DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 99

CARBONIZATION OF LUBRICATING OILS

NOVEMBER 12, 1920
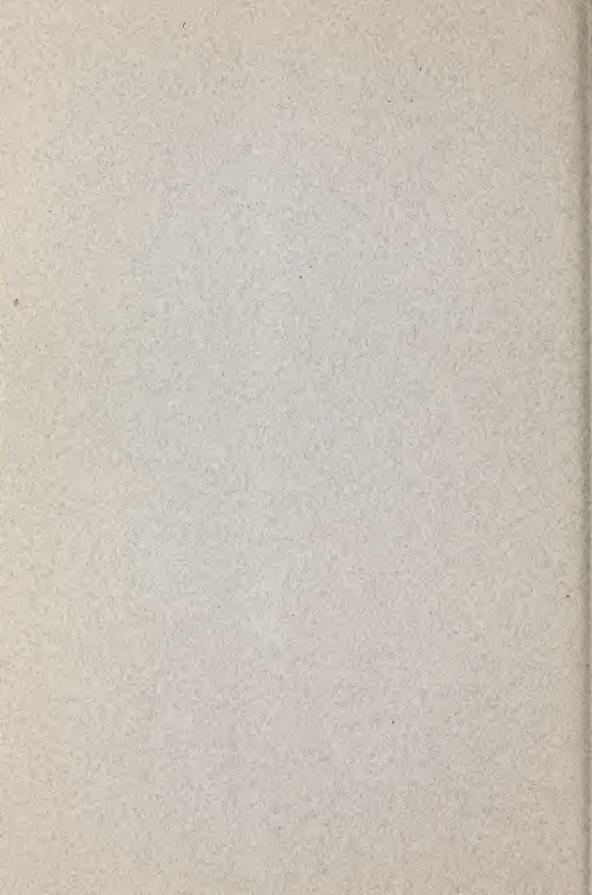
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CONTENTS

[a] Prepared by C. E. Waters, Chemist, Bureau of Standards.

I. INTRODUCTION

In the days of the old stationary gas engine, little was heard of the sort of troubles which are now experienced with the lubrication of the cylinders of gasoline engines. This was, no doubt, due to the comparatively small number of engines, and, if statistics were available, they would probably show that, in proportion to the number of engines in use, there was as much trouble as now. The oil was not as good as now, for refiners did not have the present-day incentive to produce lubricants especially for internal-combustion engines. A gas engine was a novel sight to most persons. The writer remembers two, each installed in a grocery window, where it served as an attraction and advertisement while it ground coffee. The intermittent, irregular exhausts at the curbstone called attention to the novel sight and to the enterprise of the proprietor.

Although the oil was probably inferior to what is used in internal-combustion engines to-day, it did not have to meet the heavy duty of a truck engine or overcome the effects of dusty air, poor gasoline, and unskillful mangement. These are real difficulties that must be overcome, and even the careful and conscientious refiner is not always successful in producing an oil which meets them.

II. CARBON DEPOSITS

1. NATURE OF CARBON DEPOSITS

The enormous number of internal-combustion engines in use, particularly in automobiles, trucks, and motor boats, has been the means of giving a new and special significance to the word "carbon," and of making it a household word. "Carbon" has come to mean, to most people, the deposits which form on the inside of these engines. Strictly, these deposits are not really carbon, but are composed of mixtures of this substance with tarry or asphaltic

matter, with oil which has become more or less oxidized or otherwise changed during the running of the engine, and with metallic particles and dust. The proportions of these constituents vary in the deposits in different parts of the engine. Even the oil in the sump finally becomes turbid from the presence of finely divided "carbon."

At least a partial separation of this material into its constituents can be made by successive treatments with suitable solvents. The following experiments were made on a deposit taken from an airplane engine. As it was a typical deposit, the experiments are described in detail so that others can make similar tests. The oil was removed by grinding the material with just enough petroleum ether to make a paste, which was transferred to a Gooch crucible and thoroughly washed with the solvent, then dried at 100° C (212° F). The powder was digested overnight with benzene (benzol) and next day warmed on the steam-bath with several successive portions of benzene. After this washing the residue was sucked dry in a Gooch crucible and then digested in the same way with carbon tetrachloride. It was finally dried at room temperature over the next night, because the digestions just described took all day. The following tests were then made:

When heated in a test tube it gave off oily vapors which could be lighted at the mouth of the tube. Some moisture and a considerable amount of a deep yellow oily liquid condensed on the walls of the tube.

On boiling with pyridine for a few minutes enough dissolved to yield a dark-brown solution.

Carbon bisulphide, alcohol, and turpentine appeared to dissolve not more than traces, if any at all.

Melted paraffin wax and acetic anhydride dissolved a little.

Dilute caustic soda solution dissolved a considerable amount. When filtered, the solution was of a clear-brown color, so dark that it appeared black by reflected light. To make sure whether or not it was a suspension of colloidal carbon, it was strongly acidified with hydrochloric acid. The flocculent precipitate which formed had the appearance of hydrated manganese peroxide. It was filtered off and washed once by filling the funnel with water. The same volume of alcohol was then poured upon it. This filtrate was clear and of a deep-yellow color. The addition of two or three volumes of water caused only a faint opalescence in it. The residue on the filter was then treated with benzene, which

gave a colorless filtrate. The paper and adherent precipitate were dried at room temperature. The precipitate was now very dark brown with a dull-gray cast. It did not dissolve in carbon bisulphide, and after an hour or two gave only a trace of color to alcohol. It was almost completely soluble in pyridine. Natural asphalt behaves in much the same way when boiled with caustic soda solution.

No further examination was made of the material, but enough has been said to show that much work might profitably be done on it. It can not be gainsaid that the "carbon" is by no means pure carbon.

When the so-called carbon is burned to ash, it is found to have a higher percentage of incombustible matter than the oil before use. Oil of good quality should contain not more than one or two hundredths of a per cent of ash, which is mainly iron oxide. The ash from the engine deposits contains dust (clay, grit, etc.) and metallic oxides. Fine particles of metal are worn from the engine, become mixed with the oil and "carbon," and are changed to oxides when the mixture is burned to ash.

2. EFFECTS OF CARBON DEPOSITS

As just stated, the so-called carbon deposits contain dust which is made up of clay, fine grit, etc., which are drawn in during the suction stroke of the piston. It eventually gets into the crank case, where it is worked up with the oil, gets into the bearings, and may again reach the cylinder. The mixture of solid and oily matter in the cylinder gradually thickens and hardens with the heat. Owing to the grit, it is abrasive enough to cause wear between the piston rings and the cylinder walls.

Under some conditions the deposit becomes granular or scaly. Small, projecting particles of it which remain in the upper part of the cylinder may be incandescent or at least retain enough heat to ignite the incoming gas during the charging stroke. Such pre-ignition troubles are indicated by a pounding noise or "knocking" in the cylinders. Failure of ignition, or "missing," may be caused by small particles of scaly deposit which collect on the spark plug. They conduct the current and thus short-circuit the spark.

If small pieces of the deposit work up under the exhaust valve and cause bad seating, there will be leakage of gases and loss of compression. This means loss of power.

III. NATURE OF PETROLEUM OILS

1. HYDROCARBONS

Some of the ways in which carbon deposits can be formed in the engine will be discussed further on, but before doing so it will be well to say something about the chemical nature of petroleum oils.

All petroleum is made up almost entirely of different chemical substances which are composed of the elements carbon and hydrogen and which, therefore, are known as "hydrocarbons." The hydrocarbons differ from one another in the number and arrangement of the carbon and hydrogen atoms in the molecule, and with these differences there are corresponding changes in the chemical and physical properties. The hydrocarbons are classified according to their chemical constitution; that is, the arrangement of the carbon atoms in the molecule. The arrangement of the hydrogen atoms follows from that of the carbon atoms. By taking these facts into account we find that crude petroleum is composed of representatives of only a few series of hydrocarbons. By far the greater part of the oil belongs to two chief series, the paraffins and the naphthenes.

In some series the lower members, or those which contain only from one to four or five carbon atoms in the molecule, are gaseous at ordinary temperatures, although they can be liquefied by sufficient cooling. As the number of carbon atoms becomes greater the boiling points are higher, the specific gravities and the viscosities increase, and the freezing points rise. Because all crude petroleum contains different members of each of the series represented, it is possible to obtain from it a great variety of products, ranging from the lightest and most volatile distillates to the heaviest and most viscous oils, or even waxes.

2. PARAFFIN BASE OILS

The first petroleum deposits which were used commercially in this country were those found in western Pennsylvania and in adjacent parts of the neighboring States. The principal hydrocarbons contained in them belong to the series known to the chemist as "paraffins," a name applied to them because of their chemical inertness. This name, from the Latin parum, too little, and affinis, allied, calls attention to the fact that they have slight affinity for, or do not readily combine with, other substances.

The lowest member of the series, and incidentally the simplest of all hydrocarbons, is methane or marsh gas. It contains one

carbon atom and four hydrogen atoms in the molecule, and in chemical notation is written CH_4. It is a gas which boils at $-160°$ C ($-256°$ F) under atmospheric pressure. Butane, C_4H_{10}, boils at about $0°$ C ($32°$ F). Pentane, C_5H_{12}, boils at $36.5°$ C ($97.5°$ F), and is therefore found in those distillates from crude oil which boil off first, and also in casing-head naphtha. At the other end of the series are very viscous oils and the paraffin waxes. Because the crude oils from Pennsylvania contain these waxes, they are known as "paraffin base oils."

3. NAPHTHENE OR ASPHALT BASE OILS

By far the greater part of the crude petroleum which is produced consists of the so-called naphthene or asphalt base oils or of mixtures of these with paraffin base oils. When these crudes are distilled, asphalt is left behind. It is said that when they first came into use, much was made of this fact by the producers of paraffin base oils. The obvious intention was to cast discredit upon the asphalt base oils and to create the impression that because of the nature of the distillation residue lubricants made from these crudes were not suitable for use.

The name as applied to the refined oils is misleading, so much so that even some chemists have the idea that they actually contain asphalt. A glance at a well-refined oil made from one of these crudes will show that there is no comparison between its color and that of oil which contains even a few tenths of 1 per cent of dissolved asphalt.

