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DATA ON THE OXIDATION OF AUTOMOBILE CYLINDER OILS

BY

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I. INTRODUCTION

It has long been known that mineral oils become oxidized when subjected to the combined action of sunlight and air. The literature of the subject was rather fully reviewed in a paper published some time ago,[1] and need not be referred to again, except perhaps occasionally in the following pages.

The so-called "carbonization" of automobile cylinder oils is due to only a very limited extent, if at all, to cracking, but is caused by oxidation [2] and subsequent polymerization. This will be discussed more fully further on. In order to learn whether there is any close connection between the rate of oxidation of different oils on exposure to light and air, and their carbonization values at elevated temperatures, both before and after oxidation in the light, an extended series of tests was made with three automobile cylinder oils of well-known brands. Certain other constants were also determined. As supplemental to the above, the influence of the time and temperature of heating upon the carbonization value was

[1] Bull., Bur. Standards, 7, pp. 227–234, 1910; J. Ind. Eng. Chem., 2, pp. 451–454, 1910.

[2] Bull., Bur. Standards, 7, pp. 372, 375, 1910; Techn. Paper, Bur. Standards, 4, p. 11, 1911; J. Ind. Eng. Chem., 3, pp. 236, 237, 815, 1911.

also studied. A sufficient supply of each of the oils was purchased in the open market. In order to remove adventitious particles of iron rust or other material that might affect the carbonization values and possibly other determinations,[3] the samples were filtered directly into clean cans. One-liter portions were kept for convenience in dark-brown bottles.

The flash and fire points were as follows, the determinations being made in the Pensky-Martens closed-cup apparatus:

	Oil No. 1	Oil No. 2	Oil No. 3
	Degrees	Degrees	Degrees
Flash point	215	210	205
Fire point	270	260	250

II. OXIDATION IN SUNLIGHT

In the earlier paper on this subject[4] it was shown that when an oil is oxidized in the sunlight some water and carbon dioxide are given off. The oil becomes highly acid and an insoluble oxidation product is thrown down, sometimes after only a few hours' insolation. In order to follow the changes in weight of the oils under investigation, seven 10-g portions of each were placed in 150-cc Erlenmeyer flasks, the mouths of which were covered with filter paper to exclude dust. The flasks were held in racks, the bases of which were covered with white paper. On every bright day, for a total of 438 hours, they were placed outside a window facing south. At first the flasks were weighed every day, but later on, as the rate of oxidation became less rapid, this was done only every three or four days. All weighings were made against a tare. Much time was saved by arranging the flasks according to their weight rather than in numerical order.

Twenty-one flasks were all that could be placed, without shading one another, upon the window sill. Great care was taken to keep the racks level and to avoid getting the oil on the sides of the flasks, thus increasing the area of oil surface exposed. Only three flasks of each set were exposed for the entire 438 hours, because on two occasions two flasks of each oil were used for special tests. Although the remaining flasks were those showing gains furthest from the respective averages, yet at the end of the experiment the

[3] Techn. Paper, Bur. Standards, 4, pp. 10, 13, 1911; J. Ind. Eng. Chem., 3, p. 815, 1911.
[4] Bull., Bur. Standards, 7, p. 232, 1910; J. Ind. Eng. Chem., 2, p. 453, 1910.

differences between the highest and the lowest gain for each oil were only 7.5, 4.5, and 6.9 mg, respectively. These are the maximum differences found during the test. Aside from variations in the rate at which the oils gained in weight from day to day, according to the weather, there were fluctuations in the rate for the flasks of each set. One would be ahead, then drop behind, and possibly catch up again in the race.

The following table gives the average gains in weight for the three oils at approximately equal intervals:

TABLE 1

Average Gain in Weight of Oils Exposed to Sunlight and Air

Total exposure	Oil No. 1	Oil No. 2	Oil No. 3
	Milligrams	Milligrams	Milligrams
9 hours	9.1	19.3	18.2
51.5 hours	62.6	79.7	75.5
90 hours	88.0	107.7	104.0
130 hours	123.5	141.7	139.2
167.5 hours	154.0	170.9	169.6
205 hours	172.6	188.8	188.2
249 hours	180.7	197.4	197.0
289 hours	195.4	212.7	212.6
327 hours	210.5	227.2	227.2
364 hours	220.4	237.8	237.4
402 hours	229.9	247.4	246.7
438 hours	236.2	252.9	252.1

