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## CHEMICAL CONSTITUTION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MID-CONTINENT PETROLEUM<sup>1</sup>\*

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### ABSTRACT

A correlation has been made of the properties of 179 fractions of oil prepared by extensive distillation and extraction of the extract portion of the lubricant fraction from a midcontinent petroleum. The correlation includes a comparison of the properties of these fractions with those of a selected 15 of the same fractions after complete hydrogenation, with those of synthetic hydrocarbons of high molecular weight, and with those of fractions of "water-white" oil previously prepared from this same lubricant fraction.

The following physical and chemical properties have been compared: Specific optical dispersion, specific optical refraction, specific optical rotation, aniline point, viscosity at 100° and at 210° F, kinematic-viscosity index, and boiling point at 1 mm Hg. The sulfur, oxygen, and nitrogen content and the value of  $x$  in the expression  $C_nH_{2n+x}$  have also been considered.

Concerning the chemical constitution of the lubricant fraction of a midcontinent petroleum from which the "wax" and "asphaltic" constituents have been removed, the following conclusions are drawn: (1) about 60 percent of the material consists of naphthenes with from 1 to 3 rings per molecule (a very small amount of material containing 4 naphthenic rings is probably present also); (2) about 15 percent of the material consists of molecules with 1 aromatic ring and from 1 to 3 naphthenic rings per molecule, together with a small amount of sulfur and oxygen compounds; (3) about 14 percent of the material consists of molecules with 2 aromatic rings (linked through two common carbon atoms) and about 2 naphthenic rings per molecule, together with a small amount of sulfur and oxygen compounds; (4) about 11 percent of the material consists of molecules with more than 2 aromatic rings (each probably linked through two common carbon atoms) and 1 or 2 naphthenic rings per molecule, together with some sulfur, nitrogen, and oxygen compounds.

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## I. INTRODUCTION

Two years ago this laboratory prepared several series of fractions of water-white oil by extensive distillation and extraction of the lubricant fraction from a midcontinent petroleum. Certain physical properties of these fractions were determined and conclusions were drawn as to the chemical nature of the fractions [1, 2].<sup>3</sup> To obtain a more complete picture of the constitution of the lubricant fraction five series of fractions were prepared in an analogous manner from the extract portion of the same oil and a number of their physical properties determined [3]. Fifteen of these fractions were completely hydrogenated to naphthenes and their physical properties again determined [4]. In this paper data on the extract fractions, the hydrogenated fractions, and the water-white oil are correlated with data available in the literature on synthetic hydrocarbons. Although special consideration is given to the chemical composition of the extract portion, conclusions are drawn as to the constitution of the entire lubricant fraction, except for wax and asphaltic constituents.

## II. ORIGIN OF THE PETROLEUM FRACTIONS AND SOURCES OF THE DATA USED IN THIS CORRELATION

The lubricating-oil stock came from well No. 6 of the South Ponca Field, Kay County, Okla. The lubricant fraction was distilled in vacuo by the Sun Oil Co., Philadelphia, Pa., before receipt at this Bureau. Its treatment in this laboratory is illustrated diagrammatically in figure 1. It consisted in (1) the separation of an extract portion by extraction with liquid sulfur dioxide at room temperature, (2) the separation of a wax portion by crystallization from ethylene chloride at  $-18^{\circ}\text{C}$ , and (3) the separation of the remainder by filtration through silica gel into two portions (a) a water-white portion, and (b) a portion recovered from silica gel and listed in figure 1 as silica gel "hold-up." As shown in figure 1, the extract portion was further separated, by extraction with sulfur dioxide and petroleum ether at  $-55^{\circ}\text{C}$ , into two portions, one of which, denoted as "asphaltic material", was placed in storage. The petroleum ether-soluble portion was mixed with the silica gel hold-up and the mixture systematically distilled. Five charges, denoted as *A*, *B*, *C*, *D*, and *E*, were prepared from the distillation fractions and each charge was separated into a series of 30 to 40 fractions by extraction with methyl cyanide in 16.7-m (55-ft) columns. The properties of these fractions have been compared with each other and with the properties of 3 fractions from series *B*, with 10 from series *C*, and with 2 from series *E*, after their complete hydrogenation [4]. They have also been compared with the properties of several series of water-white oil fractions previously prepared by distillation and extraction from the same lubricant fraction [1].

The data used for comparison come, for the extract fractions, from tables 9 and 10 of reference [3]; for the hydrogenated fractions, from table 4 of reference [4]; and for the water-white oil fractions, from tables 2 and 3 of reference [1].

<sup>3</sup> Figures in brackets indicate the literature references at the end of this paper.

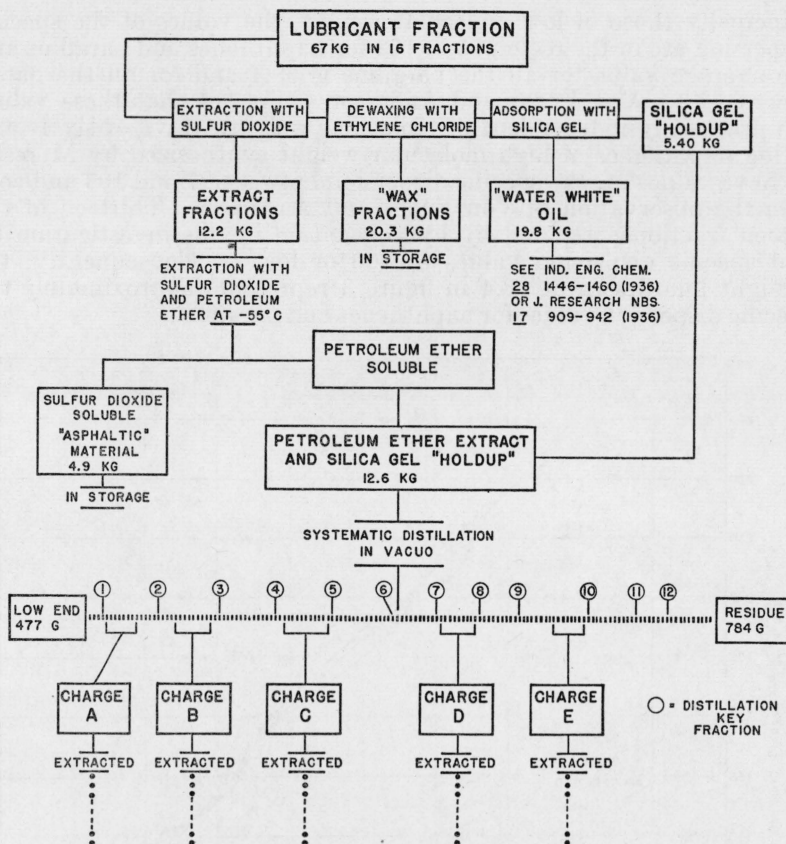


FIGURE 1.—Chart showing treatment and disposition of lubricating oil fractions.

### III. DISCUSSION OF PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

#### 1. SPECIFIC REFRACTIVE DISPERSION <sup>4</sup>

It is evident from figure 2 that there is a general similarity in the shape of these curves for the specific dispersion and that pronounced changes in slope occur at approximately the same percentage extracted. Curves for series *A* and *E*, though not unlike those of *B*, *C*, and *D*, are not included since their presence would mechanically complicate the figure.

Both Vlugter, Waterman, and Van Westen [5] and Von Fuchs and Anderson [6] have used specific dispersion as a means of obtaining information concerning the chemical constitution of petroleum fractions. The former have used the *G* and *C* lines, and have pointed out that an oil is practically free from aromatic hydrocarbons when  $(n_a - n_c)/d$  is less than  $158 \times 10^{-4}$ . In Von Fuchs and Anderson's [6] recent review of specific dispersion values of synthetic hydrocarbons,

<sup>4</sup> For convenience values of the specific dispersion given in the text refer to values of  $\frac{n_F - n_C}{d} \times 10^4$ .

principally those of low molecular weight, the values of the specific dispersion are in the region 95 to 102 for naphthenes and paraffins and the average value for all the paraffins is 98.4 and for all the naphthenes 98.3. Von Fuchs and Anderson point out that these values are practically independent of molecular weight. Five of six 1- and 2-ring naphthenes of high molecular weight synthesized by Mikeska [7] have values for the specific dispersion between 97 and 100 and confirm the observation of Von Fuchs and Anderson. Thirteen of the fifteen fractions prepared by hydrogenation in this investigation [4] had specific dispersion values of 100 or lower. Consequently, the straight line drawn at 98.4 in figure 3 represents approximately the specific dispersion values for naphthenes and paraffins.

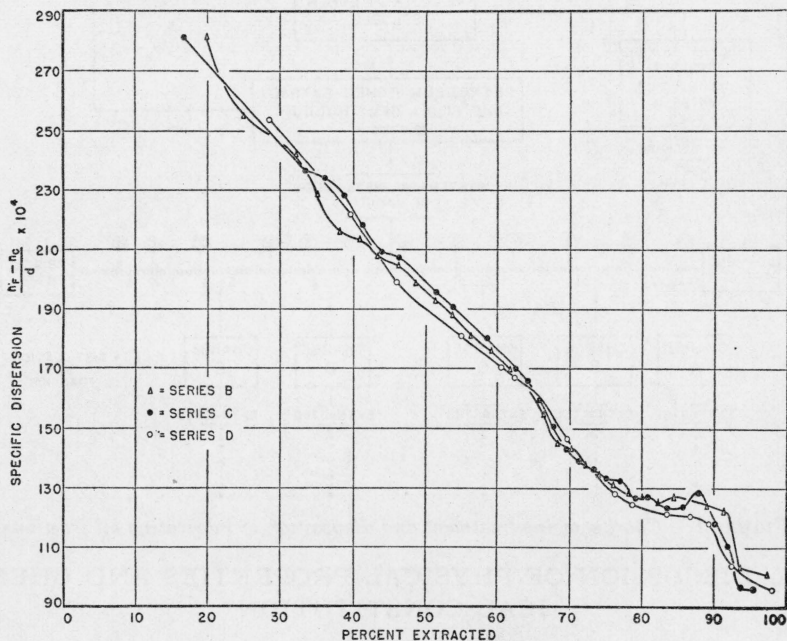


FIGURE 2.—Specific dispersion of petroleum fractions.