To the chemist these hydrocarbons are known as the naphthenes, and that name will be applied to them throughout the rest of this circular. In their molecular structure, as well as in some of their chemical and physical properties, they are quite different from the paraffins. The naphthenes are more stable when heated alone, their viscosity decreases more rapidly with rising temperature, for a given viscosity their specific gravity is higher and they are more volatile, and they can be chilled to a lower temperature before they cease to flow. Just as with the paraffins, the naphthenes become more viscous and their boiling points rise as the number of carbon atoms in the molecule increases.

4. OTHER CONSTITUENTS OF PETROLEUM

Besides hydrocarbons of the paraffin and naphthene series petroleum always contains representatives of other series. By "cracking" during distillation still others may be formed. Free

sulphur, hydrogen sulphide, organic compounds which contain sulphur, and nitrogen compounds are all constituents of crude petroleum, though they are not all necessarily found in the same oil. A discussion of these is outside the scope of this paper.

5. FREE CARBON

With the belief that the deposits in the engine are carbon comes the notion that they are due to the presence of free carbon in the oil or are at least in some way dependent upon the percentage of that element in the lubricant.

No oil which can be called refined contains free carbon. It is true that during distillation some may be formed, but it is not volatilized and carried over with the distillates, while any that may be in the residual cylinder stock would be removed by filtration. An oil which had suspended in it even as little as 0.10 per cent of free carbon would be very dark in color.

The formation of deposits in the engine is not due to the greater proportion of carbon in the heavier oils; that is, those which contain the larger number of carbon atoms. Of the paraffins which occur in kerosene, an increase of one carbon atom raises the proportion by 0.10 per cent or less. In the lubricating oil fractions the addition of one carbon atom causes a still smaller change in the percentage of carbon. Decane, $C_{10}H_{22}$, which is found in kerosene, contains only about 0.6 per cent less carbon than eicosane, $C_{20}H_{42}$, a solid having the melting point 37° C (98° F). It is unlikely that this slight increase in the percentage would of itself be the cause of the deposition of carbon by one oil and not by the other when heated. Further, in the naphthene series there are always two hydrogen atoms for every carbon atom, so that the percentages of the two elements are the same for all members of the series.

The cause of the formation of free carbon from the lubricant is the breaking down of the large, relatively unwieldy molecules by heat. The lower members of a series are comparatively volatile, if not gaseous, at ordinary temperatures and at atmospheric pressure, and they can be distilled without excessive heating. But the boiling point rises with each added carbon atom until soon temperatures are reached at which the molecules "crack," or break down into simpler hydrocarbons and free carbon before the oil can all be changed to vapor. At reduced pressures, especially in high vacua, it is possible to distil even the higher hydrocarbons with little or no decomposition. No doubt a part of the carbon

in the engine comes from the partial combustion of the gasoline and of the lubricant. Even in the open air they burn with smoky flames. The chances that soot will be formed in the engine are increased because most persons are apt to run it with too rich a mixture; that is, one which contains too little air for the most nearly complete combustion. Part of the soot will be trapped by the oil, and thus help to build up the deposits.

6. ASPHALT

The usual test for the presence of asphalt is to dilute the oil with light gasoline or petroleum ether. According to the practice in different countries and laboratories, one volume of oil is diluted with from 9 to 40 volumes of gasoline. If much asphalt is present, the oil will not only have a dark-brown color, but the mixture will at once become turbid, owing to the formation of a precipitate. If there is no turbidity at first, the mixture is allowed to stand in a stoppered cylinder for some hours, when the appearance of a precipitate will show that there is some asphalt in the oil. In this way a small fraction of 1 per cent can be detected.

The better-refined oils whether intended for use in internal-combustion engines or not, give no indication of the presence of asphalt, by this test, no matter from what crudes they may have been obtained. On the other hand, poorly refined naphthene base oils or even paraffin base oils contain more or less. This will be discussed further on in greater detail.

In general, therefore, well-refined oils can not deposit either free carbon or asphalt except as the result of changes which are brought about in them during the running of the engine. The amount of deposit will depend not only on the oil, but also upon the conditions in the engine; that is, the temperature, the carburetor adjustment, etc.

IV. THEORIES CONCERNING CARBON DEPOSITION

In view of the importance of the subject, it is not surprising that numerous tests have been devised for the purpose of learning in the laboratory how oils may be expected to behave in use. Many papers on the subject have been published, from which it can be seen that there are two entirely different lines of attack, two schools of thought, as to the fundamental reason for the formation of the deposits in the engine.

Some think that partial oxidation of the oil causes the formation of asphaltic matter, which first comes down in gummy form and

afterwards hardens. Others think that this formation of asphalt is negligible, but that the important factor is the destructive distillation, or "cracking," of the oil with deposition of actual carbon. Without attempting to make a choice, it will be well to discuss the whole subject in some detail.

1. OXIDATION OF PETROLEUM

In earlier papers of this Bureau [1] references have been given to many papers on the oxidation of petroleum oils. It is not necessary to repeat them here. What is meant is, of course, the partial oxidation of the oil, with formation of other substances, and not its combustion in the usual sense.

(a) EFFECTS OF HEAT AND SUNLIGHT.—Petroleum oils are by no means chemically inert, but are susceptible of oxidation at ordinary temperatures. This action proceeds very slowly in the dark, and oil can be stored for a long time in closed barrels or cans without any considerable change. Some oils, when heated in the dark nearly to the boiling point of water, show but slight evidence of oxidation. At temperatures in the neighborhood of 200° C (392° F), or above, all oils will oxidize more or less rapidly, and some with great ease.

Sunlight greatly hastens the action of oxygen upon petroleum. This is not due to the heating effect, because the oxidation proceeds at a measurable rate even if the glass vessel which contains the oils is surrounded by cracked ice.[2] It is a photochemical effect of the light, and perhaps chiefly of the rays of shorter wave length. No doubt any of the lamps which produce ultra-violet radiations would have much the same effect as sunlight.

That oxidation takes place in sunlight is shown by the formation of carbon dioxide and finally by the formation of a precipitate in the oil. The latter is an acid substance which contains carbon, hydrogen, and oxygen. It dissolves in certain organic solvents, as well as in caustic potash solution.

(b) EFFECTS OF IMPURITIES IN THE OIL.—Many different kinds of substances hasten the oxidation of petroleum by their catalytic action. Among the most important and effective catalyzers are certain little-known "resinous" substances which are either in the crude oil or are produced at some stage of the refining. These

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[1] Waters, B. S. Bulletin, **7**, pp. 227–234 and 365–376; 1910 (Scientific Papers Nos. 153 and 160). B. S. Tech. Papers, No. 4, 1911, and No. 73, 1916. See also J. Ind. Eng. Chem., **2**, pp. 451–454, 1910; **3**, pp. 233 and 812, 1911; **8**, p. 587, 1916.

[2] Waters, B. S. Bulletin, **7**, pp. 227–234, 1910 (Scientific Paper No. 153); and J. Ind. Eng. Chem., **2**, pp. 451–454, 1910.

substances are oxidation products and are most efficient oxygen carriers, which even at low temperatures accelerate the action of sunlight and air. By heat they become polymerized and changed into asphaltic matter, which can be precipitated by means of light gasoline. Finally, they can be removed by filtration through boneblack or fuller's earth. If they are not removed, heating the oil in the air produces more asphalt than would otherwise be the case.[3]

Facts such as these have been the chief arguments of those who believe that asphaltic matter, either present or formed when the oil gets hot in the engine, is the primary cause of the deposits. The oil is heated to a rather high temperature in contact with air, and it must, therefore, become oxidized. The laboratory test based upon this theory is intended to reproduce the essential conditions in the engine, while it eliminates such important but variable factors as changing temperature, dust, metallic particles more or less oxidized, and deposits left over from earlier lots of oil.

It has also been argued that because these resinous substances can be removed in the refinery, as shown by tests of many brands of automobile oils, their presence is evidence of careless or improper refining.

(c) CATALYZERS WHICH CAUSE OXIDATION.—*Alkalies, etc.*— Other substances which cause rapid oxidation of oil are alkalies, soap, rosin, iron oxide (rust), and sulphur compounds.[4] Perhaps most of these act as "oxygen carriers" in much the same way as the driers used in paints and varnishes for the purpose of hastening the drying of the film by oxidation. The soap, and especially the alkalies, neutralize, and thus in effect remove the acids which are formed by the oxidation of the oil.

Dust and Dirt.—The effect of particles of dust and dirt was well shown by one sample of oil which was tested. It contained numerous particles distributed through it. These were allowed to settle for 24 hours before the oil was tested. The amount of asphaltic matter formed by heating was 0.91 per cent. Evidently the time allowed for settling was not long enough, because after the oil had stood undisturbed for some weeks it was again tested. This time it gave only 0.55 per cent of asphalt, an amount in close agreement with that found for other samples of the same brand. Perhaps the high result was due to the presence of iron rust in the particles of dust and dirt.

[3] Waters, B. S. Tech. Papers, No. 73, p. 10.
[4] Waters, B. S. Tech. Papers, No. 4; and J. Ind. Eng. Chem., 3, p. 812, 1911.

Sulphur.—Because the oxidation of oil is influenced by so many different substances, it is unsafe to say that if any one of them is absent, or present in only very small amount, little asphaltic matter will be formed when the oil is heated. The effect of other catalyzers which are present may be great enough to give high results. This is shown by the oxidation of 10 oils which contained varying amounts of sulphur in organic combination. Table 1 gives the percentages of sulphur ˉand of asphaltic matter formed by heating the oil in contact with air.

TABLE 1.—Percentages of Sulphur and of Asphalt Formed by Heating

Material	Percentages of sulphur and of asphalt formed with various oils									
	1	2	3	4	5	6	7	8	9	10
Asphalt.........................	0.01	0.02	Trace.	Trace.	0.29	0.34	0.56	0.84	1.43	3.55
Sulphur.........................	.05	.08	0.04	0.04	.05	.36	.29	.40	.38	.37

The results on oils 1 to 4 show that those which yield little asphalt are low in sulphur. The reverse of this is not always true, for No. 5 gives a considerable amount of asphalt although it is low in sulphur. Nos. 6 to 10 are comparable as regards sulphur content, but quite different in their yields of asphalt.