The curves shown in Fig. 1 are plotted from the average gains for each set of flasks and the number of hours they were exposed to light. It will be seen that, except for breaks caused by unfavorable weather, the curves apparently show that the oxidation proceeds at a gradually decreasing rate. But it must be remembered that the gain is the algebraic sum of the oxygen absorbed and the carbon dioxide and water lost.[5] Hence, curves showing the actual rate of oxidation would lie somewhat above those drawn. Oil No. 1 gained 20.1 mg in weight in 12.5 hours after the first weighing. During this time the amounts of water and carbon dioxide that escaped must have been very slight, so that the slope of the curve represents quite closely the true rate of absorption of oxygen in that time. If we assume that the oil was oxidized at the same rate and that the carbon dioxide and water were all weighed with the oil, the total gain in 438 hours would be about 690 mg, or 450

[5] See footnote 4.

mg more than was observed. From the results of earlier tests it is probable that the gain in weight is slightly more than the combined weights of carbon dioxide and water. In other words, even if values corrected for these losses were used in plotting the curves, their slope would still lessen. We are thus practically forced to the conclusion that oxidation in sunlight proceeds more and more slowly while, as will be shown below, at elevated temperatures the reverse is true.

The decided break in each of the curves at about 200 hours is due to a succession of cloudy or hazy days following a stretch of clear weather, but after this unfavorable period other bright days came, without again causing any marked upward trend. The first nine hours of exposure caused a sharp separation of one of the oils from the other two, which remained close together throughout the entire time. The deviations from this initial difference of about 10 mg were slight, and at the end of 438 hours the total gains were less than 17 mg apart.

To follow the changes in weight, carbonization, and acidity, not to mention a few special tests, more than 200 ten-gram portions of oil were used. To have had these in separate flasks would have been impracticable, so that about 1½ liters of each oil was oxidized in crystallizing dishes, 24 cm in diameter. The dishes were covered with watch glasses, which excluded dust but did not prevent access of air. At certain intervals enough to make the desired tests was removed, after thoroughly stirring the contents of the dishes. Satisfactory sampling was not difficult even after the insoluble oxidation product[6] began to form, because the particles settled very slowly through the oil.

It was foreseen that the oil in the dishes could not be oxidized as rapidly as that in the flasks, on account of its being in a much deeper layer. For this reason the curves showing the increase in acidity and carbonization are not strictly comparable with those showing the gain in weight. This does not, however, affect the general results. The more important determinations were made on samples that had received the same treatment.

III. INCREASE IN ACIDITY BY OXIDATION

From time to time representative samples were removed from the dishes. Ten-gram portions were warmed with measured volumes of alcohol and gasoline and titrated with 0.1 N alkali,

[6] Bull., Bur. Standards, 7, p. 230, 1910; J. Ind. Eng. Chem., 2, p. 452, 1910.

using phenolphthalein as indicator. At first there was no difficulty about this, but as the oils became more strongly acid the end point was increasingly difficult to detect, owing to their great tendency to emulsify. This is not surprising when it is remembered that soap is formed by the reaction with the alkali.[7]

The results are tabulated below and also plotted in Fig. 1. The ordinates show the number of milligrams of potassium hydroxide required to neutralize 1 g of oil. It will be seen that the curves for oils 2 and 3 lie very close to one another throughout the greater part of their extent, the maximum deviation being equivalent to only 0.07 mg of caustic potash. In this respect they resemble the curves showing the increase in weight. In both cases, also, oil No. 1 lies below these two. The general trend of the curves indicates that the rate of formation of acids gradually increases. A maximum acidity must eventually be reached, but the curves give merely an uncertain indication of this by their slightly decreased slope. The two abrupt breaks in the curves between 69 and 149 hours are the result of unfavorable weather.

TABLE 2

Gain in Acidity of Oils Exposed to Sunlight and Air

Acidity.	Oil No. 1	Oil No. 2	Oil No. 3
Initial acidity (milligrams KOH)	0.06	0.04	0.03
Acidity after 22 hours	.08	.08	.08
Acidity after 40 hours	.09	.10	.09
Acidity after 69 hours	.19	.21	.22
Acidity after 90 hours	.16	.24	.22
Acidity after 101.5 hours	.17	.25	.25
Acidity after 118 hours	.38	.51	.50
Acidity after 149 hours	.50	.71	.67
Acidity after 174 hours	.86	1.03	1.08
Acidity after 208.5 hours	1.22	1.36	1.43
Acidity after 238 hours	1.44	1.65	1.67
Acidity after 289 hours	2.32	2.74	2.68
Acidity after 333 hours	2.40	2.91	2.94
Acidity after 419 hours	3.40	3.70	3.67

It was found that the percentage of the insoluble oxidation product thrown down by petroleum ether is not proportional to the gain in acidity. The percentages found at the end of the exposure test were 0.38, 0.51, and 0.60, respectively.

[7] Cf. Schaal: D. R. Pat. 32705, Chem.-Ztg., 9, p. 1520, 1885.