In figure 2 and in all subsequent figures in which a property is plotted with respect to the percentage extracted, the average value for the percentage extracted has been used. Thus fraction C-5 which was the extract obtained between 15.3 and 17.9 percent of the charge, is represented by a point at 16.6 percent.

Von Fuchs and Anderson also give values for the specific dispersion of benzene and some of its homologues and point out that the dispersion decreases as the number of nonbenzenoid carbon atoms increases. Mikeska [7] gives values for several compounds of this type of high molecular weight. Curve III, figure 3, is drawn through the values recorded by Von Fuchs and Anderson for benzene and its homologues of low molecular weight and through those benzene and tetralin homologues of high molecular weight given by Mikeska. Similarly, curve I is drawn through the specific dispersions given by Von Fuchs and Anderson for naphthalene and its homologues of low molecular weight, and through the values given by Mikeska for those of high molecular weight. As Von Fuchs and Anderson point out,

the specific dispersion of naphthalene and its homologues in which the aromatic rings have two carbon atoms in common are abnormally high when compared with hydrocarbons in which the rings are connected through a nonbenzenoid carbon atom. Curve *II* is drawn for 2-ring aromatic hydrocarbons in which the connection between rings is through nonbenzenoid carbon atoms. This curve is based on values for two hydrocarbons of low molecular weight reported by Von Fuchs and Anderson, and on the value 142 for 1,1-diphenylhexadecane and 143 for 1-phenyl-2-benzylheptadecane, synthesized by Landa and

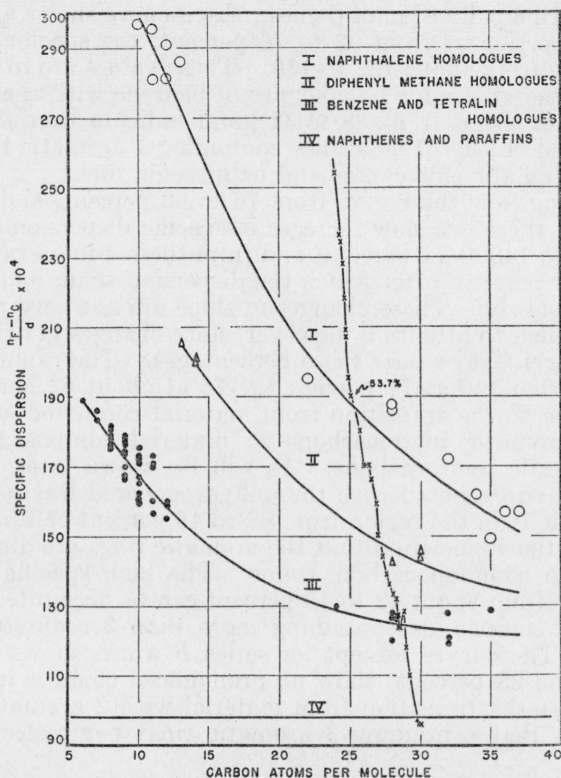


FIGURE 3.—Specific dispersion of synthetic hydrocarbons with respect to the carbon atoms per molecule.

Cech [8]. A point is also plotted for 1,1-diphenyloctadecane synthesized by Mikeska [7], although other properties reported for this compound are not what would be expected. Hydrocarbons with 2 aromatic rings directly connected at one point will have values lying between curves *I* and *II*. Included in this figure is a line showing the specific dispersions of the fractions from extractor *C*. On this line is indicated one point which represents the fraction extracted at 53.7 percent. Evidence is given later to show that this fraction contains essentially compounds with 2 aromatic rings, with the rings linked through two common carbon atoms, and this is in agreement with its specific dispersion.

An interpretation of the specific dispersions of the extraction fractions may be obtained by comparing figures 2 and 3. Here and later in this paper it is convenient in the interpretation of these figures to begin at the right-hand side of the figures and consider the curves in the direction of decreasing percentages extracted. In figure 2, each curve shows a nearly horizontal portion in the region from about 100 to 94 percent extracted. In this region the specific dispersions vary from 96 to 101, and it is evident that they contain little, if any, aromatic material. Since paraffins are probably absent because the value for  $x$  in the expression  $C_nH_{2n+x}$  is negative these fractions are composed principally of naphthenes. Each curve shows another relatively flat portion at from 92 to 76 percent, the specific dispersions here varying from about 122 to 130. These values are in good agreement with the values for homologues of benzene with the same number of carbon atoms (i. e., 28 to 32), and indicate that the fractions are composed chiefly of molecules containing 1 aromatic ring and the necessary aliphatic side chains and naphthenic rings.

Considering now the region from 76 to 62 percent, and in particular series *C*, there is a slow increase in specific dispersion from 132 at 76 percent to 140 at 71 percent, and from there a more rapid increase to 175 at 62 percent, after which the dispersion again increases somewhat more slowly. These changes in slope are not very pronounced. They are called to attention, however, since changes in other physical properties occur at or near these percentages. The rapid increase in dispersion from 140 at 71 percent to 175 at about 62 percent is presumably due to the transition from material composed substantially of 1-ring aromatic hydrocarbons to material composed largely of 2-ring aromatic hydrocarbons. As will be shown later, when comparing the hydrogenated with the unhydrogenated fractions, the specific dispersions in the region from 62 to 45 percent can be accounted for only on the supposition that the aromatic rings are directly joined through two common carbon atoms. The high specific dispersions (above 210) from about 42 to 18 percent can be accounted for by the presence of compounds containing more than 2 aromatic rings per molecule. The curves (except for series *B* which shows a break between 46 and 38 percent) show no pronounced changes in slope, and indicate that the transition from material with 2 aromatic rings per molecule to that containing 3 aromatic rings per molecule has not been sharp.

## 2. SPECIFIC REFRACTION

The curves in figure 4, like those for the specific dispersion, show a general similarity in shape, but, unlike those for the specific dispersion, they show several pronounced maxima and minima. An interpretation of the values for the refraction and the maxima and minima shown by these curves may be obtained by comparing figures 4 and 5.

Vlugter, Waterman, and Van Westen [11] have shown that the Lorentz-Lorenz specific refractions may be used for determining the number of rings in aromatic-free oils, and conversely, for determining whether an oil is aromatic-free by comparing its  $x$  value obtained from the carbon-hydrogen ratio and molecular weight with that obtained

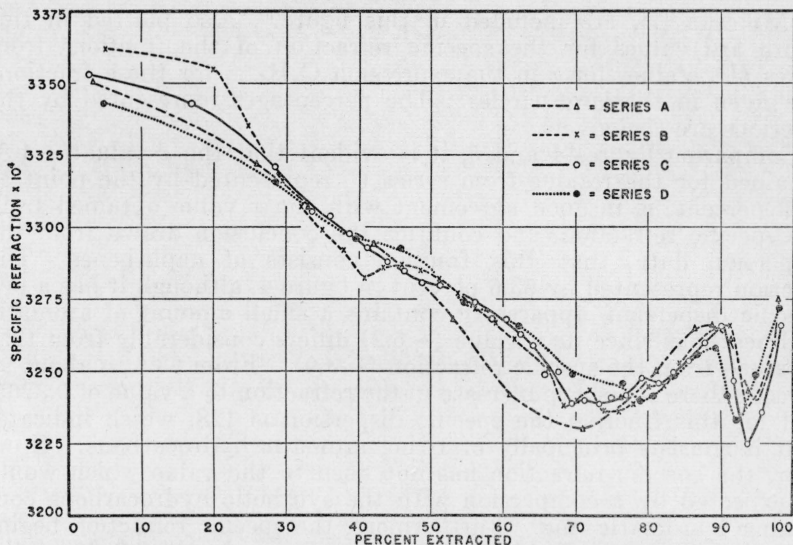


FIGURE 4.—Specific refraction (Lorentz-Lorenz) of petroleum fractions.

from its specific refraction. This latter method was used in this laboratory with the water-white oil [2] and the hydrogenated fractions prepared from the series under discussion [4]. In figure 5

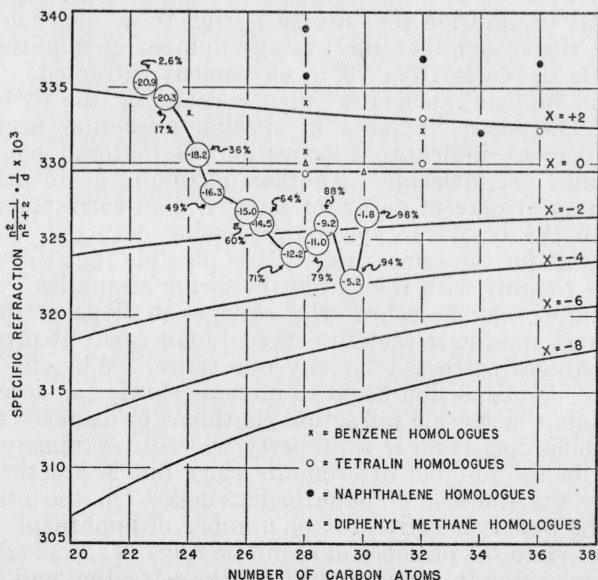


FIGURE 5.—Specific refraction of fractions from series C compared with theoretical curves for naphthenes and paraffins and with synthetic aromatic hydrocarbons.

theoretical curves, similar to those of Vlughter, Waterman, and Van Westen [11], show the variation in specific refraction with the number of carbon atoms for paraffins and for naphthenes containing 1, 2, 3, and 4 rings. Values for aromatic hydrocarbons, principally those

of Mikeska [7], are included in this figure.<sup>5</sup> Also plotted in this figure are values for the specific refraction of the fractions from series *C*. Values for  $x$  in the expression  $C_nH_{2n+x}$  for these fractions are given in the large circles. The percentages represented by the fractions are also given.