(*d*) OXIDATION AND OTHER PROPERTIES.—When it was found that oils differ greatly in their tendency to become oxidized, attempts were made to correlate this tendency with their behavior in other respects.[5] The first thought was that members of the ethylene (olefin) series were responsible. These are what the chemist calls "unsaturated" compounds, because they do not contain as many hydrogen atoms as the paraffins with the same number of carbon atoms. The parts of the molecule where these missing hydrogen atoms should be are susceptible of attack by reagents. Oxygen, and particularly chlorine and bromine, readily combine with the hydrocarbon molecule at these points. The same is true of sulphuric acid. The iodine number, or the percentage of iodine which combines with an oil, is a fair measure of the degree of unsaturation. The same is true of the Maumené number, or the rise in temperature when the oil is vigorously stirred with concentrated sulphuric acid.

Determinations were made of the iodine and Maumené numbers of three oils whose behavior on heating was known. Contrary to expectation, the oil which was least easily oxidized at

[5]Waters, B. S. Tech. Papers, No. 73, pp. 9–13, 1916; J. Ind. Eng. Chem., 8, pp. 589–590, 1916.

both high and low temperatures gave the highest values for these two numbers. The following is suggested as a possible reason, though without adequate evidence. Although the iodine and Maumené numbers show that this oil is the highest in its content of unsaturated hydrocarbons, the low value for asphalt, or its low rate of oxidation, indicates that it contains a smaller amount of the necessary oxygen carriers than the other two oils.

Certain determinations were made on these three oils before and after they had been exposed to the action of air and direct sunlight for a long time. In Table 2 are given the gains in weight (oxygen absorbed less carbon dioxide and water lost) of 10-gram samples on exposure, the iodine and Maumené numbers, the percentages of asphalt formed on heating, the acidities expressed as mg of caustic potash required to neutralize 1 g, and the demulsibilities.

TABLE 2.—Effects of Oxidation on Some Properties of Oils

Oils	Gains in weight	Acidity	Asphalt	Mau-mené number	Iodine number	Demulsi-bility
Original oils:	mg	mg, KOH	Per cent	°C		
No. 1		0.06	0.14	8.3	31.4	270
No. 2		.04	.17	7.3	29.8	270
No. 3		.03	.30	7.1	30.2	360
Oxidized oils:						
No. 1	236	3.40	.90	20.9	20.4	20
No. 2	253	3.70	1.38	19.9	19.1	32
No. 3	252	3.67	1.75	18.9	20.6	45

HOURS EXPOSURE

	438	419	419	438	438	238

The increases in the acidity and in the amount of asphalt were to be expected from previous experience. The entry of oxygen into the molecule lowered the iodine numbers. Because these oxygen compounds were presumably more reactive than the hydrocarbons, the Maumené numbers showed marked rises.

Demulsibility is the rate, in cc per hour, at which an oil separates from its emulsion with water. Other things being equal, the better refined the oil the greater the demulsibility. The data in the table show the effect of the oxidation products.

If the flash and fire points were given in the table, the conclusion might be drawn that the lower these values the greater the rate at which the oil becomes oxidized. The flash points of

the oils were 215°, 210°, and 205° C (419°, 410°, and 401° F), and the fire points 270°, 260°, and 250° C. (518°, 500°, and 482° F), respectively. This relation does not always hold, as shown by the data in Table 3.

TABLE 3.—Independence of Asphalt Formation and the Flash and Fire Points

Flash point, °C	125	165	190	195	195	200	200	205	225
Fire point, °C	205	205	220	235	235	240	250	245	265
Asphalt, per cent	0.42	0.41	0.06	0.29	0.16	1.05	0.22	0.39	0.06

The amount of asphalt formed is also independent of the volatility of the oil, that is, of the percentage which is lost by evaporation while it is being heated. This is of course to be expected, because the fire point and volatility are so closely related. The results in Table 4 are for the three oils for which data were given in Table 2. The evaporation losses on heating to 250° C (482° F) for three and five hours, respectively, and the corresponding percentages of asphalt are given. Incidentally it will be seen that the losses in duplicate determinations show much less close agreement than the percentages of asphalt.

TABLE 4.—Independence of Asphalt Formation and Evaporation Loss

[All figures are percentages.]

	Oil No. 1	Oil No. 2	Oil No. 3
Evaporation in 3 hours	17.3 19.3	19.6 23.9	21.0 22.5
Corresponding asphalt	.16 .14	.17 .18	.30 .30
Evaporation in 5 hours	21.3 24.3	27.2 30.7	26.8 29.5
Corresponding asphalt	.51 .51	.56 .55	1.09 1.05

It is shown in Table 5 that there appears to be no relation between the percentage of asphalt formed by heating and the viscosity of the oil. The figures show the percentages of asphalt and the viscosities in seconds as determined at 100° C (212° F) by the Saybolt universal viscosimeter. The percentages of carbon given in the table were determined by the Conradson carbon residue method, which will be described farther on. (See p. 34.)

TABLE 5.—Independence of Asphalt Formation and Viscosity

Asphalt (per cent)	0.32	0.18	0.72	1.26	0.15	0.10	Trace.	0.21
Carbon residue (per cent)	.05	.40	.18	.15	.54	.40	1.17	.07
Viscosity (time, in seconds)	42	42	42	56	55	68	87	115

2. CRACKING OF PETROLEUM

(*a*) Nature of Cracking.—It has already been said that many oil chemists believe that the chief cause of the formation of deposits in the engine is the breaking down, or cracking, of the oil at the high temperatures which prevail, and that the higher percentage of carbon in the heavier oils which are used, or even free carbon contained in them, is responsible. In reply to this it was pointed out on page 9 that the percentage of carbon rises very slowly, in the paraffin series, as the number of atoms of that element in the molecule increases. In the naphthene series the percentage is the same, no matter how many carbon atoms there may be. The heavier oils break down because their molecular structure becomes unstable at or below the temperatures at which they would be expected to boil under atmospheric pressure. In closed vessels at very low pressures they can be distilled with almost no change, because their boiling points are then below the temperatures at which they crack. In the engine, with high temperatures and increased pressures, the conditions are favorable to cracking.

(*b*) Conditions Which Influence Cracking.—The cracking of petroleum is said to have been discovered by Silliman in 1855, but it did not become a matter of practical interest to oil refiners until 1861, and then owing to the carelessness of a workman who was in charge of a still.[6] This happened in the days when kerosene was the most valuable product obtained from crude oil, and for many years the cracking was so controlled as to yield the greatest possible amount of kerosene. In more recent years the effort has been to increase the yield of gasoline by more complete cracking. Many processes have been devised and patented. There is an enormous literature on the subject, but it is nearly all outside of the scope of the present paper. A brief account must be given, however, of some of the conditions which affect cracking.

Effects of Temperature and Pressure.—High temperature is of first importance. At atmospheric, or even somewhat reduced pressures, oils will crack if they can be heated high enough without distilling. Oils of lower boiling points, which under ordinary pressures can be distilled without change, can be cracked in the liquid phase if subjected to sufficiently high pressures to prevent their boiling. The gaseous hydrocarbons, or the liquid ones when vaporized, can be cracked if heated to high enough temperatures.

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[6] Most of the statements about the cracking of petroleum have been adapted from Bacon and Hamor's American Petroleum Industry, pp. 554 to 571; 1916.

There is never a complete breaking down into carbon and hydrogen.[1] This would be possible only under the most extreme conditions, if at all, because there would be a partial recombination of the two elements at very high temperatures. The formation of acetylene, C_2H_2, has been observed when hydrogen and carbon were heated together at 1800° C (3272° F).

In all cracking processes there is some deposition of carbon, with simultaneous formation of hydrogen and a mixture of hydrocarbons, which are either gases, or liquids of lower boiling points than the original oil. The paraffin, naphthene, benzene (aromatic), and ethylene (olefin) series are all represented. The nature and proportions of the different products depend upon the kind of oil which is cracked, upon the temperature of the still, the pressure, etc.

The members of the ethylene, or olefin, series are less stable than the paraffins when heated. They usually make up a considerable proportion of the products of cracking. The naphthenes are still more stable than the paraffins. Even though they may be absent from the original oil, they are found in the distillates, having been formed by the polymerization of the olefins; that is, the molecules of the olefins combine with one another to form more complex molecules or groups of atoms. These two series have the same percentage composition, for in each there are two hydrogen atoms to every carbon atom. They differ greatly in their molecular structure.

Effects of Catalyzers, etc.—Besides the effect of pressure upon cracking, the chemical reactions which take place can be affected in other ways. Various metals, clay, alumina, and other substances facilitate the breaking down of the oil molecules. Use is made of such catalyzers in some of the commercial processes, sometimes in conjunction with steam, sometimes with hydrogen, to lessen the percentage of the comparatively undesirable olefins.

Of particular interest in connection with the lubrication of engines is the fact that the rate of cracking is nearly proportional to the area of oil surface in contact with the heated metal. In the engine, with its thin films of oil, it would appear as if the conditions were extremely favorable for this breaking down. Another fact is that the reactions are hastened if the new compounds are removed as fast as they are formed. In this respect, also, the conditions in the engine are favorable, because the lighter or more volatile products are burned or escape with the exhaust gases.

14115°—20——3

The relatively heavier products of cracking, which are not vaporized or burned, help to thin the lubricating oil. Leakage of gasoline past the piston rings during compression, with retention of its less volatile portions, or "heavy ends," by the oil, has usually been regarded as the chief cause of the thinning. However, experiments performed at this Bureau with an engine to which a glass intake manifold was fitted showed clearly that under ordinary operating conditions a large amount of liquid gasoline flows into the cylinder. The quantity is greater the lower the temperature of the manifold. Of course, the greater part of this gasoline is burned, but enough is retained to account for most of the thinning of the lubricating oil.

· In parts of the engine the temperatures are high enough to crack the oil, for under some conditions it will begin to break down at 300° C (572° F), or even lower. In refinery operations the temperatures employed are much higher.

V. CARBONIZATION TESTS DEPENDING ON OXIDATION

1. SLUDGING TEST

This test has been much used in testing transformer oils. One method of making it is as follows:[7] Heat 150 g of the oil, contained in a 400 cc Erlenmeyer flask, in an oil bath at 120° C (248° F) for 70 hours. Pass oxygen into the oil through a tube of at least 3 mm bore, and at the rate of two bubbles a second. After this warm 50 g of the oxidized oil with 50 cc of alcoholic soda for 20 minutes on a boiling-water bath. The flask must be connected with a return condenser. The alcoholic soda is made by mixing 1000 parts by weight of alcohol, 1000 parts of water, and 75 parts of caustic soda.