IV. CARBONIZATION OF OILS OXIDIZED IN SUNLIGHT

The carbonization values of the oxidized oils were determined on samples taken at the same times as those used for the determination of acidity. The procedure followed was the same as described in earlier papers,[8] but an electrically heated and controlled air bath was used instead of one heated by gas. Ten-gram portions of oil,

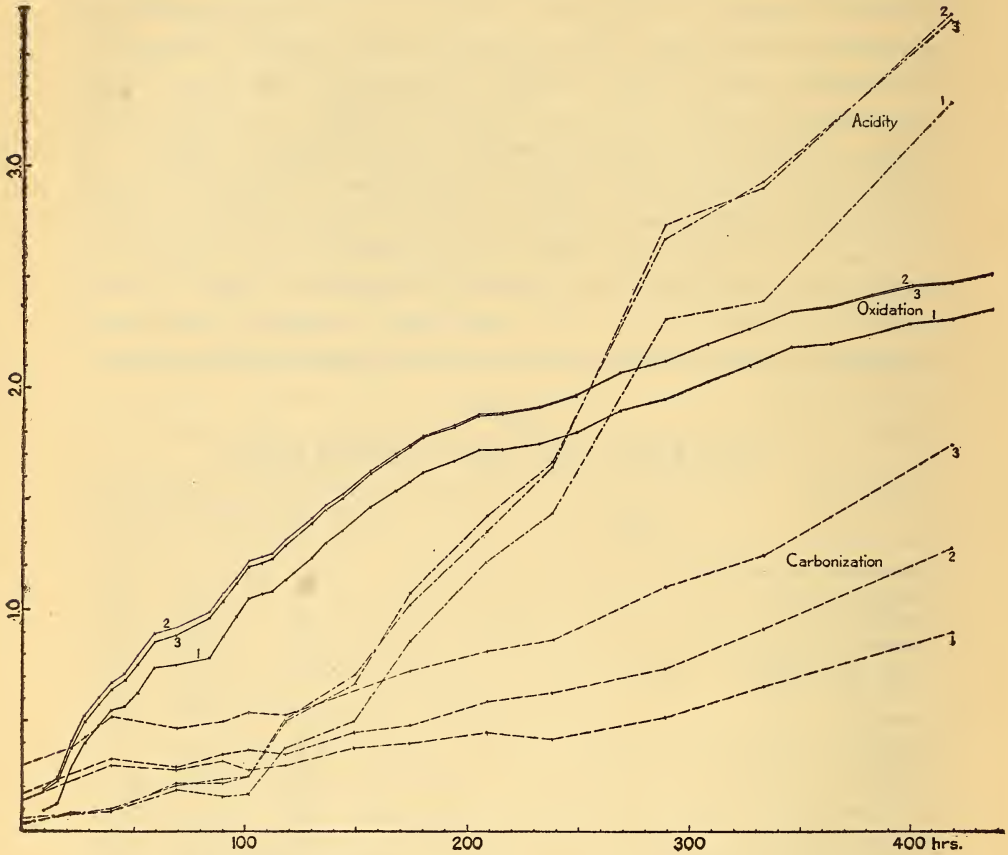

FIG. 1.—*Percentage of carbonization, gain in weight (decigrams) due to oxidation, and acidity (as milligrams of KOH required for neutralization) of oils exposed to sunlight and air*

contained in 150-cc Erlenmeyer flasks, were heated to 250° for three hours, allowed to cool, and diluted with 50 cc of petroleum ether. The flasks were then tightly corked and set aside for about 24 hours. The precipitate was filtered off in a Gooch crucible prepared with a disk of filter paper (S. & S. No. 589 blue ribbon)

[8] Bull., Bur. Standards, 7, p. 370, 1910· Techn. Paper, Bur. Standards, 4, p. 4, 1911; J. Ind. Eng. Chem., 3, pp. 235, 813, 1911.

covered with a thin layer of asbestos to keep it in place. It was washed with petroleum ether, dried at 95–100°, and weighed. The results obtained are included in Table 3 and are shown in Fig. 1.

TABLE 3

Carbonization Values of Oils Oxidized in Sunlight

Exposure	Oil No. 1	Oil No. 2	Oil No. 3
	Per cent	Per cent	Per cent
None	0.14	0.17	0.30
22 hours	.23	.26	.38
40 hours	.30	.33	.52
69 hours	.28	.29	.47
90 hours	.32	.35	.50
101.5 hours	.28	.37	.54
118 hours	.30	.35	.53
149 hours	.38	.45	.64
174 hours	.40	.48	.73
208.5 hours	.45	.59	.82
238 hours	.42	.63	.87
289 hours	.52	.74	1.11
333 hours	.66	.92	1.25
419 hours	.90	1.38	1.75

The curves showing the percentages of carbonization of the oxidized oils are strikingly different from those showing the gains in weight and in acidity. Oils 2 and 3 no longer give nearly the same values, but quite different ones. After 419 hours' exposure to sunlight, oil No. 2 has a carbonization value that is slightly greater than the mean of the values for the other two oils. A similar relationship held for the amounts of insoluble oxidation product formed, at ordinary temperatures, in sunlight.