Comparing figures 4 and 5, it is evident that the  $x$  value ( $-1.8$ ) obtained for the residue from series *C*, represented by the point at 98.2 percent, is in good agreement with the  $x$  value obtained from the specific refraction, and confirms the conclusion drawn from the dispersion data, that this fraction consists of naphthenes. The fraction represented by 93.6 percent in figure 4, although it has a low specific dispersion, apparently contains a small amount of aromatic hydrocarbons since its  $x$  value ( $-5.2$ ) differs considerably from that obtained from the specific refraction ( $-3.9$ ). From 93.6 to about 90 percent there is a sharp increase in the refraction to a value of 0.3265, and for this fraction the specific dispersion is 128, which indicates that it consists principally of 1-ring aromatic hydrocarbons. However, the specific refraction has not risen to the value which would be expected by a comparison with the synthetic hydrocarbons containing 1 aromatic ring. Furthermore, the specific refraction begins to decrease at 90 percent and attains a low value of 0.3239 in the region from 73 to 69 percent, although the specific dispersion remains fairly constant between 90 and 76 percent and increases only slightly at 71 percent.

The relatively low value for the specific refraction, and its decrease to a minimum at 73 to 69 percent, can be accounted for on the supposition that in addition to 1 aromatic ring these molecules contain naphthenic rings, and that the average number of naphthenic rings per molecule increases from 90 to 69 percent extracted. This supposition will be confirmed later when considering the hydrogenated fractions. The sharp increase in specific refraction beginning at about 69 percent indicates a transition to material containing 2 aromatic rings per molecule. Another maximum at 46 percent and a minimum at 41 percent occur for series *B*, and correspond approximately with the breaks in specific dispersion occurring between 46 and 38 percent for the same series. It is possible that this minimum corresponds roughly with the end of the 2-ring aromatics.

The question may be asked why changes in slope of the specific dispersion and specific refraction curves do not occur at precisely the same percentages extracted for any one series. Why, for example, does the specific dispersion begin to increase slowly for series *C* at 77 percent, while the specific refraction continues to decrease to 69 percent? Specific dispersion is a property which is extremely sensitive to changes in the number of aromatic rings but is practically uninfluenced by the number of naphthenic rings. On the other hand, specific refraction is sensitive to the number of naphthenic rings but not as sensitive to the presence of aromatic rings as specific dispersion. For this reason simultaneous analysis of the refraction and dispersion curves serves to yield the maximum amount of information from the data on refraction and dispersion. In the region from 77 to 69 percent there is, as will be shown later, a slight increase in the average

<sup>5</sup> Compound 48 of Mikeska [7], i. e., 1,1-diphenyloctadecane was not included because most of the physical properties of this compound are out of line. Values for two compounds synthesized by Landa and Cech [8], 1,1-diphenylhexadecane and 1-phenyl-2-benzylhexadecane, are included, however.



number of aromatic rings per molecule; that is, a few percent of 2-ring aromatic hydrocarbons are present, which causes the increase in specific dispersion, but the number of naphthenic rings are increasing at such a rate that their influence predominates (as far as the specific refraction is concerned) and causes the specific refraction to decrease to 69 percent.

In figure 6 the simpler Gladstone-Dale expression  $(n-1)/d$  is used. There is also plotted in this figure the "refractivity intercept,"  $n-d/2$ , a quantity which has been proposed by Kurtz and Headington [9] and Kurtz and Ward [10] for use in analyzing hydrocarbon mixtures. The similarity of these two curves is obvious, and for these quantities also, as with the Lorentz-Lorenz specific refraction, there is a minimum in the neighborhood of 93.6 percent, though the depth of the minimum is not as great. Between 90 and 70 percent, instead of the

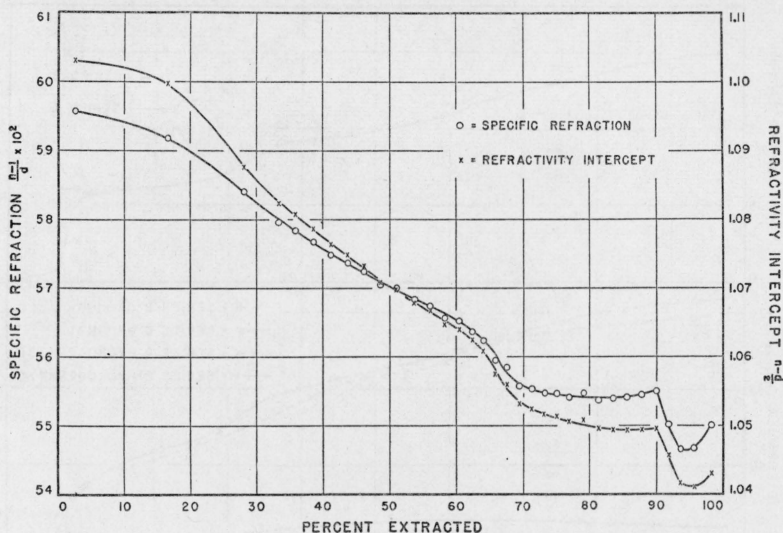


FIGURE 6.—Specific refraction (Gladstone-Dale) and refractivity intercept of fractions from Series C.

very pronounced minimum given by the Lorentz-Lorenz refraction, these curves are more nearly horizontal and indeed begin to rise in the neighborhood of 78 percent. Evidently the two quantities used in figure 6 are not as sensitive to the presence of naphthenic rings as the Lorentz-Lorenz specific refraction and in many respects these quantities resemble the specific dispersion as closely as they do the Lorentz-Lorenz specific refraction.

### 3. INCREASE IN HYDROGEN ATOMS PER MOLECULE ON HYDROGENATION

It is now in order to examine by a fundamental method the conclusions drawn from the specific-dispersion and specific-refraction data. Ten fractions from series *C* and three fractions from series *B* were completely hydrogenated, their physical properties recorded, and evidence produced to show that the hydrogenation to naphthenes

was substantially complete and that there was no loss of carbon atoms in the hydrogenation process [4]. For such fractions the difference in  $x$  values (from the expression  $C_nH_{2n+x}$ ) before and after hydrogenation (except for olefinic unsaturation and possible small errors due to the removal of sulfur, nitrogen, and oxygen in the hydrogenation process, which will be considered later) is a measure of the aromatic content.<sup>6</sup>

In the lower half of figure 7 are plotted the  $x$  values for the fractions from series *C* with respect to the percentage extracted both before and after hydrogenation. Unfortunately, after the determination of its physical properties, a sufficient quantity of the important fraction represented by 93.6 percent was not available for hydrogenation. This fraction had a specific dispersion value of 97, which would indicate that it was substantially naphthenic. Nevertheless, it is thought that

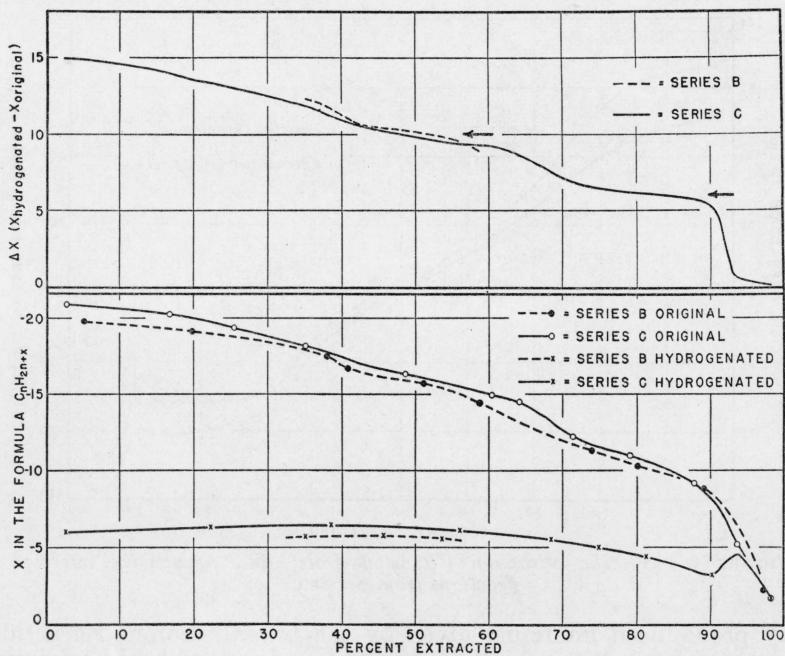


FIGURE 7.—Lower half:  $x$  in the formula  $C_nH_{2n+x}$  for fractions before and after hydrogenation; upper half: Increase in hydrogen atoms per molecule on hydrogenation.

it contained a small amount of aromatic hydrocarbons because its  $x$  value, determined experimentally, was  $-5.2$  and that obtained from its specific refraction  $-3.9$ . The true value, were it free from aromatic hydrocarbons, would probably lie between these values, and the value  $-4.6$  is believed to be nearly correct. Consequently, the curve for  $x$  (hydrogenated) is drawn through this point.