Remove the flask from the bath, attach a condensing tube, and shake vigorously for 5 minutes. Transfer the mixture to a separating funnel and draw off as much as possible of the alcoholic layer through a filter. Acidify 40 cc of the filtrate with hydrochloric acid and extract the tar which separates with two successive portions of benzene. Wash the tar solution twice with water, evaporate off the benzene in a glass dish, dry the residue at 100° C (212° F) for 5 minutes, weigh, and calculate the percentage on the basis of the 50 g of oil taken.

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[7] See Höfer, Das Erdöl, 4, pp. 88–89. The General Electric Co.'s test (the "G. E." test) is similar to this. It consists essentially in blowing a fine stream of bubbles of oxygen through the oil while it is heated, either with or without the presence of copper. The test may not be described in detail at present, because it is undergoing investigation to determine modifications which appear to be necessary, or desirable, for the purpose of standardization.

2. GUMMING TEST [8]

For this test prepare nitrosulphuric acid as follows: Dilute 560 cc of commercial sulphuric acid to 1 liter. This gives acid of specific gravity 1.47. Add a few drops of nitric acid and saturate with the oxides of nitrogen prepared by the action of nitric acid upon copper. Cool in ice water and again saturate with the gases. This liquid is known as Roth's liquid.

The test is performed as follows: Thoroughly mix 5 g of oil in a cordial glass with 11 g of nitrosulphuric acid and cool by setting in water at 10 to 15° C (50 to 59° F). "Brownish spots, or, in case of a bad oil, masses, form around the edges and become red in the course of two hours. The cordial glass is filled successively three times with 70 to 86° naphtha and the oil dissolved off the surface of the acid, the gasoline solution being sucked off into a bottle with an air pump. Care is taken not to suck off any of the tarry matter formed. The acid can be neutralized with ammonia, and the tar can be collected on a tared filter, washed with gasoline that leaves no residue on evaporation, dried at a low temperature, and weighed as gummy matter. As shown by long practical experience, the oil showing the least tar or gum is the best oil; it also absorbs the least oxygen."

3. TAR AND COKE TESTS

These tests were devised by Kissling,[9] who determined two "numbers" both before and after heating the oil.

The resin or tar number is determined by warming the oil in a flask with an alcoholic solution of sodium hydroxide made up as prescribed for the sludging test for transformer oils. In fact, the entire procedure is the same in the two cases, except that the oil is not first heated.

The coke number is found by diluting the sample, of which the tar number has been found, with 500 cc of petroleum ether. The precipitate is filtered off next day, washed with the ether, dried, and weighed.

After another portion of the oil has been heated to 150° C (302° F) for 50 hours, the operations just mentioned are repeated. The results give the tar-forming and coke-forming numbers.

4. WATERS TEST

The method about to be described has come to be known by the name just mentioned. It is very much like Kissling's method

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[8] A. H. Gill, J. Amer. Chem. Soc., 24, p. 467, 1902; and Oil Analysis, later editions. Gill's description of the method in Scott's Standard Methods of Chemical Analysis, ed. 2, p. 578, is used here.

[9] Kissling, Chem.-Ztg., 30, p. 932, 1906; 31, p. 328, 1907; 32, p. 938, 1908; 33, p. 521, 1909.

for the determination of the coke-forming number. It differs from it in that the treatment with alcoholic soda is omitted, as well as in other less important details.

(*a*) Condensed Directions for Waters Test.—The procedure, in brief, is as follows: Weigh 10 g of oil in each of four flasks and place these in the air bath. Then turn on the heating current and raise the temperature of the bath to 250° C (482° F) in 30 minutes, as nearly as possible. Maintain the bath at this temperature for two hours, turn off the current, and allow the flasks to cool for about one hour. Remove them, add 50 cc of petroleum ether to each, cork tightly, and gently swirl the contents to dissolve the thickened oil. Next day filter off the precipitate in a Gooch crucible in which is a disk of filter paper covered with a thin layer of asbestos. Wash with petroleum ether, dry at 100° C (212° F), cool in a desiccator, weigh, and calculate the percentage of asphaltic matter on the basis of the original 10 g of oil. This percentage is the "carbonization value."

(*b*) Preliminary Experiments.—In the preliminary experiments the flask containing the oil was heated in a large iron crucible provided with a cover in which were two holes. Through one of these holes the neck of the flask passed and through the other a thermometer. The flask was to be kept at 250° C (482° F) while a slow current of heated air was bubbled through it. It was found impossible to regulate either the temperature or the air current, so for these and other reasons the arrangement was abandoned. In its stead a cubical copper bath was made with a special slotted cover which held four flasks suspended by their necks. In this way the mouths of the flasks were open to the air outside of the bath. Convection currents were depended upon to renew the air in contact with the surface of the oil. It is essential that the oil be given every opportunity to become oxidized.

This bath was heated by gas, but it has been replaced by one which is electrically heated and controlled. Apart from the difficulty of maintaining a uniform temperature with gas, it was recognized that the products of combustion from the flame were a possible source of error. Even with a flame placed symmetrically under the bath, a slight draft might make the conditions on one side more favorable to oxidation than those on the other side.

(*c*) The Air Bath.—The bath is a copper box, 23 cm square and 22 cm deep. The metal is bare on the inside because this helps to distribute the heat more uniformly. Outside on the sides and bottom the bath is covered with asbestos board. That on

the sides is in three layers, each about 2 mm thick. The layers are kept slightly apart by narrow strips of asbestos board, so as to have the extra insulating effect of the air spaces. Only one layer is on the bottom because the bath rests in a shallow wooden tray.

The cover consists of two principal parts. One of these, *A*, Fig. 1, is little more than a narrow horizontal rim projecting inward around the upper edge of the bath. As it is not often removed, it is held in place by 8 vertically projecting strips
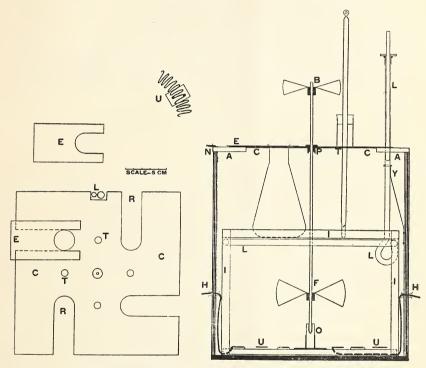

FIG. 1.—*Vertical section through air bath, plan of cover, and detail of heating coil*

of brass, 2 at each corner of the upper edge of the bath, which pass through holes in wider, horizontal strips, *N*, on the rim. Brass escutcheon pins which fit in holes in the vertical strips hold the rim firmly in place. The rim, *A*, is covered with asbestos board riveted on. The edges of the rim and of the body of the bath are given a neat finish by means of asbestos "baking sheets" cut into strips and glued on.

Resting upon the rim or fixed part of the cover is a movable one, *C*, of sheet copper which holds the flasks and thermometers. Four openings, shown at *R* in the plan, are cut to admit the necks of the flasks. Four other pieces, *E*, completely close the bath

when the flasks are in place.   Asbestos board is riveted to the undersides of C and E.   In addition, the top of C is covered with sheet asbestos put on wet and with its edges turned over to the board on the underside.   Four holes, T, were made for the thermometers, so as to ascertain how uniformly the bath was heated. In testing oils two thermometers are used.

The heating coil, U, consists of nichrome ribbon about 0.79 by 0.28 mm in cross section and having a resistance of 4.2 ohms per meter.[10]   At the suggestion of a former chemist of the Bureau, the ribbon is bent in zigzags, as shown at U near the top of Fig. 1. This makes it easy to attach the ribbon in a flat spiral with three turns to a square piece of heavy asbestos board.   It is tacked on with short escutcheon pins.   At intervals of about 5 cm (2 inches)
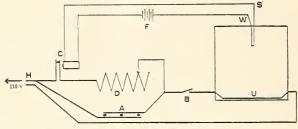

FIG. 2.—*Wiring diagram (not drawn to scale)*

small squares of asbestos board are placed under the spiral, so that nearly all of it is free in the air.

The ends of the ribbon are silver-soldered to heavy copper wires which run down through the board and then out through holes in the sides of the bath.   Short lengths of glass tubing, H, pass through these holes and serve to insulate the wires.   The tubes are flared at the ends to hold them in place.   The wires are insulated from the bottom of the bath by a piece of thin asbestos board laid beneath the heating element.

The wiring outside of the bath is shown in Fig. 2, which requires little explanation.   It is not drawn to scale.

The terminals W and S are at the upper part of the thermoregulator.   They are connected with the primary battery F and the relay C.   The latter is so arranged that the portion of the heating current which flows through the sliding resistance D is broken when contact is made in the regulator.   When this occurs, all of the heating current must flow through the bank of lamps A.   Usually only one of the three lamps is kept screwed down in

[10] The data given on the spool of ribbon are: 1/32 by 0.011 inch, and 1.28 ohms per foot.

the socket after the bath has reached the desired temperature. The action of the relay has the same effect as increasing the resistance outside of the bath. By not cutting off all of the current which flows through the heating coil U in the bath, the fluctuations in the temperature are diminished.

B is a knife switch, and at H are wires leading to a socket on the 110-volt lighting circuit.

In order to distribute the heat more uniformly throughout the bath, a four-bladed fan F, 8 cm in diameter, rotates about 5 or 6 cm above the coil. (See Fig. 1.) The blades are turned so that the air is thrown down upon the coil. The motive power is an 8-bladed propeller B, 7 cm in diameter, at the upper end of a light steel shaft. Upon it impinges a stream of air from the laboratory blower. The air issues from a glass tip which has a nearly vertical opening about 0.5 by 3 mm. Owing to its size and shape it furnishes a considerable current of air at a velocity high enough to cause the propeller to make several hundred revolutions a minute. The tip is at the end of a glass tube which is about 45 cm (18 inches) long and is bent at a right angle near the middle. The end which is connected with the compressed air system is held nearly vertically in a clamp on an iron stand at the back of the bath. With this arrangement the end with the tip can be swung back out of the way when the cover is placed on or removed from the bath. (All of this is omitted from the drawing Fig. 1.) Such a propeller, attached to a glass stirrer, has been used for determining the Maumené numbers of oils. B and F are made from circular disks of thin sheet brass silver-soldered to short pieces of brass rod which are drilled to fit the steel shaft. Set screws (not shown) hold them in place. The lower end of the shaft is conical and revolves in a hole drilled in a block of Acheson graphite. This is held in a brass socket, which is screwed down at the center of the heating coil. A small brass bushing P in the cover keeps the shaft vertical. It is a convenience to have the lower end of P funnel shaped.

