	3·6%	Less than 1·0%
Pentanes	15·8%	30·0%
Hexanes	29·7%	36·1%
" Heptanes and Heavier "	50·9%	32·9%+

The high content of pentanes in Aviation Natural Gasoline is largely responsible for its abnormally high volatility.

Vapour Pressure.—Aviation Naturals generally have higher vapour pressures than normal aviation fuels. Thus the Reid vapour pressures of the two fuels considered above are 9·7 pounds and 7·8 pounds per square inch at 100°F. respectively. Because of their high vapour pressures and high front end volatility aviation natural gasolines do not meet the requirements of the latest U.S. specifications but, doubtless, suitable fractionation will enable them to do so if part of the high pentane content is eliminated.

The Effect of Pentanes Content upon the Properties of Aviation Natural Gasolines.—The effect of a given amount of pentanes upon the vapour pressure measured at 100°F. is much less than the effect of the same amount of butanes. Thus 1 per cent. of pentane raises the vapour pressure approximately 0·1 pounds and 1 per cent. of butane 0·5 pounds. These and other effects of varying the hydrocarbon composition are shewn in Figures 232 and 233, reproduced from the published work of Oberfell, Legatski and Parker.[12]

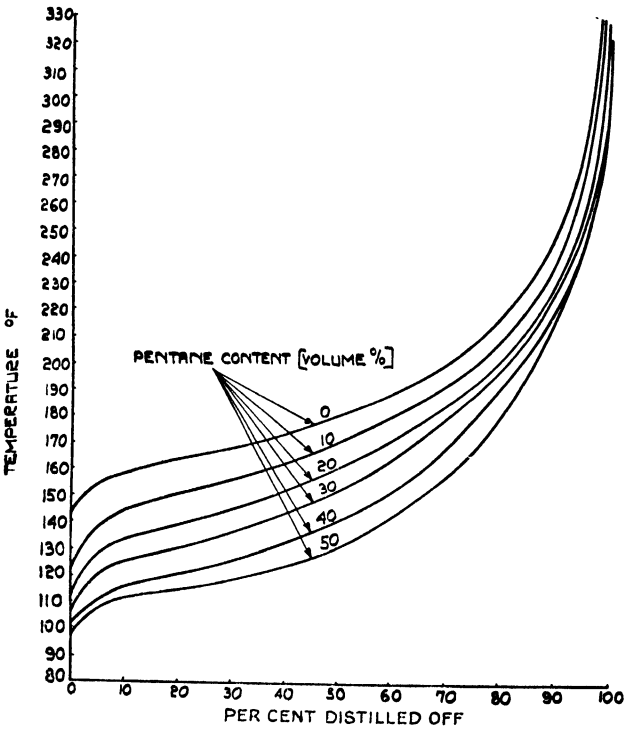


FIG. 232.—THE EFFECT OF PENTANES ON THE DISTILLATION CHARACTERISTICS OF AVIATION NATURAL GASOLINE.

Numerous tests have been made under actual flight conditions to demonstrate the advantages of the peculiar properties of Aviation Natural Gasolines, and the Boeing Air Transport, Inc., adopted such a fuel for use on its line from Chicago to Salt Lake City in 1927, and from that date to the beginning of 1930 consumed upwards of three million gallons with apparent complete satisfaction.

844. Future Developments in Aircraft Fuels.—Developments in aircraft fuels likely to receive attention in the near future are many

and varied, but the following may be considered as among the most important—

(*a*) The use of cracked spirits.
(*b*) The use of high flash-point fuels in the normal type of internal combustion (petrol) engine.
(*c*) The development of the aero Diesel engine.

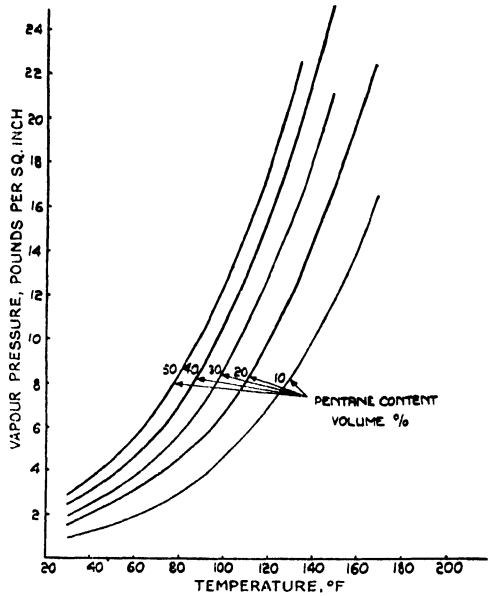


FIG. 233.—THE EFFECT OF PENTANES ON THE VAPOUR PRESSURES OF AVIATION NATURAL GASOLINES.

The Use of Cracked Spirit.—Up to the present cracked spirits have been rigidly excluded from aviation fuels because of their chemical instability and gum forming properties, the view being held that their use constitutes a hazard, which it is the duty of aircraft users to avoid. Nevertheless, agitation for the use of cracked spirit in aviation fuels has occurred, statements having been made that the anti-knock requirements of aviation fuels are already such that they can only be met by a comparatively small number of straight run spirits without the employment of special anti-knock materials, such as benzole, coal-tar solvent-naphtha and tetra-ethyl-lead. The point remains, however, that the demand for high anti-knock aviation fuels, free from cracked spirit, is being met, and will continue to be met for some time, now that the addition of appreciable amounts of tetra-ethyl-lead is permitted. Moreover, the hydrogenation process will, in the near future, be in a position to satisfy any demand for perfectly stable aviation fuels of very high

knock-rating. On the other hand, the use of inhibitors to prevent gum formation may enable cracked spirits to be used to an appreciable extent, but it would appear that this expedient is an unwelcome complication in this field.

845. The Use of High Flash-Point Fuels.—Perhaps the greatest argument in favour of high flash-point fuels for use in aircraft is the elimination of the fire risk that is ever present when normal aviation fuels are employed. The elimination of this fire risk would do much to popularize aircraft and to make the public at large more "air-minded." Two important attempts have been made to use such high flash-point fuels. One has made use of a white-spirit fraction to which tetra-ethyl-lead was added to give the requisite anti-knock properties. The other, which appears to be rather more important, is one of the out-comes of the adoption of the hydrogenation process. In this case fuels have been produced, as shewn in Chapter VIII, which have flash-points as high as 107°F. (41·6°C.) and octane numbers above 90 at 300°F. and which have a boiling range of 150° to 210°C. The satis-factory use of such fuels demands special carburetting arrangements because of their non-volatile character, but developments recently made in the use of solid injection indicate that this method is better able to use the valuable properties of such fuels. Conventional carburettors have many limitations and disadvantages. They demand a sufficiently high fuel volatility so that the latter may be vaporized into, and carried by, the air stream into the cylinders, and as a metering device for both air and fuel leave much to be desired. Moreover, they limit the volumetric efficiencies of engines on which they are used because of pressure drop through their restrictions and actual mechanical load of carrying the fuel.

846. For some time the idea of using the mechanical system of injection, as used in the Diesel engine, has been receiving attention, particularly in America, and much experimental and development work has been carried out. Mechanical fuel pumps are used to inject the fuel into the engine cylinders and the moment of injection is timed to take place at any convenient moment between the beginning of the suc-tion stroke and the end of the compression stroke. Generally better fuel economy and greater power is obtained by injecting after the closing of the inlet valve. In this way the fuel is metered mechanically and is distributed in exact quantities directly to the cylinder for which it is intended, thus overcoming all the distribution problems of the con-ventional carburettor. In some cases the fuel is injected into the air stream entering the cylinders.

The advantages of this type of operation are numerous. In the first

place the peak power output is increased from 10 to 20 per cent. due to increased volumetric efficiency and improved distribution. The engine becomes more responsive to variations in fuel supply because the fuel is handled mechanically and positively and the time lag of the carburettor is completely eliminated. Starting is also claimed to be improved, because of the atomization obtained on injection. A further advantage, with particular regard to aviation conditions, is that freezing of the carburettor at high altitudes is completely eliminated.

Such a development is likely to play an important part in aircraft operation in the near future. The hydrogenation process is able to supply high flash-point fuel of very high knock-rating (up to 100 octane number) without the addition of tetra-ethyl-lead, and the use of mechanical fuel injection should materially increase the flexibility of aero engine operation. Manœuvrability should also be considerably improved if a suitable automatic altitude compensating device can be devised. This is necessary to maintain the fuel-air ratio constant irrespective of altitude.

However, one difficulty would appear to be the development of a suitable pump for the continued handling of non-viscous fuels. Such pumps must not wear appreciably during prolonged service, otherwise accurate metering of the fuel would not be possible and one of the main advantages of the system would be lost. There is, however, no reason to suggest that this problem will not be solved satisfactorily.

847. Experimental work on the direct injection of fuel into spark ignition engines has been carried out by Taylor and Williams.[14] The engine used was a standard 3½ in. by 4½ in. Co-operative Fuel Research engine coupled to a dynamometer and a Bosch cam-operated plunger type fuel pump driven through a planetary-gear drive, which permitted easy adjustment of the injection timing, was employed. The injection valve was of special design as shewn in Figure 234. The position of the spray valve with respect to the combustion chamber was arranged as shewn, the axis of the spray cone making an angle of 45° with the cylinder axis. A shrouded inlet valve was employed to give various types and degrees of turbulence.

Tests were carried out on aviation spirit, boiling range approximately 40°C.—165°C., hydrogenation " safety " fuel, 190°—310°C. and a straight petroleum distillate I.B.P. 240°C., 80% distillate at 316°C., all of which were examined at a compression ratio of 5 to 1, at full throttle and at 1,000 r.p.m. With the aviation spirit it was found that the best performance was obtained when injection began simultaneously with the closing of the inlet valve and under these conditions the power output increased 5—7 per cent. and the specific fuel consumption decreased 6—11 per cent. as compared with a carburettor. The heavier

fuels, surprisingly enough, had a wider range of injection timings than the aviation spirit and could be injected at the low compression ratio of 4 : 1, as late as 110 degrees after bottom centre, whereas aviation spirit could not be injected later than 90 degrees without misfiring. However,

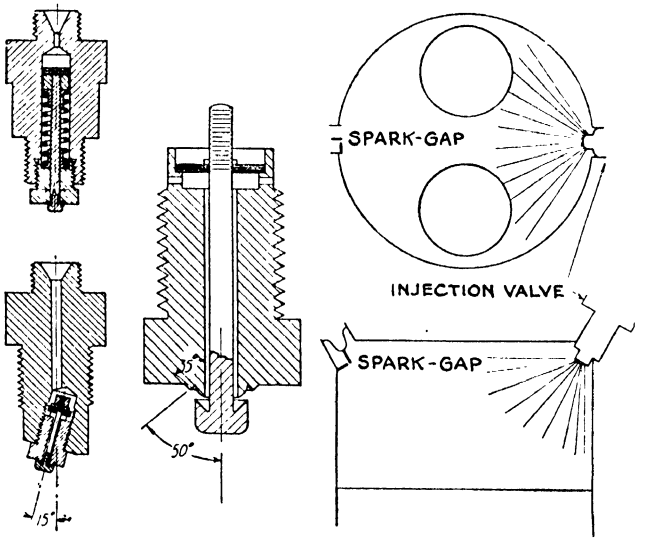


FIG. 234.—DETAILS OF INJECTION VALVE AND ITS POSITION IN THE CYLINDER USED BY TAYLOR AND WILLIAMS.
(Courtesy, Editor, Journal of the Society of Automotive Engineers.)

with injection later than bottom centre, a fair degree of directed turbulence was found essential to give proper distribution of the fuel through the combustion space and to assure homogeneity of the charge to obtain good combustion. The results obtained with the three different fuels are shewn in Figure 235.

Announcements have been made [15] to the effect that the Pratt and Whitney Aircraft Company of East Hartford, Connecticut, have been successful in perfecting the fuel injection mechanisms so as to be able to benefit by these advantages and that a Series A-2 Hornet engine has been fitted with the requisite gear and has passed its rigid fifty hour block test. This engine has proved itself efficient in flight tests.

848. The Development of the Aero Diesel Engine.—Great efforts are at the present time being made to develop Diesel engines suitable for use in aircraft because of the following arguments in favour of the Diesel engine in this sphere. [16]

(1) Elimination, or at least reduction, of the fire risk in the event of a crash.

(2) Elimination of the magneto—which causes interference in radio communication.
(3) Increased range, due to the lower fuel consumption under all conditions and more particularly at cruising speeds.
(4) Greater reliability due to the freedom from electric ignition apparatus and the employment of a cooler engine generally.
(5) Reduced cost of fuel. (As Diesel fuel becomes used to a greater extent, its cost will of course rise.)

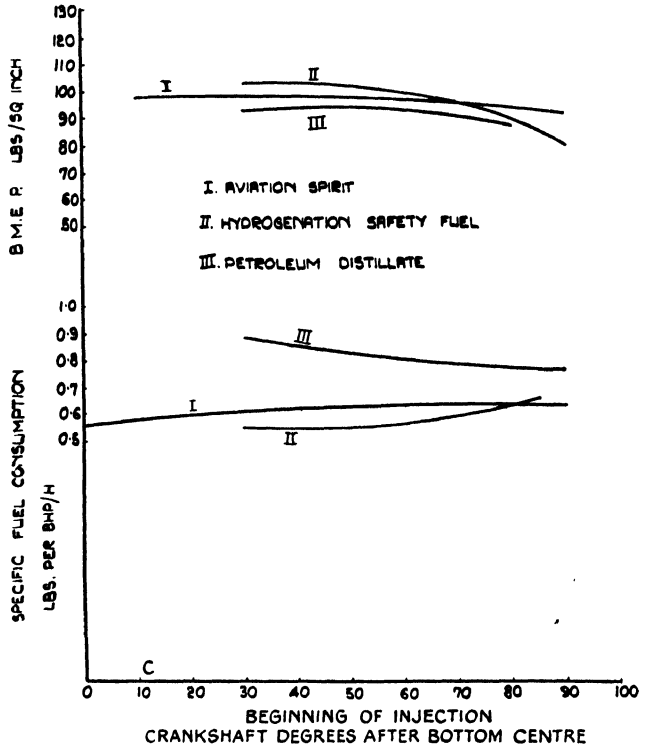


FIG. 235.—THE EFFECT OF INJECTION TIMING ON THE PERFORMANCE OF VARIOUS FUELS WITH DIRECT INJECTION AT 1,000 R.P.M. AND COMPRESSION RATIO 5—1. SPARK ADJUSTED FOR MAXIMUM POWER. (TAYLOR AND WILLIAMS.)

For long distance bombing planes and planes used for troop carrying, the Diesel engine has much to commend it, but the fact that it is about 50 per cent. heavier than a petrol engine of the same power will probably prevent its adoption on fighting planes which must have high manœuvrability. For commercial aircraft pay load is a vital consideration and Ricardo[16] has stated that at present the pay load of an aeroplane and the weight of its engine are in the ratio of about 2 to 1. If therefore, 50 per cent. is added to the weight of the engine, the earning capacity of the machine is reduced by 25 per cent. Against this the reduced weight of

fuel carried does not count for much, for, except in oversea flights, there is no reason why the commercial plane should not land and replenish its fuel tanks at frequent intervals. We are thus left with the outstanding argument of the fire risk—which cannot be assessed in any quantitative terms. The privately owned light aeroplane, built entirely for pleasure, is in a different category as in this case pay load is of little or no importance.

During 1929 an aeroplane fitted with a Packard nine cylinder static radial air cooled Diesel engine made successful cross country flights in America. The engine subsequently passed the U.S. Army 50 hour endurance acceptance test. It was rated at 225 H.P. at 1,900 r.p.m. and weighed 510 lbs., i.e., 2·26 lbs. per H.P. The maximum cylinder pressure was stated to be about 1,200 lbs. per sq. inch. Since 1930, however, very little has been heard about this engine. Several freight planes in Germany are equipped with Junkers Diesel engines. These engines are water cooled, with two opposed pistons working in each cylinder and two crankshafts geared together. There are six cylinders of 120 mm. bore arranged vertically in line and the engine, which is of the 2 stroke variety with direct injection, is rated at 720 B.H.P. at 1,700 r.p.m. The weight of the engine is 800 Kg., that is, 2·34 lbs. per B.H.P. and the fuel consumption 0·371 lbs. per B.H.P. hour.

Important trials have recently been made by the Air Ministry with Messrs. Napier & Sons' modified designs of the German "Junkers Jumo" compression ignition aero engine. These have been successful. These new engines, the "Culverin" of 720 h.p., and the "Cutlass" of 550 h.p., are stated to weigh about 2·25 lbs. per h.p., with a fuel consumption at the most favourable mixture strength of about 0·35 lb. per B.H.P.H.

Towards the end of 1932, the Air Ministry issued some particulars regarding the first British Diesel aero engine. This is a Rolls-Royce Condor engine, strengthened where necessary to take the increased stresses due to raising the compression ratio from 6·5 to 12·5. The maximum explosion pressure is 900 pounds per square inch and the output 500 B.H.P. at 1,900 r.p.m. The weight of the engine is 3 lbs. per B.H.P. representing an increase in weight over that of the petrol engine from which it was developed of less than 10 per cent. Flight tests were reported to be in progress in a Hawker "Horsley" aeroplane, during which it was hoped to investigate the extent to which the radiator and the weight of cooling water could be reduced as compared with petrol engines.

The Bristol Aeroplane Company (England) have recently announced their "Pheonix," 9 cylinder air-cooled radial diesel engine. This engine has been fully tried out on the bench and in actual flights. Starting is easy and the general performance of the engine has given

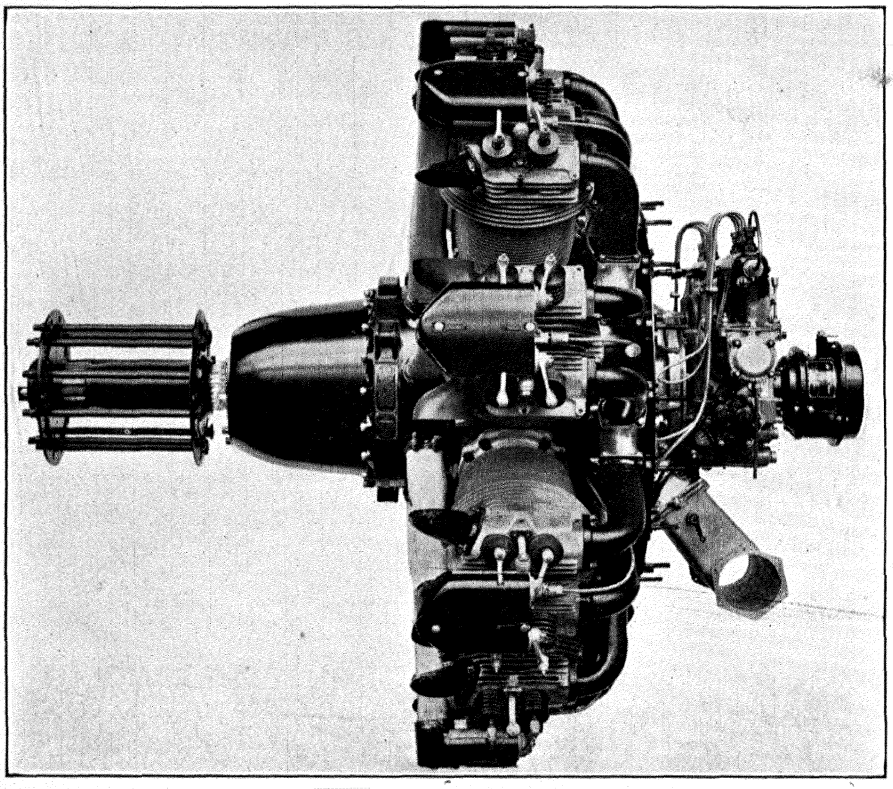


FIG. 236.—SIDE VIEW OF BRISTOL PHŒNIX RADIAL DIESEL AERO ENGINE.
(Courtesy, Bristol Aeroplane Co.)

Facing p. 421]

satisfaction. It is designed on the same general lines as the "Bristol" Pegasus engine and has the same capacity, viz. 28·7 litres. It works on the usual 4-stroke cycle. The maximum power output is 400 B.H.P. and the cruising power available at normal R.P.M. of 1,900 is 350 H.P. while the nett dry weight is 990 lbs., and the overall diameter 53 inches, or 2 inches less than the "Bristol" Pegasus. Compared with this engine, the Phoenix Diesel Engine has the same weight, but gives a one-third less power output and has a 25 per cent. lower fuel consumption. A view of the engine is given in Figure 236.

Diesel engines have also been used in airships, where the question of weight is not quite so important. In this country the Beardmore water-cooled 4-cycle direct injection engine has been used for this purpose. This engine has 8 cylinders $8\frac{1}{4}$ ins. by 12 ins., is rated at 650 B.H.P. at 1,000 r.p.m. and weighs about 8 lbs. per B.H.P.

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CHAPTER XIX

AUTOMOTIVE DIESEL ENGINES AND DIESEL OILS

850. Introduction.—The term "Diesel engine" is now universally accepted when reference is made to the modern type of high speed compression ignition engine which has been developed from the older Diesel engines operating at much lower speeds for use in propelling motor vehicles.

Various opinions have been stated regarding the possible future use of compression-ignition engines for this purpose, some authorities assert that in a few years' time most motor coaches and heavy lorries will be so equipped and others go so far as to predict that such engines will entirely displace the petrol engine in all types of motor vehicles. Both in the United Kingdom and on the Continent, much development work on the Diesel engine has been carried out during the past few years and a large number of high speed engines for use in the heavier types of motor vehicles have been produced. These have been in service for some time, and, on the whole, have given complete satisfaction.

The interest shown in the automotive high speed Diesel engine has been mainly brought about by the high import duties on motor spirits and the consequent high cost of such fuels to the consumer. In the case of large transport concerns, such as London Transport, the high cost of motor fuels has appreciably reduced their profits and naturally they have given considerable encouragement to the development of engines using cheaper fuels.

In the absence of petrol import duties, that is, if petrol were sold in this country at $9\frac{1}{2}$—10 pence per gallon, there would be far less interest shown in the Diesel engine, although the greater efficiency of the latter and the greater calorific value of Diesel oil per gallon as compared with petrol would result in definite savings in fuel costs. On the other hand, the future development of high speed Diesel engines in the United Kingdom will be appreciably hindered by the recent imposition of 1d. per gallon tax on Diesel oils, etc., and by the greatly increased taxes on Diesel driven vehicles which became effective on January 1st, 1934.

A further point is that, as the demand for a satisfactory high speed Diesel fuel becomes appreciable, the price of the latter is bound to increase. The increase in price that will result will be

dependent upon the demand and will also be governed by the nature of the oils required as being most suitable.

With regard to the quality necessary in high speed Diesel engine fuels, at the moment only oils of predominantly paraffin-base type are really satisfactory, others causing combustion shock and high maximum pressures. Unless engine improvements are made whereby the use of naphthenic and aromatic oils is made possible, it is likely that a shortage of suitable fuel will result. On the other hand, it seems probable that engine design will proceed in such a way that engines will become less sensitive to fuel quality than they are at the moment. Noticeable improvement has already been made in this direction, but it would appear that some time must pass by before such highly aromatic oils as coal-tar fractions, creosote, etc., can be considered as possible Diesel engine fuels.

The Diesel Engine Cycle

851. Before the advent of the Diesel engine, all internal combustion engines had relied upon volatile fuels, for liquid fuels could be utilized only after they had first been vaporized to a gaseous state. The heavier petroleum oils, in virtue of their high boiling point and chemical instability cannot be vaporized completely without thermal decomposition taking place and, hence, have to be introduced into the cylinder in the liquid state.

The essential principle of the Diesel engine is the compression of the air within the cylinder to a temperature and pressure such that, when the liquid fuel is injected, it is either burnt or else already in the process of being burnt, before it has time to reach, and deposit upon, the relatively cold walls of the cylinder or piston. In the petrol engine, the fuel is present, mixed with the air, during the compression stroke and imposes a limit upon the compression ratio which may be employed, this limit being determined by the chemical stability and ignition temperature (i.e., knocking tendency) of the fuel. In the Diesel engine, however, air alone is compressed, to a pressure of about 450 pounds per square inch and to a temperature of the order of 600°C. Into this highly compressed and heated air the fuel is injected in the form of a fine spray at just such a rate that it shall, by its burning, maintain the pressure more or less constant during the first portion of the outward stroke, after which the supply of fuel is discontinued and expansion proceeds in the usual manner. The satisfactory operation of the engine depends entirely upon the introduction and distribution of the fuel in the engine cylinder.