V. MISCELLANEOUS DETERMINATIONS

1. DEMULSIBILITY

When oils are vigorously stirred or shaken with water, more or less permanent emulsions are produced. The rates at which the two liquids separate differ widely, some emulsions lasting for days, while with others the two original layers reappear in a few minutes. The "demulsibility,"[9] or rate of separation of an emulsion into two layers, is an indication of the quality of an oil. A high demul-

[9] The expression "demulsification value" has been used by Arnold Philip (J. Soc. Chem. Ind., 34, p. 700, 1915) to denote the percentage of oil which separates in 24 hours. The word selected by Mr. Herschel is not only a shorter expression but refers to a different unit.

sibility, measured in cubic centimeters per hour, for instance, indicates an oil of good quality.

W. H. Herschel, of this Bureau, using an apparatus devised by him,[10] determined the demulsibilities of the original oils, of the oils after 238 hours' insolation, and of the latter after they had been filtered through bone-black. The carbonization values of two of the filtered oils were also determined.

TABLE 4

Demulsibility and Carbonization Values

	Original oils			Oxidized oils			Oxidized and filtered oils	
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 2	No. 3
Demulsibility, cubic centimeters per hour	270	270	360	20	32	45	90	163
Carbonization, per cent	0.14	0.17	0.30	0.42	0.63	0.87	0.34	0.55

It is plain that oxidation caused a decided deterioration of the oils, and that a distinct improvement was effected by shaking with bone-black and filtering soon thereafter. This is in agreement with the work of Schwarz and Marcusson,[11] who were able to extract from oils certain resinous substances which, when heated to 120° in the air, blackened and were transformed into asphalt that was insoluble in benzine. These resins were first concentrated by solution in acetone, which dissolved a little of the oil.[12] After distilling off the solvent the residue was mixed with animal charcoal and sand and then extracted with low-boiling benzine, according to Holde and Eickmann.[13] The resins were removed from the bone-black by extraction with chloroform. Schwarz and Marcusson regard these resins, which contain a considerable percentage of oxygen and in which most of the sulphur of the oil is concentrated, as transition stages between the hydrocarbons and asphalt. The evidence that has been adduced in the past few years is preponderatingly in favor of the view that the formation of asphalt is essentially a combination of oxidation and polymerization. Sulphur and sulphur compounds are rarely brought into the discussion, though Southcombe[14] found that when lubricating

[10] There is in course of preparation a paper describing the apparatus and procedure for making this determination.

[11] Z. angew. Chem., 26, A, p. 385; 1913.

[12] Schwarz and Schlüter, Chem.-Ztg., 35, pp. 413–415; 1911.

[13] Mitth. kgl. Materialprüfungsamt, p. 145, 1907; Cf. Z. angew. Chem., 20, pp. 1263, 1923, 1907.

[14] J. Soc. Chem. Ind., 30, pp. 261–264, 1911; see also Holde and Eickmann, loc. cit.

oils are heated in a current of air containing sulphur vapor or sulphur dioxide, much more asphaltic matter is formed than in air alone.

It is unnecessary to do more than mention polymerization by the action of such catalyzers as anhydrous ferric chloride, phosphorus pentoxide, aluminium chloride, manganese dioxide, etc.[15] An illuminating suggestion was made by Gurwitsch, who found that finely divided, porous materials, such as "floridin" (fuller's earth from Florida), can cause polymerization.[16] According to him the asphaltic substances exist in a colloidal state in the oil and coagulate upon the porous material. In this condition they are not soluble in such "weak" solvents as benzine; but they can be extracted by means of benzene, whereupon they revert to their original sol state.[17]

2. MAUMENÉ NUMBER

Chiefly as a matter of interest the Maumené numbers of the oils, before and after exposure to sunlight for 438 hours, were determined. Fifty-gram samples were mixed with 10 cc of concentrated sulphuric acid and stirred vigorously until no further rise of temperature was observed. The oil-acid mixture was contained in a 100-cc tall beaker surrounded with a thick layer of cotton batting in a larger beaker. A simple mechanical stirrer, using the laboratory blast for motive power, was employed. Temperatures were read on an Anschütz thermometer having a range of 50° and graduated to 0.2°. The following results were obtained:

TABLE 5

Maumené Numbers of Original and Oxidized Oils

	Original oils			Oxidized oils		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
	°	°	°	°	°	°
Observed rise in temperature.....	8.3	7.3	7.1	20.6	20.0	18.8
	8.2	7.2	7.1	21.1	19.7	18.9

The Maumené number, like the heat of bromination and the iodine number, is supposed to be a measure of the degree of unsaturation of an oil. The nondrying oils give lower values than the drying oils. Jenkins[18] found that boiled linseed oil had lower

[15] Zaloziecki and Zelinski: Eighth Internat. Cong. Appl. Chem., **10**, pp. 335–341, 1912; Chem.-Ztg., **36**, p. 1305, 1912.