To prevent, as far as possible, any contamination of the oil while it is being heated, a light, brass frame supports a sheet-brass screen about 5 cm (2 inches) above the cover C. These are not shown in the drawing. The screen must be below B because the oil vapors which condense on the propeller are sufficiently acid to attack brass, and drops of the resulting green liquid are flung off the blades. They would affect the results if they fell into the flasks which contain the oil. The screen is perforated for the

passage of the shaft and two thermometers. A curved glass screen, cut from the side of a large bottle, is placed close to the propeller to prevent the spattering of oil drops upon the floor and the clothing of the operator.

The thermometers T pass through corks inserted in short lengths of glass tubing, which rest upon C. This prevents the burning of the corks. The bulbs are at the level of the oil in the flasks.

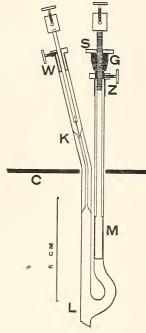(d) *The Thermoregulator.*—The thermoregulator LL, Fig. 1, consists of a horizontal mercury reservoir made of glass tubing, which runs around close to the four sides of the bath slightly below the level of the flasks, and a vertical part which branches some distance below the cover of the bath. (See Fig. 3, which shows this vertical part as viewed from another position.) The body of the regulator is horizontal and is supported by copper wires silver-soldered to a light frame I. This is made of strips of sheet brass, bent lengthwise to form angle pieces, which are silver-soldered together at the corners. The legs are of such a height that, if desired, a square of wire netting laid upon the frame will support shallow dishes at the same level as the bottoms of the flasks. To lessen the danger of breakage, the vertical part of the regulator is wired to a brass strip Y, one end of which is riveted to the wall of the bath.

FIG. 3.—*Details of Thermo-regulator*

The essential features of the regulator are shown in Fig. 3, where the details of the upper portion are given. The brass cap W and the collar Z are fastened to the ends of the glass tubes by means of a cement made by melting together 1 part of shoemaker's wax and $2\frac{1}{2}$ parts of shellac. The cap W holds a binding post at its upper end; at its lower end is a nickel wire which runs a short distance into the capillary tube at K. Nickel is preferable to platinum for this purpose because it has less tendency to become amalgamated by the mercury in the tube, and the contact is broken more sharply.[11] The soft solder which holds the nickel wire in the end of the rod is covered with a thin layer of the above cement to protect it from the mercury.

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[11] W. M. Clark, J. Amer. Chem. Soc., **35**, pp. 1899–1890; 1913.

The collar Z holds a second brass piece, G, which slips easily along the threaded steel rod from S to M. The upper end of this rod is provided with a binding post. The lower end M acts as a plunger and is therefore made to fit the glass tube so closely that mercury will not flow past it. It is not a tight fit, but has a lateral play of two or three tenths of a millimeter in the tube. In assembling the apparatus, M is depressed to its lowest point while the cement which holds Z is hardening, so that the rod will be as nearly as possible coaxial with the tube. The reason for having the collar G is to permit the convenient removal of the steel rod on the few occasions when it is necessary to clean out the glass tubes or to change the amount of mercury.

S is a brass disk threaded so as to turn on the steel rod. By turning S the plunger is raised or lowered so that it displaces more or less mercury. In this way contact can be made with the nickel wire at any desired temperature over a wide range. Without changing the amount of mercury the present apparatus can be held anywhere between 210 and 290° C (411 and 522° F). So wide a range is not necessary, except perhaps for special work.

A regulator embodying the same ideas was constructed about 1908 for use in a bath heated by gas. Instead of the brass cap W and the rod which carries the nickel wire, there was a tapering steel tube fastened in place by cement. It ended just above the capillary part of the glass tube. The gas entered through the steel tube and passed out to the burner through a glass side tube sealed on just above the capillary. In the side of the steel tube was a tiny hole, just large enough to allow the passage of sufficient gas to keep the burner lighted when the main supply was cut off by the mercury rising in the capillary. The temperature at which this took place was adjusted by means of a plunger.

It is plain that this regulator is a modification of the familiar Reichert form, but has the advantage that the mercury can not leak out at the adjusting screw. Long after it was constructed similar regulators were described by Slator [12] and by Fontaine.[13]

(e) ESSENTIAL CONDITIONS OF TEST.—It should be understood clearly that elaborate and expensive apparatus is not necessary for making the test. The essential conditions are: (1) An ample supply of air circulating over the surface of the oil; (2) flasks or dishes in which practically the same area of oil surface is exposed to the air; (3) adequate temperature control.

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[12] J. Soc. Chem. Ind., **30**, pp. 61–62; 1911.   [13] Ann. chim. anal., **16**, pp. 52–53; 1911.

The Flasks.—The first and third of these conditions will be cared for by the above or any other suitable air bath. The size of the flasks which are used at this Bureau was decided upon by measuring the internal diameter at the widest part, as well as the bore of the neck, of a new lot of Erlenmeyer flasks of 150 cc capacity. More flasks of 65 mm ($2\frac{9}{16}$ inches) diameter could be found than of any other size, so that these were adopted as standard. Flask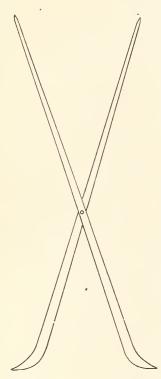s of this size have always been found in later shipments and of other makes. The bore of the neck is of secondary importance. The size selected was 21 or 22 mm (about $\frac{27}{32}$ inch). In measuring the flasks it was surprising to see how nearly circular in cross section the majority of them were.

Contrary to expectation, the thickness of the glass is of no practical importance. In one set of 12 the extreme weights were 29.37 and 42.64 g, yet they gave the same results in testing a given oil.

If a suitable inside caliper is not at hand one can be made easily from two strips of sheet metal filed to the shape shown in Fig. 4 and riveted together near the middle. The caliper is opened until the curved ends touch the inside of the flask at the widest part; the distance apart of the straight tips is then measured with a ruler. The caliper shown is 20 cm (8 inches) long. When opened 65 mm at the curved ends the points at the other are 52 mm apart. This ratio permits of sufficiently accurate measurements.

FIG. 4.—*Caliper for measuring oxidation flasks*

(*f*) TECHNIC OF OPERATION—*Heating.*—The technic of operating the bath is not as complicated as it may appear from the following description: In making a determination of the "carbonization value" 10 g samples are weighed, to the nearest drop, in the flasks. The necks of the flasks are inserted in the slots *R*, the small covers *E* are adjusted, and then the whole is placed on the bath. In doing this the steel propeller shaft is easily slipped through the funnel-shaped lower end of the bushing *P*. This done, the thermometers are inserted, the dust screen is put in

place, and the propeller B is fixed at the right height by means of the set screw (not shown). The stirrer is started by swinging the arm which carries the glass tip into place and turning on the air. All this takes but two or three minutes after the oil has been weighed out.

The heating current is now turned on. The sliding resistance and the lamps are arranged so as to bring the bath up to the desired temperature as rapidly as possible. This takes about 30 minutes for 250° C (482° F). When the bath is hot enough only one lamp is left in the circuit and the sliding resistance is so adjusted that the primary battery circuit which actuates the relay is closed only every three or four minutes. Considerable experience has shown that this is the best working condition, principally because the mercury is heated slowly and is less apt to force its way up past the end of the nickel wire K, where a drop of it will become trapped when the circuit is broken. This in effect lessens the amount of mercury in the regulator, so that the temperature must go to a higher point before contact is again made at K. With proper adjustment of the sliding resistance the mercury gradually approaches the wire and is not forced up above the capillary, so that the primary circuit will be closed for not more than a very few seconds at a time and will be broken again before the temperature of the bath has had time to drop as much as 1°.

The regulator is so constructed that practically all of the mercury is inside of the bath. The steel rod, however, is nearly all outside and it does not attain its maximum temperature at once. The result is that it has not expanded to its full length when the bath first reaches the required temperature, and contact at K is not made until a point 1 or 2° higher is attained. By suitable manipulation of the sliding resistance, or of the disk S, this difficulty is overcome.

In all of the testing at this Bureau the oils are heated to 250° C (482° F). The bath reaches that point in 30 minutes and is kept there for 2 hours, after which the current is turned off and the flasks are left to cool for about an hour before they are removed. A complete run thus takes three and one-half hours and two runs. or eight analyses, can be made in one laboratory day.

Precipitation and Filtration.—If the evaporation loss is to be determined, the cooled flasks are weighed after they have been removed from the bath. Then to each flask is added quickly 50 cc of petroleum ether (86 to 88° gasoline), a soft, tight cork is

inserted, and the contents of the flask are gently swirled to dissolve the oil. Next day the insoluble precipitate is filtered off in a Gooch crucible, washed with petroleum ether and dried in an air-bath at about 100° C (212° F), cooled in a desiccator, and weighed. The percentage is calculated on the basis of the original 10 g of oil.

In transferring the precipitate to the crucible it is sometimes necessary to use a stiff feather from which all the barbs, but enough for a small flag at the end, have been removed. A rubber policeman is worthless. No attempt is made to remove the "varnish" from the walls of the flask. Its amount, like the loss by evaporation, is quite variable. There is no apparent quantitative relation between it and the amount of precipitate.

A porcelain Gooch crucible which holds 30 cc is used. A disk of close-fibered filter paper is placed in the crucible, wetted with a drop or two of water and covered with a thin layer of finely shredded asbestos, which is then dried in an air bath to constant weight. The reason for using the asbestos is to keep the edges of the filter paper from curling up when dried in the air bath. Enough paper disks for many determinations can be cut out in a few minutes from several thicknesses of larger papers by means of a sharp cork-borer. By cutting against a large cork the borer is less quickly dulled.

If the suspension of asbestos in water is measured in a small beaker (about 10 cc), practically the same amount will always be used and much time will be saved by having the approximate weights of the crucibles on a card. The combined variations in weight of the paper disk and the asbestos rarely amount to more than 10 mg.