It will be apparent that in order to obtain complete combustion of the fuel, the latter must be evenly distributed throughout the air in the

combustion chamber, so that the fuel particles may, in the short time available, find enough oxygen for their combustion. When air injection is employed, i.e., when the liquid fuel is sprayed into the cylinder by means of highly compressed air, it is comparatively easy to pulverize the liquid fuel and to distribute it. There are, however, serious objections to the use of such an arrangement on engines intended for automobile propulsion, foremost of which is the cost and complication of the air compressor necessary, which consumes about 10 per cent. of the total power output of the engine with which it is used.[1] When fuel injection is accomplished without the use of compressed air, it is referred to as " air-less " or " solid " injection. In this case, the fuel is injected by a suitably timed valve pump under a pressure so great that it can be both pulverized and distributed by its passage, at high velocity, through the injection nozzle without the help of air. This method, although much simpler and far less cumbersome than the air injection system, is, however, not free from troubles. The fuel has to be injected into the cylinder during the latter part of the compression stroke when the pressure existing therein is in the neighbourhood of 30 atmospheres. High fuel-line pressures are therefore necessary. Moreover, in order to obtain good fuel distribution within the cylinder, the fuel must be broken up into very fine particles, but, unfortunately, the finer the particles, the sooner they lose their impetus gained on passing from the fuel nozzle and are borne down by the resistance of the compressed atmosphere within the cylinder. Solid injection therefore involves many compromises. In nearly all the small high speed Diesel engines, distribution and in some cases, pulverization also, is assisted by setting the air within the cylinder in violent motion, on the principle that it is easier for the air to find the fuel than for the fuel to find the air. In all cases, of course, the air inside the cylinder is already in a state of turbulence, due to the velocity it has acquired in entering the cylinder, but in the case of solid-injection engines, it is usual either to supplement this turbulence by forcing it through a restricted passage during compression, or to exchange the irregular turbulence for an orderly rotational swirl. The former method appears to be favoured when poppet valves are used and the latter when the air is admitted to the cylinder through ports, as in the case of sleeve-valve or two cycle engines. Whichever is used, it is necessary to keep the relative motion between the burning fuel particles and the air as rapid as possible to give the fuel a sufficiency of oxygen.

852. Ignition in the Diesel engine is procured by compressing the air charge in the cold cylinder to a temperature well above the self-ignition temperature of the fuel. To ensure starting from cold, compression pressures of the order of 450 lbs. per square inch were at one

time required, with the risk of higher pressures in the event of accidental early injection or other mishap. This necessitated a somewhat heavy and costly engine, and attempts were made to reduce these starting pressures. An engine, in which a part of the combustion space was left uncooled and allowed to reach a high temperature was therefore developed. A much lower compression pressure, of the order of 150 lbs. per square inch. was possible and the necessary high temperature needed for ignition was obtained by the help of heated surfaces, or hot bulbs, in the combustion chamber.

A few years ago the surface ignition type of engine was in extensive use, but various considerations such as lack of flexibility with regard to load and speed, rough running due to uncertain time of ignition and the liability of uncooled combustion chambers to crack, led engine builders gradually to abandon this design. Slowly the compression ratio has been raised and the area or temperature of the uncooled surface reduced.

Combustion in the Diesel Engine

853. The process of combustion, or oxidation, which occurs in the Diesel engine, is very complex and is more complicated than petrol engine combustion because liquid fuel is injected into the cylinder. On injection, oxidation of the fuel first takes place very slowly, but because of its exothermic nature, the reaction accelerates and soon reaches a point when the rate of heat generation by the oxidation is greater than the rate of heat dissipation, and a flame is established. Of much importance in this connection is the so-called Spontaneous Ignition Temperature (S.I.T.) of the fuel, because if this is very much above the temperature of the compressed air into which it is injected, it will not ignite at all or else will only ignite after the lapse of an appreciable interval of time, the so called "Delay Period." The shorter this interval, the better the engine performance obtained, but it is not possible to eliminate it altogether. There must always be a short delay period.

One obvious method of reducing the delay period between fuel injection and ignition is to increase the compression ratio, because this raises the compression temperature and, moreover, increases the ease of starting. There is, however, a limit to which the compression ratio may be raised because of the resulting higher maximum pressures and the extra engine weight made necessary to cope with this. These points are dealt with later in discussions on Diesel engine fuels.

The variation in air temperature and the variation of the S.I.T. of the fuel during the compression stroke of a Diesel engine is shown in Figure 237. The figures are only approximate and are based on the well known work of Professor Neumann.[2] Once the delay period is

over and ignition is established, the rate of burning depends principally upon the rate at which each nucleus of flame can find fresh oxygen to keep it burning, in other words it depends upon the intimacy of contact between the air and the fuel. The fuel injected in the first part of the injection comes in contact with air which is at a temperature only a little above its S.I.T., and the delay period is more or less pronounced. However, that part of the fuel injected later meets air which has become heated to a much higher temperature by the ignition of the fuel injected during the earlier part of the injection, so that this portion of the fuel burns straight away, almost as soon as it leaves the injection nozzle, even though a part of the air charge in the cylinder has already been used up.

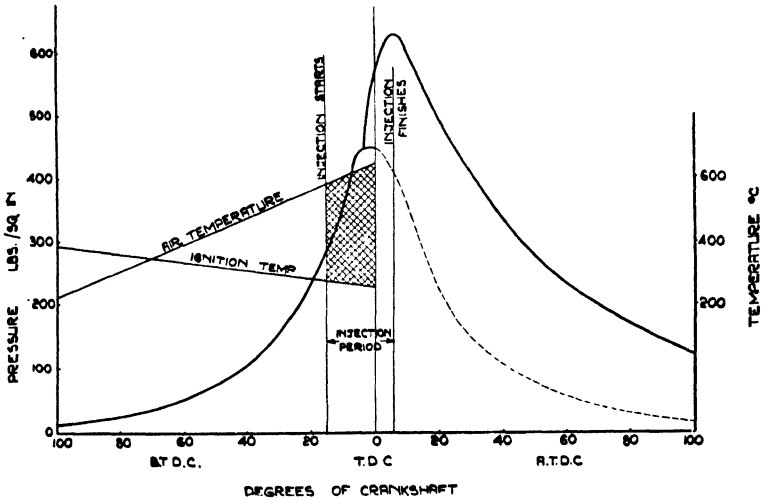


FIG. 237.—CURVES SHEWING THE VARIATION IN AIR-TEMPERATURE AND SPONTANEOUS IGNITION TEMPERATURE OF A FUEL DURING THE COMPRESSION STROKE OF A DIESEL ENGINE. (RICARDO.)

854. If the rate of burning could be made closely to follow, at a very short interval, the rate of admission of the fuel into the cylinder, the latter could be controlled so as to maintain a nearly constant pressure during the period of fuel injection. This may be nearly possible with air injection engines, but is not possible with solid injection, and, in this case, the combustion may be considered as taking place in three distinct stages. First of all there is the delay period, or as it is sometimes called, the "ignition lag," during which fuel is admitted but does not ignite. This is succeeded by ignition accompanied by a period of very rapid pressure rise. At the end of this second stage the temperature and pressure are so high that any fuel remaining to be injected during this period burns as it enters the cylinder and any further pressure rise can be controlled. These three separate stages are numbered 1, 2 and 3 in Figure 238, which shows an artificial indicator diagram in which the

pressure time curve has been given an angular form in order to show up the distinct phases. By comparison with Figure 239, the three stages can be quite well distinguished upon the experimental diagram.

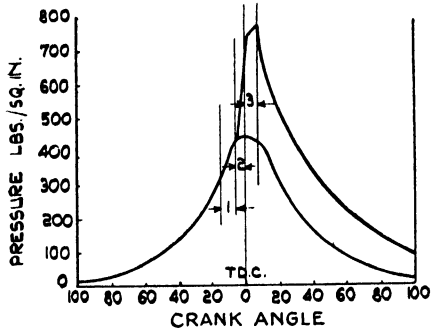


FIG. 238.—DIAGRAM SHEWING THE THREE PHASES OF COMBUSTION IN COMPRESSION IGNITION ENGINES.

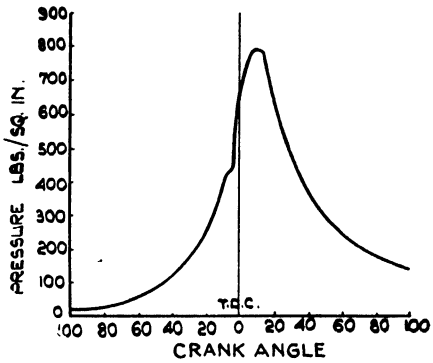


FIG. 239.—ACTUAL INDICATOR DIAGRAM TAKEN ON A COMPRESSION IGNITION ENGINE.

It will be obvious that, for any given injection timing, the pressure reached during the second stage will depend upon the duration of the delay period, since with longer the delay, the more rapid and the higher the pressure rise, since more fuel will be present in the cylinder before the rate of burning comes under direct control. Such control may be exerted by admitting the fuel slowly at first. In all cases, the aim is to keep the delay period as short as possible, both for the sake of smooth running and in order to maintain control over the pressure changes.

"Roughness" of running is a factor of great importance in Diesel engine operation, and in extreme cases is characterized by what has come to be described as "Diesel knock," or "combustion shock," a hammer-like blow very similar to that produced by knocking in a petrol engine. This causes rapid wear of any gears through which the load is transmitted and damage to connecting rods and main bearings. It has been shown by experiment that "roughness" is not dependent upon the maximum pressure in the cylinder, but that it is closely associated with the rapidity of the pressure rise during the second stage of the combustion process. On the other hand, engines must be designed to withstand maximum pressures without risk of breakdown.

FUEL INJECTION SYSTEMS

855. Fuel injection systems may be divided into two classes, (1) Storage systems and (2) Timed-Pump or Jerk-Pump systems.

In the first class the fuel is compressed to the desired injection pressure and delivered to a fuel line in which are the injection nozzles of the

cylinders. The nozzles are closed by a mechanically controlled valve and the opening of this valve times the fuel charge to the cylinder.

With the full pressure maintained constant the charge is metered either by controlling the time during which the fuel valve is open or by varying the valve lift. Another design meters the charge by varying the pump pressure while maintaining the valve lift constant. With the storage system only one pump is used and any variation in the pump discharge does not affect smoothness of running. There may, however, be variations in injection timing and metering from irregularities in the fuel valve mechanism. The valve lift is very small and wear must be negligible while temperature effects may have serious results with an engine which is sensitive to small changes in injection. The fuel valve must seat itself accurately if waste of fuel is to be prevented.

Separate pumps for each cylinder are required for the Jerk-Pump system or a fast running pump and a distributor. Even metering can be obtained by the latter design, but there is a risk of leakage. Pressure waves and air pockets resulting in a secondary discharge cause dribble, and valve lift is sluggish. When air finds its way into the fuel, misfiring may result and timing may vary, due to air locking. These are the objections which must be overcome in order that the Jerk-Pump system may function efficiently.

The type of spray produced by the injection nozzle has been studied, the velocity and discharge coefficients determined and the size of the oil drops has been measured with some degree of accuracy.

The shape of the spray, its power of penetration and its degree of atomization are effected by the nozzle and these factors must be considered together when designing a nozzle orifice. The penetration, which depends upon the length of the orifice, the diameter of the outlet and the pressure of the fuel, increases with an increase in the $\frac{\text{length}}{\text{diameter}}$ ratio, whilst atomization increases with increased pressures and with a decrease in this same ratio.

It has been pointed out previously that the more fully atomized a fuel is, the sooner will the particles lose their impetus. Thus, atomization and penetration are opposed and in order to obtain efficient working a compromise is necessary. The best possible atomization for a given penetration should be the objective.

856. The majority of direct injection systems require the maximum distribution of oil spray from the injection nozzle. The plain parallel sided hole gives a spray angle varying from 12° to 15°, the pressure required is very high, and the spray is considerably affected by variations in workmanship. An increase in distribution can be obtained by the use of multiple hole nozzles, but due to the fact that these holes must

of necessity be small there is a loss in penetration with the consequent risk of choking. These holes are difficult to drill and the cost of the nozzle is high. Assuming that the degree of penetration remains sufficient a wide distribution depends mainly on the angle of the spray cone.

This angle may be increased in various ways by the use of (1) an annular orifice, (2) a lip orifice or (3) by employing a centrifugal spray.

When an annular orifice is used, the effect is increased and a finely atomized hollow spray results. Erosion and coking may be the cause of trouble, but if the pin, which should be accurately centred, is part of the injection valve, the movement of this pin tends to free itself from carbon, and gives an even discharge of fuel into the cylinder.

The lip valve gives a finely atomized and broad spray, which is, however, thin, and the penetration is not great.

A centrifugal spray is induced by spiral flutes placed in the oil passages of the centrifugal nozzle. A rotational speed of 7,000,000 r.p.m. is theoretically attained with a 45° spiral and a 0·02 in. orifice at 8,000 lbs. injection pressure. The friction loss is heavy and if this is to be reduced the passage should be short.

A decrease in the angle of the centrifugal jet spray is noticed with an increase of combustion chamber pressure and an increase in the angle with increase of injection pressure. This is, of course, contrary to the spray from a simple orifice which shows an increase of angle with an increase of combustion chamber pressure and a decrease of angle with an increase of injection pressure. Under test conditions, a centrifugal jet showed a decrease of penetration of 23 per cent. as compared with a simple spray from an orifice of the same diameter.[3]

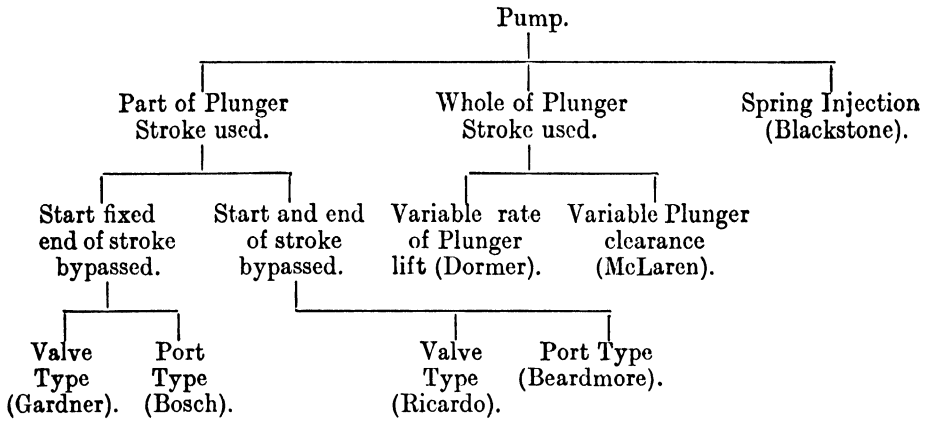
Investigations made on the mechanism of the formation of a spray show that the spray does not leave the nozzle fully formed but that an appreciable distance is covered by the fuel before the spray formation becomes visible. Highly turbulent flow through the nozzle is assumed, so that eddy motion prevails throughout the fluid stream, and it is considered that on leaving the orifice these eddies separate and an atomized spray is produced.

An alternative theory is that small particles of the liquid are lost to the air in the form of fine ligaments joined at one end to the main mass. These ligaments are rapidly severed and by the action of surface tension form a spherical drop. In effect, atomization would appear to resemble the explosion of the liquid into fine droplets and these ligaments must, therefore, be very short lived.[4]

An application of Lord Rayleigh's[5] work on the collapse of liquid columns assists in the explanation of this phenomena.

857. The development of a large number of pumps of different

designs resulted from the necessity for timing and metering the charge. The following classification will give an idea of their diversity :—



It may be stated generally that for high speed work more satisfactory results will be obtained if the middle of the stroke only is used, bypassing the delivery at the beginning and the end of the stroke through ports which may be controlled by valves or by the plunger itself.

Farmer and Alcock[6] have studied the flow of the fuel charge from the pump into the combustion chamber, and in addition to taking indicator diagrams have propounded a mathematical analysis of the process.

858. The Bosch Fuel Injection System.—The Bosch fuel pump and fuel injection nozzles are among the best known and most widely used for high speed C.I. engines and have been adopted for several British Commercial vehicles.

The Bosch fuel pump belongs to the "single plunger per cylinder" constant stroke type, and gives accurate metering and timing of the fuel at all speeds and loads ; the quantity of fuel injected per stroke on multicylinder engines is identical for each cylinder. Each pump embodies a special anti-dribble device and the pumps are of simple and robust construction. The Bosch pump is made for 2, 4 or 6 cylinder engines, and in different models the plunger diameter varies from 6 mms. to 10 mms., the stroke being kept constant at 10 mms. and the outputs vary from 100 to 280 cubic millimetres per stroke.

Each pump element consists of a steel plunger which is a piston fit in the barrel and which is provided with a suitable guide and tappet roller which bears on a cam, as shown in Figure 240.

There is also a discharge valve fitted at the upper end of the barrel. Fuel is supplied from a tank and flows through a suitable filter to the

fuel inlet connection and keeps the common suction chamber in the pump casing always flooded with clean fuel, whence it can readily be drawn into the pump barrels of the various elements through the two small ports provided. To enable the pump to vary the quantity of fuel delivered per stroke, the plunger is provided with a vertical channel as shown in Figure 241, extending from its top edge to an annular groove, a little way down the plunger length. External means are provided whereby the plunger can be rotated slightly in its barrel while working.

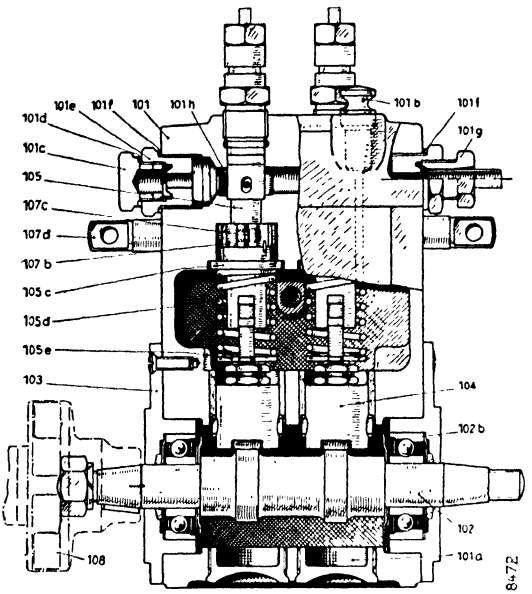


FIG. 240.—SECTION THROUGH THE BOSCH DIESEL ENGINE FUEL PUMP.
(Courtesy, C. A. V. Bosch, Ltd.)

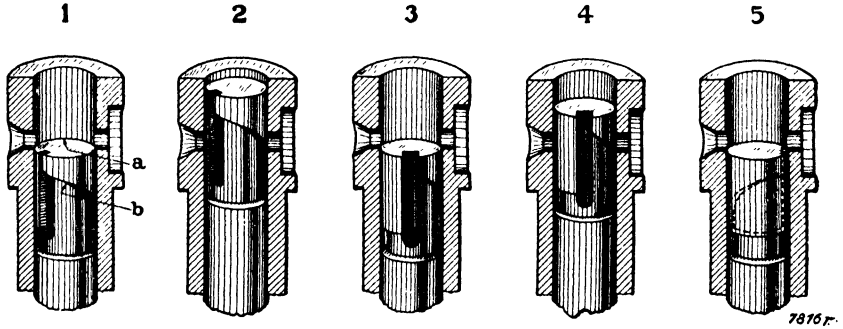


FIG. 241.—SECTION THROUGH THE BOSCH FUEL PUMP PLUNGER AND BARREL.
(Courtesy, C. A. V. Bosch, Ltd.)

The operation of a two cylinder pump is illustrated in Figure 240. When the pump element is at the bottom of its suction stroke the

two small ports are open through which the fuel can be drawn, thus filling the pump barrel. On the next delivery stroke the plunger displaces fuel back through the two small ports until its top edge covers them, so that the remaining fuel is passed out through the delivery valve, via the connecting piping, to the nozzle in the engine cylinder. Because the plunger is of constant stroke, its top edge always covers the ports in the pump barrel at the same position of the cam rotation, so that the commencement of fuel injection at the nozzle is always the same relative to the position of the engine crank. As long as the ports are kept covered by the plunger, the pump continues to inject fuel at the nozzle, but before the plunger reaches the top of its stroke, the helical edge of its annular groove uncovers the right hand port, which enables the enclosed fuel to take the path of least resistance (via the vertical channel and annular groove in the plunger) back through the port in the barrel to the common suction chamber. The position of the plunger at which the helical edge will uncover the port is adjusted by rotating the plunger through a certain angle axially by means of a toothed quadrant. This is clamped to a sleeve having slots engaging the lugs of the plunger at its lower end. The quadrant meshes with a rack provided on the control rod, which embraces the whole of the pump elements in the unit. It is coupled externally to the governor or hand control by suitable links.

Anti-Dribble Device.—When the helical edge of the pump plunger uncovers the port in the pump barrel near the end of the delivery stroke, the pressure of the fuel is immediately reduced so that the delivery valve at once drops on its seating, thus cutting off communication between the pump and the nozzle. The delivery valve also performs another function, namely that of releasing the pressure in the pipe. The effect of this is to cause the nozzle valve in the fuel nozzle to "snap" on its seat, thus suddenly terminating the spray of fuel and eliminating dribble.

The Bosch fuel pump also embodies an injection advance device for varying the fuel injection timing.

859. Bosch Fuel Nozzles.—These are suitable for injection pressures of 900 pounds per square inch and upwards and are normally supplied in two distinct types, i.e., Pin and Hole nozzles.

The complete nozzle consists of two parts, the nozzle valve and the nozzle body. The nozzle valve is formed as a circumferentially grooved barrel which at its lower end is reduced to form a valve face and ends in the "Pin" which projects through the mouth of the nozzle body. Fuel is fed to the nozzle mouth by means of small tunnels bored in the nozzle body, which terminates in a small reservoir just behind the

face of the nozzle valve seat. As the nozzle valve is a highly ground plunger fit for the nozzle body, these two parts are not interchangeable.

The pin nozzles will give spray angles of 4°, 6°, 8°, 15° and 30°. Hole nozzles are supplied with from 1 to 7 holes with hole diameters from 0·2 mm. upwards.

The nozzle valve is kept on its seat by means of a valve spring and a spindle, as shown in Figure 242. The pressure at which the nozzle valve will lift depends upon the amount of compression placed on the spring, which is adjustable by means of a compression screw. A feeling pin passes through the centre of the compression screw, which enables the functioning of the nozzle valve to be felt with the finger while the engine is running, slight shocks indicating that the nozzle is in operation. Any slight leakage of fuel which may accumulate above the valve can be led away to a drain tank by means of a pipe connection to the leak off nipple stud.

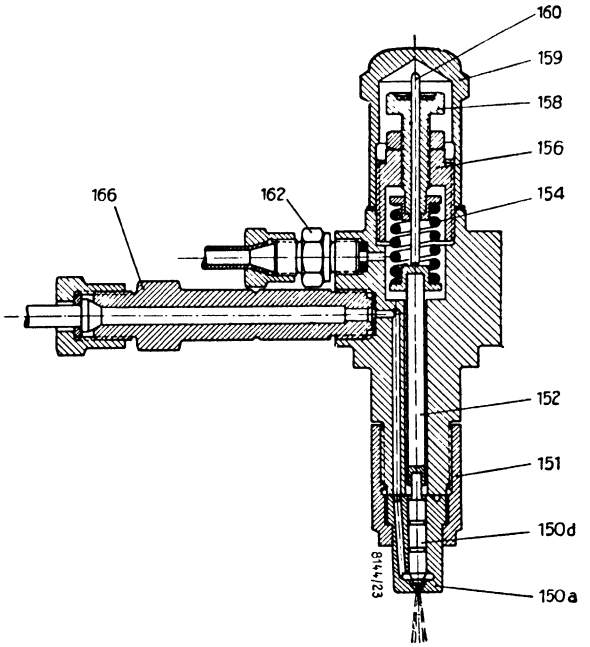


FIG. 242.—SECTION THROUGH THE BOSCH NOZZLE HOLDER.
(Courtesy, C. A. V. Bosch, Ltd.)

TYPES OF COMBUSTION CHAMBERS USED IN MODERN HIGH SPEED DIESEL ENGINES

860. Such high speed Diesel engines as have been developed may be divided into three main classes :—

(1) Those which depend upon high velocity and carefully aimed fuel

injection, in an open combustion chamber ; that is, those in which the fuel has to find the air. This system is also called the direct-injection method.

(2) Pre-combustion chamber engines.

(3) Those which depend upon an orderly rotational air swirl across which the fuel is projected ; that is to say, those in which the air has to find the fuel.

There is also the Acro-Bosch system, which does not in a strict sense fall into either of these three separate categories.

Direct Injection Systems.—These are in no way novel, but were developed for submarine engines more than twenty years ago. According to this method (one example of which is shown in Figure 243), the fuel is injected directly into the combustion chamber through a special design of fuel nozzle carrying a number of very fine jets (often aimed in various directions), under sufficient pressure to carry the fuel particles well into the mass of the compressed air. The injector in this case is fitted into the cylinder head, there being no ante-chamber. The plain cylinder head is usually, but not always, of symmetrical shape and in some cases the piston is given a special dome, or dish shape, to assist the spraying action.