[16] Z. Kolloide, **11**, p. 17.

[17] Petroleum, **8**, pp. 65–68; Chem. Zentr., **83**, II, p. 1792, 1912.

[18] J. Soc. Chem. Ind., **16**, pp. 193–194; 1897.

Maumené and iodine numbers than raw oil, as he expected. On the other hand, blown cottonseed and blown rapeseed oils, though having lower iodine and "bromo-thermal" values than the raw oils, gave higher figures for the Maumené number. This is analogous to the behavior of olive oil when exposed to light and air, according to Archbutt.[19] Ballantyne found that not only olive oil but five other oils behaved in the same way.[20] These facts are cited by Lewkowitsch.[21]

None of the four authors just mentioned attempted any explanation of the phenomenon. The following suggestions are offered, according to which boiled linseed oil is the exception, and not the two blown oils, as stated by Jenkins. When an unsaturated hydrocarbon with a double bond reacts with sulphuric acid, there is formed an alkylsulphuric acid. For instance, ethylene yields ethylsulphuric acid:

$$H_2C{:}CH_2 + H_2SO_4 = H_3C.CH_2OSO_3H.$$

Ethyl alcohol and ethyl ether also form ethylsulphuric acid when they react with sulphuric acid, but water is produced at the same time. If the oils contain compounds with the ethylene linkage, it is not unlikely that the effect of oxidation in the sunlight would be to introduce hydroxyl groups at the double bond. The Maumené number should then be higher because the heat of formation of water would be added to that of the alkylsulphuric acid. Also the iodine number and the heat of bromination should be low, because there is no longer a double bond at which addition can take place. It must not be forgotten that the halogen numbers will never equal zero, even though all the double bonds should become saturated, because there is always some substitution.

In determining the Maumené numbers of the oils there was always perceptible a strong odor of sulphur dioxide, which persisted for some time after the attainment of the maximum temperature. The mixture also became dark as if charred. This does not invalidate the suggestion in the preceding paragraph, because a "smooth" organic reaction is the exception. Even in the comparatively simple case of making ethylene from alcohol, there is always some charring and evolution of sulphur dioxide.[22]

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[19] Ibid., 5, p. 312; 1886.
[20] Ibid., 10, p. 32; 1891.
[21] Chem. Techn. and Anal. of Fats, etc., 5th ed., 1, pp. 484–485.
[22] Erlenmeyer and Bunta, Ann. Chem. Pharm., 168, p. 64; 1873.

3. IODINE NUMBER

Kissling long ago pointed out that for different oils the resinification number (carbonization value) may vary much more than the Maumené and iodine numbers.[23] The iodine numbers of oils 1, 2, and 3 and of the same oils after 438 hours' insolation were determined by J. H. Bower, of this Bureau. His results confirm the statement of Kissling, and also show that the oils behave in the same way as the blown oils discussed above.

TABLE 6

Iodine Numbers of Original and Oxidized Oils

	Original oils.			Oxidized oils		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
Iodine number	31.2 31.5	29.8 29.8	30.0 30.3	20.4 20.4	19.1 19.1	20.6 20.6

Oils 1 and 2 show a slightly greater drop in the iodine number than does oil 3, but the difference is perhaps not great enough to be worthy of special comment.

VI. EFFECT OF THE TIME OF HEATING UPON THE PERCENTAGE OF CARBONIZATION

In order to learn whether the percentage of carbonization is directly proportional to the time of heating or whether the reaction is progressively more or less rapid, a series of determinations was made upon the three oils under investigation. Ten-gram samples were heated to 250° for one, two, etc., up to seven hours, the insoluble precipitate being thrown down and determined in the usual way. The results are shown in Table 7 and are plotted in Fig. 2.

TABLE 7

Variation in Carbonization with Time of Heating to 250°

	Oil No. 1	Oil No. 2	Oil No. 3
	Per cent	Per cent	Per cent
Carbonization in 1 hour	0.03	0.04	0.04
Carbonization in 2 hours	.10	.10	.16
Carbonization in 3 hours	.14	.17	.30
Carbonization in 4 hours	.34	.37	.60
Carbonization in 5 hours	.51	.54	1.02
Carbonization in 6 hours	.83	.94	1.37
Carbonization in 7 hours	1.26	1.25	2.01

[23] Chem.-Ztg., 30, pp. 932–933; 1906.