With moderate suction a precipitate which amounts to a few tenths of a per cent can be filtered off and washed in four or five minutes. The flask is rinsed three times with petroleum ether, and then laid on its side, or inverted in a rack, to drain and to hasten the escape of the ether vapor in case the "varnish" is to be determined. In half an hour, at room temperature, it can be weighed.

If an all-glass wash bottle is used for the wash ether, a flask can be rinsed out three times with 10 or 15 cc, and three washings of the precipitate and walls of the crucible will take about as much more.

When there is a large amount of gummy precipitate, the filtration is slow, and there is much crawling of the oily solution, espe-

cially if there is a strong draft in the room. Fortunately the precipitate does not also crawl. When the filtration is slow, the crucible had better be covered with a small watch glass. In any case as much as possible of the clear solution should be poured through the crucible before the precipitate is transferred to it. The precipitate should not be sucked dry until after the last washing, for it may crack and the next lot of ether will pass between instead of through the lumps. If the pasty layer should crack, the lumps are to be broken up under 2 or 3 cc of petroleum ether by means of a stirring rod.

Cleaning the Flasks.—Preparatory to a new run, or if they have not been used before, the flasks are cleaned as follows: They are filled with a moderately strong solution of caustic soda in alcohol, closed with small watch glasses and allowed to stand for a few hours. They are then rinsed out thoroughly, shaken with coarse sand and water, rinsed with distilled water, and placed in a rack to drain and dry. The rack is a horizontal board supported on legs and having holes in which the flasks are placed. It is imperative that the flasks be thoroughly cleansed, for any of the varnishlike coating or precipitate, or any soda that may remain in them, will cause high results in the next determination. Drying the flasks on pegs may also introduce undesirable dust.

Pyridine is the only solvent for the varnish which has been found, but it goes without saying that it could not be used, owing to its disagreeable properties. Alcoholic soda dissolves only a little of the deposit, but loosens it from the walls of the flasks. By means of it the flasks can be cleaned much more rapidly than by heating on the steam bath with strong chromic-acid mixture.

Cleaning the Crucibles.—The crucibles are most easily cleaned by scrubbing them out with a little powdered fluorspar on the end of the moistened finger. This mineral does not scratch porcelain or glass. The crucibles are then rinsed out and prepared for another filtration. All of these operations can be performed in a very short time. As a test 8 crucibles which contained precipitates have been cleaned as described, prepared with new pads, and placed in the air bath within 15 minutes.

(*g*) NATURE OF THE PRECIPITATE.—Even after drying, the precipitate in the Gooch crucible is soluble in benzene (benzol), carbon bisulphide, and similar organic liquids. This shows that in spite of cracking during the heating there is no formation of free carbon. The appearance of the oil also shows this. It is, of course, darker than before it was heated, but is almost always

perfectly clear.   Not more than one or two out of a hundred oils
is turbid before the petroleum ether is added. . The phenomenon
is so infrequent as to attract attention.   One of the most remark-
able cases was that of a white medicinal oil made from a Cali-
fornia crude.   It was strongly clouded when removed from the
bath.   The precipitate formed by the addition of petroleum ether
was of a peculiar gummy consistency instead of being flocculent.
It hardened in glossy masses which could not be scraped off the
glass without danger of breaking the flask.

(*h*) VARIATIONS IN THE APPARATUS.—The method and appa-
ratus in use at this Bureau have been described in great detail,
not because they are the best possible, but because they have
been found to give reproducible results with comparatively little
trouble.   They are not the last word on the subject.   The bath
and the technic are not as complicated as may appear from the
description.   Most of the work on the bath and regulator was
done, not by a mechanician and skilled glassblower, but by one
of the chemists.

As stated on page 25, one of the essentials in making the test
is to have an ample supply of air circulating over the surface of
the oil.   This is self-evident, because the method depends on
oxidation.   It has been found that when the oil is heated in closed
flasks there is practically no formation of asphaltic matter.   If
the test is made in an air bath in which the flasks are placed so
that the outer air does not reach the surface of the oil directly,
there will be a smaller amount of precipitate unless the bath is
unusually well ventilated.   Two or three air baths, known to have
been specially designed for making the test and which cost a great
deal, were failures because of insufficient ventilation.

The objection should not be raised that the bath in use at this
Bureau imposes unduly severe conditions upon the oils.   Many
samples are received which yield only traces, or at most a few
hundredths of a per cent, of precipitate.

Tests made with an electric hot plate of a familiar type on the
market indicate that with certain changes it would be satisfactory.
The chief difficulty is uneven heating in different parts of the cir-
cular top.   With constant voltage it would be easy to maintain
the plate at any desired temperature by regulating the resistance
in the circuit.   With the usual lighting current, however, the
voltage is rarely sufficiently constant for the length of time required
for a run, so that control by hand or the use of a thermoregulator
is necessary.   If a hot plate is used, it should have a sheet-metal

cover which fits down over the flasks, but with holes through which their necks project. A small motor-driven stirrer equalizes the temperature inside of the cover.

In at least two laboratories connected with refineries oxidation baths are in regular use. They are not of the same design as the one at this Bureau.

(*i*) VARIATIONS IN TECHNIC.—An important variation in the method of making the oxidation test is to bring the flasks to the desired temperature before introducing the oil. This is done in at least one laboratory,[14] and there is much to be said in favor of it. The strongest argument is that the oil is brought to the desired temperature almost instantly, in spite of fluctuations in the heating current. At this Bureau a set of determinations must once in a while be rejected because the voltage is so low that the bath does not reach 250° within the time limit. The modification of the usual procedure has not been tried, however, because the apparatus does not seem adapted to it.

In some laboratories shallow dishes of glass, nickel, iron, or other metal have been used instead of flasks. Even if there were no catalytic effects due to the oxides of the metals, or to the metals themselves, dishes are not as satisfactory as flasks. Iron dishes, always somewhat oxidized, give slightly higher results than nickel ones. In order to properly precipitate the asphalt it should be allowed to stand for 12 hours or more in a tightly closed vessel after the addition of the petroleum ether. To transfer the thickened oxidized oil without loss to a flask by means of a definite, known volume of petroleum ether is difficult. It has been claimed that dishes should be used in spite of this difficulty, because they can be matched in size so much better than flasks. Some have gone so far as to say that a variation of only 0.025 mm (0.001 inch) will make a noticeable difference in the amount of asphalt formed.

Some who use dishes heat a large sample, say 50 g, of oil and afterwards transfer 10 g to the precipitation flask. There are several reasons why results by this procedure may not agree with those obtained by heating only 10 g in flasks. The rate of oxidation depends upon the area of the oil surface, and the dishes should therefore be of proportionately greater diameter than the flasks. Many oils yield very small amounts of precipitate and the test must be made strenuous enough to show differences between them rather than between the more easily oxidized oils.

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[14] Private communication from P. H. Conradson.

With the above proportions, 10 g represents more than one-fifth of the original 50 g, because some has evaporated. Not only that, but different oils, or even two portions of the same oil, will not lose the same amount by evaporation. The differences between the losses in duplicate determinations are by no means small, but are often as much as 5 or 6 per cent, and may be even 10 or 12 per cent. The figures in Table 4 do not represent extreme values. Owing to these differences in the amount of evaporation, the quantity of oxidized oil to be taken for precipitating the asphalt should be calculated for each sample, or the evaporation loss should be taken into account in figuring the percentage of asphalt. This is especially true of oils which yield large amounts.

Another important variation in the technic is to measure the volume occupied by the precipitate instead of filtering it off and weighing it. The mixture of oxidized oil and petroleum ether is placed in a glass bulb or tube, the constricted lower end of which is graduated. The tube is then whirled in a centrifuge until there is no further diminution of the volume occupied by the precipitate. There are several objections to the adoption of this procedure for general use. The force with which the precipitate is packed into the bottom of the tube depends not only upon the number of revolutions per minute of the centrifuge but also upon the radius of the circle described by the end of the tube. Both the tube and the centrifuge would have to be standardized and a definite speed of revolution agreed upon. The volume of the precipitate also depends upon how long it has stood after the addition of the petroleum ether. With most oils the asphalt comes down in a very loose, flocculent condition. It is at first not easy to filter off, but after some hours it seems to become more compact and granular. How compact and granular depends on the nature of the oil. Usually the precipitate makes a putty-like or clayey mass when first filtered off, but that which is formed from some oils is in granular particles too coarse to adhere to one another. These particles would not settle to the same volume as an equal weight of the finer ones.

If proper allowance is made for the sources of possible error, the centrifuge method is no doubt as good as any for refinery control. In a testing laboratory where oils from many, and usually unknown, sources are tested, the method by weighing seems preferable.

(*j*) CHOICE OF TEMPERATURE AND TIME OF HEATING.—The temperature at which the test is run was originally selected because

it is an easy one at which to maintain the bath, it is sure to be below the boiling points of any oils that are likely to be tested, and it is high enough to cause oxidation. Data have been obtained which show that the oils might be tested at temperatures well below or above 250° C (482° F), but for the same time of heating the results will be lower or higher than at that point. The same is true if the time of heating at 250° is less or more than 2½ hours. This length of time was chosen for convenience, as already explained. Graphs drawn by plotting the carbonization values against the time and the temperature show that the conditions finally adopted give reliable comparative data.[15] At temperatures below 250°, or for shorter runs than 2½ hours, different oils may yield nearly the same amounts of asphalt, but heating at 250° for 2½ hours causes the oils to diverge enough from one another to show how they may be expected to act under more strenuous conditions.

It has been argued that the test should not be run at the same temperature for all oils; if 250° C is suitable for medium oils, the light oils should not be heated to so high a point, while the heavy ones should be raised to a higher temperature. Data accumulated in the laboratory show that of three grades of the same brand of oil, the heaviest is apt to have the lowest carbonization value. Assuming that all three grades are equally "good," it might be claimed that they should be tested at such different temperatures as to make them all yield the same percentages of asphalt. This would be an extreme attempt at refinement of method. It is believed that little would be gained by working at different temperatures. The heaviest oil of a brand does not always have the lowest carbonization value, while the medium grade as often as not gives results higher than those of the light oil. Among different brands there are no set limits of viscosity for the three grades, and any dividing line would have to be drawn entirely arbitrarily. If an oil which was classed by the refiner as medium fell above this arbitrary line and were tested at the higher temperature chosen for the heavy oils, complaint could justly be made.