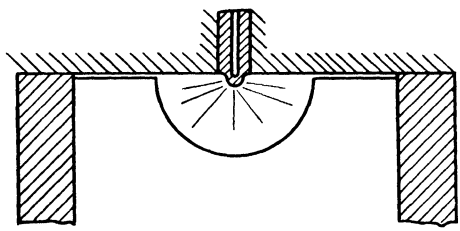


FIG. 243.—DIAGRAM OF THE GARDNER DIRECT INJECTION FLAT CYLINDER TYPE COMBUSTION CHAMBER.

With regard to turbulence, a certain amount, of course, exists because of the entering velocity of the air, but usually no attempt is made to stimulate this or to give it any organized directional flow, contact between the fuel and the air being achieved by the direction of the fuel spray and the general indiscriminate turbulence. The great advantages of this system are that, owing to the lack of intensive turbulence and to the compact form of the combustion chamber, the loss of heat during compression is at a minimum, hence the delay period is short, running is fairly smooth, the engine starts easily from cold and is not particularly fuel sensitive. These advantages are substantial but, nevertheless, the direct injection system has its limitations. These are as follows :—

(1) Engine speed is limited by the speed at which the liquid fuel can travel through the compressed air in the combustion space.

(2) High fuel pressures are necessary in order to give the proper penetration and atomization. This complicates, to some extent, the design of the fuel pump and injection system and tends to increase leakage losses.

(3) It is necessary to employ a number of very small fuel jets and to maintain at all times precisely the same direction of flow from each of these jets. Not only is it very difficult to produce, and subsequently to maintain, the correct angle between all the various minute jets, but this angle is liable to be deflected by partial choking of the jet orifices.

(4) For small engines, the fuel injection system becomes more intricate, greater accuracy in metering being essential.

For these reasons, the principle of directed spray, where there is no induced turbulence to assist combustion, has lost favour except in the case of large, slow running engines where the size of fuel jets is large and where low fuel line pressures suffice.

861. Pre-Combustion Chamber Engines.—The combustion chamber of the Pre-combustion chamber type engines is in two parts. A small auxiliary chamber communicates with the main combustion chamber through one, or a series of, small holes, and the fuel is sprayed into this auxiliary chamber. Here it proceeds to burn, and as the pressure rises, the partially burnt fuel is forced through the small communicating holes at high velocity into the main combustion chamber where additional oxygen is picked up to complete the combustion. The delay period and pressure rise therefore take place in the auxiliary chamber and also the stage corresponding to the burning of the fuel as it leaves the nozzle in the main combustion chamber. The rapid rise of pressure in the auxiliary chamber is utilized both to pulverize and to distribute the fuel and the effect is similar to that obtained with ordinary air injection. Certain advantages are shown when using this method. The size of the fuel orifice is not of great importance, the fuel does not need to be injected in any precise direction and a relatively low fuel injection pressure can be used. The work placed upon the fuel pump is thus made comparatively simple and, due to the low pressure used, leakage troubles are reduced, and timing and metering are not seriously affected by the elasticity of the piping nor by the elasticity of the liquid fuel itself.

Against these advantages, there is the disadvantage that a large proportion of the air during compression and nearly the whole of the burning fuel during combustion must be forced through a number of small holes at a high velocity resulting in a heavy heat loss. Thus, if a sufficiently high temperature for combustion is to be reached, a high

compression ratio must be employed, and this increases the pressure range and necessitates the use of heavy working parts. The power output and efficiency are greatly reduced due to the high heat loss and because of this heat loss during compression the engine is difficult to start from cold.

862. Engines Embodying Directed Turbulence. The third category consists of engines which employ the principle of causing the air in the combustion chamber to rotate at a high velocity past the fuel jet. The air is admitted to the cylinder tangentially during the suction stroke to induce an orderly rotary motion instead of the usual general turbulence. The combustion chamber may be simple in design, an ordinary cylindrical chamber almost half the diameter of the cylinder being sufficient. In this chamber, the whole of the air is compressed and rotates at an extremely high speed, and into the rapidly rotating mass of air a stream of fuel is projected at right angles to the air flow. This stream of fuel is admitted at a point towards one side of the combustion chamber so that, as the air rotates, it sweeps past the fuel jet. By this means, the fuel is burnt in a rapidly moving air current allowing fresh oxygen to be continuously supplied to replace that which has been consumed.

Thus the pulverization and distribution of the fuel is accomplished by the combustion air and, as in the previous case, a low fuel injection pressure and relatively large single orifice can be used.

Since the air finds the fuel, the velocity and direction in which the jet is projected are not of vital importance. The speed of rotation of the air will vary with the speed of the engine, and since the speed is unlimited by any conditions of injection, fixed injection can be used throughout the whole speed range of the engine. Provided some form of check valve is installed to prevent air being forced back into the fuel system, a plain jet is all that is required and no fuel valve is needed.

This principle works to best advantage in either a sleeve valve engine, or a two-stroke engine. In order to obtain the requisite amount of air swirl in a poppet valve engine the ports have to be shrouded to an extent such as to impair their volumetric efficiency.

As the swirl increases, the heat loss by scrubbing the cold cylinder walls increases, the delay period also increases and the running becomes rough. This can be obviated to a great extent by fitting a loose liner inside the cylindrical combustion head. Starting from cold is a little more difficult, but this can be overcome by fitting movable guide vanes outside the air intake ports, so that they can be set normal for starting and tangential for running.

863. The Acro-Bosch System utilizes a combustion chamber

divided into two compartments of nearly equal capacity, separated by a narrow neck. The first compartment is open directly to the cylinder and the air in this portion is relatively unagitated, but that in the second compartment is forced through a narrow neck and acquires a high degree of turbulence. The fuel jet is injected across the first compartment and is aimed at the opening into the second. The exact position where ignition takes place is speculative, but probably takes place at or about the mouth of the second compartment (or air cell as it is generally termed). Combustion may then oscillate rapidly on either side of the restricted neck and is completed during the expansion stroke by the discharge of the remaining air from the air cell. The system is extremely sensitive, and over penetration of the jet, or too long a delay period may allow fuel to penetrate into the air cell where it will rapidly burn, due to the excessive turbulence and cause excessive maximum pressures and knocking.

Typical Types of Automotive Diesel Engines and Diesel Driven Vehicles

864. It has already been stated that the advances made in the high speed compression ignition engine have, in the main, resulted from the interest taken in the type suitable for road transport use.

As the characteristics of the Diesel engine differ considerably from those of the petrol engine, particularly in regard to the high power output at low engine speeds, modifications to the transmission mechanism are necessary. Clutches of greater area are needed, and gear ratios generally should be higher so that a satisfactory road speed may be attained in spite of the lower maximum engine speed. On the other hand, as the maximum power is the same as that of a corresponding petrol engine, it is also necessary, for severe hill climbing, that the lowest ratio shall be as low as that used on a petrol chassis. A slightly higher back axle ratio has been found satisfactory on passenger vehicles, but on very heavy transport vehicles, where more arduous conditions of working are encountered, it is usual to combine a supplementary gear with the existing four-speed gear box. Occasionally this gear is used to step up the ratios so that a high road speed may be available at low engine revolutions when the vehicle is running empty. On the majority of vehicles, however, this gear is a reducing gear and is only brought into play under heavy conditions, giving the effect of a lower back axle ratio.

The power developed at low speeds tends to promote roughness when the engine is running slowly and to prevent any shock from this cause being transmitted to the vehicle a flexible mounting for the engines is desirable.

The braking of the compression ignition vehicle is a factor requiring some study. On the petrol chassis the Vacuum system operated by the depression in the induction pipe is common, but this method is impossible in the heavy oil engine, since no vacuum is maintained in its "open" inlet manifold. Various means have been adopted to overcome this difficulty. Some of the Continental engines utilize one or more of the cylinders as vacuum pumps to operate the vacuum brake, the fuel being cut off. The majority of British engines are equipped with rotary exhausters for the vacuum brakes or reciprocating air pumps for pressure brakes, these auxiliaries being driven off the timing gear shafts. On one model, a magnetically operated braking system has been evolved.

Just as the engine is unsuited for the direct working of vacuum brakes, so is it unable to raise fuel to the pumps by means of the usual vacuum tank used on petrol engines. When the rotary exhauster is installed the vacuum tank is used, or, if not, small electrically or mechanically driven pumps are fitted for this purpose.

The starting of a heavy oil engine presents some difficulty due to the high compression pressure. It has, however, one advantage over the petrol engine in that it will take its load almost at once and does not need warming up before developing full power as does the petrol engine.

Two principles have been adopted to overcome the problem of cold starting. One is to provide some form of power to overcome the compression pressure and the other is to relieve the compression pressure whilst the engine is being turned by hand and to restore it when the momentum is sufficient to overcome the compression.

As in the case of the petrol engine, the electric motor has been widely adopted for starting even though means have been provided to permit starting by hand. The power required is, of course, greater than that for the petrol engine, and this usually takes the form of a 24 volt motor. In some instances, two 12 volt batteries are provided and by means of an automatic switch these two batteries are connected in series to supply the 24 volts required. When the engine starts, the switch disconnects the motor from the batteries and connects them in parallel as required for the lamps and for charging by the 12 volt dynamo.

Another method provided on some engines is to increase the fuel injection pressure to ensure adequate delivery through the injection nozzles under starting conditions.

The method adopted for starting the engine by hand is similar to that provided for motor cycles. The engine is equipped with a decompression mechanism actuated by a small hand lever. This mechanism prevents one valve of each cylinder from closing, so that no pressure is created when the pistons rise on the compression stroke. This permits the crankshaft to be turned by hand. On throwing the decompression

mechanism out of action, when the engine is turning by its own momentum, regular firing begins.

In some cases means are provided for increasing the compression on some or all the cylinders to compensate for the heat lost to the cooling system during the slow turning speed at starting. On pre-combustion and air-cell types, the general practice is to employ electric heater plugs. In the former type of engine, the plugs are placed so that the heating coils enter the pre-combustion chambers and thus heat the air inside to ensure a quick start. For the air-cell type of engine the heating coils are placed so that they heat the air between the injection nozzle and the mouth of the air cell.

865. The A.E.C. Diesel Engines for Lorries and Buses. — The late London General Omnibus Company, in conjunction with the Associated Equipment Company of Southall, Middlesex, began actual service tests on Diesel driven vehicles in January, 1931, when three four-wheeler omnibuses, fitted with A.E.C.—Acro high speed engines, were operated. In March of the same year, the experiments were extended by the addition of nine six-wheeler omnibuses.

The engines were operated on the Acro principle, the air-cell being located in the cylinder head, the success of the system depending on very delicate balance between the size and shape of the venturi, injection characteristics and compression ratio. The performance of the engine was then far in advance of most of its contemporaries, its most valuable feature probably being its wide speed range. The actual operation of the engine was satisfactory in service; during idling, "Diesel knock" was apparent, but this was not noticeable at road speeds greater than about 10 miles per hour.

As a result of these early experiments with the Acro system, the A.E.C. developed a new type of engine in conjunction with Mr. Ricardo, and in October, 1931, twelve Acro engines in L.G.O.C. omnibuses were converted to this type. This new design embodied Mr. Ricardo's principle of "Rotational Air Swirl" and enabled a larger amount of the available oxygen to be utilized than occurred in the Acro engines, and hence the specific output and consumption were improved. The combustion process was also more efficient and a smokeless exhaust was obtained under all operating conditions: the only time when smoke was apparent was on acceleration, when a slight momentary puff was emitted.

Details of the A.E.C.-Acro and A.E.C.-Ricardo Diesel engines are given in Table 203.

The latter engine has a cast Elektron alloy crankcase, ribbed to give adequate support for the crankshaft. The main bearing caps are of drop forged steel with the white metal bearing surfaces run directly into

them. The main bearing bolts are carried right up through the crankcase and the upper ends serve as studs for securing the cylinder. The cylinder is in the form of a monobloc casting and two cylinder heads are fitted, each covering three cylinders. The heads carry the valves, valve rockers, etc., and combustion chamber. A single cylinder head cover is fitted over the two heads and incorporates the air intake manifold. The crankshaft is of very generous proportions and of sufficient rigidity to avoid any troubles from torsional vibration. Seven main bearings of 85 mms. diameter are provided. The pistons are of heat treated aluminium alloy and are provided with three pressure and two oil scraping rings. The fuel pump and injectors are standard C.A.V.-Bosch equipment and work at an injection pressure of 1,500 pounds per square inch.

TABLE 203.—CHARACTERISTICS OF A.E.C. HIGH SPEED DIESEL ENGINES

	A.E.C.-Acro	A.E.C.-Ricardo
Number of cylinders	6	6
Bore and stroke, mms.	110 × 142	115 × 142
Swept volume, litres	8·10	8·86
B.H.P. and speed (r.p.m.)	95 at 2,500	130 at 2,400
Max B.M.E.P., lbs./sq. in.	83	103
B.H.P. per litre	11·7	14·7
Total weight with electrical equipment (lbs.)	1,350	1,415
Ditto per B.H.P. (lbs.)	14·2	10·9

The A.E.C. also produce a 70 H.P. four-cylinder A.E.C.-Ricardo Diesel engine for use in vehicles normally equipped with four-cylinder petrol engines.

Various views of the six-cylinder engine are shown in the accompanying illustrations.

Comparison of A.E.C. Petrol and Diesel 6-Cylinder Engines.—It is of interest to compare the A.E.C. Mammoth-Major 120 h.p. 6-cylinder petrol engine, already mentioned in Chapter XIV, with the 6-cylinder A.E.C. Diesel engine, described above. The performance curves of these two engines are given in Figure 247, which shows that:—

(1) The Diesel engine has a markedly lower fuel consumption. This, together with the lower cost of Diesel fuel as compared with petrol, results in an appreciable saving in running costs.

(2) The brake-horse-power of the Diesel engine is appreciably greater than that of the petrol engine although the brake mean effective pressure is a little lower.

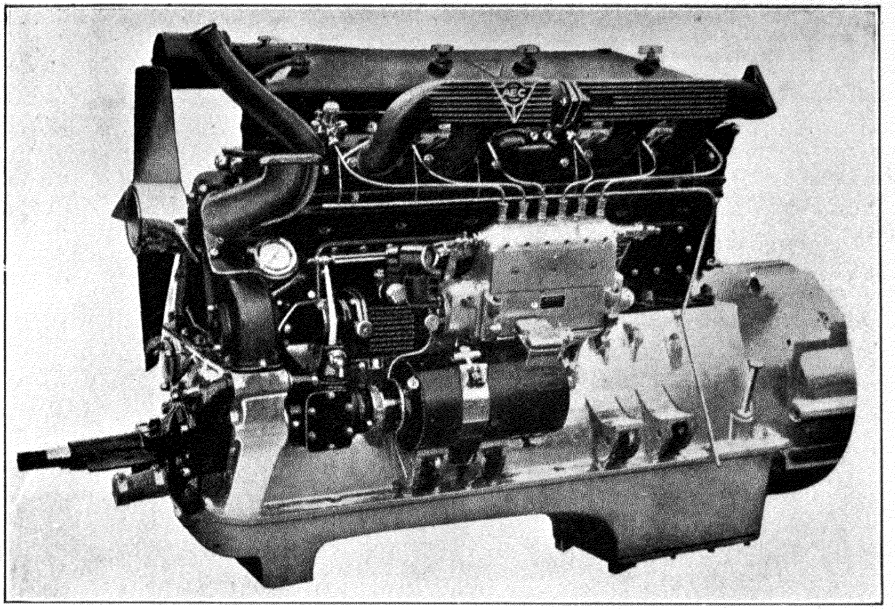


FIG. 244.—THE A.E.C. 130 H.P. 6-CYLINDER HIGH SPEED DIESEL ENGINE.
(Courtesy, Associated Equipment Co.)

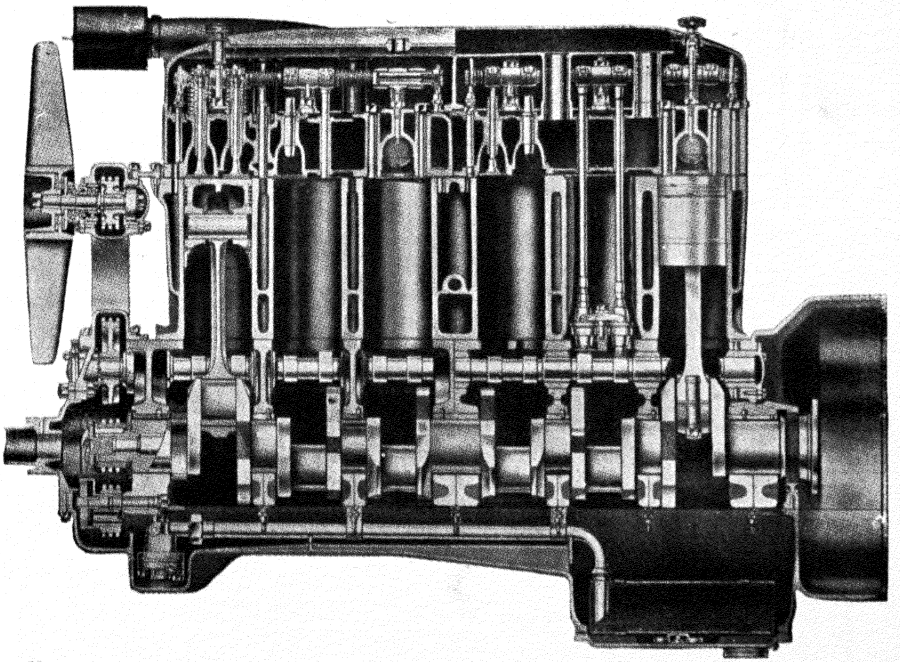


FIG. 245.—SECTION of the A.E.C. 130 H.P. HIGH SPEED 6-CYLINDER DIESEL ENGINE.
(Courtesy, Associated Equipment Co.)

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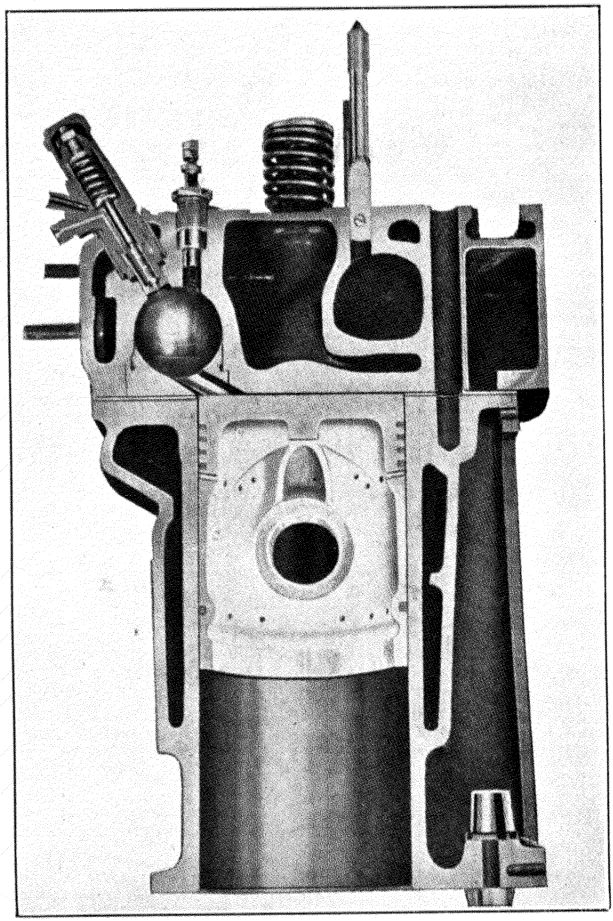


FIG. 246.—SECTION THROUGH CYLINDER HEAD OF A.E.C.–RICARDO ENGINE.
(Courtesy, Associated Equipment Co.)

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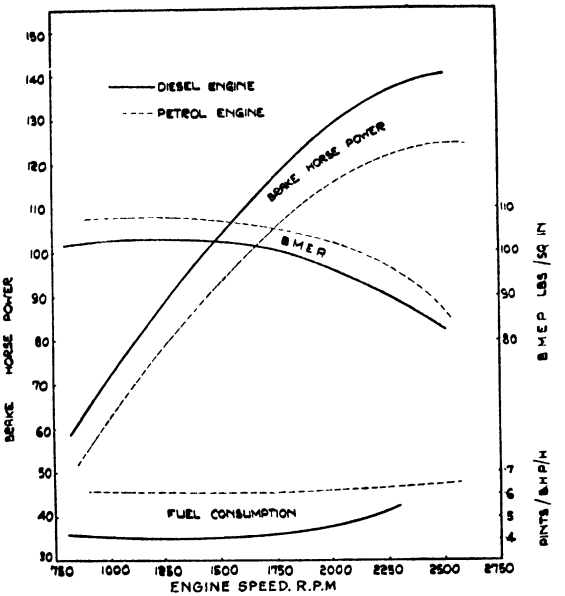


FIG. 247.—CURVES SHEWING COMPARISON OF PERFORMANCES BETWEEN A.E.C. 110 M.M. × 130 M.M. 6 CYLINDER PETROL ENGINE AND A.E.C. RICARDO 115 M.M. × 142 M.M. 6 CYLINDER DIESEL ENGINE.
(Courtesy, Associated Equipment Co.)

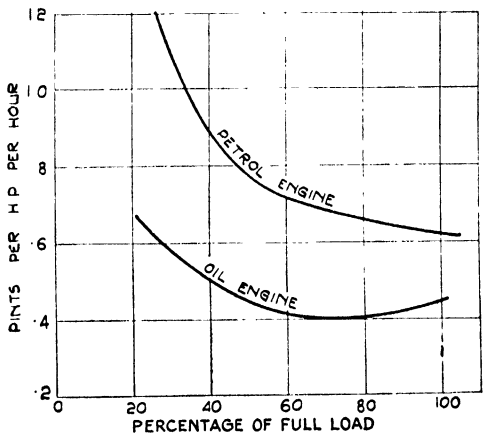


FIG. 248.—PART LOAD CONSUMPTION CURVES OF A.E.C. 6 CYLINDER PETROL AND DIESEL ENGINES.
(Courtesy, Associated Equipment Co.)

865a. Gardner High Speed Diesel Engines.—The well known firm of L. Gardner & Sons, Manchester, make a series of 4, 5 and 6 cylinder high speed Diesel engines for automotive purposes. These are of the direct injection type and have cylinders of 4¼ in. bore, 6 in. stroke and 1·4 litres swept volume. Bosch fuel pumps and injection valves are fitted as standard. To ensure easy starting, arrangements are pro-

vided whereby the compression can be relieved and the inlet valve timing altered ; this allows starting by hand, electric starting only being required on very rare occasions. No electric glow plugs are used.

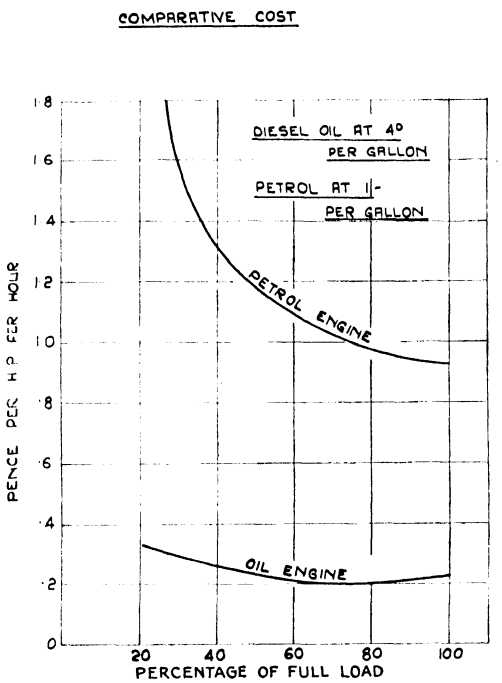


FIG. 249.—FUEL COSTS OF A.E.C. 6 CYLINDER PETROL AND DIESEL ENGINES AS FITTED IN LORRY CHASSIS UNDER ACTUAL LOAD CONDITIONS.
(*Courtesy, Associated Equipment Co.*)

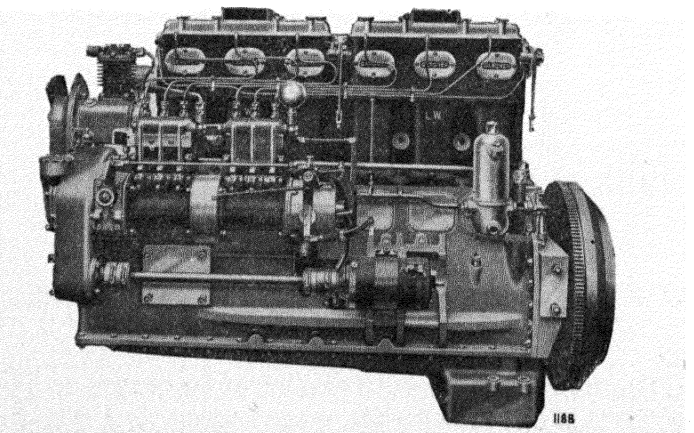


FIG. 250.—NEARSIDE VIEW OF THE 6 CYLINDER GARDNER DIESEL ENGINE.
(*Courtesy, Norris, Henty and Gardners Ltd.*)

A near side view of the 6 cylinder Gardner engine is shown in Figure 250. This engine has a weight (including the flywheel) of 1,500 lbs.

and an R.A.C. rating of 43·5 horse power. It delivers 102·5 horse power at 1,700 r.p.m., a governor limiting the engine speed to this figure. The compression ratio employed is about 13 to 1. Typical performance curves are reproduced in Figure 251. A point of importance is the very low fuel consumption.