The time was counted from the moment the heating current was turned on. About half an hour was required to heat the bath to 250°, but long before this temperature was reached oxidation began.

All the oils gave practically the same results on heating for one hour, but by the end of two hours oil 3 showed a decided

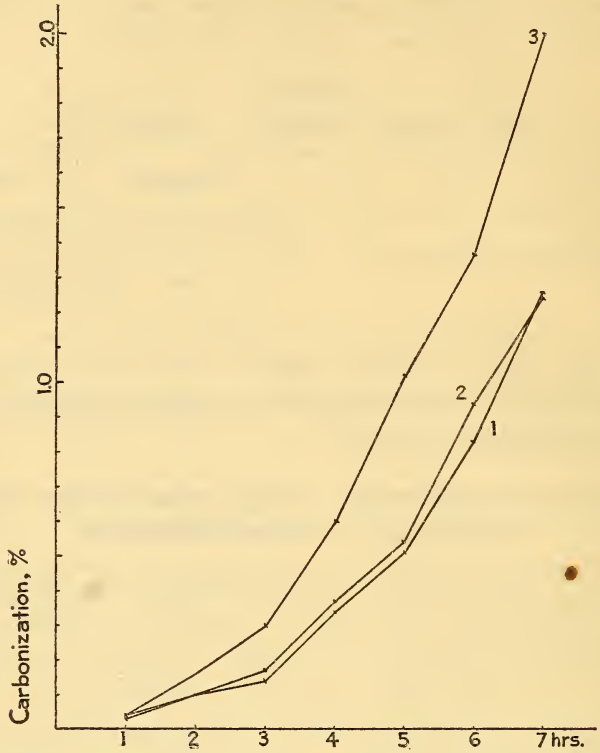

FIG. 2.—*The effect, upon the percentage of carbonization, of heating to 250° for different lengths of time*

deviation from the other two. This deviation became increasingly greater as the period of heating was lengthened, while oils 2 and 3 kept close together throughout. The ordinary physical and chemical tests gave no indication that the oils would behave so differently on heating. As Kantorowicz says, "the slight differences in the asphalt content of cylinder oils, in contrast with the great differences in practice, would make it appear advisable to test oils quantitatively as to their ability to form new asphalt under definite conditions."[24]

[24] Chem.-Ztg., 37, pp. 1594–1595; 1913.

The curves show that the conditions obtaining at elevated temperatures effect a grouping of the oils different from that due to oxidation at ordinary temperatures in sunlight, if we consider only the gains in weight and in acidity. The carbonization values of the oxidized oils will be discussed further on.

It is important, from the standpoint of routine laboratory testing, to learn whether or not two oils that yield nearly the same percentages of carbonized matter, when heated for two or three hours, remain equally close together if heated for a longer time. Eight oils of well-known brands were heated for two and one-half, three and one-half, and four and one-half hours and the insoluble matter was determined as usual. A and C were light and heavy grades of the same brand. B and D were light and heavy grades of a second brand. E, F, and H were from the same company, while G was a fourth brand. The data obtained are given in Table 8 and are plotted in Fig. 3.

The data obtained, confirming as they do the results found for oils 1 to 3, do not call for any especial comment. In saying this it must be understood that the amount of carbonized matter formed by heating to 250° for only one hour is disregarded.

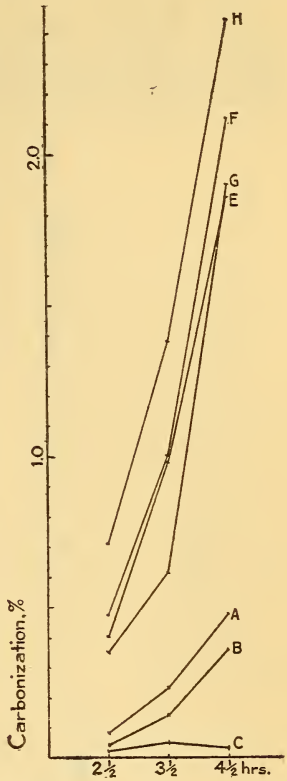

FIG. 3.—*The effect upon the percentage of carbonization, of heating seven special oils to 250° for different lengths of time*