In actual use the oils are subjected to the most varied conditions of temperature, richness of the gasoline-air mixture, amount and kind of dust, duration of run, etc. For all these reasons the most that can be expected of a laboratory test is that it shall give

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[15] Waters, B. S. Tech. Papers, No. 73, pp. 13–17; 1916.

comparative data which show how different oils will behave under identical conditions. For these reasons, then, this Bureau has adopted the practice of heating the oils at one fixed temperature and for the same length of time. The data given in Tables 3 and 5 tend to justify this position. The fire points roughly indicate how heavy the oils are. The same is true of the viscosities.

A concession which indirectly meets the objections of those who think that the temperature of the bath should be changed to suit the oil, would be to so word specifications that a higher carbonization value would be permitted for the light than for the heavy oils. This would avoid the practical difficulties that would be encountered by running the test at different temperatures.

VI. CARBONIZATION TESTS DEPENDING ON CRACKING

The chemical nature of cracking and some of the conditions which affect it have already been discussed briefly. Free carbon, in hard cokelike masses, as flakes or in powdery form, is one of the products. Some cracking must always occur in the engine, so that it is perfectly logical to make laboratory tests which will show the relative tendencies of different oils to deposit carbon. Any such test must be made under definite and carefully controlled conditions. Such tests, like those which depend upon oxidation, are entirely empirical. They do not determine how much of a given constituent is in the oil, but they do attempt to ascertain how the oil will behave under certain conditions. This distinction should be clearly made. To illustrate further: Various methods can be used to find out how much sulphur is in a sample of oil, and they will all give the same result if the analyses are carefully made and certain known errors are corrected for. On the other hand, to vary the method in determining the carbon residue or the carbonization value is to insure differences in the results.

1. CONRADSON CARBON RESIDUE TEST

(a) EARLIER METHODS.—It is not necessary to describe any of the earlier tests which were devised for the purpose of finding out to what extent an oil might be expected to form carbon deposits in the engine. Only the test devised by Conradson has been generally adopted. In some of the earlier procedures the oil was distilled to dryness in a glass distilling bulb or in one made of fused silica in which the residue of carbon could be burned off in order to determine the amount of ash. Such bulbs are fragile and the

distillation requires a comparatively long time. It is also not easy to raise the final temperature to such a point that the hydrocarbon vapors which fill the bulb will be completely broken down, or at least be converted into gaseous compounds which will not condense on the glass as it cools and thus be weighed together with the carbon. It was a great improvement to distil the oil from a porcelain crucible which is contained in a closed iron one. This is the essential feature of the Conradson method.
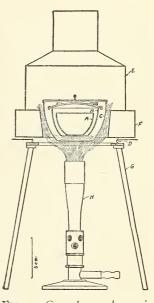
In the earlier form of the apparatus, a current of carbon dioxide or other suitable gas was used at the beginning of the test to sweep out the air and at the end to remove the last oil vapors. This was a complication which proved to be unnecessary, as well as one which involved the possibility of obtaining low results. Too strong a current of gas could easily carry out particles of the light carbonaceous residue. These might be seen in the receiver into which the oil was distilled, but they could not be collected and weighed without considerable extra trouble. Another possibility was the burning of part of the carbon to monoxide, with simultaneous reduction of the dioxide. Loss could occur in this way if the current of dioxide were passed for too long a time while the crucible was heated to redness.

FIG. 5.—*Conradson carbon residue apparatus*

(b) PRESENT CONRADSON APPARATUS.—These two difficulties have been overcome in the present form of the apparatus and with the present procedure. Many specifications for oils now set a limit to the "Conradson carbon residue." [16]

The apparatus is shown in Fig. 5. The oil to be tested is placed in the glazed porcelain crucible, *A*, of the form shown. This rests directly on the bottom of the iron Skidmore crucible, *B*. There are no delivery tubes attached to the cast-iron cover of the latter, and one of the outlets is closed. The Skidmore crucible is placed on a layer of sand deep enough to bring its cover nearly up to the top of the covered wrought-iron crucible, *C*. The latter

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[16] Amer. Soc. Test. Mat. Standards, pp. 620–622; 1918. Various specifications of the Army, the Navy, the Panama Canal, etc. Bulletins of the Comm. Stand. Petrol. Spec.. issued by the Bur. Mines. The drawing and the description of the apparatus and procedure were obtained through P. H. Conradson.

rests on a pipestem triangle, *D*, on the tripod, *G*.   Surrounding *C* is an asbestos or hollow sheet-iron block, *F*, and upon this a sheet-iron hood and chimney, *E*.   The burner *H* is seen to be one of the improved type now familiar in most laboratories.

(*c*) METHOD OF OPERATION.—Weigh the crucible *A*, place in it 10 g of the oil, and set it in the center of the Skidmore crucible, which in turn must be placed in the exact center of the outer crucible *C*.   Cover the iron crucibles, and assemble the apparatus as shown in the figure.

Light the burner and allow a high flame to play around the sides of the outer crucible for 4 to 7 minutes, according to the character of the oil.   The time is less for a thin oil with a low flash point than for a heavy oil with a high flash point.   Now reduce the height of the flame to 5 to 7 cm (2 or 3 inches) until oil vapors begin to burn over the crucible.   This point should be watched for with the greatest care to avoid overheating, which might cause the oil to boil over in the crucible.   The burner flame should be so regulated that the vapor comes off at a uniform rate and burns with a flame which extends not more than 5 cm (2 inches) above the top of the chimney.   It is much easier to regulate the height of the flame if the entire apparatus is thoroughly heated before the porcelain crucible is introduced.   This greatly lessens the risk of overheating the oil.   When the vapors cease to come off, the gas flame should be turned as high as at the start and maintained so for 5 minutes.   The bottom of the crucible becomes red hot.

After the burner flame has been turned off, the apparatus must be left undisturbed for 5 minutes.   If the covers are removed too soon, some of the carbon will burn away.   Cool the porcelain crucible and contents in a desiccator, weigh and calculate the percentage of carbon residue.

With proper regulation of the heat the entire operation can be completed in about one-half hour, although the time varies according to the oil.

The simplest way to clean the crucible is to burn off the adhering carbon.   If none of the residue is lost before this is done, one more weighing will give the amount of ash.

Objection has been raised against the Conradson test because so much depends upon the judgment of the operator, who unless he regulates the burner flame properly may get unreliable results. However, after making a few determinations a careful person can obtain surprisingly close agreement in duplicate analyses.

VII. DISTILLATION TESTS

Although, strictly speaking, not a carbonization method, distillation is in a way related to the procedure of Conradson, according to which the oil is distilled to dryness. At least two methods have been used to learn whether or not a given oil is a blend of light and heavy oils. This has a bearing upon its use in internal-combustion engines.

1. DISTILLATION WITH STEAM

According to the method devised at the United States Naval Experiment Station at Annapolis, Md.,[17] the oil is fractionally distilled with the aid of superheated steam. It "meets all the requirements of a successful laboratory routine method for the examination of mineral lubricating oils as to the quality and quantity of component light oils, heavy oils, and intermediate oils." This information is valuable as indicating what changes in the viscosity may be expected with long-continued use, because the less viscous oils will be lost by evaporation. The test was not devised especially for the examination of oils for internal-combustion engines.

2. VACUUM DESTILLATION.

Having a more direct bearing upon the oils just mentioned is a method for their fractional distillation under considerably reduced pressures. The still of two liters capacity and the receiver, which holds several graduated bottles in which the fractions of the distillate are measured, can be evacuated to a very low pressure.[18] With a good vacuum there is almost no cracking, so that much information as to the components of a blended oil can be gained. This gives an idea of the consumption of the oil in the engine. In this connection Parish,[19] in an account of oil tests made in airplane engines, says that "the consumption of oil is entirely and only related to the body of the oil as indicated by the viscosity at 212° F. The two curves, representing consumption and viscosity, are exactly opposed at all points."

A glass apparatus for fractional distillation under reduced pressure has been used in the Pittsburgh laboratory of the Bureau of Mines.[20]

At the Bureau of Standards much work has been done on the distillation of oils by several methods. It has been demonstrated

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[17] O'Neill, J. Amer. Soc. Naval Eng., 28, pp. 465–486; 1916.

[18] The original still, designed by C. W. Stratford, was lent to this Bureau, and many interesting and valuable data have been obtained with it.

[19] J. Amer. Soc. Naval Eng., 32, pp. 45–99: 1920. See p. 62.

[20] E. W. Dean, private communication.

that under pressures of only a few mm of mercury there is very little cracking, except, perhaps, with the heaviest oils, or when the temperature of the still gets above 300° C (572° F).

3. DISTILLATION AT ATMOSPHERIC PRESSURE

It has been argued that the oil should be distilled, not in a partial vacuum, but rather at atmospheric or even at a somewhat increased pressure, because this is more nearly like the conditions in the engine.[21]   If the oil will crack in use, its behavior in the distillation test will show what is to be expected of it.   This method comes nearer than the other distillation method to Conradson's test.

Distillation tests, like those which depend on oxidation and on cracking, are empirical.   They are at best but comparative and cannot duplicate the conditions in the engine.

VIII. DISCUSSION

It will be asked what is the actual, practical significance of the tests which have been described and how much do they tell about the behavior of oils in the engine.   Evidently laboratory tests must be made on engines before these questions can be answered, and then the whole story will not be told.   There are many makes of engines, and no two of them are run under exactly the same conditions as to speed, temperature, kind of gasoline, richness of mixture, compression, clearance of piston rings, dust, etc.   Only on the test block can all of these factors be made approximately constant.   Unfortunately there are few data which have been obtained with the intention of correlating laboratory tests with engine experience.

Beginning late in 1917, a series of tests on airplane engines was made at the navy yard, Washington, D. C., under the auspices of the Signal Corps of the Army and the Navy.   The necessary laboratory work was divided between several Government laboratories and those of four refineries.   W. F. Parish, who planned and was in charge of the tests, has published an account of them.[22] Among other conclusions reached are the following: The Waters method gives higher results with naphthene base than with paraffin base oils.   The Conradson method gives results which are the reverse of this.   "With oils of the same classification as to crude, the carbon content, Conradson, is directly related to the viscosity at 212° F, and the carbon content by the Waters method

[21] Private communication from F. G. Wahl.
[22] J. Amer. Soc. Naval Eng., **32**, pp. 45–99; 1920.   See especially pp. 55–56.

is directly opposed to the viscosity at 212° F." Further, oils which "gave the greatest amount of carbon in the engine were those that showed the greatest carbon content by the Conradson method and the lowest value by the Waters method," with one possible exception which was explained as due to excessive consumption, owing to its light body. In other words, the paraffin base oils crack more readily and become oxidized less easily than the naphthene base oils.