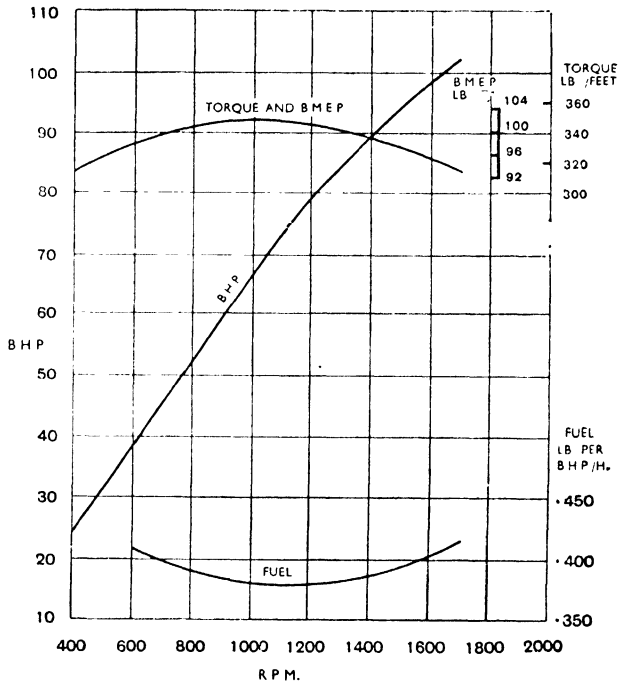


FIG. 251.—TYPICAL PERFORMANCE CURVES FOR THE GARDNER DIESEL ENGINE.
(*Courtesy, Norris, Henty and Gardners, Ltd.*)

866. Armstrong Saurer Automotive Diesel Engines. — Armstrong Saurer Commercial Vehicles, Ltd., manufacture a range of Diesel engine driven vehicles fitted with both four and six cylinder engines. These engines, which are shown in the accompanying illustrations are of the air-cell type. The cylinder blocks are of special cast iron, cast in one piece with the crankcase; the cylinder bores are fitted with cast iron liners and the cylinder heads housing the air cells are detachable. Overhead valves are employed, operated by a camshaft through push-rods and rocker levers. The crankshaft is of unique design and consists of six sections built together, the ends of which are flange shaped and carry the main roller bearings. Bosch fuel injection equipment is used throughout and glow plugs are fitted to give easy starting.

The four cylinder engine develops 72 B.H.P. at 1,800 r.p.m., with a fuel consumption of 0·535 lbs. per B.H.P.H., and the six cylinder engine 103 B.H.P. at the same speed and with the same specific fuel con-

sumption. Performance curves referring to the latter engine are reproduced in Figure 254.

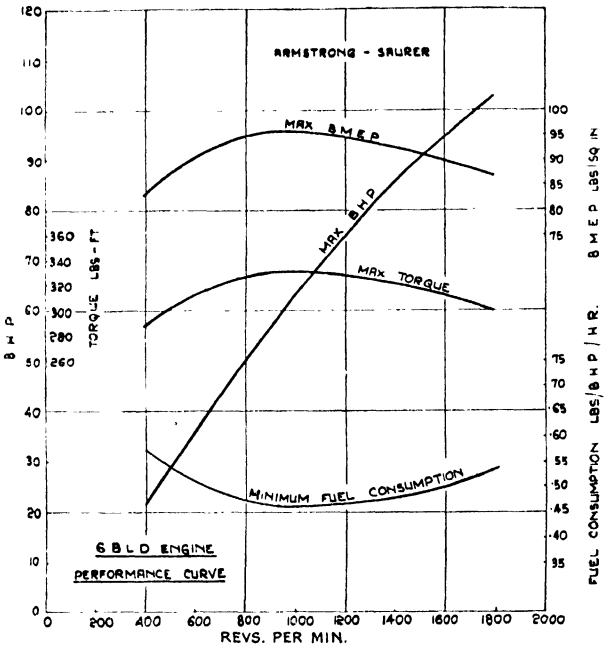


Fig 254.—Typical Performance of the Armstong-Saurer 6 Cylinder Diesel Engine. (*Courtesy, Armstrong-Saurer Commercial Vehicles, Ltd.*)

The above short descriptions of three typical types of automotive Diesel engines are sufficient to indicate the progress made in this field during the past few years. Many other makes of engines have, of course, also been developed.

Fuels for Diesel Engines

867. The automotive Diesel engine and its fuel constitute a joint problem and development of the former cannot proceed without due consideration of the latter. Already much work is being carried out by the major Oil Companies to determine the fuel requirements of high speed Diesel engines and the fuels marketed embody the results of many important investigations carried out with this object in view. One can also see that the position existing about ten years ago, with regard to petrol engines and their fuels, now occurs with respect to the Diesel engine. The phenomenon of Diesel knock has already been appreciated and the knock-ratings of Diesel engine fuels are being actively studied. Important as other properties of Diesel oils are, such as ash and sulphur contents, flash points, etc., these are now no more important than knock ratings and are likely to assume relatively less importance in the future.

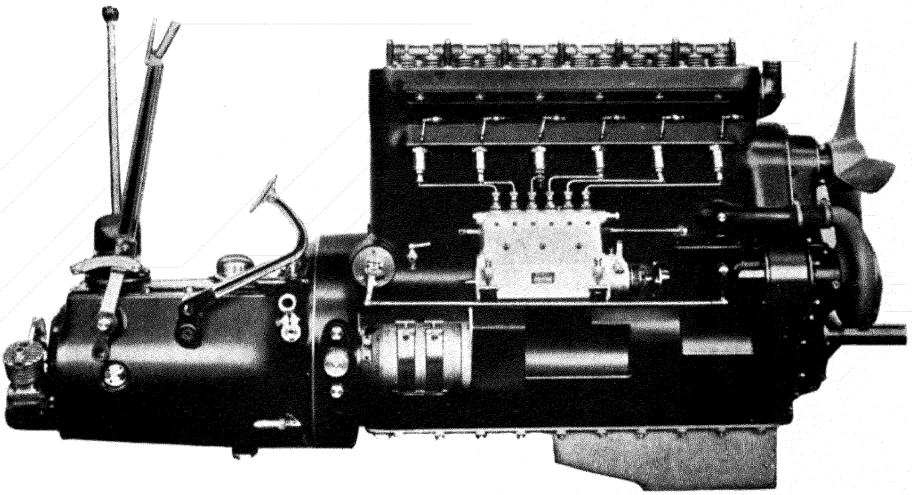


FIG. 252.—OFFSIDE VIEW OF ARMSTRONG-SAURER 6-CYLINDER DIESEL ENGINE.
(Courtesy, Armstrong-Saurer Commercial Vehicles, Ltd.)

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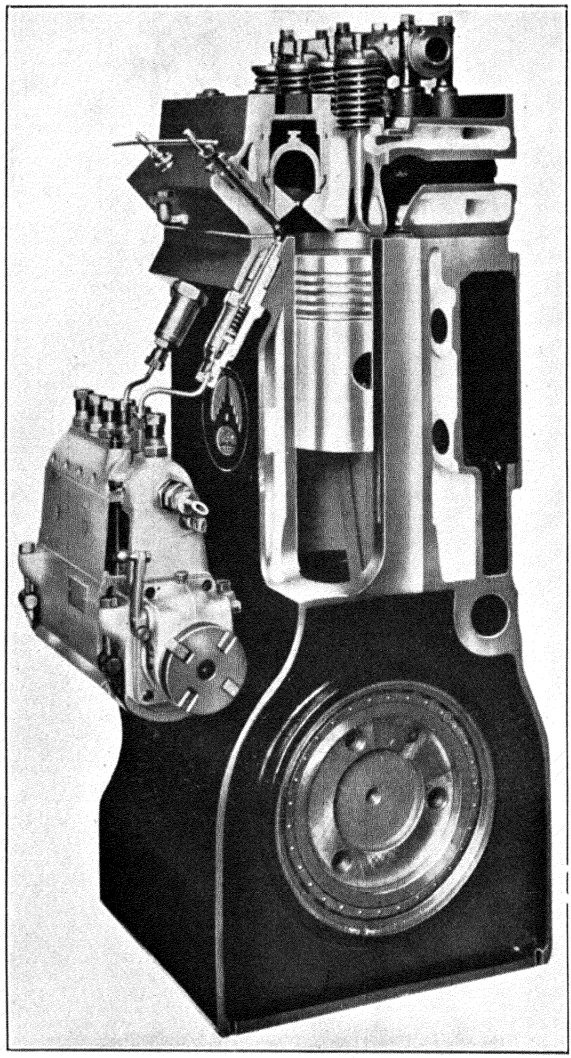


FIG. 253.—SECTION THROUGH ARMSTRONG-SAURER 6-CYLINDER DIESEL ENGINE.
(*Courtesy, Armstrong-Saurer Commercial Vehicles, Ltd.*)

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The General Properties of Diesel Oils.—Slow speed marine Diesel engines and similar engines operating in power stations, etc., are fairly tolerant to variations in fuel quality so long as properties such as ash content are kept within reasonable limits, but this state of affairs does not obtain with the automotive Diesel engine, whose fuel requirements are stringent. These will now be briefly considered.

868. Specific Gravity.—This is of importance in only one connection. At the present time, when the demand for such fuels is still small, and negligible compared with that of petrol, Diesel oils are sold on a weight basis instead of on a gallonage basis. When, however, they are marketed at roadside service stations, retailing by the gallon will be the only feasible method. When this comes about, an oil of a high specific gravity, provided it is satisfactory in all other respects, will have the advantage of a high calorific value per gallon and will give a correspondingly better mileage. At the moment, sale by weight, which is more rational than sale by volume, though more troublesome, prevents any such differentiation.

It is of interest to compare petrols and Diesel oils with respect to their specific gravities and calorific values. The latter, as at present marketed, have an average specific gravity of about 0·87 and a net calorific value of 18,250 B.T.U.'s per pound, equivalent to 158,775 B.T.U.'s per gallon. The corresponding figures for an average English No. 3 grade petrol are 0·74, 18,750 B.T.U.'s and 138,750 B.T.U.'s, respectively. At the present market prices, therefore (4·0 and 17·5 pence per gallon, respectively), the costs of the fuel equivalents of 1 therm (100,000 B.T.U.) are 2·5 pence in the case of Diesel fuel and 12·7 pence in the case of petrol.

Generally speaking, however, Diesel oils having high specific gravities are less satisfactory from the viewpoint of engine behaviour than those of lower specific gravity. This is because they are less paraffinic in character than the latter and, consequently, give longer delay periods, with which are associated running roughness, excessive pressures and knocking. However, this must only be accepted as a very rough guide as there is no hard and fast relationship existing between the two properties, no more than the octane numbers and specific gravities of petrols are related.

869. Flash Point.—The flash points of Diesel engine fuels are of importance in two directions which are practically the same in essentials. One applies to the fire risk in storage which affects storage in bulk insurance premiums and the other applies to the fire risk on vehicles using such fuels. A low flash-point naturally increases the cost of storage and increases insurance premiums. With regard to the fire

risk on automotive vehicles, it is obviously an advantage to use fuels which have high flash-points, other things being equal. Diesel oils marketed in the United Kingdom for this purpose have flash-points, as measured in the Pensky-Martens apparatus, of from 180°F.—240°F. (82°C.—115·6°C.).

870. Ash Content.—The ash content of a Diesel oil should be kept as low as possible because the whole of this is injected into the engine cylinder with the fuel and if excessive in amount leads to cylinder liner wear. This is not surprising because an ash content of 0·003 per cent. (a figure often met) is approximately equivalent to nearly 1 ounce of ash per 100 gallons of Diesel oil. These ashes are often very abrasive and they cannot be removed by filtering or centrifuging. However, the amount of wear caused by the ash content of a normal high speed Diesel fuel is only responsible for the fraction of the total wear, the major part being caused, under normal driving conditions, by the abrasive dust present in the air taken into the engine cylinders. Ash contents of present high speed Diesel fuels vary from a trace (i.e., less than 0·001%) to ·006 per cent. Usually a limit is set at ·005 per cent.

871. Sulphur Content.—The sulphur content of Diesel oils is not important. Various limitations are imposed in specifications, but it would appear that no harm could result with sulphur contents as high as 2 per cent. No relation appears to exist between the sulphur content of the fuel and the amount of cylinder wear which takes place. The sulphur contents of present high speed Diesel fuels vary widely but rarely exceed 1·5 per cent. They are sometimes as low as 0·1—0·2 per cent.

872. Adventitious Matter.—The presence of foreign material such as dirt and water is to be avoided wherever possible because it is liable to cause choked fuel lines and filters and often gives trouble in the form of choked injection nozzles.

873. Fuel Viscosity.—This is extremely important. Low viscosity at low temperatures is necessary to ensure adequate flow through the fuel lines, which are often in exposed positions near the fuel tanks and also to ensure satisfactory working of the fuel pump. Fuels of high viscosity also tend to choke filters and gauzes. Fuel viscosity is also of importance in determining the type of fuel spray formed in the cylinder and the extent of fuel penetration, fuels of higher viscosity giving a spray of larger drop size and greater penetration. The viscosity must not be allowed to rise too high, however, if incomplete combustion and exhaust smoke is to be avoided. Similarly, low viscosities can also be a

disadvantage as they cause wear in fuel pumps and "seizing" of fuel nozzles, due to lack of "lubrication." Poor fuel penetration in the engine cylinder also often results.

It will be evident from these remarks that the viscosity of high speed diesel fuels is determined by numerous factors dependent to a large extent upon engine design. Figures for the viscosities of high speed diesel oils used in this country are given later.

874. Boiling Range.—Boiling range is of no importance in itself, viscosity being the determining factor. It rarely appears in specifications. Distillate oils used in high speed engines have initial boiling points about 200°C., and end points somewhere between 325°C. and 425°C.

875. Specifications for High Speed Diesel Fuels.—The only general specification in existence at the moment in this country for Diesel oils is specification "A" No. 1 of the British Engineering Standards Association. This is as follows :—

Flash point (closed). Not less than 150°F.
Hard asphalt content. 0·5 per cent. maximum.
Ash content. 0·01 per cent. maximum.
Viscosity (Redwood No. 1) at 100°F. 75 secs. (maximum).
Water Content. 0·5 per cent. (maximum).
Cold test. Oil to remain liquid at −20°F. (−29°C.).

The Company possessing perhaps the greatest experience in this country in the field of Diesel driven road vehicles, is the London General Omnibus Company, now known as London Transport, who have recommended the following tentative specification.[7]

Description.
The fuel to be a hydrocarbon oil of petroleum and/or shale origin. To be free from mineral acid, grit and other foreign materials of all descriptions.
Closed Flash Point. 150°F. (min.).
Viscosity (Redwood No. 1 at 100°F.). 45 secs. (max.).
Cold Test. Not above 20°F. (−7°C.).
Water. Nil.
Adventitious matter. 0·03 per cent. (max.)
Ash content (inherent). 0·01 per cent. (max.).
Sulphur content. 0·5 per cent. (max.).
Spontaneous Ignition Temperature. As low as possible.
Performance. The fuel must give satisfactorily smooth running when tested in the engine.

The properties of the oils generally used as high speed Diesel engine fuels have recently been given by numerous investigators in this field. Thus, Goddard[8] states that oils of the following characteristics are suitable :—

Specific gravity at 60°F.	0·875.
Flash point.	150°F. (min.).
Pour point.	30°F. (max.).
Water.	0·05 per cent. (max.).
Sediment.	0·012 per cent. (max.).
Ash.	0·005 per cent. (max.).
Sulphur.	0·850 per cent. (max.).
Calorific value.	19,400—19,600 B.T.U./lb.
Viscosity, Redwood No. 1.	
40°F.	116 secs.
60°F.	75 ,,
75°F.	60 ,,
100°F.	45 ,,

Generally speaking, the present automotive diesel engines require fuels that are classed as " light diesel oils " or " gas oils." They must, in any case, be distillate oils, for no fuels containing residues can be tolerated except in engines of the low speed variety used for stationary purposes. Table 204 shows the properties of various Diesel fuels now available and is reproduced from the published work of Le Mesurier and Stansfield.[9]

It will be observed that only one of the above specifications, namely that drawn up by the London General Omnibus Company, contains any reference to engine performance, similar to a knock rating test for petrols. Nevertheless, without such a condition, all specifications are practically valueless, because many oils of suitable viscosity, ash content, etc., cannot be used in high speed engines because of their rough running and knocking properties. It has now been established that the high speed Diesel engine fuel requires as much care in its selection as does a petrol engine fuel.

876. The Knock-Ratings of Diesel Fuels.—It has already been shown that the process of combustion in a Diesel engine may be divided into three more or less distinct stages, (*a*) the delay period, (*b*) a period of rapid combustion and (*c*) a period in which the rate of combustion may be controlled by the fuel pump and nozzle. The smoothness of running obtained on any fuel is determined by the extent of the delay which it gives in the first stage and, consequently, the maximum pressures which it develops in the second stage. Fuels vary widely in their suitability for Diesel engines. In general, it has been found that

TABLE 204.—PROPERTIES OF DIESEL FUELS. (LE MESURIER & STANSFIELD)

	1. Distillate from Mixed Base Crude (Mainly Paraffinic)	2. Scotch Shale Gas Oil	3. Distillate from Mixed Base Crude (Mainly Paraffinic)	4. Distillate from Naphthenic Base Crude	5. Distillate from Naphthenic Base Crude	6. Distillate from Naphthenic-Aromatic Crude
1. Specific Gravity at 60°F.	0·867	0·833	0·852	0·867	0·855	0·904
2. Flash Point (Pensky-Mortens), °F.	236	182	188	184	208	206
3. Set Point, °F.	8	12	0	—20	—10	—20
4. Kinematic Viscosity at 32°F.	0·1946	0·0735	0·0840	0·1379	0·1297	0·1528
70°F.	0·0846	0·0425	0·0453	0·0640	0·0599	0·0653
100°F.	0·0520	0·0295	0·0307	0·0403	0·0396	0·0412
140°F.	0·0317	0·0212	0·0209	0·0250	0·0254	0·0254
5. Calorific Value—Gross, B.T.U.'s/lb.	19,500	19,700	19,800	19,700	19,675	19,150
Net, B.T.U.'s/lb.	18,290	18,460	18,600	18,490	18,460	18,050
6. Sediment, %	0·003	0·007	0·009	0·007	0·008	Trace
7. Ash, %	0·001	0·003	0·004	0·003	0·003	Trace
8. Carbon	85·60	85·61	85·69	86·50	85·41	86·80
9. Hydrogen	12·69	13·03	12·65	12·77	12·82	11·63
10. Carbon/Hydrogen ratio	6·7	6·6	6·8	6·8	6·7	7·5
11. Sulphur, %	1·07	0·54	0·85	0·11	0·63	0·50
12. Hard Asphalt, %	Nil	Nil	Nil	Nil	0·10	Trace
13. Soft Asphalt, %	Nil	Nil	Nil	Nil	Nil	Nil
14. Carbon Residue, %	0·06	0·01	0·01	0·02	0·17	0·13
15. Spontaneous Ignition Temperature, °C.	262	268	263	261	262	272
16. Initial Boiling Point °C.	256	205	205	214	226	236
Volume to 200°C., %	—	—	—	—	—	—
225°C., %	—	3	3	3·5	—	—
250°C., %	—	20·5	22	17·5	20	18
275°C., %	10·5	53	61	44	48·5	51
300°C., %	42·5	77	80	68·5	70·5	75·5
325°C., %	71	90	91	83	83	87
350°C., %	89	96·5	96·5	93	91·5	95
Residue, %	11	3·5	3·5	7	8·5	5

paraffinic oils are the most satisfactory, in that they give low ignition delays and reasonable maximum pressures and that aromatic oils such as creosotes and coal tar oils are quite unsuitable. Naphthenic oils occupy an intermediate position. Often highly aromatic oils will not ignite at all.

The actual differences obtained with various fuels are well shown in Figure 255, which refers to tests carried out in a Junkers opposed piston engine (8 B.H.P., 1,000 r.p.m., 65 mms. bore and 210 mms. combined stroke) and shows the maximum pressures obtained.[10] The numbers of the fuels in this diagram do not correspond to those given in Table 204.

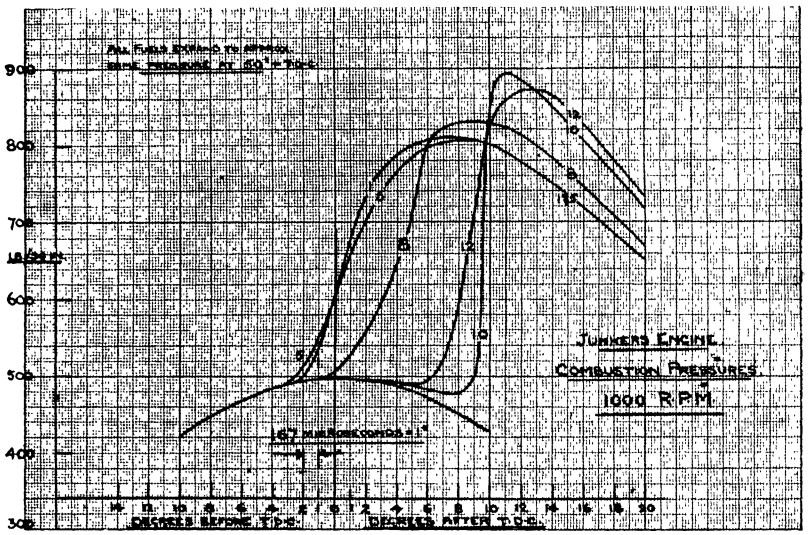


FIG. 255.

In these tests, Fuel No. 5 (Scotch shale gas oil) was the smoothest as regards freedom from combustion shock, Nos. 10 and 12 gave pronounced shock (No. 10 Fuel is the same as No. 6 of Table 2). The actual delay angles (i.e., delay times in terms of crank angle degrees elapsing between fuel injection and the beginning of pressure development) obtained in this series of tests on the various fuels of Table 204 in this engine, were as follows :—

Fuel Number.	*Delay Angle.*
No. 1	10°.
No. 2	9½°.
No. 3	11°.
No. 4	11°.
No. 5	10½°.
No. 6	16°.

Creosote could not be used owing to the excessive delay angles obtained.

Chemical analysis of Diesel fuels does not give sufficient data for grading them, just as analysis does not give sufficient information regarding the knocking tendencies of motor spirits.

Combustion shock has been measured by means of the Strobophonometer (see Chapter XVI) in terms of both vibration and noise produced in a single cylinder Gardner engine by Le Mesurier and Stansfield.[10] Figure 256 shows meter readings of noise and vibration intensities plotted against delay angles. These vary together, increasing with greater rates of rapid pressure rise and falling again as the descending piston reduces the rate below the maximum. No absolute values can be assigned to the vertical scale, and it may not be strictly linear with vibration amplitude. It does, however, give a true indication of changes in amplitude.

Such results as these show that the "knocking" properties of Diesel oils are of considerable importance.

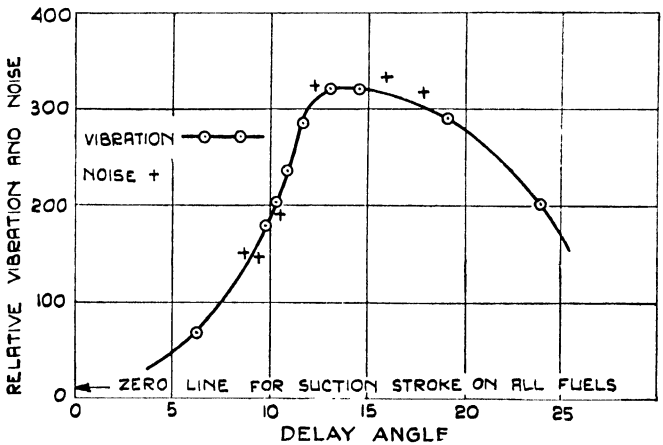


FIG. 256.—EFFECT OF DELAY ANGLE ON VIBRATION OF ENGINE CYLINDER HEAD. (LE MESURIER AND STANSFIELD). (GARDNER ENGINE, 4¼″ BORE, 6″ STROKE, 1,000 R.P.M., DIRECT INJECTION (4 JETS) CONSTANT B.M.E.P.)