TABLE 8

Carbonization of Eight Special Oils Heated to 250° for Different Periods of Time

Oil	Flash point	Fire point	Percentage carbonization when heated for—		
			2½ hours	3½ hours	4½ hours
	Degrees	Degrees			
A	190	245	0.08	0.23	0.48
B	225	250	.04	.14	.36
C	235	280	.02	.05	.03
D	230	265	Trace	Trace	Trace
E	145	200	.40	.98	1.86
F	165	200	.47	1.00	2.12
G	185	230	.35	.62	1.90
H	160	190	.70	1.38	2.45

VII. EFFECT OF DIFFERENT TEMPERATURES UPON THE CARBONIZATION VALUE

Just as the carbonization value depends upon the length of time the oil is heated, so also it must vary with the temperature. In order to determine the magnitude of the changes, a series of

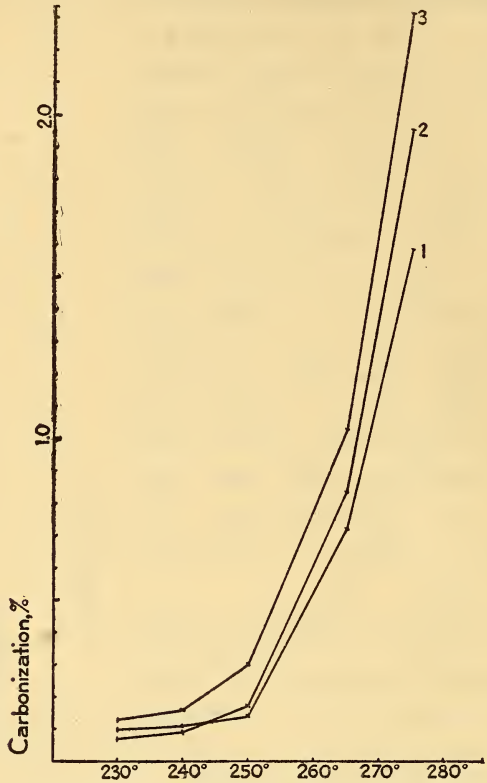

FIG. 4.—*The effect, upon the percentage of carbonization, of heating at different temperatures for the same length of time*

tests was made at temperatures varying from 230° to 275°. The data are given in Table 9 and are plotted in Fig. 4. The time of heating, in each series, was three hours.

TABLE 9

Influence of Temperature Upon the Carbonization Value

Sample	Carbonization value when heated to—				
	230°	240°	250°	265°	275°
No. 1	0.10	0.11	0.14	0.72	1.59
No. 2	.07	.09	.17	.84	1.96
No. 3	.13	.16	.30	1.03	2.32

The curves are of the same general form as those showing the effect of lengthening the period of heating, although in this series of determinations no two of them lie close together at the highest temperatures. The carbonization value for oil 2 at 265° is very nearly, and at 275° exactly, the mean of the values for the other two oils at the respective temperatures. It was shown above that the curves plotted from the carbonization values of the oils oxidized in sunlight are rather widely separated from one another, instead of having the decided tendency, noticed in the other tests, for two of them to behave quite differently from the remaining one. In both of these sets of curves there seems to be a tendency for oil 2 to draw away from oil 1 and to become parallel with oil 3. If this has any special significance, the explanation is not apparent.

The eight oils, A to H, which were tested as a further check upon the influence of the time of heating, were carbonized for two and one-half hours at each of three temperatures. The following table gives the data obtained. The corresponding curves are shown in Fig. 5.

TABLE 10

Carbonization of Eight Special Oils Heated to Different Temperatures

Oil	Percentage carbonization when heated to—		
	250°	260°	270°
A	0.08	0.43	1.18
B	.04	.40	.81
C	.02	.11	.45
D	Trace	Trace	.31
E	.40	1.11	2.02
F	.47	1.22	2.51
G	.35	.77	1.68
H	.70	1.33	2.54

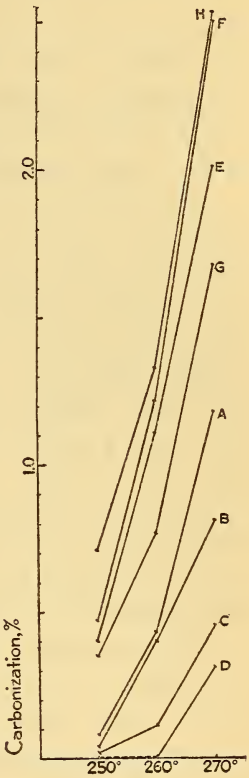

FIG. 5.—*The effect, upon the percentage of carbonization, of heating eight special oils to different temperatures for the same length of time*

It is interesting to see that oil D, which gave only traces of carbonized matter even when heated for four and one-half hours at 250°, and which in this series of tests did not carbonize to any extent at 260°, shows a sudden increase in insoluble matter at 270°. The curves of the other oils are of the expected form. They are a further justification of the conclusion already drawn that the greater the carbonization value is at 250° the more rapidly does it increase when the oil is heated to a higher temperature.