For series *B* the  $x$  (original) value is also plotted over almost the entire range, while the  $x$  (hydrogenated) value is given only in a region of particular interest for this series. In the upper half of the same figure is plotted the difference in the  $x$  values after and before hydrogenation,  $\Delta x = (x \text{ hydrogenated} - x \text{ original})$ , which is the in-

<sup>6</sup>Vlugter, Waterman, and Van Westen [11] have used this method extensively.

crease in the number of hydrogen atoms per molecule on hydrogenation. For series *C* this curve shows a nearly horizontal portion from about 88 to 71 percent, in which  $\Delta x$  varies from 5.7 to 6.8. This is considered definite proof that this material consists principally of 1-ring aromatic hydrocarbons and the necessary naphthenic rings and aliphatic side chains.

In the region from 71 to 61 percent there is a rapid increase in  $\Delta x$  to the value 9.2. From 62 to 44 percent there is some indication of a plateau, the  $\Delta x$  value increasing only to 10.5 at 44 percent. The corresponding plateau for series *B* in the region from 56 to 44 percent is slightly more pronounced and the  $\Delta x$  value varies only from 9.6

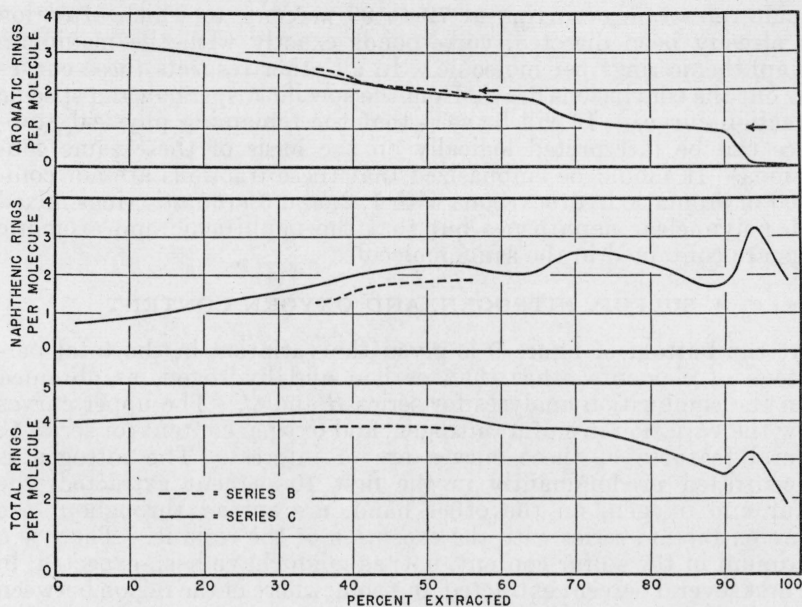


FIGURE 8.—Rings per molecule of petroleum fractions.

Lower curve: Total rings per molecule; middle curve: Naphthenic rings per molecule; top curve: Aromatic rings per molecule.

to 10.5. Doubtless, the plateau is associated with 2-ring aromatic hydrocarbons, and the fact that  $\Delta x$  for this plateau is approximately equal to 10 instead of 12 is considered strong evidence that in these hydrocarbons the aromatic rings are linked through two common carbon atoms. If the specific dispersion values are considered in conjunction with the values for  $\Delta x$ , the evidence appears to be conclusive that the aromatic rings are condensed. For example, fraction *C-19*, represented by 53.7 percent with 25.1 carbon atoms, has a specific dispersion value of 190 and a  $\Delta x$  value equal to 9.5. As can be seen from figure 3, it lies reasonably close to the curve for condensed 2-ring aromatic hydrocarbons. If this fraction were composed of rings linked through nonbenzenoid carbon atoms, its specific dispersion would be much lower, about 154, and its  $\Delta x$  value much higher, 12. It is, of course, possible that small amounts of aromatics with noncondensed rings do exist in these fractions, but, if any, the percentage must be small. In figure 8, three curves are given: The

lower curve gives the total number of rings per molecule, the intermediate curve the number of naphthenic rings per molecule, and the upper curve the number of aromatic rings per molecule. The calculation of the number of aromatic rings is based on a change in  $x$  value of 6 for the first ring hydrogenated and of 4 for each succeeding ring. This method of calculation assumes that all of the aromatic rings are condensed, an assumption, evidently, reasonably close to the truth. The number of naphthenic rings is given by the difference between the total number and the number of aromatic rings per molecule.

It is interesting to note that even the most soluble fractions with about 3 aromatic rings per molecule contain, on the average, nearly 1 naphthenic ring per molecule. It is evident that the minimum in specific refraction occurring at 72 to 69 percent, to which attention has already been directed, corresponds exactly with the maximum in naphthenic rings per molecule. In all other respects these curves bear out the conclusions drawn from the specific dispersion and specific refraction curves. It will be seen that the remaining physical properties can be interpreted logically on the basis of these same conclusions. It should be emphasized that these fractions are not composed of aromatic hydrocarbons with 1, 2, and 3 aromatic rings mixed with polynuclear naphthenes but that the naphthenic and aromatic rings are contained in the same molecule.<sup>7</sup>

#### 4. SULFUR, NITROGEN, AND OXYGEN CONTENT

At the bottom of figure 9 is given the variation in the total percentage of elements other than carbon and hydrogen, as obtained from the combustion analyses for series *B* and *C*. The upper curves show the variation in sulfur, nitrogen, and oxygen content for series *C*. Several features of these curves are of interest. The nitrogen is concentrated predominantly in the first 10 percent extracted, the sulfur and oxygen, on the other hand, are spread throughout the entire extraction series with the exception of the residue. There is a maximum in the sulfur content, not, as might have been expected, in the first several percent extracted, but somewhere in the region between 20 and 40 percent. Another small but definite maximum in the sulfur content occurs in the neighborhood of 88 percent extracted. The oxygen content also shows a small but definite maximum in this region. This maximum in sulfur and oxygen content corresponds with monocyclic aromatics with the minimum number of naphthenic rings found (1.6), and the decrease in sulfur and oxygen content at slightly lower percentages extracted is associated with increase in the number of naphthenic rings. No explanation is offered for the maximum in sulfur content in the region from 20 to 40 percent. It does not seem probable that sulfur so modifies the solubility of all types of hydrocarbon molecules with which it is combined that it can ever be concentrated by solvent extraction into one narrow region.

<sup>7</sup> Consider a fraction with the formula  $C_{30}H_{22}$ , which after hydrogenation, has the formula  $C_{30}H_{38}$ . In 100 molecules of this fraction there are 100 naphthenic rings and 100 aromatic rings. It is apparent that this fraction could not be composed of equimolar portions of the monocyclic aromatic  $C_{30}H_{14}$  with the monocyclic naphthene  $C_{30}H_{26}$ , since 100 molecules of such a mixture would contain only 50 aromatic and 50 naphthenic rings. The fraction could, however, be composed of an equimolar mixture of a dicyclic naphthene  $C_{30}H_{38}$  with a dicyclic homologue of diphenyl  $C_{30}H_{46}$ . Such a mixture would have the empirical formula  $C_{30}H_{22}$  and 100 molecules would contain 100 naphthenic and 100 aromatic rings. The coexistence of a 2-ring naphthene and a 2-ring aromatic in extensively extracted fractions like those described above is, however, not possible because of their different solubilities (see aniline point curves for 2-ring naphthene hydrocarbons and 2-ring aromatic hydrocarbons in fig. 13).

Instead, it seems probable that the hydrocarbon portion of the molecule plays a predominant part in governing the solubility of the entire molecule, and consequently the regions in which sulfur is concentrated by extraction depend largely on the type of the hydrocarbon portion of the molecule with which it is combined. As a matter of fact, for the fraction from series C, which contains the largest amount of sulfur, the average number of atoms per molecule is 0.14 for sulfur, 0.02 for nitrogen, and 0.15 for oxygen. These are to be compared with hydrogen and carbon atoms to the number of 23.2 and 26.1, respectively.

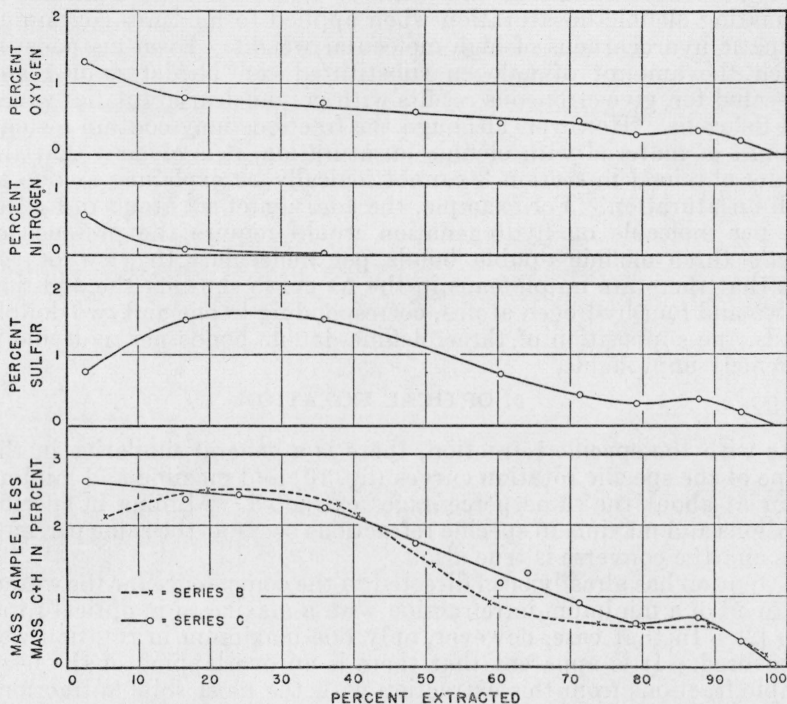


FIGURE 9.—Sulfur, nitrogen, and oxygen content of petroleum fractions.