877. Measurement of the "Knock Ratings" of Diesel Fuels.—Various methods have been developed during the past two or three years, but, as yet, no procedure has been singled out as being suitable for standardization because of the wide variety of Diesel engines now in operation and because sufficient time has not yet elapsed for the necessary research to be carried out. This research is being carried out mainly by the Oil Companies who are, of course, able to use to advantage the experience they have gained in the development of petrol knock rating tests. Progress will be slow, but the next few years should see the es-

tablishment of routine Diesel oil knock rating tests on a standardized basis.

878. Measurement of "Delay Angle."—Perhaps the most direct testing method is the measurement of the actual delay period which takes place in an engine under normal operating conditions, as developed by the Anglo Persian Oil Company. This method of test has the advantage of comparative simplicity and quickness. It requires an engine that is sensitive to small changes in fuel quality, but when this condition is satisfied, it is capable of giving delay angle determinations accurate to 0·5 degrees crank angle. The Farnborough (R.A.E.) electrical indicator may conveniently be used to record the pressure-crank angle diagrams and also to record the precise moment of fuel entry into the cylinder, the latter being accomplished by fitting an indicator to the end of the needle valve in the fuel injection nozzle. Both records are thus obtained on one diagram, from which the delay angle may be obtained by inspection (and also the maximum pressure developed).

The actual figures for delay angles vary, of course, on different engines, but the difference in delay angles between various fuels are, with minor exceptions, in very good agreement between one engine and another and between different speeds.

879. Test Methods of the Royal Dutch Shell Company.—Boerlage and Broeze[11] have recently described the test methods for Diesel oil knock ratings developed in the laboratories of the Royal Dutch Shell group. In order to obtain a relative rating of fuels, an endeavour was made to find one or more important and quickly variable engine factors, which would make it possible, by changing them, to vary the behaviour of the fuel in the engine, i.e., to make smooth fuels run roughly and *vice versa*. It was found that varying the air pressure by throttling produced the desired effect, a slight supercharge reducing the knock and a reduced air pressure aggravating it. In this way, the liability to roughness of each fuel could be judged in a simple and reproducible way. At first this was done by ear by determining the compression pressure at which the limit for smooth running was reached. The compression pressure, obtained from an indicator diagram, served as the "knock" figure for the fuel concerned, after dividing it by the normal compression pressure of the engine, corrected to 760 mms. For commercial fuels, these knock figures ranged from 0·60 (i.e., smooth running ceased at $0{\cdot}6 \times 35 = 21$ atmospheres) to over 1·2 (40 atmospheres), at which compression pressure the combustion pressures reached levels which it was thought unwise to exceed. These first investigations were carried out on a 40 H.P. Thomassen engine, built in order to obtain a wide range as well as accuracy of measurement. It was possible to determine the ratings of about twelve fuels in a day in this manner.

From this method, a more accurate test procedure was developed, using a 20 H.P. Thomassen engine, which was more easily operated than the one of larger size. This engine was fitted with a variable compression plug, permitting variations in compression of from 600—375 pounds per square inch, but this was only used in exceptional cases. An improved optical indicator was used for measuring combustion pressures and delay angles.

Fuel ratings obtained on this engine using the above procedure were found to agree very well with those obtained on a wide variety of other Diesel engines.

880. Cetene Numbers.—Boerlage and Broeze also suggested that Diesel fuels be compared against pure standards in the same manner as petrols are rated in terms of equivalent octane-heptane blends and recommended blends of a special high grade gas oil and a coal-tar oil for this purpose. Later, they proposed blends of cetene and α-methyl naphthalene and suggested that fuels should be rated in terms of "cetene numbers"; (cetene number = per cent. by volume of cetene in a mixture of cetene and α-methyl naphthalene which is equivalent in Diesel knock rating to the fuel under test).[12] Of these two substances, cetene is of low knocking properties and is therefore equivalent to a good Diesel fuel. The same investigators found, for straight distillate Diesel oils of petroleum origin, that when the specific gravity was plotted against the 50 per cent. A.S.T.M. point, (T), a sheaf of lines could be drawn through fuels of equal cetene number. These lines are of the type

$$G - aT + bT^2 = \text{constant},$$

where G = specific gravity.

For gas oils the term bT^2 is of no importance and, for a large part of the straight lines,

$$G - 0{\cdot}0075T = \text{constant}$$

may serve as well, whereby a high constant means a low cetene number. This led to the adoption of an "ignition" index, I, as given by the formula

$$I = G - 0{\cdot}0075T\ (50\%\ \text{A.S.T.M. point} - 250°\text{C.}).$$

For natural hydrocarbon fuels, there is a curve relating cetene number with "ignition index" but the application of the formula must be confined to narrow limits. Naphthenic fuels are rated too high and mixtures of straight paraffins and aromatics too low, while cracked products and pure hydrocarbons may not agree with the relationship at all. Thus, tetra-iso-butylene which has the same ignition index as cetene, is vastly different from it in knock rating, causing heavy knock-

ing. For distillate fuels, the average values obtained agree generally to within about 10 cetene numbers, but the use of the formula is not to be recommended.*

Diesel fuels from American crudes vary from about 68 to 40 cetene number. The cetene numbers required in practice for European engines vary from 55 for the better class of engine with good combustion chamber characteristics, to about 64 for the poorer class of high speed direct injection engines.[13]

The use of cetene and α-methyl naphthalene as the high and low standards is generally agreed as being at least a preliminary basis for grading, with secondary standards calibrated against these for routine testing. The change of the cetene numbers of average fuels with change of engine conditions is very much less than the corresponding change in the octane numbers of motor fuels.

881. Critical Compression Ratio Method for the Rating of Diesel Fuels.—In the early part of 1932, Pope and Murdock[14] described work carried out in the determination of Diesel fuel knock ratings in a modified C.F.R. petrol knock testing engine (see Chapter XVI). As the basis of measurement the critical compression ratio for audible combustion was employed and the results expressed in terms of blends of standard fuels, in this case heptane and iso-octane.

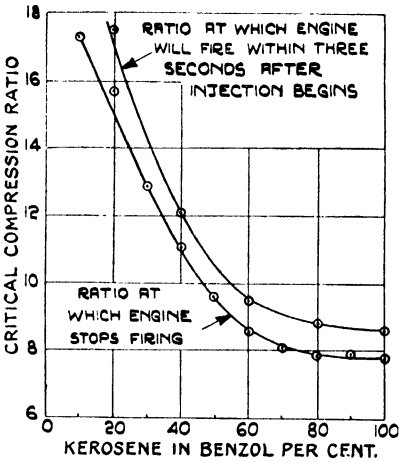


FIG. 257.—CRITICAL COMPRESSION RATIOS OF KEROSENE-BENZOLE BLENDS. (POPE AND MURDOCK.)

Fig. 257 shows the critical compression ratios of a series of benzole-

*, Various relationships have recently been found to exist between the knock ratings of Diesel fuels and certain other properties, such as aniline point, specific gravity and unsaturated hydrocarbon content. These relationships are only approximate and reference should be made to a paper on this subject by A. E. Becker and H. G. M. Fisher, J.S.A.E., 1934, 35, (4), 376.

kerosene blends as determined by two methods. The lower curve was obtained by operating the engine under standard conditions and then lowering the compression ratio until firing ceased. The upper curve was obtained by motoring the engine under standardized conditions and noting the compression ratio at which audible combustion started. For these tests, the standard C.F.R. engine was fitted with a special cupped-piston, to provide a combustion chamber conforming to the shape of the spray. A Bosch fuel pump with adjustable advance was driven from the end of the camshaft and used in conjunction with a Bosch fuel nozzle with a pintle-type orifice, injection timing being measured by the use of contact points above the needle-valve stem connected in the circuit of the normal neon tube spark timing indicator.

Experiments were first carried out in an attempt to operate the engine as a normal Diesel engine and then lower the compression ratio until audible firing ceased, but this method gave trouble because of difficulty in standardizing operating temperature conditions and also because of carbonization and poor combustion as a result of wide variations in compression ratio. Consequently this method was abandoned and the engine used without operating it under power.

The following engine conditions were employed :—

Speed, r.p.m.	600
Jacket temperature, °F.	210
Air inlet temperature, °F.	100
Oil temperature, °F.	130
Injection pressure, lbs. per square inch	1,000
Injection advance, degrees	12
Quantity of fuel injected, mls.	0·023

Intervals of 1 minute are allowed for stabilization of temperature conditions after moving the cylinder head before taking a reading. The injector bye-pass valve is then closed for three seconds. If an audible explosion is heard at the exhaust within this time, the ratio is lowered and observations are repeated until a 0·007 inch movement of the cylinder head up and down removes or brings in audible combustion. It is important that the interval of injection be carefully regulated, as the longer it is prolonged, the more likely combustion is to occur. Recognition of this fact was essential to the success of the method.

The relative position of various engine fuels with respect to critical compression ratio is shown in Table 205.

The above method of Pope and Murdock is still being developed and cannot be said yet to have reached finality. However, it has recently been shown that the relative ratings of fuels obtained in this way agree with those obtained in actual running conditions, except in the case of doped fuels, such as those containing ethyl-nitrate. It would appear

that the measurement of critical compression ratio is analogous to the determination of Spontaneous Ignition Temperature under elevated pressure conditions.

TABLE 205.—CRITICAL COMPRESSION RATIOS FOR VARIOUS FUELS ON THE C.F.R. ENGINE. (POPE AND MURDOCK)

	Critical Compression Ratio
Benzole	Above 20
Iso-octane	17·3
Premium Motor Fuel	14·2
60 Octane Number Motor Fuel	11·0
Rough Running Diesel Fuel	10·6
n-Heptane	8·5
Good Diesel Fuel	8·0
Kerosene	7·5

882. The Use of Spontaneous Ignition Temperature Measurements in the Determination of Diesel Fuel Quality.—Many references have been made regarding the use of Spontaneous Ignition Temperature (S.I.T.) measurements for the estimation of the knock ratings of Diesel oils, and numerous pieces of apparatus have been designed for the determination of such measurements. The present discussion may well be limited to a consideration of those two pieces of apparatus developed by the Royal Aircraft Establishment, Farnborough,[15] and by Moore,[16] respectively, as these are the most widely used.

The Royal Aircraft Establishment (Farnborough), S.I.T. Apparatus.—This apparatus was developed by Squadron Leader W. Helmore and F. C. Code-Holland, at the Royal Aircraft Establishment and is, accordingly, known as the R.A.E. apparatus. It embodies many novel features and was especially developed for use in the testing of Diesel oils, as distinct from the other methods of S.I.T. measurement. It is a noteworthy attempt to simulate actual engine conditions in a simple apparatus.

General Description of the Apparatus.—The apparatus consists of (*a*) an electrically heated explosion vessel, (*b*) a fuel injection system, (*c*) a timing mechanism for recording the moment of injection and the moment of explosion and (*d*) a thermocouple for temperature measurements. A photograph of the apparatus is reproduced in Figure 258.

The explosion vessel consists of a wrought iron cylinder, 6 inches

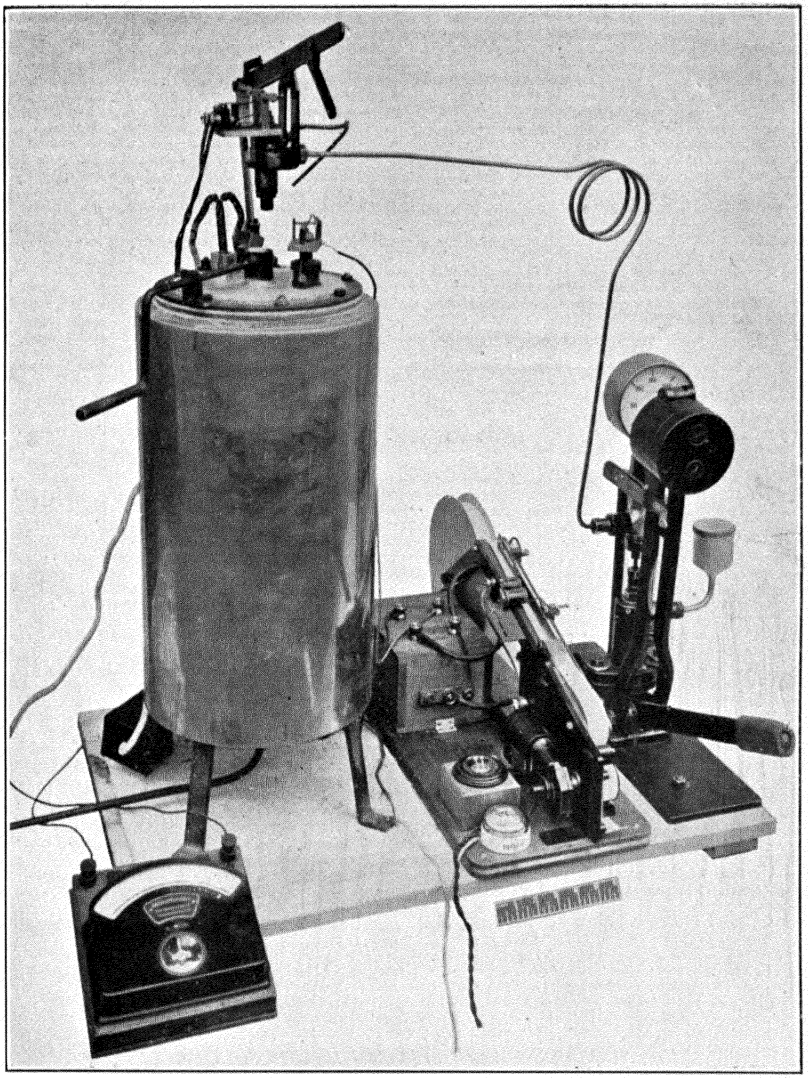


FIG. 258. THE ROYAL AIRCRAFT ESTABLISHMENT SPONTANEOUS IGNITION TEMPERATURE APPARATUS. (FOORD.)

[*Facing p.* 456

diameter and 18 inches long, the sides of which are electrically heated and lagged. The top end of the cylinder is formed of layers of steel and asbestos and carries the fuel injection valve, a thermocouple, a vent and an air tube and also a connection for the explosion time recorder. The fuel injection valve (Bosch pintle type) and explosion vessel are so arranged to give a free spray having a cone angle of 8°, i.e., an angle less than the cone angle subtended by the perimeter of the bottom end of the vessel with the point of entry of the fuel into the vessel, so as to prevent the fuel spray from striking the heated sides of the vessel. The bottom end of the cylinder is of inverted conical shape, unlagged and separated from the body part by a joint ring of asbestos. This is necessary in order to ensure that any fuel from the jet which may impinge on the bottom does so on a relatively cool surface.

The fuel injection system consists of a standard Bosch outfit and the pump is operated by a falling weight and lever fulcrumed on the pump base, which ensures that the rate of injection of the charge is constant for each test.

The injection timing recorder takes the form of a pair of contacts in an electrical circuit which are closed when the fuel valve opens by means of a tappet pin, while the moment of explosion is recorded by means of a disc valve fitted into the top end of the explosion vessel and which lifts and opens a pair of contacts when the explosion occurs. A time record is obtained by means of a calibrated electrical tuning fork which traces a record on a moving tape on which are also recorded the instants of injection and explosion.

Method of Operation.—The temperature of the vessel having been raised to the highest point which it is desired to investigate, the current is switched off and sufficient time allowed for temperature conditions to become stable. A charge of air is then drawn into the apparatus and the apparatus allowed to stand for a few minutes until the air temperature reaches a maximum and then begins to fall. The fuel is then injected by the retractable injector nozzle and the time lag between injected and ignition recorded. The products of combustion are then drawn out of the apparatus, a fresh charge of air introduced and the operation repeated at a lower temperature. In this way, a series of readings are taken every 20 or 30 degrees over a gradually falling temperature until, finally, at the lowest temperature, no explosion occurs after an indefinite delay. The results so obtained can conveniently be expressed in the form of curves in which ignition delay is plotted against temperature.

This method of S.I.T. measurement constitutes a very marked advance over the older methods and is free from many objections associated with the latter. On the other hand, the method and the apparatus,

as described by Foord (loc. cit.), has its limitations. Work conducted by one of the authors (D. A. H.) in the laboratories of Imperial Chemical Industries (Fertilizers and Synthetic Products), Limited, (to whom the authors are indebted for permission to publish these results), has shown that :—

(1) The moment of explosion, as recorded by the movement of a piston indicator, is not the true moment of explosion and differs from the latter by amounts which vary for different fuels. Paraffinic fuels, such as Scotch shale oil, suffer cracking almost as soon as they enter the apparatus and often the pressure rise due to this cracking is rapid enough to lift the piston indicator from its seat. Aromatic fuels, on the other hand, when injected into the apparatus decompose with the separation of a cloud of smoke and carbon particles before the explosion takes place. The explosion is much more violent than in the case of paraffinic fuels. If the piston indicator is held down by a spring sufficient to prevent it lifting on sudden pressure rise due to cracking, it is found that the inertia of the system becomes so great that the indicator only lifts some appreciable time after the explosion occurs. It would appear that the moment of explosion could be best ascertained by a continuous pressure recorder. This would also give greater information about the changes taking place prior to explosion.

(2) The heat capacity of the apparatus is not very large and a temperature gradient exists down the centre line of the vessel, being coldest at the bottom and hottest a few inches from the top (because it is lagged at the top and unlagged at the bottom). It is found, on making S.I.T. determinations in this apparatus, that the temperature of the unlagged bottom conical plate gradually rises from 120°C. to 160°C., during the course of about three or four hours. This changes the temperature gradient in the apparatus from experiment to experiment.

(3) Fuels of different viscosity penetrate to varying depths in the apparatus with a given fuel injection pressure. As a uniform temperature does not exist in the explosion chamber, it is not possible to decide upon the true ignition temperature with certainty.

(4) Although precautions have been taken to prevent the fuel spray from striking the hot walls, experiments conducted with a paraffinic gas oil distillate and using a 30° cone angle of spray, which definitely strikes the hot walls, showed that no measurable difference in ignition lag was obtained. From this, it may be inferred that with the present design of apparatus, even when using a very narrow angle fuel spray, fuel does ignite from the hot walls and that the hot surfaces play an important part.

Despite these observations, however, Le Mesurier[17] has shown that results on the Farnborough S.I.T. apparatus are of definite value

in indicating the ease of engine starting with various fuels. This being so it should be of value in determining the relative behaviour of fuels under running conditions.

883. The Moore S.I.T. Apparatus.—The Moore apparatus, as commonly employed, consists of an iron pot which is heated in a bath and through which a stream of air is passed heated to the same temperature. A drop of fuel is allowed to fall into the pot from a burette and the S.I.T. is taken as the lowest temperature at which explosion can be obtained after an indefinite delay.

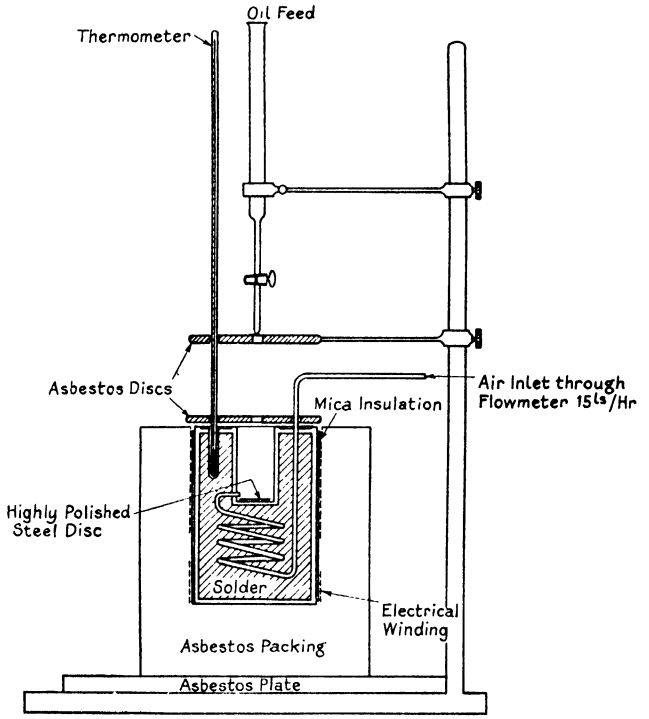


FIG. 259.—THE MOORE SPONTANEOUS IGNITION TEMPERATURE APPARATUS.

This procedure may be modified so as to allow the measurement, by a stop watch or similar device, of the time interval elapsing between the moment of the falling of a fuel drop into the pot and the moment of ignition, as indicated by a flash. The apparatus used is shown in Figure 259, and Figures 260 and 261 show typical delay-temperature curves obtained. The reproducibility of results is much improved by this method of operation. Because of the inability to measure very short time intervals, measurements must be made at temperatures considerably lower than those commonly used in the Farnborough S.I.T. apparatus.

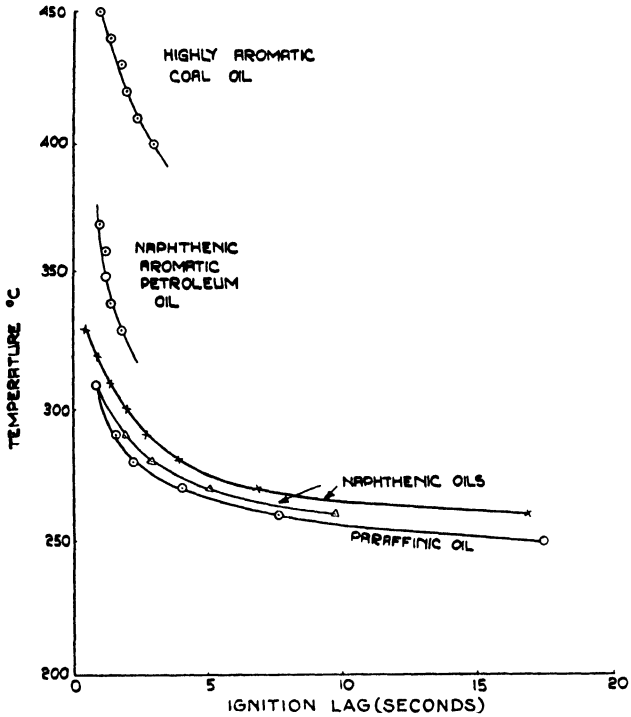


FIG. 260.—TEMPERATURE-DELAY CURVES OF VARIOUS FUELS DETERMINED BY THE MOORE S.I.T. APPARATUS.

ANTI-KNOCK DOPES FOR DIESEL ENGINES

884. Various attempts have been made to find a substance which is effective in reducing the knocking properties of diesel oils in the same way as tetra-ethyl lead and other substances act as anti-knock dopes in petrols. So far these attempts have not been particularly successful.

It has already been shown that aromatic and napthenic oils, while possessing desirable properties from the petrol anti-knock standpoint, give rise to more or less severe knocking in Diesel engines and that the best Diesel oils are paraffinic in character. This is equivalent to stating that the Diesel engine fuel requirements, as far as chemical composition is concerned, are exactly opposite to those of the petrol engine. It has also been found that those substances which act as anti-knock dopes in petrol engines, e.g., tetra-ethyl lead, phenols, aromatic amines, etc., are pro-knocks in Diesel oils and that pro-knocks in petrol engines, e.g., aldehydes, alkyl nitrates, etc., have anti-knock effect in Diesel engines.

In 1928, a patent was issued in the name of C. J. Simms,[18] in which the use of so called "primers" to reduce the delay characteristics of Diesel fuels was advocated. The following substances were mentioned

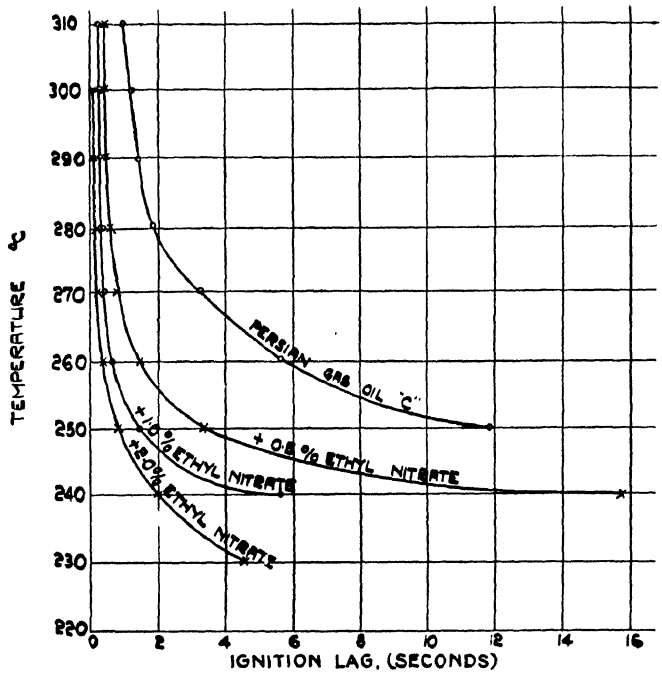


FIG. 261.—TEMPERATURE-DELAY CURVES OF BLENDS OF ETHYL NITRATE IN PERSIAN GAS OIL—MOORE S.I.T. APPARATUS.

as being suitable: trinitroresorcinol, nitrous and nitric esters, e.g., methyl nitrate or amyl nitrite; azo compounds; chlorates and organic perchlorates, e.g., hydrazine diperchlorates; acetylenic compounds, e.g., copper acetylide: superoxides, e.g., benzene ozonide; nitro amines, e.g., pecramide; mercury organic compounds, e.g., mercury fulminate; also phenylnitramine and phenyl selenious acid. The quantity of primer required was said to be small, e.g., 5 per cent. by volume.