VIII. GENERAL CONSIDERATIONS

Experience has shown that, while it is easy to obtain concordant results in determining the carbonization values of "good" oils, it is an entirely different matter when the percentage of precipitate is in the neighborhood of 1 per cent or more. It is believed that this is not due to unequal heating of the flasks in different positions in the bath, and is certainly not due to differences in the thickness of the flasks. The most reasonable explanation appears to be that occasional particles of foreign matter, such as metal or rust, act catalytically, giving the portion of oil in which they happen to be a start over the others.

An interesting case bearing upon this came to light in testing a sample in which there were numerous black particles. The bottle was left undisturbed for 24 hours to allow these to settle and the oil was then tested. The value found was 0.91. A few weeks later, the bottle having been untouched meanwhile, the carbonization value was 0.55, a figure that agreed closely with the value for other samples of the same brand. This experience emphasizes the need of taking every precaution in sampling, as well as in testing the oil. In this connection may be mentioned the work of Schlüter[25] who found that in most of the cylinder deposits examined by him, the trouble did not lie in the quality of the oil used, but was caused by sand and other foreign matter accidentally introduced or carelessly left in the engine cylinders, etc.

When an oil is carbonized there is usually formed on the walls of the flasks a brown coating, the properties of which justify the use of the name "varnish" for it. The large mass of data accumulated in the present experiments verifies the statement made in earlier papers that there is no regularity in the amount of varnish formed, and no connection between this and the amount of precipitate thrown down by petroleum ether. Fortunately for the success of the method, the varnish is not loosened from the flask walls by this solvent, and none, or at most only a few negligible flakes of it, is washed out of the flask. On the other hand, the precipitate can as a rule be transferred easily to the filter. Occasionally it is necessary to use a feather to dislodge the particles.

It may be well to repeat, parenthetically, the statement that there is no direct connection between the loss by evaporation when an oil is heated and the percentage of carbonized matter formed at

[25] Chem.—Ztg., 37, pp. 221–223; 1913.

the same time.[26] Because this statement has been questioned, though not in print, it may be well to give the following data showing that this is true, not only for the same, but also for different oils.

TABLE 11

Showing Independence of Carbonization Value and Evaporation Loss on Heating to 250°

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

It so happens that these oils have carbonization values that increase as the flash and fire points become lower. That this is accidental can be seen from the following table which gives data on a few oils recently tested, and shows that the flash and fire points are also independent of the carbonization value.

TABLE 12

Showing Independence of Carbonization Value and the Flash and Fire Points

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

IX. SUMMARY

In order to determine whether there is any close connection between the rate of oxidation of automobile oils when exposed to sunlight and air and their carbonization values when heated to comparatively high temperatures, a study was made of three brands of oil. The gains in weight and in acidity and the increase in the carbonization value were determined at frequent short intervals. In the first two of these tests, two of the oils showed nearly identical gains, the third differing quite noticeably. In the carbonization test the values for the three oils were quite far apart.

Of minor importance were determinations of the demulsibility, the iodine number, and the Maumené number. The effect of

[26] Techn. Paper, Bur. Standards, 4, p. 12, 1911; J. Ind. Eng. Chem., 3, p. 815, 1911.

oxidation was to increase the tendency to form emulsions with water. The iodine numbers were lower and Maumené numbers higher for the oxidized than for the original oils.

The changes in the carbonization values caused by heating the above three oils and eight others to 250° for different lengths of time were then studied, as well as the changes caused by heating to different temperatures for three hours. It was found that in both cases the greater the carbonization value at first, the more rapidly did it increase as the temperature was raised or the time of heating extended. In other words, an oil which has a low carbonization value if heated to 250° for two or three hours and an oil showing a somewhat higher value under the same conditions will be farther and farther apart as the conditions become more strenuous.

The carbonization value of an oil is coming to be recognized as a valuable criterion in routine testing, and methods for its determination are finding their way into textbooks, as well as into the journals. Most of these methods prescribe heating the oil for many hours, but it seems, from the work described above, that this is unnecessary. In most cases, heating for two and one-half hours is sufficient, and has the advantage of permitting two runs in a working day, with the necessary interval of an hour or more for the bath to cool. Of far greater and, indeed, of vital importance, is the exercise of extreme care in taking and preserving samples, as well as in testing them.

A study of all the data obtained shows that there is no direct proportionality, but only a rough parallelism, between the results of the different tests described above.

In conclusion, it is shown that the carbonization value is independent of the flash and fire points and of the evaporation loss on heating.

WASHINGTON, December 23, 1916.