In a preceding section it was pointed out that the removal of sulfur, oxygen, and nitrogen in the hydrogenation process might cause a change in the value of  $\Delta x$  and introduce an error in the calculation of the aromatic content. If the nitrogen, sulfur, and oxygen through all their valencies were linked only to carbon, their removal and the substitution of hydrogen in their place would result in an absorption of three, two, and two atoms, respectively, for each atom of nitrogen, sulfur, and oxygen removed. If, however, the sulfur and oxygen were attached by one valence to carbon and the other to hydrogen, the removal of these elements in the hydrogenation process would cause no change in hydrogen content. In the case of the removal of nitrogen, if two of the valencies were attached to hydrogen

and only one to carbon, a decrease in hydrogen content would occur. Assuming that all the valencies of the sulfur, nitrogen, and oxygen are linked to carbon, for the two fractions in series *C* represented by 79 and 49 percent extracted, it is possible to attribute changes in  $\Delta x$  of 0.22 and 0.46 to the removal of these elements. The actual change in  $\Delta x$  attributable to this source is likely to be much smaller.

#### 5. OLEFINIC UNSATURATION

Halogen numbers were not determined on any of these fractions, since such determinations are without significance as a means of estimating olefinic unsaturation when applied to mixtures containing aromatic hydrocarbons of high molecular weight. Even methods by which the amount of halogen substituted can be determined and corrected for, give erroneous results with polynuclear aromatics which add halogens. However, although the fractions may contain a small amount of material with olefinic unsaturation, it is evident that the results obtained in section 3 cannot logically be explained as due to such unsaturation. For example, the addition of six atoms of hydrogen per molecule on hydrogenation would require the presence of *exactly* three olefinic double bonds per molecule. In view of the fact that there are no plateaus in the  $\Delta x$  curve showing the addition of two and four hydrogen atoms, corresponding to one and two double bonds, the supposition of three olefinic double bonds per molecule is extremely improbable.

#### 6. OPTICAL ROTATION

As with the specific refraction, there is a general similarity in the shape of the specific rotation curves (fig. 10) and maxima and minima occur at about the same percentages extracted. Minima in specific rotations and maxima in specific refractions occur at the same percentages and/the converse is true also.

Attention has already been directed to the coincidence for the water-white oil of a minimum in refraction with a maximum in optical rotation [2]. In that case, however, only one maximum in rotation was discovered. It is apparent that there is an overlapping of the least soluble fractions from this extraction with the most soluble fractions of the water-white oil, and the maximum in rotation of the water-white oil corresponds with the maximum in rotation occurring with this oil in the neighborhood of 93 percent extracted. Considering series *C*, there is a sharp increase in specific rotation from 98.2 to 93.6 percent, which shows that in this naphthenic material the rotation increases as the number of naphthenic rings increase. The minimum at 90 percent corresponds with the 1-ring aromatic material with the minimum number of naphthenic rings (1.6). The rotation then increases and reaches another maximum in the neighborhood of 68 percent extracted. This increase is associated with an increase in the number of naphthenic rings; in this case, the addition of naphthenic rings to a 1-ring aromatic.

The decrease in rotation from 68 to lower percentages extracted is associated with the transition from 1-ring aromatic hydrocarbons to hydrocarbons with 2 or more aromatic rings and a smaller number of naphthenic rings per molecule.

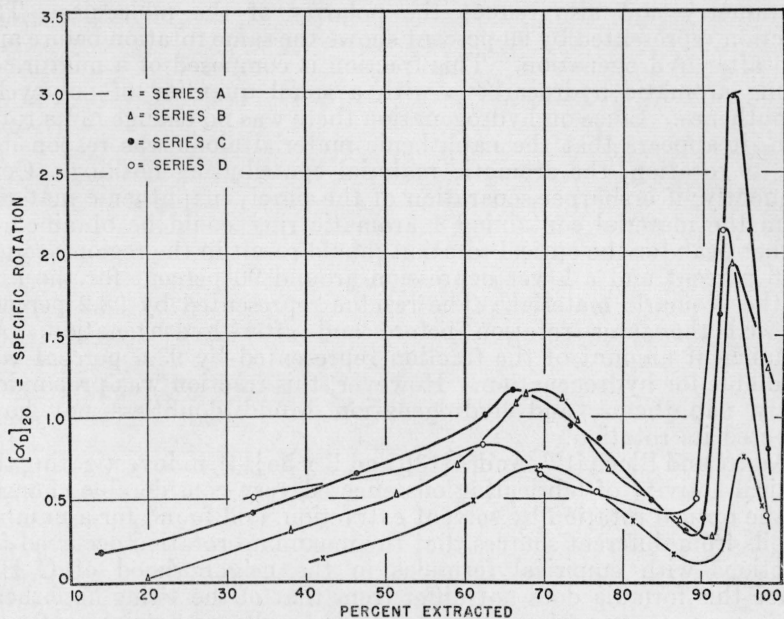


FIGURE 10.—Specific optical rotation of petroleum fractions.

In figure 11 the specific optical rotation of the fractions from series C has been plotted before and after hydrogenation. It will be observed that the shape of the curve is the same after as before hydro-

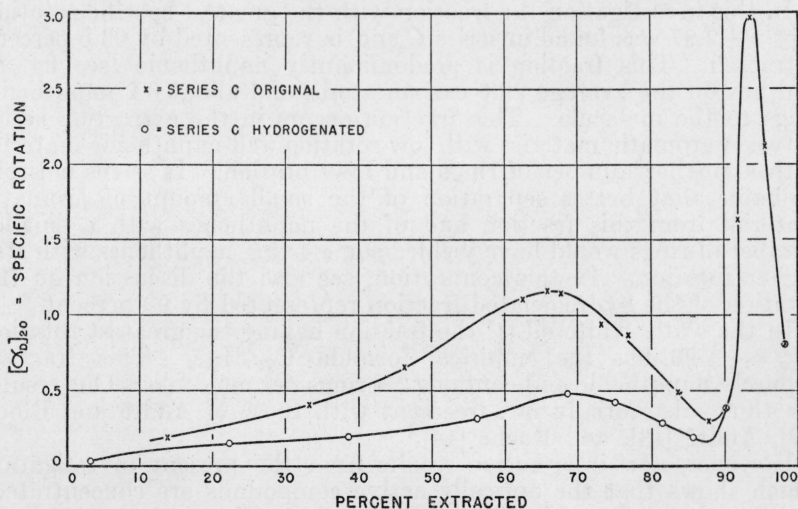


FIGURE 11.—Specific optical rotation of fractions from series C before and after hydrogenation.

genation, a maximum again occurring in the neighborhood of 68 percent. However, the magnitude of the rotation has been markedly reduced for all the fractions up to 86 percent; a result which is to be expected, since hydrogenation probably would reduce the centers of

asymmetry and also reduce the polarity of the molecules. The fraction represented by 90 percent shows the same rotation before and after hydrogenation. This fraction is composed of a mixture of 1-ring aromatic hydrocarbons with a small quantity of polycyclic naphthenes. Since on hydrogenation there was no change in its rotation, it appears that the naphthenic material alone was responsible for its rotation, the aromatic material contributing nothing. Consequently, if a sharper separation of the purely naphthenic material from the material containing 1 aromatic ring could be obtained, a higher peak for the optical rotation should result in the region around 93.6 percent and a lower depression around 90 percent for the first of the aromatic material. The residue represented by 98.2 percent showed the same rotation before and after hydrogenation. An insufficient amount of the fraction represented by 93.6 percent was available for hydrogenation. However, this fraction was preponderantly naphthenic, and hydrogenation would doubtless not have affected its rotation.

André and Bloch [12], André [13], and Roche [14], in investigating the optical activity of lubricating oils effected very considerable changes in the optical rotation by solvent extraction, and found for a number of oils from different sources that the maximum rotation occurred for fractions with empirical formulas in the neighborhood of  $C_{28}H_{50}$ . Since this formula does not differ from that of the 4-ring naphthene cholestane, these authors consider their results as partial confirmation of the hypothesis of Marcusson, who suggested that the sterols might be the source of material for optically active compounds in petroleum. However, these authors have given no evidence to indicate that their fractions were purely naphthenic and they may well have contained considerable aromatic material.

In this investigation the fraction with the greatest specific rotation  $[\alpha]_D^{20} = +2.97$  was found in series *C* and is represented by 93.6 percent extracted. This fraction is predominantly naphthenic (see fig. 8) and has on the average 29.6 carbon atoms and about 3.2 naphthenic rings to the molecule. This fraction occurs in the extraction series between aromatic material with low rotation and naphthenic material with a smaller number of rings and low rotation. It seems entirely probable that better separation of the small amount of aromatic material from this fraction and of the naphthenes with a smaller number of rings would have yielded some 4-ring naphthenes with still higher rotation. In this connection, see also the discussion on the rotation of the hydrogenated fraction represented by 90 percent.

In the water-white oil [1] the fraction having the greatest rotation  $[\alpha]_D^{20} = +1.96$  has the empirical formula  $C_{27.7}H_{52.6}$ . This fraction is purely naphthenic and contains 2.4 rings per molecule. Our results are thus substantially in agreement with those of André and Bloch [12], André [13], and Roche [14].<sup>8</sup>

However, new information results from the present investigation which shows that the optically active compounds are concentrated, also by solvent extraction, in another region. The second region most optically active occurs from 68 to 66 percent extracted for series *C*, for which  $[\alpha]_D^{20}$  was 1.14 to 1.16. Fractions in this region consist

<sup>8</sup> A maximum in optical activity with  $[\alpha]_D^{20} = 8$  has been reported by Engler and Steinkopf [15] for the fraction of an Argentine (Mendoza) crude distilling at 216° C at 0.5 mm Hg. Such a fraction might be expected to have somewhere in the neighborhood of 28 carbon atoms per molecule.



substantially of 1 aromatic ring with about 2.6 naphthenic rings per molecule. The similarity between these fractions and cholestane is apparent, since the dehydrogenation of one 6-membered ring in cholestane results in a hydrocarbon with 1 aromatic and 3 naphthenic rings.