Of these various compounds only the alkyl nitrates and nitrites have been used to any great extent. In 1930, an English patent was granted to W. Helmore,[19] in which two or more primers were used, one of which is a so called "igniting primer" such as ethyl or methyl nitrate and the other an "exploding primer" such as benzoyl peroxide, amylene peroxide, picric acid, dinitro benzene, trinitrobenzene, and trinitrotoluene, etc.

The use of ethyl nitrate as a Diesel fuel anti-knock dope has been covered in other patents,[20] and this material has, apparently, been singled out as the most satisfactory.

Figure 262 is a reproduction of two indicator diagrams taken by the Associated Equipment Company on one of their Acro engines at a speed of 1,000 revolutions per minute and with a brake mean effective pressure

of 83·5 pounds per square inch. The continuous line was obtained on an Asiatic Fuel and the broken line diagram was obtained on the same fuel to which 5 per cent. of ethyl nitrate had been added. The improvement in the performance is noticeable, both as regards the maximum pressure and the rate of pressure rise.

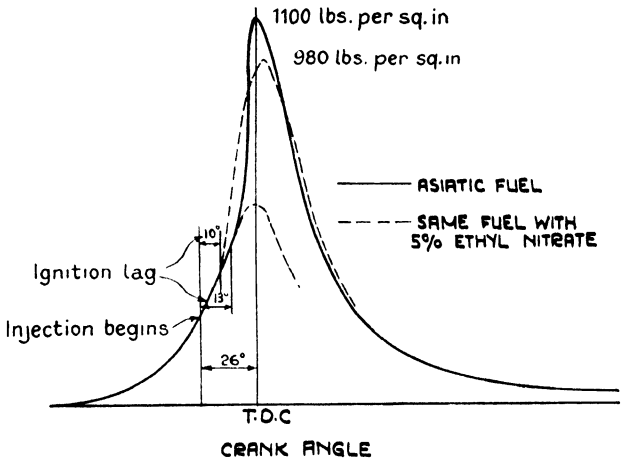


FIG. 262.—INDICATOR DIAGRAMS SHEWING THE EFFECT OF ETHYL NITRATE UPON THE COMBUSTION CHARACTERISTICS OF A DIESEL OIL.

In a recent patent (E.P. 404,682), D. A. Howes and I.C.I., Ltd., have claimed that the effect of ethyl nitrate may be improved by the addition of small amounts of bromine compounds and/or copper compounds. For example, a middle oil produced by the destructive hydrogenation of coal had a spontaneous ignition temperature of 400°C. and a delay period of 3·0 seconds at this temperature. When 0·5 per cent. of ethyl nitrate and 0·5 per cent. of benzyl bromide was added to this oil, the spontaneous ignition temperature was reduced to 330°C. and the delay period at 400°C. was reduced to 0·9 seconds. When 1 per cent. of ethyl nitrate alone was added to the oil the spontaneous ignition temperature was 345°C., and when 1 per cent. of benzyl bromide alone was added the spontaneous ignition temperature was 330°C. and the delay period at 400°C. was 1·5 seconds. A fuel containing 0·9 per cent. ethyl nitrate and 0·1 per cent. butyl bromide gave results in a Diesel engine equal to that of the same fuel containing 2 per cent. of ethyl nitrate.

The following substances have also been proposed by D. A. Howes and I.C.I., Ltd., as Diesel oil dopes:

Aliphatic and aromatic diketones. E.P. 403,124.

Non-explosive aliphatic nitroso compounds. E.P. 405,658.

885. Regarding the precise mode of action of Diesel oil dopes, comparatively little is known. Ethyl nitrate may work in either (or both) of two ways. It may act by becoming spontaneously inflamed at an instant prior to that at which an appreciable flame nucleus is set up in the fuel-air mixture, and causing the fuel to burn earlier by the development of heat from the combustion of the ethyl nitrate. On the other hand the substance may not be effective in itself as such, but the nitrogen oxides formed in its decomposition may act as oxidation catalysts. In this connection, it is of interest to record that Bibb and Lucas[21] and Smith and Milner[22] found that these substances had marked catalytic activity in the oxidation of natural gas and benzene by air.

According to Broche, Ehrmann and Scheer,[23] the spontaneous ignition temperature of naphthalene is reduced from 575° to 210°C., in the presence of platinum, vanadium pentoxide and thoria and the suggestion has been made that these substances might be used in compact form in the engine cylinder head to make possible the satisfactory use of coal tar oils. This may be possible, but the chances of success seem to be remote. The main point of interest is that, of the substances proposed, two are well known oxidation catalysts. As in the petrol engine knocking is induced when organic peroxides are formed in the charge during compression, it would appear that if the yield of peroxides from Diesel oils under the conditions existing in the Diesel cylinder during the process of injection could be increased, Diesel knock might be reduced. Stable peroxides, such as benzoyl peroxide, have no effect upon knock when added to Diesel oils, but this is no argument against the possibility of the unstable peroxides acting in this way. However, it is unwise to attempt predictions because of the very small amount of work which has been done on the subject.

Although ethyl nitrate is the most effective Diesel oil dope so far known, it is by no means the ideal substance for this use. It is required in fairly large concentrations (from 1·0 to 2·0 per cent. for medium class oils), it is expensive compared with Diesel oils, it has a low boiling point (86°C.), it is not safe to handle in great bulk in an undiluted state and it lowers the flash-point of any oil with which it is blended.

If a dope could be discovered which was so effective that it need only be used in the same concentrations as tetra-ethyl lead in petrols (i.e., 2—3 ccs. per gallon), then perhaps commerical application on a large scale would follow. On the other hand, the present low price of Diesel oil would severely limit this development.

It might be argued, however, that the employment of an anti-knock dope in Diesel oils will eventually be essential, because of the limited supply of fuel of suitable paraffinic character from petroleum and because there are no alternative sources of good quality Diesel oil available. Against this argument is the possibility that Diesel engine design is pro-

ceeding in such a way as to widen the range of suitable fuels, a condition of affairs vastly different from that obtaining in the petrol engine, where improvements in design to obtain greater power outputs, etc., generally result in a diminished range of suitable fuels.

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890.

Gravities, Pounds, Gallons and Tons.
(15·56°C., 60°F.)

A.P.I. Gravity	Specific Gravity	Pounds Per U.S. Gallon	Pounds Per Imperial Gallon	U.S. Gallons Per Ton	Imperial Gallons Per Ton
10	1·0000	8·331	10·0017	268·875	223·961
11	·9930	8·273	9·9317	270·771	225·54
12	·9861	8·215	9·8627	272·665	227·118
13	·9792	8·158	9·7937	274·587	228·718
14	·9725	8·102	9·7267	276·478	230·294
15	·9659	8·047	9·6607	278·368	231·868
16	·9593	7·992	9·5947	280·283	233·463
17	·9529	7·939	9·5307	282·165	235·031
18	·9465	7·885	9·4666	284·073	236·621
19	·9402	7·833	9·4036	285·977	238·206
20	·9340	7·781	9·3416	287·875	239·787
21	·9279	7·730	9·2806	289·768	241·363
22	·9218	7·680	9·2196	291·685	242·961
23	·9159	7·630	9·1606	293·564	244·526
24	·9100	7·581	9·1016	295·467	246·111
25	·9042	7·533	9·0436	297·363	247·690
26	·8984	7·485	8·9856	299·282	249·289
27	·8927	7·437	8·9286	301·193	250·881
28	·8871	7·390	8·8725	303·095	252·464
29	·8816	7·345	8·8175	304·986	254·039
30	·8762	7·300	8·7635	306·865	255·605
31	·8708	7·255	8·7095	308·768	257·190
32	·8654	7·210	8·6555	310·696	258·795
33	·8602	7·166	8·6035	312·573	260·359
34	·8550	7·123	8·5515	314·474	261·943
35	·8498	7·080	8·4995	316·398	263·546
36	·8448	7·036	8·4495	318·271	265·105
37	·8398	6·996	8·3995	320·166	266·884
38	·8348	6·955	8·3495	322·083	268·281
39	·8299	6·914	8·3004	323·985	269·865
40	·8251	6·874	8·2524	325·870	271·435
41	·8203	6·834	8·2044	327·777	273·023
42	·8156	6·795	8·1574	329·966	274·597
43	·8109	6·756	8·1104	331·576	276·188
44	·8063	6·717	8·0644	333·468	277·764
45	·8017	6·679	8 0184	335·381	279·358
46	·7972	6·641	7·9734	337·275	280·935
47	·7927	6·604	7·9284	339·189	282·529
48	·7883	6·567	7 8844	341·082	284·106
49	·7839	6·531	7·8464	342·997	285·701
50	·7796	6·495	7·7974	344·889	287·277
51	·7753	6·459	7·7543	346·802	288·870
52	·7711	6·424	7·7123	348·691	290·444
53	·7669	6·389	7·6703	350 600	292·034
54	·7628	6·355	7·6293	352·485	293·604
55	·7587	6·321	7·5883	354·389	295·190
56	·7547	6·287	7·5483	356·268	296·755
57	·7507	6·254	7·5083	358·166	298·336
58	·7467	6·221	7·4683	360·085	299·934
59	·7428	6·188	7·4293	361·975	301·509
60	·7389	6·156	7·3903	363·886	303·101
61	·7351	6·124	7·3523	365·767	304·667
62	·7313	6·092	7·3143	367·668	306·251
63	·7275	6·061	7·2763	369·588	307·850
64	·7238	6·030	7·2393	371·477	309·424
65	·7201	5·999	7·2023	373·386	311·014
66	·7165	5·969	7·1662	375·262	312·575
67	·7128	5·938	7·1292	377·210	314·199
68	·7093	5·909	7·0942	379·071	315·749
69	·7057	5·879	7·0582	381·005	317·360
70	·7022	5·850	7·0232	382·904	318·942
71	·6988	5·822	6·9892	384·767	320·494
72	·6953	5·793	6·9542	386·704	322·107
73	·6919	5·764	6·9202	388·604	323·690
74	·6886	5·737	6·8872	390·467	325·241
75	·6852	5·708	6·8532	392·404	326·855
76	·6819	5·681	6·8202	394·303	328·437
77	·6787	5·654	6·7882	396·162	329·985
78	·6754	5·627	6·7552	398·098	331·598
79	·6722	5·600	6·7232	399·993	333·176
80	·6690	5·573	6·6912	410·906	334·770
81	·6659	5·548	6·6602	403·777	336·328
82	·6628	5·522	6·6292	405·666	337·961
83	·6597	5·496	6·5981	407·572	339·489
84	·6566	5·470	6·5671	409·496	341·092
85	·6536	5·445	6·5371	411·376	342·658

891.

Specific Gravities and Baumé Gravities for Liquids Heavier than Water.

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific Gravity}} \quad \text{for liquids heavier than water.}$$

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
0·0	1·0000	23·5	1·1934	47·0	1·4796
0·5	1·0035	24·0	1·1983	47·5	1·4872
1·0	1·0069	24·5	1·2033	48·0	1·4948
1·5	1·0105	25·0	1·2083	48·5	1·5026
2·0	1·0140	25·5	1·2134	49·0	1·5104
2·5	1·0175	26·0	1·2185	49·5	1·5183
3·0	1·0211	26·5	1·2236	50·0	1·5263
3·5	1·0247	27·0	1·2288	50·5	1·5344
4·0	1·0284	27·5	1·2340	51·0	1·5426
4·5	1·0320	28·0	1·2393	51·5	1·5508
5·0	1·0357	28·5	1·2446	52·0	1·5591
5·5	1·0394	29·0	1·2500	52·5	1·5676
6·0	1·0432	29·5	1·2554	53·0	1·5761
6·5	1·0469	30·0	1·2609	53·5	1·5847
7·0	1·0507	30·5	1·2664	54·0	1·5934
7·5	1·0545	31·0	1·2719	54·5	1·6022
8·0	1·0584	31·5	1·2775	55·0	1·6111
8·5	1·0623	32·0	1·2832	55·5	1·6201
9·0	1·0662	32·5	1·2889	56·0	1·6292
9·5	1·0701	33·0	1·2946	56·5	1·6384
10·0	1·0741	33·5	1·3004	57·0	1·6477
10·5	1·0781	34·0	1·3063	57·5	1·6571
11·0	1·0821	34·5	1·3122	58·0	1·6667
11·5	1·0861	35·0	1·3182	58·5	1·6763
12·0	1·0902	35·5	1·3242	59·0	1·6860
12·5	1·0943	36·0	1·3303	59·5	1·6950
13·0	1·0985	36·5	1·3364	60·0	1·7059
13·5	1·1027	37·0	1·3426	60·5	1·7160
14·0	1·1069	37·5	1·3488	61·0	1·7262
14·5	1·1111	38·0	1·3551	61·5	1·7365
15·0	1·1154	38·5	1·3615	62·0	1·7470
15·5	1·1197	39·0	1·3679	62·5	1·7576
16·0	1·1240	39·5	1·3744	63·0	1·7683
16·5	1·1284	40·0	1·3810	63·5	1·7791
17·0	1·1328	40·5	1·3876	64·0	1·7901
17·5	1·1373	41·0	1·3942	64·5	1·8012
18·0	1·1417	41·5	1·4010	65·0	1·8125
18·5	1·1462	42·0	1·4078	65·5	1·8239
19·0	1·1508	42·5	1·4146	66·0	1·8354
19·5	1·1554	43·0	1·4216	66·5	1·8471
20·0	1·1600	43·5	1·4286	67·0	1·8590
20·5	1·1647	44·0	1·4356	67·5	1·8710
21·0	1·1694	44·5	1·4428	68·0	1·8831
21·5	1·1741	45·0	1·4500	68·5	1·8954
22·0	1·1789	45·5	1·4573	69·0	1·9079
22·5	1·1837	46·0	1·4646	69·5	1·9205
23·0	1·1885	46·5	1·4721	70·0	1·9333

892.

Thermal Expansions of Gasoline-Benzole Mixtures.

(C. S. Cragoe, U.S. Bureau of Standards, Miscellaneous Publication, No. 97, 1929.)

Ratio of Volume at 60°F. to Volume at t°F., $\frac{V_{60}}{V_t}$, for Mixtures containing 0, 25, 50 and 100 per cent. Motor Benzole by Volume.

Temp. °F.	45° A.P.I. at 60°F. Specific Gravity 0·8017 at 60°/60°F.			50° A.P.I. at 60°F. Specific Gravity 0·7796 at 60°/60°F.			55° A.P.I. Specific Gravity 0·7587 at 60°/60°F.			Motor Benzole 100 Per Cent.
	Percentage Motor Benzole									
	0	25	50	0	25	50	0	25	50	
0	1·0301	1·0342	1·0386	1·0324	1·0367	1·0410	1·0347	1·0391	1·0440	1·0387
5	1·0276	1·0314	1·0354	1·0297	1·0337	1·0376	1·0318	1·0359	1·0404	1·0355
10	1·0251	1·0286	1·0322	1·0270	1·0307	1·0343	1·0290	1·0326	1·0368	1·0323
15	1·0226	1·0257	1·0290	1·0243	1·0276	1·0309	1·0261	1·0294	1·0332	1·0291
20	1·0201	1·0229	1·0258	1·0216	1·0246	1·0275	1·0232	1·0261	1·0295	1·0259
22	1·0191	1·0217	1·0245	1·0205	1·0233	1·0261	1·0220	1·0248	1·0280	1·0246
24	1·0181	1·0206	1·0232	1·0194	1·0221	1·0248	1·0209	1·0235	1·0266	1·0233
26	1·0171	1·0194	1·0219	1·0184	1·0209	1·0234	1·0197	1·0222	1·0251	1·0220
28	1·0161	1·0183	1·0207	1·0173	1·0197	1·0220	1·0186	1·0209	1·0237	1·0207
30	1·0151	1·0171	1·0194	1·0162	1·0184	1·0206	1·0174	1·0196	1·0222	1·0191
32	1·0141	1·0160	1·0181	1·0151	1·0172	1·0193	1·0162	1·0183	1·0207	1·0181
34	1·0131	1·0149	1·0168	1·0140	1·0160	1·0179	1·0151	1·0170	1·0192	1·0168
36	1·0121	1·0138	1·0155	1·0130	1·0148	1·0165	1·0139	1·0157	1·0178	1·0156
38	1·0110	1·0126	1·0142	1·0119	1·0135	1·0151	1·0128	1·0144	1·0163	1·0143
40	1·0100	1·0115	1·0129	1·0108	1·0123	1·0138	1·0116	1·0131	1·0148	1·0130
42	1·0090	1·0103	1·0116	1·0097	1·0111	1·0124	1·0104	1·0118	1·0133	1·0117
44	1·0080	1·0092	1·0103	1·0086	1·0099	1·0110	1·0093	1·0105	1·0119	1·0104
46	1·0070	1·0080	1·0090	1·0076	1·0086	1·0096	1·0081	1·0092	1·0104	1·0091
48	1·0060	1·0069	1·0078	1·0065	1·0074	1·0083	1·0070	1·0079	1·0089	1·0078
50	1·0050	1·0057	1·0065	1·0054	1·0061	1·0069	1·0058	1·0066	1·0074	1·0065
52	1·0040	1·0046	1·0052	1·0043	1·0049	1·0055	1·0046	1·0053	1·0059	1·0052
54	1·0030	1·0034	1·0039	1·0032	1·0037	1·0041	1·0035	1·0039	1·0044	1·0039
56	1·0020	1·0023	1·0026	1·0022	1·0025	1·0028	1·0023	1·0026	1·0030	1·0026
58	1·0010	1·0011	1·0013	1·0011	1·0012	1·0014	1·0012	1·0013	1·0015	1·0013
60	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
62	·9990	·9988	·9987	·9989	·9987	·9986	·9988	·9987	·9985	·9987
64	·9980	·9977	·9974	·9978	·9975	·9972	·9977	·9974	·9970	·9974
66	·9970	·9965	·9961	·9968	·9963	·9958	·9965	·9960	·9955	·9961
68	·9960	·9954	·9948	·9957	·9951	·9944	·9954	·9947	·9940	·9948
70	·9950	·9942	·9935	·9946	·9938	·9930	·9942	·9934	·9925	·9935
72	·9940	·9931	·9922	·9935	·9926	·9917	·9930	·9921	·9911	·9922
74	·9929	·9919	·9909	·9924	·9913	·9903	·9919	·9908	·9896	·9909
76	·9919	·9908	·9896	·9913	·9901	·9889	·9907	·9895	·9881	·9896
78	·9909	·9896	·9883	·9902	·9888	·9875	·9896	·9881	·9866	·9883
80	·9899	·9885	·9870	·9891	·9876	·9861	·9884	·9868	·9851	·9870
82	·9889	·9873	·9857	·9880	·9864	·9847	·9871	·9855	·9836	·9857
84	·9879	·9862	·9844	·9869	·9852	·9833	·9860	·9842	·9821	·9844
86	·9869	·9850	·9831	·9859	·9839	·9819	·9848	·9828	·9806	·9830
88	·9859	·9839	·9818	·9848	·9827	·9806	·9837	·9815	·9791	·9817
90	·9849	·9827	·9805	·9837	·9814	·9792	·9825	·9802	·9776	·9804
92	·9839	·9816	·9792	·9826	·9802	·9778	·9813	·9789	·9761	·9791
94	·9829	·9804	·9779	·9815	·9789	·9764	·9802	·9776	·9746	·9778
96	·9819	·9793	·9766	·9805	·9777	·9750	·9790	·9763	·9731	·9765
98	·9809	·9781	·9753	·9794	·9764	·9736	·9779	·9749	·9716	·9752
100	·9799	·9770	·9740	·9783	·9752	·9722	·9767	·9736	·9701	·9739
105	·9773	·9741	·9707	·9756	·9727	·9687	·9737	·9703	·9663	·9706
110	·9748	·9712	·9675	·9729	·9690	·9652	·9708	·9670	·9626	·9673
115	·9723	·9684	·9642	·9702	·9659	·9617	·9679	·9637	·9588	·9640
120	·9698	·9655	·9609	·9674	·9628	·9582	·9650	·9604	·9550	·9607
125	·9673	·9626	·9577	·9647	·9597	·9547	·9620	·9571	·9513	·9574

893.

Corrections to Readings of Hydrometers in Gasoline-Benzole Blends to Reduce to °A.P.I. at 60°F.

Mixtures containing 0, 25 and 50 per cent. Motor Benzole by Volume.
(Cragoe, U.S. Bureau of Standards, Miscellaneous Publication, No. 97, 1929.)

Observed Temperature °F.	45° A.P.I. Observed			50° A.P.I. Observed			55° A.P.I. Observed		
	Percentage Motor Benzole								
	0	25	50	0	25	50	0	25	50
	Add to Observed ° A.P.I.								
0	5·7	6·5	7·5	6·3	7·2	8·4	6·9	7·9	9·3
5	5·1	5·9	6·8	5·7	6·5	7·6	6·3	7·2	8·4
10	4·6	5·3	6·1	5·2	5·9	6·8	5·7	6·5	7·5
15	4·1	4·8	5·4	4·6	5·3	6·1	5·1	5·8	6·7
20	3·7	4·2	4·8	4·1	4·6	5·3	4·5	5·1	5·9
25	3·2	3·7	4·2	3·5	4·0	4·6	3·9	4·4	5·1
30	2·7	3·1	3·5	3·0	3·4	3·9	3·3	3·8	4·4
32	2·5	2·9	3·3	2·8	3·2	3·7	3·1	3·5	4·1
34	2·3	2·7	3·0	2·6	3·0	3·4	2·8	3·2	3·8
36	2·2	2·5	2·8	2·4	2·7	3·1	2·6	3·0	3·5
38	2·0	2·3	2·6	2·2	2·5	2·9	2·4	2·7	3·2
40	1·8	2·0	2·3	2·0	2·3	2·6	2·2	2·5	2·9
42	1·6	1·8	2·1	1 8	2·0	2·3	1·9	2·2	2·6
44	1·4	1·6	1·8	1·6	1·8	2·1	1·7	2·0	2·3
46	1·2	1·4	1·6	1·4	1·6	1·8	1·5	1·7	2·0
48	1·1	1·2	1·4	1·2	1·3	1·5	1·3	1·5	1·7
50	0·9	1·0	1·1	1·0	1·1	1·3	1·1	1·2	1·4
52	0·7	0·8	0·9	0·8	0·9	1·0	0·9	1·0	1·1
54	0·5	0·6	0·7	0·6	0·7	0·8	0·6	0·7	0·8
56	0·4	0·4	0·5	0·4	0·4	0·5	0·4	0·5	0·6
58	0·2	0·2	0·2	0·2	0·2	0·3	0·2	0·2	0·3
	Subtract from Observed ° A.P.I.								
60	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
62	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·3
64	0·4	0·4	0·4	0·4	0·4	0·5	0·4	0·5	0·5
66	0·5	0·6	0·7	0·6	0·7	0·7	0·6	0·7	0·8
68	0·7	0·8	0·9	0·8	0·9	1·0	0·8	0·9	1·1
70	0·9	1·0	1·1	1·0	1·1	1·2	1·0	1·2	1·3
72	1·0	1·2	1·3	1·1	1·3	1·4	1·2	1·4	1·6
74	1·2	1·4	1·5	1·3	1·5	1·7	1·4	1·6	1·9
76	1·4	1·6	1·7	1·5	1·7	1·9	1·6	1·9	2·1
78	1·5	1·7	2·0	1·7	1·9	2·2	1·8	2·1	2·4
80	1·7	1·9	2·2	1·9	2·1	2·4	2·0	2·3	2·6
82	1·9	2·1	2·4	2·0	2·3	2·7	2·2	2·5	2·9
84	2·0	2·3	2·6	2·2	2·5	2·9	2·4	2·8	3·1
86	2·2	2·5	2·8	2·4	2·7	3·1	2·6	3·0	3·4
88	2·4	2·7	3·0	2·6	2·9	3·3	2·8	3·2	3·6
90	2·5	2·9	3·2	2·8	3·1	3·6	3·0	3·4	3·9
92	2·7	3·0	3·4	2·9	3·3	3·8	3·2	3·7	4·1
94	2·8	3·2	3·6	3·1	3·5	4·0	3·4	3·9	4·4
96	3·0	3·4	3·8	3·3	3·7	4·2	3·6	4·1	4·6
98	3·1	3·6	4·0	3·4	3·9	4·4	3·8	4·3	4·9
100	3·3	3·8	4·2	3·6	4·1	4·7	4·0	4·5	5·1
105	3·7	4·2	4·7	4·0	4·6	5·2	4·5	5·0	5·7
110	4·1	4·6	5·2	4·5	5·1	5·7	4·9	5·6	6·3
115	4·5	5·1	5·7	4·9	5·6	6·3	5·4	6·1	6·9
120	4·8	5·5	6·2	5·3	6·0	6·8	5·8	6·6	7·4

894.