Without any intention of starting a controversy it should be pointed out that the conditions in an airplane engine are such as to favor cracking and deposition of carbon, because of the high temperatures and pressures which prevail. It is also true that five-hour tests, such as those at the navy yard may not have been long enough for any trouble to have arisen from the formation of asphaltic deposits. That some can be formed is shown on page 5. It may be that after the deposit has been built up to a certain thickness, a further increase is prevented by the cracking, and consequent flaking off, of the asphaltic matter. It is said of one of the oils tested that "it formed a great amount of carbon which came out of the exhaust in a remarkable manner, but this carbon was not of a nature that allowed it to stick and accumulate inside the engine, * * *."[23] This oil had a very high carbonization value, by the oxidation method, but the "lowest Conradson carbon value." If the carbon is formed only by cracking, it is hard to see how this oil could have had a low carbon value in the laboratory test while in the engine it formed a great amount of carbon. As to the carbon not sticking in the engine, that will be spoken of a little farther along. On the other hand, if there is much asphalt formed by oxidation it may collect in a layer on the piston and when it is thick enough may become so hot as to decompose into hydrocarbon vapors and flaky carbon which escapes.

Although there is some doubt as to whether there is any great amount of cracking in an airplane engine, it is theoretically not impossible. This would involve the formation of olefins, which are easily oxidized. Then the results upon which Parish based his conclusions could be explained as due to the oxidation of the olefins rather than of the other hydrocarbons. This oxidation does not necessarily go as far as complete combustion or the production of asphaltic matter, but other products can also be

[23] Parish, J. Amer. Soc. Naval Eng., **32**, p. 56. In a private conversation the carbon was described as issuing from the exhaust in a shower of sparks. A similar phenomenon has been observed at this Bureau. It could not be decided whether the shower of sparks was due to carbon or to minute drops of burning oil.

formed. Indeed, "the acidity of all oils increases during operation in a quite consistent manner." [24] Acids are oxygen compounds. Work done at this Bureau has shown that aldehydes, which represent a lower stage of oxidation, are also formed.

As regards the oxidation test, Tables 2 to 5 show that the carbonization value, or percentage of asphalt formed, is independent of the physical properties, but is related to the chemical reactivity of the oil as measured by its iodine and Maumené numbers, and by its rate of oxidation in sunlight and air. It is also related to the demulsibility, which depends to a great extent upon the chemical properties and less so upon the viscosity. Table 5 shows also that the Conradson carbon residue seems not to be related either to the Saybolt viscosity at 212° F or to the carbonization value by the oxidation method.

The subject is of too much importance to be dismissed without reference to other published statements. Unfortunately it has come to be a subject for dispute between the protagonists of the paraffin base and the naphthene base oils.

In a paper on motor-cylinder lubrication, Bryan [25] says that high temperature and a limited supply of oxygen (air) are the conditions which cause carbon to be formed.

Unless air is present in excess of that required for the combustion of the gasoline or fuel oil, and usually it is not, the oil can not really burn. Under the intense heat, however, the inner surface of the oil film will be vigorously affected, and in the absence of the air necessary for burning three things may happen:

Case 1. The compounds may volatilize without decomposition.

Case 2. The compounds may decompose with the formation of free carbon and hydrogen.

Case 3. The compounds may decompose with the formation of other hydrocarbons of a different nature.

In discussing these cases, Bryan says that "the carbon may be blown out with the gases, or may remain in the cylinder," according to "the condition of the oil film on the cylinder walls. Some oils form a thick, viscous, gummy, asphalt-like deposit, which retains the carbon formed on its surface and prevents it from being blown out through the exhaust." According to Bryan, the compounds formed in case 3 are responsible for these gummy deposits, which are further acted on by heat and "finally, a hard, brittle deposit results." No attempt is made to explain why a film of unchanged oil is not able to trap and retain the light, loose particles of carbon. It is hard to see why the hot, thin oil, which

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[24] Parish, J. Amer. Soc. Naval Eng., **32**, p. 56.

[25] J. Amer. Soc. Naval Eng., **27**, pp. 1-14; 1915.

must wet and hold the particles the instant they touch it, should not also build up deposits.

1. An anonymous writer [26] takes Bryan to task quite sharply for these and other statements.

F. C. Robinson,[27] after giving an account of tests of four oils in an automobile, which was run from 976 to 1339 miles with each oil, came to the following conclusions: "(*a*) Highly viscous oils from any source cause excessive and unnecessary losses in miles per gallon of gasoline. (*b*) Irrespective of viscosity, the oils with low flash (typical of Texas field oils) are considerably less efficient than the higher flash oils from Pennsylvania crude; i. e., they require about 1.2 gallons of Texas field oil to do the same work as 1 gallon of Pennsylvania oil. (*c*) The amount of carbon averages, broadly, about the same for low viscosity and high viscosity oils and about the same for Texas field oil and Pennsylvania oil; and the consistency of all four samples of carbon is identical." Two of the oils tested were paraffin base and two naphthene base. The statement about the amount of carbon is interpreted by Robinson "to mean that any hydrocarbon burned under the conditions that are found on the walls of an engine cylinder will produce some unconsumed residue and that the amount of this residue will be governed very largely by the amount of oil that actually reaches the compression space of the engine."

Robinson's statement that all of the oils he tested gave carbon of about the same consistency is confirmed by tests made on an airplane engine at this Bureau. The layers of carbon which formed on the pistons were so much alike in their properties and general appearance that they gave no hint as to the nature of the oil used.

An anonymous writer of a paper on motor-oil specifications [28] comments favorably on new specifications issued by the War Department, and says. "The carbon residue test, especially the qualifying clause, 'hard carbon residue in service will be cause for rejection,' should be ample provision to guard against the admission of a poorly refined oil or one unsuited for internal-combustion engines." Such a requirement, in effect, takes the specification away from the testing laboratory because no carbonization method can show how much residue will be formed "in service." Fortu-

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[26] The Atlantic Connecting Rod, June, 1917, pp. 11–17.
[27] The Atlantic Lubricator, 3, p. 8; February, 1920.
[28] Lubrication, 6, pp. 6–7; February, 1920.

nately there is no such clause in any of the specifications issued by the Committee on Standardization of Petroleum Specifications.

Finally, in a paper on the examination of oils before and after use in engines, Atkins presents a number of interesting facts.[29] Besides making the usual measurements of the physical constants, he studied the oxidation, the carbonization, and the iodine numbers. His results on the last are confirmatory of the data given in Table 2, because they show that the iodine number falls when the oil is oxidized. Two oils which had iodine numbers of 12.7 and 12.6, respectively, were heated, whereupon these numbers fell to 9.5 and 9. From these figures and from the losses by evaporation Atkins concluded that evidently the first was "the more economical oil to use."

Atkins found that the finely divided carbon which is suspended in used oil is precipitated the more rapidly the greater the acidity of the oil. Oxidation causes the oil to become acid,[30] but "good mineral oils, when examined after use, are found to retain the carbon in suspension for very long periods—after as long as 18 months much is still in suspension." Atkins's "spot test" is to "allow a drop of the oil to fall on a piece of white filter paper. The extent of the carbonization may be judged by the depth of the black deposit, from which the clear oil is drawn away by the fibers of the paper." * * * "This simple test reveals how small the amount of 'carbon' is in oil that appears inky black, and its adoption would probably save much good oil now poured out because it looks black."

There are ample theoretical reasons for believing that both the oxidation and the cracking tests give trustworthy indications of the character of oils. The difficulty comes when one attempts to apply the laboratory data to the engine. On numerous occasions the oxidation method has been discussed with chemists and others connected with oil refineries, but rarely have any serious arguments been brought up against it. As a rule, it has been admitted that it is a theoretically sound method. The chief objections to it have been the alleged difficulties involved in making the test, and the complicated and expensive apparatus necessary. These objections are believed to be invalid. The method is in use at more than one refinery, while others are sufficiently interested to be giving it serious attention.

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[29] The Automobile Engineer, December, 1919.   [30] See pp. 11 and 14.

The cracking method, too, has its share of adverse criticism, which has not always been well founded. Not all of the objections have come from those who prefer the oxidation test.

In this circular the attempt has been made to present both sides of the case in an unbiased manner. If the oxidation method appears to have been given undue attention, it is partly because so many requests for full descriptions of the apparatus and procedure have been received, and partly because the numerous disturbing factors had to be discussed. The oxidation method, more than the carbon-residue test, has been subjected to adverse criticism, and it seemed necessary to point out how the facts brought up against it might be interpreted in its favor.

The statements which have been made in this general discussion must make it clear that much remains to be learned about the lubrication of internal-combustion engines. Possibly new methods of testing must be devised before one will be able to rely upon the findings of the laboratory in the selection of suitable oils. No matter what these new methods may be, oxidation and cracking tests can not be disregarded, because they are concerned with the determination of important, and even fundamental, yet very different properties. When more data on engine tests are available, it may be possible to find some way in which to correlate the results obtained by the two laboratory methods, so as to enable the best oil to be selected. Perhaps this will be done by averaging directly the percentages of residue found, or it may be necessary to "weight" the percentages before calculating the final values.

What is known about the behavior of lubricants in the engine is enough to indicate how much more must be learned. It is hoped that this circular will at least furnish suggestions of value to other workers in this field.

IX. SUMMARY

The nature and effects of the deposits formed in internal-combustion engines are discussed. It is shown that the term "carbon" is a misnomer, because the deposits consist largely of asphaltic matter.

Brief accounts are given of the nature of petroleum oils and of the theories concerning the formation of deposits. The oxidation and cracking of petroleum are discussed in detail.

Carbonization tests which depend upon oxidation and upon cracking are next taken up. Full descriptions of the apparatus

and procedures for the "Waters" and "Conradson carbon residue" tests are given.   Distillation methods are touched upon.

The general discussion gives brief summaries of certain controversial papers, and finally it is pointed out that there is yet much to be learned upon the whole subject of the lubrication of internal-combustion engines.

WASHINGTON, July 23, 1920.