Although the results so far considered are in agreement with the supposition that the sterols with 27 to 30 carbon atoms might be the source of the optically active compounds in petroleum, another factor is to be considered. In the water-white oil [1], which had been repeatedly distilled before extraction, fractions which still had appreciable optical rotation were found considerably removed both in boiling point and in the number of carbon atoms from the fraction with the maximum activity. Thus, although the maximum activity, with specific rotation equal to 1.96, occurred for a fraction with 27.7 carbon atoms and a boiling point of 204° C at 1 mm Hg, a fraction with 37.4 carbon atoms and a boiling point of 269.5° C at 1 mm Hg had a specific rotation of 0.51. For a material thoroughly fractionated by distillation, it seems quite impossible that a sufficient quantity of the hydrocarbons with high rotation from the fraction boiling at 204° C could be present in the fraction boiling at 269.5° C to account for its still very considerable rotation. The present investigation with material extensively distilled shows optical rotation in fractions with boiling points at 1 mm Hg from 185° to 260° C and covering a wide range of carbon atoms (23 to 34). Thus, if the sterols alone are to be considered as the source material of optically active compounds in petroleum, it is necessary to postulate the generation from them of compounds of higher and lower molecular weight.

#### 7. ANILINE POINTS

In figure 12 is a plot of the aniline points of the fractions from series *A*, *B*, *C*, *D*, and *E*, with respect to the percentages extracted. As with the other physical properties, there are pronounced breaks in the slope of these curves occurring at approximately the same percentages extracted.

In figure 13, curves are drawn which show the aniline points with respect to the number of carbon atoms for a number of different types of hydrocarbons. The upper curve,  $x=+2$ , is based on the normal paraffin hydrocarbons. The values for the paraffins of lower molecular weight are those reported by Evans [16], who converted most of these values from the data of Shepard, Henne, and Midgley for critical solution temperatures [17]. The data for the two paraffins of higher molecular weight, *n*-nonacosane (122.0° C) and *n*-dotriacontane (128.0° C) were obtained in this laboratory. The value 127.6° C for the critical solution temperature in aniline for dotriacontane was recently reported by Tilitshyev [18]. Immediately below the curve for the normal paraffins are drawn curves which show the aniline points of naphthenes containing 1, 2, 3, and 4 rings, respectively. The aniline points for the monocyclic and dicyclic naphthenes of low molecular weight on which one end of each curve is based, are those reported by Evans [16]. In the region of high molecular weight, the curves are based on the naphthene fractions of the water-white oil [1] prepared by extraction and on the fractions obtained by hydrogenation [4]. In

determining the location of these curves, there were used only fractions with specific dispersions of 100 or less, which were considered substantially free of aromatic hydrocarbons. Mikeska [7] gives aniline points for two monocyclic and one dicyclic naphthene of high molecular weight. His values for the two monocyclic hydrocarbons are much lower than the corresponding curve, while the value for the dicyclic hydrocarbon is fairly close to the corresponding curve.

Also shown in the figure is a curve for the homologues of benzene ( $x = -6$ ). The region from 15 to 22 carbon atoms is based on the

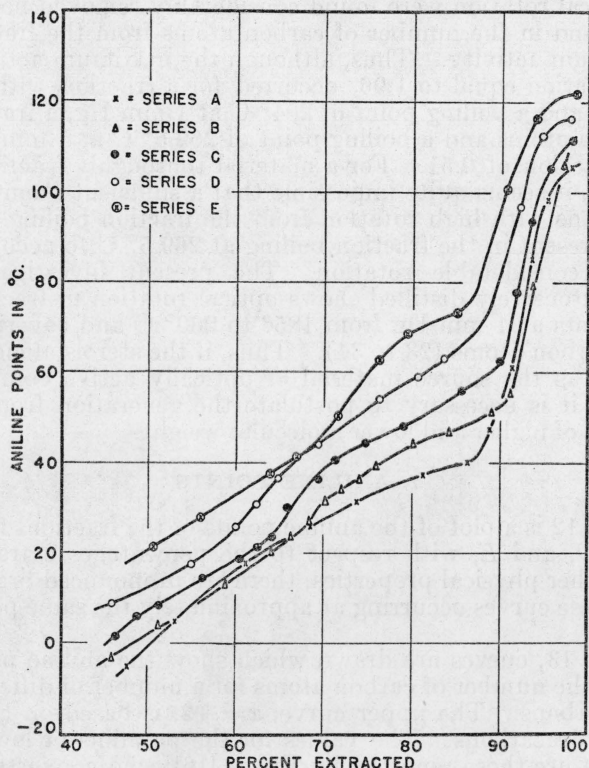


FIGURE 12. Aniline points of petroleum fractions.

critical solution temperature data given by Tilitsheyev [18],<sup>9</sup> while from 24 to 60 carbon atoms the data are those of Mikeska [7].

Below this curve, another curve is drawn through Mikeska's [7] data for homologues of tetralin. This curve shows approximately what would be the aniline points of material containing 1 aromatic and 1 naphthenic ring. The lowest curve is based on Mikeska's data for homologues of naphthalene.

The aniline points of fractions from series *C* are also shown in figure 13, and certain fractions of importance to the discussion have been indicated. Considering now series *C*, the fraction represented by 98.2 percent has an  $x$  value of  $-1.83$ , in fair agreement with that

<sup>9</sup> Evans [16] has pointed out that for many hydrocarbons the critical solution temperatures in aniline usually do not differ as much as 2° C from the aniline points.

expected from the corresponding curve. The fraction is therefore substantially naphthenic. For the fraction represented by 93.6 percent, the  $x$  value is  $-5.2$  and the aniline point is  $93.6^\circ\text{C}$ . This aniline point is somewhat low for a pure naphthene and indicates, as was expected from the specific refraction data, the presence of a small amount of aromatic material. From 93.6 to 90 percent extracted, transition from substantially naphthenic material to material consisting substantially of hydrocarbons with one aromatic ring occurs; the aniline point drops sharply and has a value of  $55.9^\circ\text{C}$  for the fraction represented by 86 percent extracted. As can be seen from figure 8, this material contains 1 aromatic ring and an average of

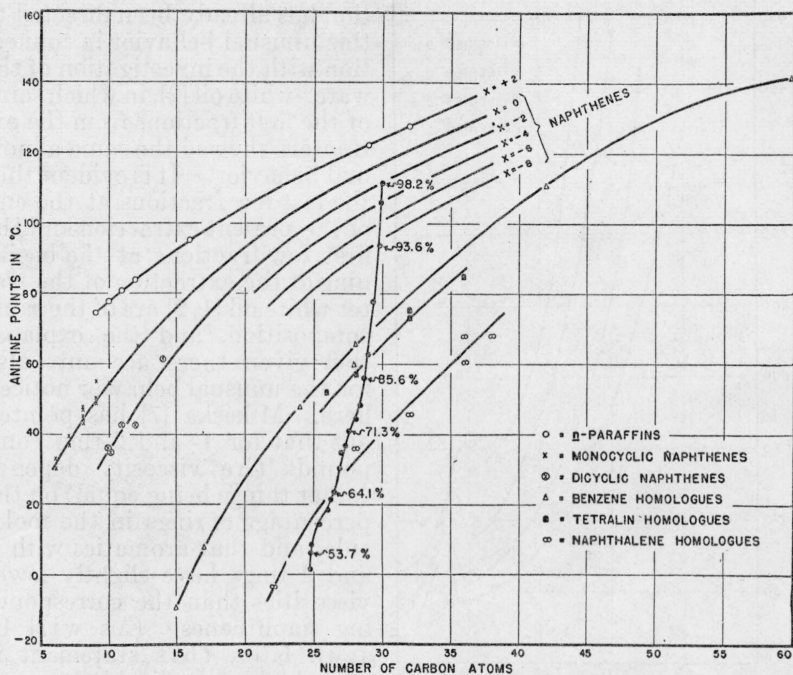


FIGURE 13. Aniline points of various types of hydrocarbons with respect to the number of carbon atoms per molecule.

1.8 naphthenic rings. It is evident that its aniline point is in agreement with this composition.

From 86 to 71 percent extracted, the aniline points are in agreement with the conclusions drawn from figure 8, that is, that this material contains 1 aromatic ring with increasing numbers of naphthenic rings. The sharp break occurring in the aniline point curve for series C, (fig. 12) between 71.3 and 64.2 percent extracted, corresponds exactly with the transition to 2-ring aromatic hydrocarbons (see fig. 8). The aniline point of the fraction represented by 64 percent extracted is close to the curve for homologues of naphthalene. The aniline points of the fractions from 64.2 to 53.7 percent extracted are somewhat lower than those for aromatic hydrocarbons with 2 condensed rings, but this is exactly what would be expected since this material also contains some naphthenic rings.