Corrections to Readings of Hydrometers in Gasoline-Benzole Mixtures to Reduce to Specific Gravity at 60°/60°F.

Mixtures containing 0, 25 and 50 per cent. Benzole, by Volume.
(C. S. Cragoe, U.S. Bureau of Standards, Miscellaneous Publication, No. 97, 1929.)

Observed Temperature °F.	Observed Specific Gravity = 0·760			Observed Specific Gravity = 0·780			Observed Specific Gravity = 0·800		
	Percentage Motor Benzole								
	0	25	50	0	25	50	0	25	50
	Subtract from Observed Specific Gravity								
0	·0270	·0307	·0360	·0263	·0296	·0342	·0251	·0285	·0325
5	·0248	·0280	·0328	·0239	·0270	·0311	·0228	·0260	·0296
10	·0224	·0253	·0296	·0215	·0245	·0281	·0207	·0235	·0268
15	·0201	·0227	·0265	·0193	·0219	·0251	·0184	·0210	·0240
20	·0177	·0201	·0234	·0171	·0194	·0222	·0164	·0186	·0212
25	·0155	·0175	·0204	·0149	·0169	·0193	·0142	·0162	·0185
30	·0132	·0150	·0174	·0127	·0144	·0165	·0121	·0139	·0158
32	·0123	·0140	·0162	·0118	·0134	·0154	·0113	·0129	·0147
34	·0114	·0129	·0150	·0110	·0124	·0142	·0105	·0120	·0136
36	·0105	·0119	·0138	·0101	·0114	·0131	·0097	·0111	·0126
38	·0096	·0109	·0126	·0093	·0105	·0120	·0089	·0111	·0115
40	·0087	·0099	·0114	·0084	·0095	·0109	·0081	·0092	·0104
42	·0078	·0089	·0103	·0076	·0085	·0098	·0072	·0083	·0093
44	·0069	·0079	·0091	·0067	·0076	·0087	·0064	·0073	·0083
46	·0061	·0069	·0079	·0059	·0066	·0076	·0056	·0064	·0073
48	·0051	·0059	·0068	·0050	·0057	·0065	·0048	·0055	·0062
50	·0043	·0049	·0056	·0041	·0047	·0054	·0040	·0046	·0052
52	·0035	·0039	·0045	·0033	·0038	·0043	·0032	·0036	·0041
54	·0025	·0029	·0033	·0025	·0028	·0032	·0024	·0027	·0031
56	·0017	·0019	·0022	·0017	·0019	·0022	·0016	·0018	·0020
58	·0008	·0010	·0011	·0008	·0009	·0011	·0008	·0009	·0010
	Add to Observed Specific Gravity								
60	·0000	·0000	·0000	·0000	·0000	·0000	·0000	·0000	·0000
62	·0009	·0010	·0011	·0008	·0009	·0011	·0008	·0009	·0010
64	·0017	·0019	·0022	·0017	·0019	·0021	·0016	·0018	·0021
66	·0026	·0029	·0033	·0025	·0028	·0032	·0024	·0027	·0031
68	·0034	·0039	·0044	·0033	·0037	·0042	·0031	·0036	·0041
70	·0042	·0048	·0055	·0041	·0046	·0053	·0039	·0045	·0051
72	·0051	·0058	·0066	·0049	·0056	·0063	·0047	·0054	·0061
74	·0059	·0067	·0076	·0057	·0065	·0074	·0055	·0063	·0071
76	·0068	·0077	·0087	·0065	·0074	·0084	·0063	·0072	·0081
78	·0076	·0087	·0098	·0073	·0083	·0094	·0070	·0081	·0091
80	·0084	·0096	·0108	·0081	·0092	·0104	·0078	·0089	·0101
82	·0092	·0105	·0119	·0089	·0101	·0115	·0086	·0098	·0111
84	·0101	·0115	·0129	·0097	·0110	·0125	·0094	·0107	·0121
86	·0109	·0124	·0140	·0105	·0119	·0135	·0101	·0115	·0130
88	·0117	·0133	·0151	·0113	·0128	·0145	·0109	·0124	·0140
90	·0125	·0142	·0161	·0120	·0137	·0155	·0116	·0133	·0150
92	·0133	·0152	·0171	·0128	·0146	·0165	·0123	·0141	·0160
94	·0141	·0161	·0182	·0135	·0155	·0175	·0131	·0150	·0169
96	·0150	·0170	·0192	·0143	·0164	·0185	·0137	·0159	·0179
98	·0158	·0179	·0203	·0150	·0173	·0195	·0145	·0167	·0188
100	·0166	·0188	·0213	·0158	·0181	·0205	·0153	·0176	·0198
105	·0186	·0211	·0239	·0178	·0203	·0230	·0172	·0197	·0222
110	·0206	·0234	·0264	·0198	·0225	·0254	·0191	·0218	·0246
115	·0224	·0257	·0289	·0215	·0247	·0279	·0209	·0239	·0270
120	·0244	·0279	·0314	·0234	·0269	·0303	·0227	·0260	·0293

895.

SODIUM HYDROXIDE SOLUTIONS. (LUNGE.)

Specific Gravity $\frac{60°F.}{60°F.}$	Degrees Baumé	% NaOH	Grams NaOH Per Litre	Degrees Twaddell
1·007	1·0	0·61	6	1·4
1·014	2·0	1·20	12	2·8
1·022	3·1	2·00	21	4·4
1·029	4·1	2·70	28	5·8
1·036	5·1	3·35	35	7·2
1·045	6·2	4·00	42	9·0
1·052	7·2	4·64	49	10·4
1·060	8·2	5·29	56	12·0
1·067	9·1	5·87	63	13·4
1·075	10·1	6·55	70	15·0
1·083	11·1	7·31	79	16·6
1·091	12·1	8·00	87	18·2
1·100	13·2	8·68	95	20·0
1·108	14·1	9·42	104	21·6
1·116	15·1	10·06	112	23·2
1·125	16·1	10·97	123	25·0
1·134	17·1	11·84	134	26·8
1·142	18·0	12·64	144	28·4
1·152	19·1	13·55	156	30·4
1·162	20·2	14·37	167	32·4
1·171	21·2	15·13	177	34·2
1·180	22·1	15·91	188	36·0
1·190	23·1	16·77	200	38·0
1·200	24·2	17·67	212	40·0
1·210	25·2	18·58	225	42·0
1·220	26·1	19·58	239	44·0
1·231	27·2	20·59	253	46·2
1·241	28·2	21·42	266	48·2
1·252	29·2	22·64	283	50·4
1·263	30·2	23·67	299	52·6
1·274	31·2	24·81	316	54·8
1·285	32·2	25·80	332	57·0
1·297	33·2	26·83	348	59·4
1·308	34·1	27·80	364	61·6
1·320	35·2	28·83	381	64·0
1·332	36·1	29·93	399	66·4
1·345	37·2	31·22	420	69·0
1·357	38·1	32·47	441	71·4
1·370	39·2	33·69	462	74·0
1·383	40·2	34·96	483	76·6
1·397	41·2	36·25	506	79·4
1·410	42·2	37·47	528	82·0
1·424	43·2	38·80	553	84·8
1·438	44·2	39·99	575	87·6
1·453	45·2	41·41	602	90·6
1·468	46·2	42·83	629	93·6
1·483	47·2	44·38	658	96·6
1·498	48·2	46·15	691	99·6
1·514	49·2	47·60	720	102·8
1·530	50·2	49·02	750	106·0

896.

SULPHURIC ACID SOLUTIONS.

Degrees Baumé	Specific Gravity 60°F./60°F.	% H_2SO_4	Degrees Baumé	Specific Gravity 60°F./60°F.	% H_2SO_4
0	1·0000	0·00	37	1·3426	43·99
1	1·0069	1·02	38	1·3551	45·35
2	1·0140	2·08	39	1·3679	46·72
3	1·0211	3·13	40	1·3810	48·10
4	1·0284	4·21	41	1·3942	49·47
5	1·0357	5·28	42	1·4078	50·87
6	1·0432	6·37	43	1·4216	52·26
7	1·0507	7·45	44	1·4356	53·66
8	1·0584	8·55	45	1·4500	55·07
9	1·0662	9·66	46	1·4646	56·48
10	1·0741	10·77	47	1·4796	57·90
11	1·0821	11·89	48	1·4948	59·32
12	1·0902	13·01	49	1·5104	60·75
13	1·0985	14·13	50	1·5263	62·18
14	1·1069	15·25	51	1·5422	63·36
15	1·1154	16·38	52	1·5591	65·61
16	1·1240	17·53	53	1·5761	66·63
17	1·1328	18·71	54	1·5934	68·13
18	1·1417	19·89	55	1·6111	69·65
19	1·1508	21·07	56	1·6292	71·17
20	1·1600	22·25	57	1·6477	72·75
21	1·1694	23·43	58	1·6667	74·36
22	1·1789	24·61	59	1·6860	75·99
23	1·1885	25·81	60	1·7059	77·67
24	1·1983	27·03	61	1·7262	79·43
25	1·2083	28·28	62	1·7470	81·30
26	1·2185	29·53	63	1·7683	83·34
27	1·2288	30·79	64	1·7901	85·86
28	1·2393	32·05	64·25	1·7957	86·33
29	1·2500	33·33	64·5	1·8012	87·04
30	1·2609	34·63	64·75	1·8068	87·81
31	1·2719	35·93	65	1·8125	88·65
32	1·2832	37·26	65·25	1·8182	89·55
33	1·2946	38·58	65·5	1·8239	90·60
34	1·3063	39·92	65·75	1·8297	91·80
35	1·3182	41·27	66	1·8354	93·19
36	1·3303	42·63	—	—	—

897.

SPECIFIC GRAVITY OF FUMING SULPHURIC ACID

Grams of Free SO_3 in 100 Grams of Acid	Total Grams SO_3 in 100 Grams Acid	D_{15}^{15}
10	83·46	1·888
20	85·30	1·920
30	87·14	1·957
40	88·97	1·979
50	90 81	2·009
60	92·65	2·020
70	94·48	2·018
80	96·32	2·008
90	98·16	1·990
100	100·00	1·984

898.

CORRECTION OF SPECIFIC GRAVITY OF SULPHURIC ACID TO 15°C.
(Year Book, Coke Oven Managers' Association, 1919, p. 327.)

Specific Gravity	Correction for 1°C.
1·000—1·170	0·0006
1·170—1·450	0·0007
1·450—1·580	0·0008
1·580—1·750	0·0009
1·750—1·820	0·0010
1·820—1·840	0·0008

MOLECULAR WEIGHTS

899. For most refinery calculations, the molecular weights of distillate oils may be approximated by determining the A.S.T.M. or I.P.T. distillation *mid-points* (i.e., the temperatures at which 50 per cent. by volume of the oil distils) and taking the normal paraffin hydrocarbon of boiling point nearest to this temperature as having the same molecular weight as the oil in question. This approximation gives results more accurate than might be expected by a consideration of the diverse nature of oils available, and is seldom in error to an extent greater than $\pm$ 8 per cent. The reason for this is shown in Figure 263, in which the molecular weights of various types of hydrocarbons are plotted against their boiling points. Curve I relates to the normal paraffins, curve II relates to iso-paraffins and curve III is a plot of the aromatic hydrocarbons. Points are also shown for naphthenes and for α-olefines. All except a few of the points shown in this figure fall within $\pm$ 10 per cent. of the mean value indicated by Curve No. I.

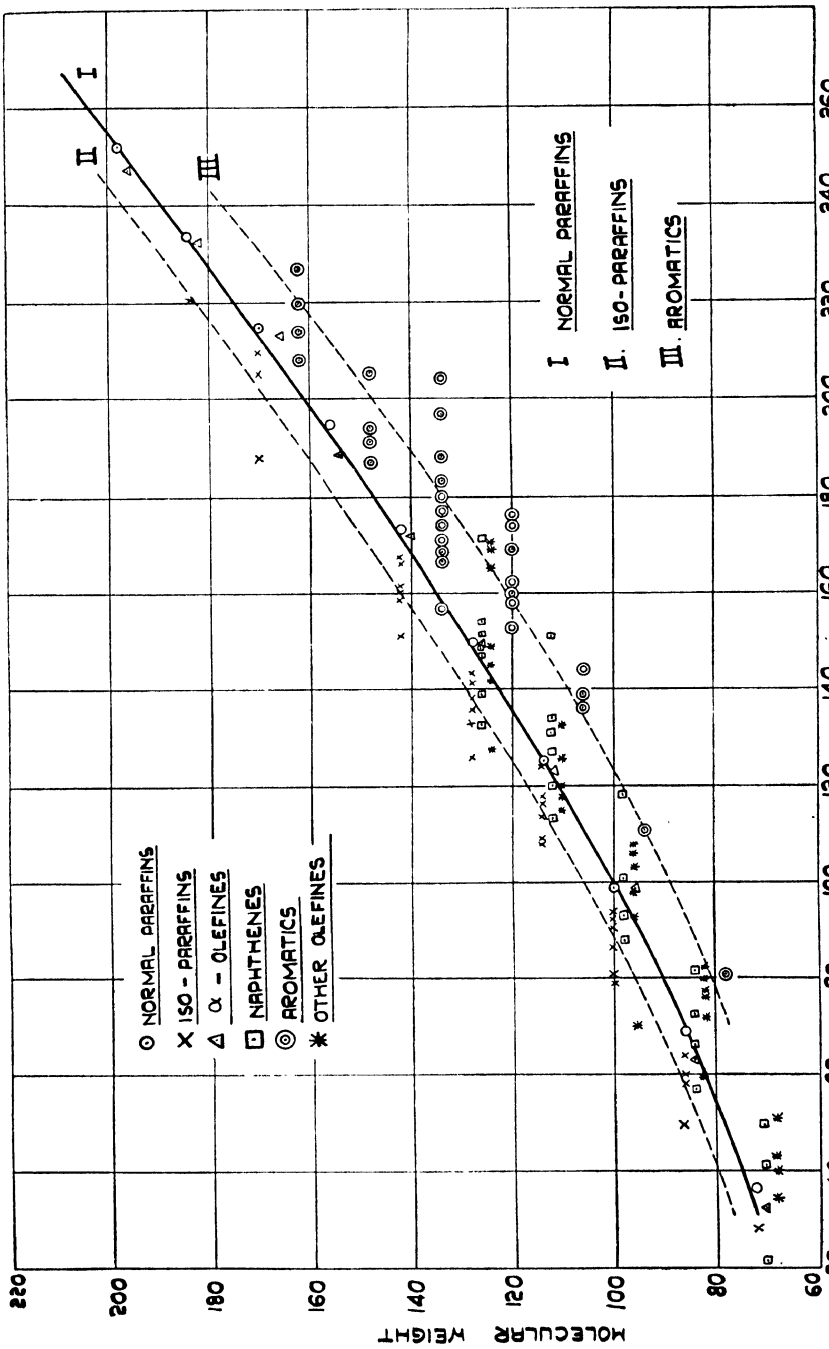


FIG. 283.—MOLECULAR WEIGHTS OF PURE HYDROCARBONS PLOTTED AS A FUNCTION OF THEIR BOILING POINTS.

Vapour Pressures

900. The approximate Clapeyron equation for the relationship between vapour pressure and temperature has the form

$$\log_e \frac{P_2}{P_1} = \frac{ML}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where P_1, P_2 are absolute pressures,
T_1, T_2 are the absolute temperatures corresponding to P_1, P_2,
M = molecular weight of the vapour,
L = latent heat of evaporation,
R = gas constant.

If, therefore, the logarithm of the vapour pressure be plotted against the reciprocal of the absolute temperature, a straight line is obtained.

Charts have been prepared in which vapour pressure data have been plotted in this way and these should be consulted. See Spiers, Technical Data on Fuel, 3rd Edition, 1932, and also H. B. Coats and G. G. Brown, Circular Series, No. 2, University of Michigan, Department of Engineering Research, December, 1928.

Vapour Pressures of Hydrocarbons (mm. Hg.) (International Critical Tables)

Temp. °C.	N-Pentane.	Iso-Pentane.	N-Hexane.	N-Heptane.	N-Octane.	2·5·Di-Methyl Hexane.	2·6·Di-Methyl Octane	Benzene.	Toluene.	Ortho-Xylene.	Meta Xylene.	Para-Xylene.	Ethyl Benzene	N-Propyl Benzene	Mesitylene.	Cumene.	Pseudo-Cumene.	Cyclo Hexane.	Naphthalene.	Tetra-Hydro Naphthalene.
−10	114·8	—	27·0	—	—	—	0·6	—	—	—	—	—	—	—	—	—	—	—	—	—
0	182·4	257·35	46·13	11·45	2·94	—	—	26·6	6·8	4·0	1·75	8·3	5·9	6·25	15·6	6·45	5·9	27·55	—	—
+10	280·5	390·4	75·5	20·5	5·62	13·0	—	45·3	12·5	6·4	3·45	11·5	9·6	7·7	20·45	8·65	7·0	47·05	—	—
20	419·8	572·2	119·7	35·5	10·45	23·0	5·0	74·3	22·0	10·05	6·45	16·35	15·3	10·0	27·15	11·8	8·7	76·9	—	—
30	608·0	819·6	182·8	58·35	18·40	38·5	—	117·5	36·7	15·55	11·45	23·5	23·75	13·55	36·4	16·45	11·3	121·3	—	—
40	867·0	1140·5	274·2	92·05	30·85	61·8	—	181·6	59·1	23·7	19·5	34·0	36·1	18·8	48·9	23·05	15·05	181·6	—	—
50	—	—	399·0	140·9	49·35	95·9	24·7	270·8	92·6	35·5	315·9	49·2	53·8	26·6	65·55	32·5	20·5	269·2	—	—
60	—	—	568·9	208·9	77·55	—	—	388·7	139·5	52·4	50·6	70·65	78·65	38·0	87·35	45·8	28·3	385·0	—	—
70	—	—	796·2	302·3	117·9	213·3	—	545·3	202·4	76·15	77·6	100·25	113·0	54·4	115·45	64·35	39·4	540·8	—	—
80	—	—	—	426·6	174·8	—	—	752·6	289·7	108·9	115·7	142·05	160·0	77·65	150·8	89·9	54·9	741·3	—	—
90	—	—	—	588·8	253·4	426·6	87·3	—	404·6	153·5	168·05	197·5	223·1	110·05	194·45	124·45	76·45	992·0	12·5	—
100	—	—	—	795·2	353·6	578·8	—	—	557·2	213·1	238·2	270·5	370·0	154·4	247·25	170·5	105·95	—	18·9	26·3
110	—	—	—	—	481·9	—	—	—	—	291·7	330·3	364·2	414·15	213·6	309·55	230·95	145·8	—	28·3	—
120	—	—	—	—	646·4	1020·0	247·0	—	—	393·85	448·85	481·3	545·9	291·0	381·1	309·0	198·55	—	—	—
130	—	—	—	—	859·0	—	—	—	—	524·6	598·6	624·9	695·95	389·6	461·7	407·55	267·6	—	—	—
140	—	—	—	—	—	—	453·2	—	—	689·6	784·6	794·8	—	511·9	550·05	530·1	355·9	—	—	118·0
150	—	—	—	—	—	—	—	—	—	—	—	—	—	659·1	643·55	679·7	466·8	—	—	—
160	—	—	—	—	—	—	—	—	—	—	—	—	—	—	740·35	—	603·9	—	—	219·0
170	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
180	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
190	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
200	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	646·0

901.

VAPOUR PRESSURES OF ENGLISH MOTOR FUELS
(Spiers, Technical Data on Fuel, 3rd Edition, 1932)

$$\log p = A - \frac{B}{T}$$

p = vapour pressure, mms., Hg.
T = absolute temperature, °C.

	Aviation Petrol	No. 1 Grade Petrol	No. 3 Grade Petrol
A.	6·76	6·72	6·65
B.	1,325	1,345	1,360
Vapour Pressure. Mms. Hg.			
— 30°C.	20·4	15	11
— 20°C.	34	25	19
— 10°C.	52	40	29
0°C.	80	62	47
+ 10°C.	115	90	70
20°C.	170	133	100
30°C.	240	185	145
40°C.	330	265	200
50°C.	450	360	280
60°C.	590	480	365
70°C.	780	630	490

902.

VAPOUR PRESSURES OF ETHYL ALCOHOL-BENZENE MIXTURES

% Weight Ethyl Alcohol	Vapour Pressure, mms. Mercury			
	34·8°C.	50°C.	60°C.	66°C.
0	147	271	389	477
2·07	174	326	471	578
3·85	185	347	503	620
9·47	195	371	545	677
17·3	198	379	562	702
25·6	198	382	570	711
32·15	197	380	569	711
50·15	190	371	557	697
64·9	178	351	530	671
79·9	155	311	479	609
93·3	122	257	403	520
100·0	103	223	354	462

903.

CRITICAL TEMPERATURES AND CRITICAL PRESSURES OF HYDROCARBONS
(International Critical Tables)

	Critical Temperature °C.	Critical Pressure Atmospheres
Methane	−82·5	45·8
Ethane	32·1	48·8
Propane	95·6	43
N-Butane	153	36
Iso-Butane	134	37
N-Pentane	197·2	33
Iso-Pentane	187·8	32·8
N-Hexane	234·8	29·5
N-Heptane	266·8	26·8
N-Octane	296	24·6
Cyclohexane	281	40·4
Benzene	288·5	47·7
Toluene	320·6	41·6
m-Xylene	348	35·8
Ethylene	9·7	50·9
Propylene	92·3	45
Naphthalene	468	39·2

VISCOSITY

904.

KINEMATIC VISCOSITIES OF ENGLISH MARKET FUELS
(C.G.S. units × 10^3)
(Spiers, Technical Data on Fuel, 3rd edn., pages 222, 224.)

Temperature, °C.	0	10	20	30
Motor Benzole	—	8·3	7·2	6·6
Aviation Petrol	7·4	6·8	6·2	5·7
No. 1 Grade Petrol	8·0	7·4	6·8	6·2
No. 3 Grade Petrol	9·5	8·5	7·6	6·9

905.

ABSOLUTE VISCOSITIES OF HYDROCARBONS

(C.G.S. units × 10^3)

(W. H. Hoffert and G. Claxton, Motor Benzole, 1931, p. 406)

Temp. °C.	Pentane	Hexane	Heptane	Octane	Cyclo-Hexane	Benzene	Toluene	Ortho-Xylene	Meta-Xylene	Para-Xylene
0	2·9	4·63	—	7·05	—	9·00	7·7	11·0	8·05	—
10	2·6	3·56	4·65	6·2	—	7·57	6·7	9·25	7·05	7·4
20	2·4	3·20	4·15	5·45	9·7	6·47	5·88	8·1	6·25	6·5
30	2·2	2·95	3·75	4·85	8·2	5·61	5·25	7·1	5·55	5·75
40	—	2·7	3·4	4·35	—	4·92	4·72	6·25	5·0	5·15
50	—	2·48	3·08	3·9	—	4·36	4·25	5·52	4·5	4·63
60	—	2·25	2·83	3·52	—	3·89	3·87	5·0	4·1	4·22
70	—	—	2·6	3·2	—	3·50	3·52	4·55	3·75	3·82
80	—	—	2·4	—	—	—	3·15	4·2	3·4	3·45

906

VISCOSITY OF WATER, 0°C. TO 30°C. (IN CENTIPOISES)

(International Critical Tables, Vol. V, p. 10)

Temperature, °C.	Viscosity	Temperature, °C.	Viscosity
1	1·7320	16	1·1156
2	1·6740	17	1·0875
3	1·6193	18	1·0603
4	1·5676	19	1·0340
5	1·5188	20	1·0087
6	1·4726	21	0·9843
7	1·4288	22	0·9608
8	1·3872	23	0·9380
9	1·3476	24	0·9161
10	1·3097	25	0·8949
11	1·2735	26	0·8746
12	1·2390	27	0·8551
13	1·2061	28	0·8363
14	1·1748	29	0·8181
15	1·1447	30	0·8004

LATENT HEATS OF VAPORISATION

907. Latent Heats of Petroleum Products.—The latent heats of vaporization of petroleum oils may be calculated with an accuracy of approximately 10 per cent. by means of the equation

$$L = \frac{1}{d}(110{\cdot}9 - 0{\cdot}09t),$$

in which L = latent heat of vaporization in B.T.U. per pound,

d = specific gravity of the liquid at 60°/60°F.,

and t = temperature in degrees Fahrenheit.

From this equation, it follows that

$$L \text{ (B.T.U./lb.)} \times \text{density (lbs./gall.)} = 8{\cdot}33722\ Ld.$$
$$= 925 - 0{\cdot}75t \text{ (B.T.U./gallon)},$$

which indicates that the latent heat of vaporization per unit volume of liquid (60°F.) is dependent only upon the temperature of vaporization.

This generalization only applies to normal petroleum oils and cannot be applied to hydrocarbons and fractions of widely different properties and chemical composition. It is not applicable to benzole mixtures.

Figure 264 shows the latent heats of vaporization of the lower aliphatic alcohols.

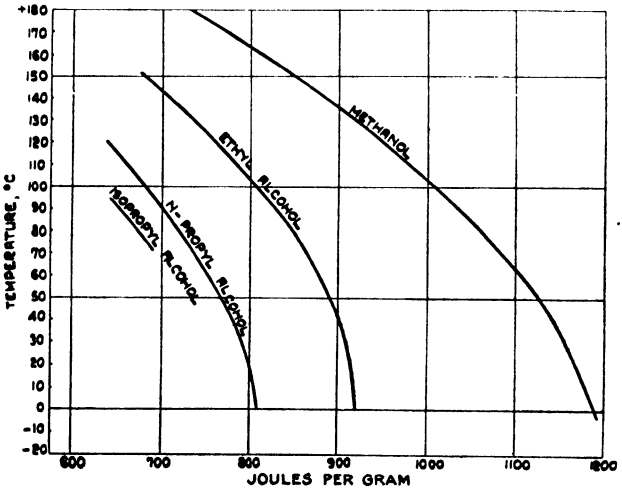


FIG. 264.—CURVES SHEWING THE LATENT HEATS OF VAPORISATION OF THE LOWER ALIPHATIC ALCOHOLS.

LATENT HEATS OF VAPORISATION OF HYDROCARBONS

(Cal_{15} per Gramme)

Temperature °C.	Benzene	Normal Pentane	Normal Hexane	Normal Heptane	Normal Octane
0	107·0	93·5	91·1	90·0	89·44
20	103·9	88·9	87·8	87·8	86·7
40	100·7	85·0	84·4	85·6	83·3
60	97·5	80·0	80·6	82·8	80·6
80	94·2	75·6	77·8	79·4	77·2
100	90·6	70·0	73·3	75·6	74·4
120	86·7	65·0	69·4	71·7	71·7
140	82·6	56·7	63·9	67·2	68·3
160	78·5	47·2	57·8	62·8	65·0
180	74·1	35·0	51·1	58·3	61·1
200	68·5	—	—	53·3	56·1

Specific Heats

908. Specific Heats of Petroleum Oils.—The specific heats of petroleum oils in the liquid state may be approximated with an accuracy of about 5 per cent., by means of the equation

$$C = \frac{1}{\sqrt{d}}(0{\cdot}388 + 0{\cdot}00045t),$$

in which C = specific heat in B.T.U.'s per pound per °F., or calories per-gram per °C.
d = specific gravity at 60°/60°F.,
t = temperature in °F.

The specific heats of petroleum oils in the vapour state at constant pressure may likewise be approximated with an accuracy of about 10 per cent., from the equation

$$\frac{dL}{dt} = C_g - C$$

in which L = latent heat of vaporization,
t = temperature,
C_g = specific heat of gaseous phase at constant pressure,
C_l = specific heat of liquid phase.

This equation may be simplified to give

$$C_g = C_l - \frac{0{\cdot}09}{d}$$

where d = specific gravity at 60°/60°F. of the liquid corresponding to the condensed vapour.

Typical specific heat values for normal petrols are as follows :— (Spiers, Technical Data on Fuel).

	Aviation Petrol	No. 1 Grade Petrol	No. 3 Grade Petrol
Specific Gravity $\frac{15{\cdot}5}{15{\cdot}5}$ °C.	0·720	0·740	0·745
t °C.	113	132	141
Mean Specific Heat between 0°C. and t°C., Cals./gram /°C.	0·523	0·528	0·531

PETROL. Specific Gravity, 0·750

Temperature t°C.	Mean Specific Heat 0°—t°C., Cals./Gramme
0	0·463
50	0·487
100	0 511
150	0·536

SPECIFIC HEATS OF PURE HYDROCARBONS IN THE LIQUID STATE
(Cal_{15}/Gramme/°C)

Hydrocarbon	Temperature, °C.	Specific Heat
Benzene	0	0 385
„	20	0·406
„	40	0·423
„	60	0·444
„	80	0·464
Toluene	0	0 386
„	50	0·421
„	80	0·447
„	100	0·470
o-Xylene	30	0·441
„	80	0·473
m-Xylene	0	0 384
„	110	0·498
p-Xylene	0	0·383
„	110	0 498
N-Hexane	0—50	0·527
„	20—100	0·600
N-Heptane	30	0·518
„	80	0·632
N-Octane	0—50	0·505
„	20—123	0·578

909.

THE SOLUBILITY OF WATER IN HYDROCARBONS, ETC.

Hydrocarbon	Solubility. Grammes Per 100 Grammes Solution						
	5°C.	10°C.	15°C.	20°C.	30°C.	40°C.	50°C.
Benzene	0 034	0 04	0 053	0·062	0·088	0·122	0·158
Toluene	0·03	0·035	0·04	0·046	0 06	0·078	0·097
Petrol (Average Values) ..	0·0025	0·003	0·004	0·005	0·01	0·017	0·026
Kerosene (Average Values)	0·002	0·003	0·004	0·005	0 01	0·015	0·023

910.

FREEZING POINTS

FREEZING POINTS OF MIXTURES OF BENZENE WITH PURE ANHYDROUS ETHYL ALCOHOL

(Pickering, J. Chem. Soc., 1893, **63**, 1019)

% Ethyl Alcohol (Weight)	Freezing Point °C.
—	5·44
4·994	3·22
14·15	1·67
27·24	−0·13
36·145	−1·78
45·166	−4·43
55·569	−8·98
65·181	−15·90
78·094	−34·01
87·285	−54·26
92·43	−71·01

911.

FREEZING POINTS OF AQUEOUS ETHYL ALCOHOL MIXTURES

(Raoult, Ann. Chem. Phys., 1880, **20**, 221)

Freezing Point °C.	Grammes Ethyl Alcohol Per 100 Grammes of Water
−1·0	2·65
−2·0	5·5
−3·0	7·95
−4·0	10·6
−5·0	13·0
−6·0	15·3
−7·0	17·8
−8·0	19·8
−9·0	21·9
−10·0	23·6
−12·0	27·6
−14·0	31·3
−16·0	35·1
−18·0	39·0
−20·0	42·8
−22·0	46·6
−24·0	50·6
−26·0	54·8
−28·0	59·2
−30·0	64·6
−32·0	70·0

912.

Properties of Dry Air

(Spiers, Technical Data on Fuel, 3rd Edition, 1932)

Composition

	Oxygen	Carbon Dioxide	Nitrogen and Rare Gases
By Volume ..	21·0%	0·03%—0·3%	78·7%—78·97%
By Weight ..	23·2%	0·046%—0·4%	76·4%—76·754%

Density.—1·2928 grammes per litre at 0°C. and 760 mms. Hg., at latitude 45° = 0·08071 pounds per cubic foot.

Mean Specific Heat at Constant Pressures.

0 — 100°C. = 0·3110 Kg. cals. per M^3 per °C.
0 — 200°C. = 0·3117 ,, ,, ,, ,,
0 — 300°C. = 0·3124 ,, ,, ,, ,,
0 — 400°C. = 0·3133 ,, ,, ,, ,,
0 — 500°C. = 0·3143 ,, ,, ,, ,,

913.

Formulæ for Horse Power, Torque and B.M.E.P.

1. $P = \frac{Tr}{5252}$
2. $P = \frac{tr}{63025}$
3. $P = \frac{pD^2rSN}{1010000}$
4. $P = \frac{pD^2KN}{168000}$
5. $P = \frac{pA{\cdot}SrN}{792000}$
6. $T = \frac{5252P}{r}$
7. $T = \frac{pD^2SN}{192}$
8. $p = \frac{792{,}000P}{ASrN}$
9. $p = \frac{192T}{D^2SN}$
10. $p = \frac{16t}{D^2SN}$
11. $p = \frac{1010{,}000P}{D^2SrN}$
12. $p = \frac{168{,}000P}{D^2KN}$

D = cylinder bore, inches.
S = stroke, inches.
A = piston area, square inches.
V = r.p.m.
N = number of cylinders.

K = piston speed, feet per minute = $\frac{rS}{6}$

p = B.M.E.P., pounds per square inch.

P = horse power.

T = torque, lb. feet.

t = torque, lb. inch.

V = total swept volume = $0{\cdot}785\ D^2SN$.

914. Statistics.

U.K. Imports of Petroleum Products by Country of Origin
(C. T. Brunner, "Problem of Oil," Ernest Benn, Ltd., 1930)

	1926 %	1927 %	1928 %	1929 %
America (Mid.)	29·8	30·3	30·1	26·3
California	10·1	8·4	9·1	9·5
Persia	25·3	26·1	23·9	23·4
Venezuela	9·3	12·4	15·8	14·9
Russia	5·8	4·5	6·9	9·8
Mexico	13·9	12·2	5·2	6·1
Roumania	2·2	2·4	3·9	3·5
Trinidad	0·7	1·8	2·6	2·1
Orient	2·1	1·5	2·0	3·7
Continental	0·8	0·4	0·4	0·7
Peru	—	—	0·1	—
	100·0	100·0	100·0	100·0

United Kingdom Imports of Crude Oil

Consignee	1932		1931	
	Gallons	%	Gallons	%
Persia	232,294,000	63·4	243,395,982	70·7
Peru	45,146,000	12·2	nil	nil
Dutch West Indies	34,459,000	9·3	23,470,796	6·8
Venezuela	32,016,000	8·6	70,008,437	20·4
Mexico	16,578,000	4·4	nil	—
Canary Islands	4,524,000	1·2	nil	—
U.S.A.	2,273,000	0·6	nil	—
Trinidad	1,168,000	0·3	7,103,732	2·1
Others	nil	—	1,310	—
	368,458,000	100·0	343,980,257	100·0

915. Cost of United Kingdom Imported Oils

Declared Value=cost of goods, including package, to the consignée, plus insurance and freight to place of importation, exclusive of any import duty.

	1932	1931	1930	1929
	Value, Pence per Imperial Gallon			
Crude Oil from Persia	2·31	2·26	2·24	2·32
Crude Oil from Other Countries ..	1·99	1·63	2·19	2·40
All Sources	2·19	2·07	2·23	2·34
Refined Oils				
Motor Spirits	3·97	3·62	6·52	6·75
Other Spirit	3·12	2·76	5·71	5·87
Kerosene	3·34	3·10	4·54	4·87
Lubricating Oil	10·50	9·85	11·14	11·91
Gas Oil	2·39	2·33	3·20	3·20
Fuel Oil	1·85	1·87	2·28	2·15
Other Sorts	13·93	22·03	18·98	12·33
All Products	3·53	3·35	5·21	5·42
Paraffin Wax, Shillings per Hundredweight	17·96	17·12	18·80	23·20

(Petroleum Times, 1933, 29, (732), 72).

916. United Kingdom Imports of Motor Fuels

Consignée	1932		1931	
	Gallons	%	Gallons	%
U.S.A.	284,842,000	29·2	383,680,612	42·4
Dutch West Indies ..	174,993,000	17·9	62,640,954	6·9
Persia	143,433,000	14·7	91,637,169	10·1
Roumania	123,670,000	12·7	109,699,056	12·1
Russia	79,963,000	8·2	122,555,516	13·5
Mexico	52,418,000	5·4	34,526,186	3·8
Dutch East Indies ..	43,803,000	4·5	51,168,086	5·7
Peru	27,059,000	2·8	nil	—
Trinidad	16,586,000	1·7	5,623,356	0·6
Egypt	13,985,000	1·4	9,589,124	1·1
Sarawak and Straits Settlements	13,820,000	1·4	28,434,471	3·1
Venezuela	nil	—	2,254,515	0·2
Others	1,365,000	0·1	4,682,619	0·5
	975,937,000	100·0	906,492,264	100·0

(Petroleum Times, 1933, 29, (738), 219).

917.

UNITED KINGDOM CONSUMPTION OF MOTOR FUELS

Year	Consumption. All Grades		Increase over Previous Year %
	Imperial Gallons	Tons	
1913	100,800,000	336,000	—
1914	117,300,000	391,000	11·6
1919	147,000,000	490,000	—
1920	176,100,000	587,000	19·8
1921	275,700,000	919,000	56·6
1922	324,000,000	1,080,000	17·5
1923	378,900,000	1,263,000	16·9
1924	447,000,000	1,490,000	18·0
1925	546,000,000	1,820,000	22·1
1926	657,000,000	2,190,000	20·3
1927	739,500,000	2,465,000	12·6
1928	832,800,000	2,776,000	12·6
1929	954,600,000	3,182,000	14·6
1930	1,026,000,000	3,420,000	7·5
1931	1,056,600,000	3,522,000	2·9
1932	1,093,000,000	3,643,300	3·4

918.

ESTIMATE OF U.K. MOTOR SPIRIT TRADE, 1929.
(BRUNNER, " The Problem of Oil," ERNEST BENN, LIMITED, 1930).

	Tons.	
Private Cars taxed on Horse Power	950,000	
Motor Cycles	150,000	
Private Vehicles ..		1,100,000
Omnibuses and Charabancs	420,000	
Other Commercial Passenger Vehicles	180,000	
Commercial Goods Vehicles	1,200,000	
Miscellaneous Vehicles ..	100,000	
Commercial vehicles		1,900,000
Grand Total ..		3,000,000

919.

SOURCES OF MOTOR FUEL IMPORTS INTO FRANCE AND GERMANY, 1930 AND 1931

	1930	1931
France		
U.S.A.	57%	36%
U.S.S.R.	13%	20%
Roumania	5%	14%
Persia	10%	25%
Others	15%	5%
Germany		
U.S.A.	50%	45%
U.S.S.R.	9%	20%
Roumania	13%	11%
Persia	6%	10%
Others	22%	14%

(World Petroleum, 1932, **3**, (1), 22)

920.

WORLD CRUDE OIL PRODUCTION

	Millions of Tons					
	1926	1927	1928	1929	1930	1931
U.S.A.	109·7	128·0	125·2	144·3	126·7	116·3
Venezuela	5·3	9·2	15·3	19·3	20·2	17·3
U.S.S.R.	8·9	10·3	12·1	13·6	18·7	22·3
Mexico	12·9	9·1	7·5	6·0	6·0	5·0
Persia	5·1	5·2	5·5	6·1	5·8	6·4
Roumania	3·2	3·6	4·4	4·6	5·7	6·7
Dutch East Indies	3·0	3·6	4·1	4·3	5·3	4·5
Colombia	0·9	2·1	2·7	2·9	2·8	2·5
Peru	1·5	1·4	1·6	1·9	1·7	1·4
Argentine	0·9	1·2	1·3	1·3	1·3	1·7
Trinidad	0·7	0·7	1·2	1·2	1·5	1·5
India	1·3	1·2	1·1	1·2	1·1	1·1
Poland	0·8	0·8	0·8	0·7	0·7	0·6
Sarawak	0·7	0·7	0·7	0·8	0·7	0·5
Egypt	0·2	0·2	0·3	0·3	0·3	0·3
Japan	0·3	0·2	0·3	0·3	0·3	0·3
Others	0·3	0·4	0·6	0·7	1·0	1·3
	154·7	177·9	184·7	209·5	199·8	189 9

921.

MOTOR VEHICLE REGISTRATIONS IN GREAT BRITAIN

	1914	1919	1921	1923	1925	1927	1929
Private Cars ..	132,015	109,715	242,500	383,525	579,901	786,610	970,275
Motor Cycles ..	123,678	114,722	373,200	430,138	571,552	681,410	705,025
Goods Vehicles	82,000	62,000	128,200	173,363	224,287	282,905	318,253
Hackney Vehicles ..	51,167	44,081	82,800	85,965	95,833	90,676	95,798
Miscellaneous Vehicles ..	—	—	17,170	32,204	34,536	36,783	41,277
Total ..	388,860	330,518	843,870	1,105,195	1,509,109	1,883,384	2,130,628

	1930	1931	1932
Private Cars	1,075,081	1,110,000	1,149,231
Commercial Vehicles ..	481,893	485,000	490,000

In order to effect a net increase of some 39,000 private cars between 1931 and 1932, 146,000 new cars were sold.

922.

AVERAGE PRIVATE CAR TAXATIONS, INCLUDING FUEL TAX

	£ Per Horse Power
Austria	2·36
United Kingdom	2·35
Italy	2·33
Denmark	2·10
Germany	1·79
Switzerland	1·65
Netherlands	1·48
France	1·43
South Africa	1·15
Australia	1·15
Sweden	1·08
New Zealand	0·95
S. Rhodesia	0·50
Mississippi	0·49
N. Rhodesia	0·45
Michigan	0·34
Pennsylvania	0·33
New York	0·33
Illinois	0·30
Chicago	0·26

923.

UNITED KINGDOM MOTOR VEHICLE TAXATION

Year	Net Direct Taxation	Net Fuel Tax Receipts	Average Total Taxation Per Vehicle
1929	£25,535,000	£12,982,000	£19·00
1930	26,598,000	15,043,000	19·34
1931	27,825,000	15,909,000	26·14
1932	27,340,000	29,277,000	28·69
1933 (est.)	27,700,000	35,224,000	—

924.

AVERAGE PETROL CONSUMPTION PER ROAD VEHICLE (EXCLUDING MOTOR CYCLES), UNITED KINGDOM

Year	Petrol Consumption, Gallons per Year
1913	486
1920	505
1928	605
1929	610
1930	638
1931	658
1932	655

925.

U.S.A. MOTOR FUEL CONSUMPTION

	U.S. Gallons	Barrels
1931	16,449,815,000	391,662,000
1930	15,786,040,000	375,860,000
1929	15,617,784,000	371,852,000
1928	13,796,538,000	328,489,000
1927	12,465,936,000	296,808,000
1926	10,995,012,000	261,786,000
1925	9,402,456,000	223,868,000
1924	7,770,210,000	185,005,000
1923	6,685,224,000	159,172,000
1922	5,372,010,000	127,905,000
1921	4,514,496,000	107,488,000
1920	4,250,694,000	101,207,000
1919	3,434,802,000	81,781,000

926.

MOTOR VEHICLE REGISTRATIONS IN U.S.A.

Year	Passenger Cars	Motor Trucks	Total Motor Vehicles
1895	4	—	4
1900	8,000	—	8,000
1905	77,400	600	78,000
1910	458,500	10,000	468,500
1915	2,309,666	136,000	2,445,666
1920	8,225,859	1,006,082	9,231,941
1925	17,512,638	2,441,709	19,954,347
1929	23,121,589	3,379,854	26,501,443

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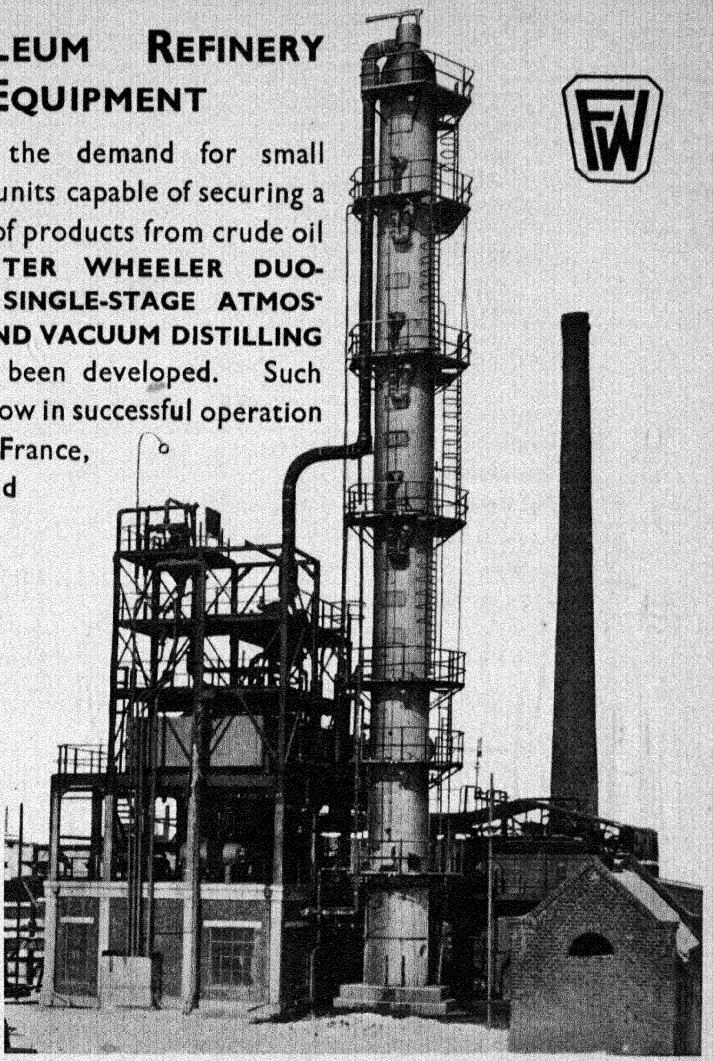
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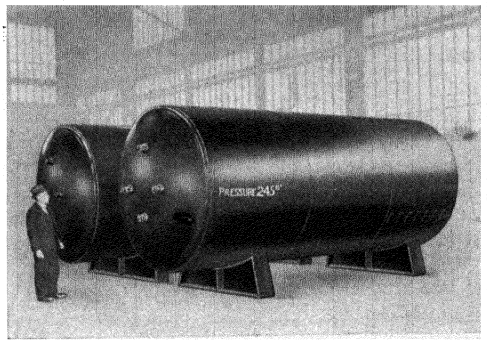
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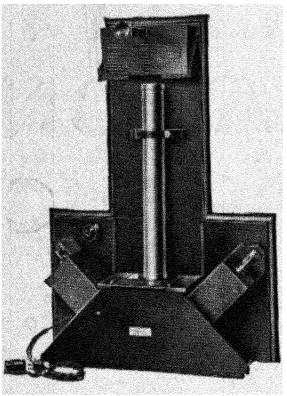
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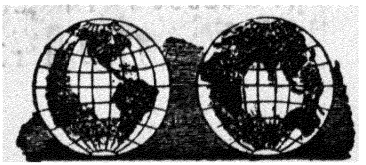
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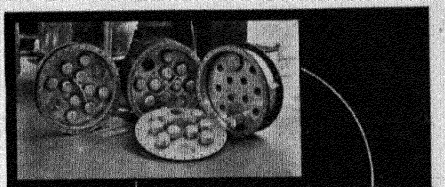
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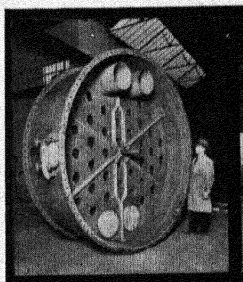
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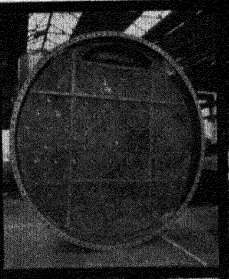
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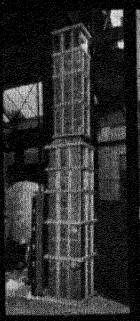




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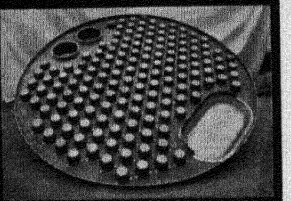
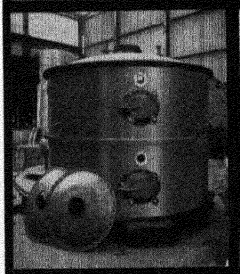
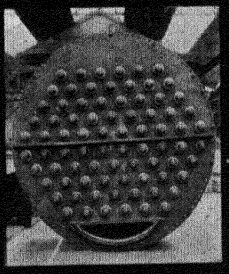
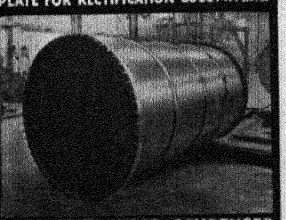


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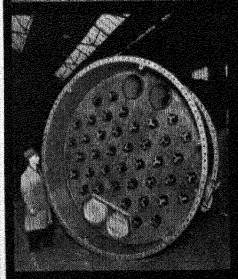




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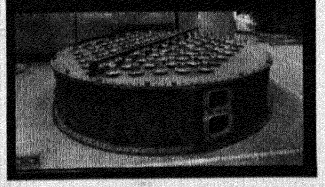
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