## 8. VISCOSITY AND THE TEMPERATURE COEFFICIENT OF VISCOSITY

In figures 14, 15, and 16 have been plotted the viscosity at 100° and 210° F and the kinematic-viscosity index for the fractions from 50 to 100 percent extracted, for series B, C, D, and E. For each series, both at 100° and 210° F, the viscosity is a minimum for one fraction in the neighborhood of 90 percent extracted, and a maximum for the next fraction, which is represented by about 94 percent. The viscosity index (a measure of the temperature coefficient of viscosity) varies in

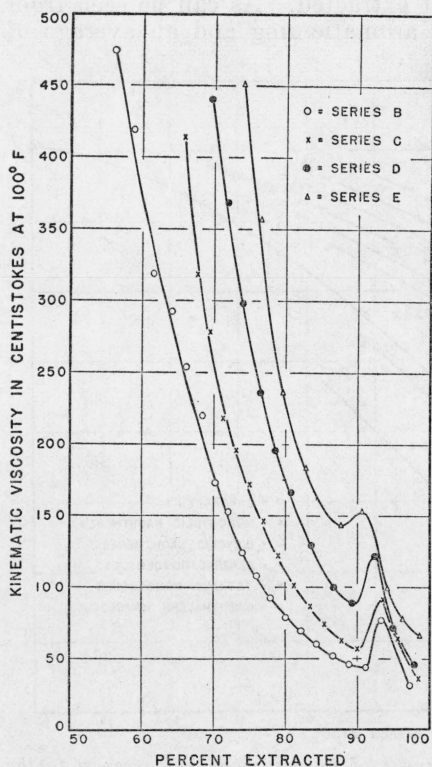


FIGURE 14.—Kinematic viscosity at 100° F of petroleum fractions.

the opposite manner, being a maximum at 90 percent and a minimum at 94 percent. Attention has already been directed to this unusual behavior in connection with the investigation of the water-white oil [2], in which some of the first fractions from the extractors showed the same abnormal behavior. It is evident that the last few fractions at the end of the present extraction and the first few fractions at the beginning of the extraction of the water white oil [1, 2] are of the same composition, and the explanation given there accounts also for the unusual behavior noticed here. Mikeska [7] has pointed out that for 1- and 2-ring compounds the viscosity depends (other things being equal) on the percentage of rings in the molecule, and that aromatics with 1 and 2 rings have slightly lower viscosities than the corresponding naphthenes. (As will be seen later, this statement is probably not applicable for compounds containing 3 or more rings.) As can be seen from figure 8, there is an increase in the total number of rings in going from the aromatic material at 90 percent extracted to the naphthenic material at 94 percent, and it is to this increase in rings that the increased viscosity and decreased viscosity index are due.

In an earlier publication [2], the authors speculated on the possibility of obtaining from petroleum aromatic material of high viscosity index. As shown here, material with 1 aromatic ring does exist but the percentage is not great, and the viscosity index of some of it, though higher than that of the naphthenic material which immediately follows it in the extraction series, attains the value of only 70. This is probably because the aromatic rings instead of being attached only to aliphatic side chains are attached also to naphthenic rings, the

fraction from series *C* with the highest viscosity index, 69 to 70, containing, in addition to 1 aromatic ring, an average of from 1.6 to 1.8 naphthenic rings per molecule.

Although there are some small fluctuations in the viscosity characteristics at lower percentages extracted, these may be due to experimental error—and no pronounced abnormalities are noticed in the region around 70 percent where the transition from 1-ring to 2-ring aromatic hydrocarbons occurs.

In figures 17, 18, and 19, the viscosities and viscosity indices of the fractions from series *C* are compared before and after hydrogenation. Considering figures 17 and 18, it is apparent that the residue represented by 98.2 percent (as was to be expected since this material was already naphthenic) shows on hydrogenation no change in viscosity either at 100° or 210° F. For the fraction represented by 90 percent there is a slight increase in viscosity on hydrogenation. Since this fraction is composed of a 1-ring aromatic with about 1.6 naphthenic rings to the molecule, this result is in conformity with Mikeska's [7] observation that naphthenes with 1 and 2 rings have viscosities slightly higher than those of the corresponding aromatics. However, from 90 to 0 percent extracted, the viscosity of the hydrogenated fractions becomes increasingly less than the original fractions, and in the neighborhood of 3 percent extracted, the viscosity at 100° F after hydrogenation is about 1 percent of its original value. This result was unexpected, and could not have been predicted from the published data on 1- and 2-ring compounds.

It appears that the hydrogenation of 1 or more aromatic rings,

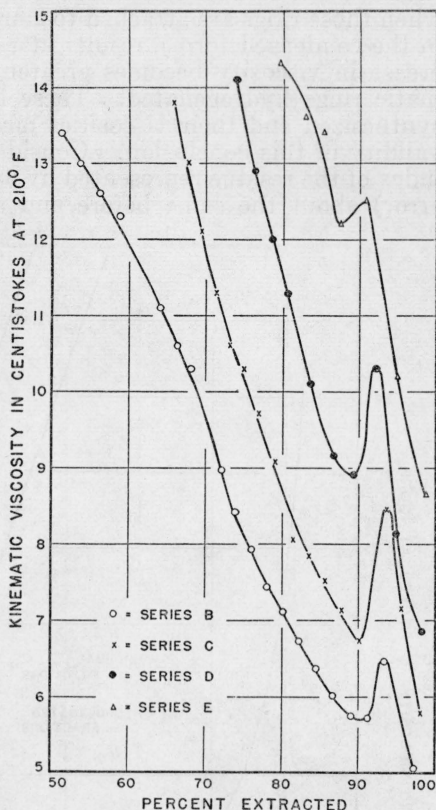


FIGURE 15.—Kinematic viscosity at 210° F of petroleum fractions.

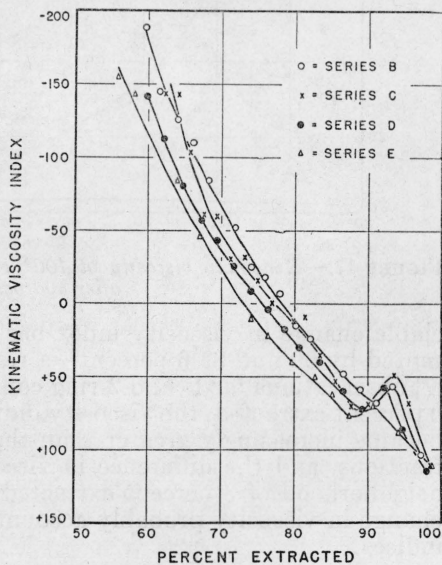


FIGURE 16.—Kinematic-viscosity index of petroleum fractions.

when those rings are attached to 2 or more naphthenic rings (probably in the condensed form), results in a decrease in viscosity, and the decrease in viscosity becomes greater, the greater the number of aromatic rings hydrogenated. These types of hydrocarbons should be synthesized and their viscosities measured to establish definitely the validity of this conclusion. Considering now figure 19, the viscosity index of the residue represented by 98.2 percent is (within the limits of error) about the same before and after hydrogenation. No appre-

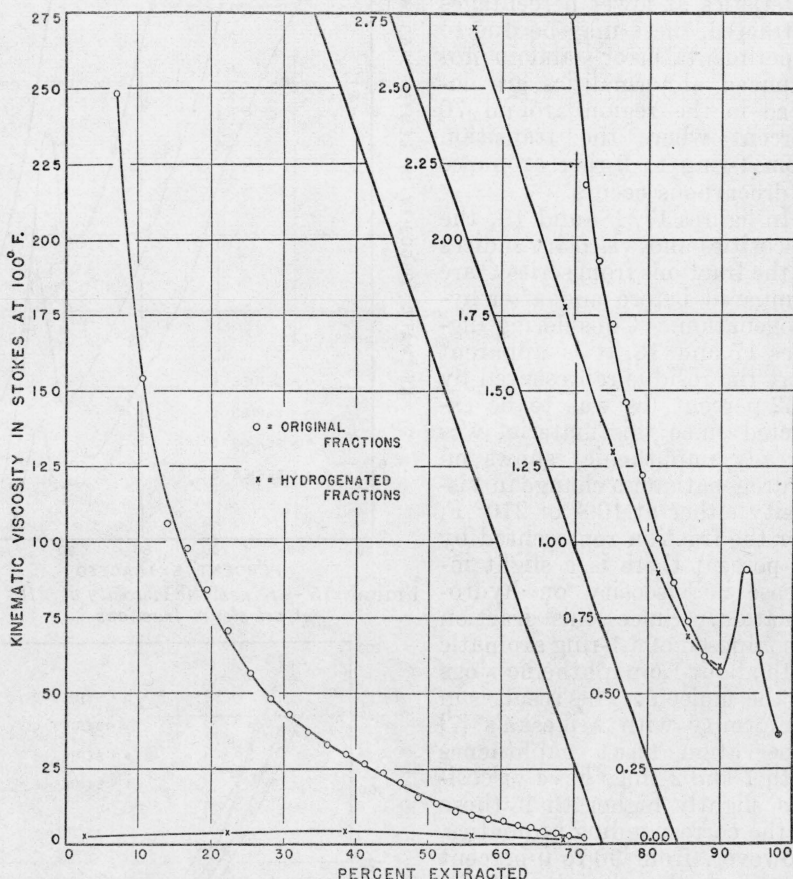


FIGURE 17.—Kinematic viscosity at 100° F of fractions from series C before and after hydrogenation.

cial change in viscosity index has occurred for the fractions represented by 90 and 85.6 percent—a result in agreement with Mikeska's [7] observations for 1- and 2-ring compounds. However, from 85.6 to 0 percent extracted, the viscosity indices of the hydrogenated fractions became increasingly greater than the viscosity indices of the original fractions, and the difference in viscosity indices is very great in the neighborhood of 3 percent extracted. The explanation given for the change in viscosity probably accounts also for the change in viscosity indices.

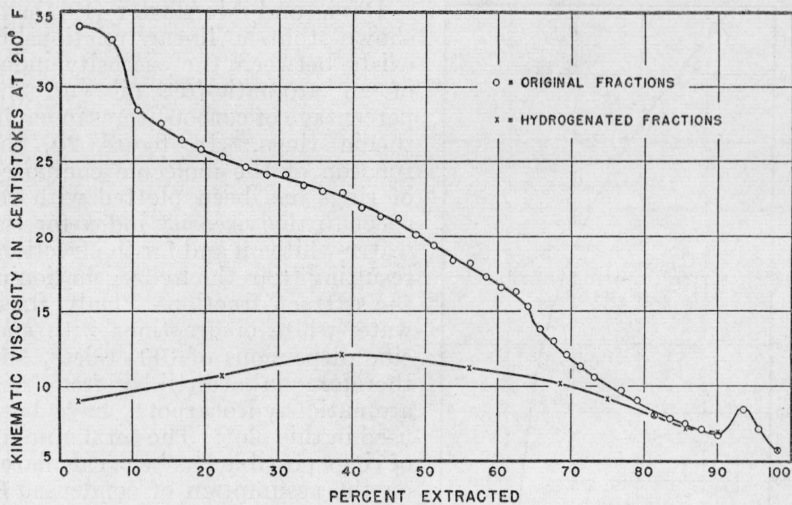


FIGURE 18.—Kinematic viscosity at 210° F of fractions from series C before and after hydrogenation.

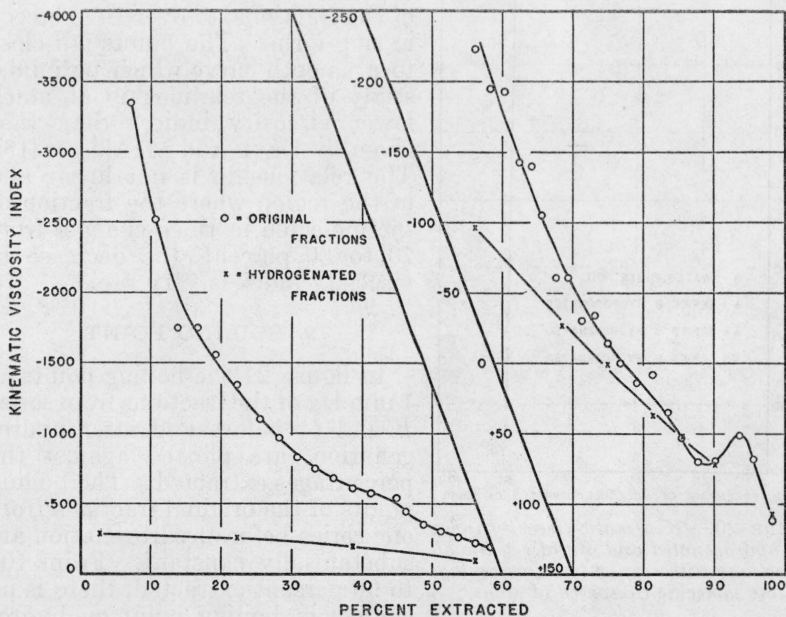


FIGURE 19.—Kinematic-viscosity index of fractions from series C before and after hydrogenation.

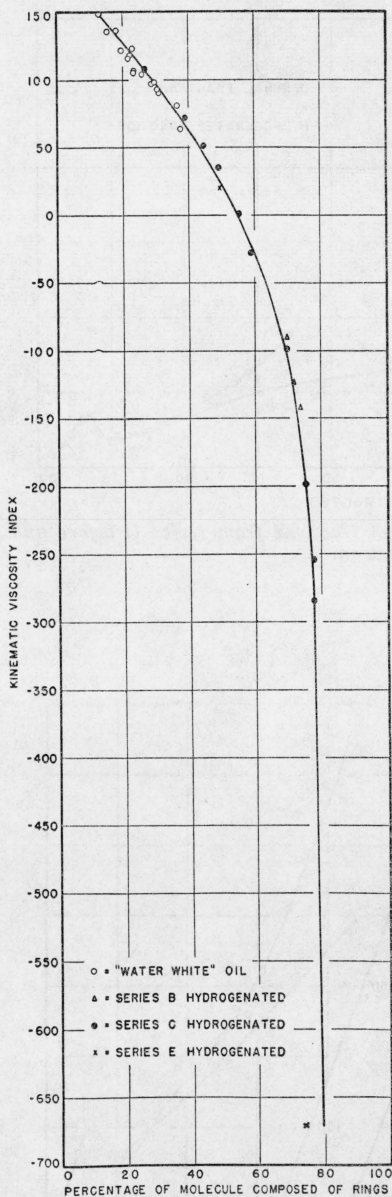


FIGURE 20.—Kinematic-viscosity index of hydrogenated and of water-white oil fractions with respect to the percentage of the molecule composed of rings.

Davis and McAllister [19] have shown that a linear relationship exists between the viscosity index of an aromatic-free oil and the percentage of carbon atoms in naphthenic rings. In figure 20, the fraction of the molecule composed of rings has been plotted with respect to the viscosity index for the water-white oil and for the fractions resulting from the hydrogenation of the extract fractions. Only those water-white oil fractions with specific dispersions of 100 or less, and therefore substantially free from aromatic hydrocarbons, have been used in this plot. The total number of rings possible has been calculated on the assumption of condensed 6-membered rings, that is, allowing six carbon atoms for the first ring and four carbon atoms for each succeeding ring. This material is not composed entirely of 6-membered uncondensed rings since a calculation on this supposition leads, for some of the fractions, to over 100 percent in ring form. The points fall close to a smooth curve which permits a study of the relationship at much lower viscosity indices than that given by Davis and McAllister [19]. The relationship is not linear and in the region where the fraction of the molecule in rings changes from 70 to 80 percent, the decrease in viscosity index is very rapid.

## 9. BOILING POINT

In figure 21 the boiling points at 1 mm Hg of the fractions from series B and C, before and after hydrogenation, are plotted against the percentages extracted. The boiling points of the original fractions from one series before hydrogenation are substantially constant. From 100 to 90 percent extracted, there is no change in boiling point on hydrogenation (within the accuracy of these measurements). From 90 to 0 percent extracted, however, there is a decrease in boiling point on hydrogenation, and the boiling point of the hydrogenated fraction (series C) represented by 2.6 percent is 50° C lower than that of the



original. This drop in boiling point is in agreement with the well-known fact that polynuclear naphthenes have much lower boiling points than the corresponding aromatic hydrocarbons. *Trans*-decahydronaphthalene, for example, has a boiling point (760 mm) 33° C lower than that of naphthalene.

In figure 22 is given a plot of the boiling points with respect to the number of carbon atoms for the hydrogenated fractions and for the water-white oil fractions [1] for which the specific dispersion is less than 100. It will be noticed that a straight line represents the data fairly well, and only in about four cases do the points fall farther from the line than could be accounted for on the basis of the precision of these determinations. Two curves are given for the extract fractions for  $x = -14$  and  $x = -18$ . These represent, within about  $\pm 3^\circ$  C, the boiling points of the extract fractions with corresponding values of  $x$ .

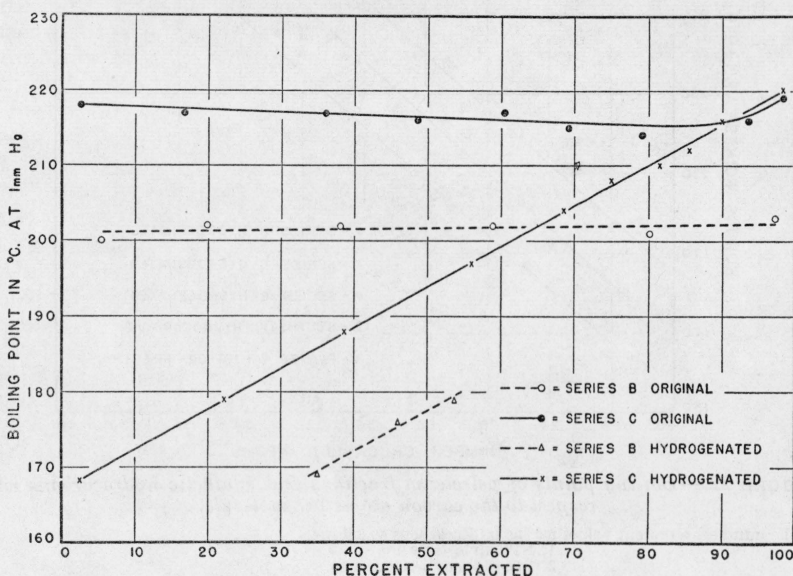


FIGURE 21.—Boiling points of fractions from series B and C before and after hydrogenation.

Also included in this figure are the boiling points determined in this laboratory on some synthetic compounds, all of which, with the exception of dotriacontane, were kindly furnished by L. A. Mikeska [7]. It will be noted that the boiling point of compound number 7, *n*-dotriacontane at 251° C, is 16° higher than that of the naphthene fractions with the corresponding number of carbon atoms. This result is not unreasonable, since the normal compounds have higher boiling points than those with branches and it is probable that the difference of 16° is due both to the rings and side chains which these fractions contain. Compound 1 consists of a benzene ring with a normal aliphatic side chain. Its boiling point is only slightly higher than its  $x$  value would indicate. In the case of compound 2 the boiling point is higher than its  $x$  value would indicate. Here the high boiling point may be due to the long unbranched side chain. Compound 3 has a

boiling point about what would be expected. In this case, the side chain is branched and contains an olefinic linkage. Compounds 5 and 6 are homologues of tetralin and decalin with a singly branched side chain. It is surprising to see the boiling point of the decalin homologue higher than that of the tetralin homologue, and this result is probably in error. If the boiling point of compound 6 had fallen just below that of compound 5, it would be in good agreement with the naphthene fractions.

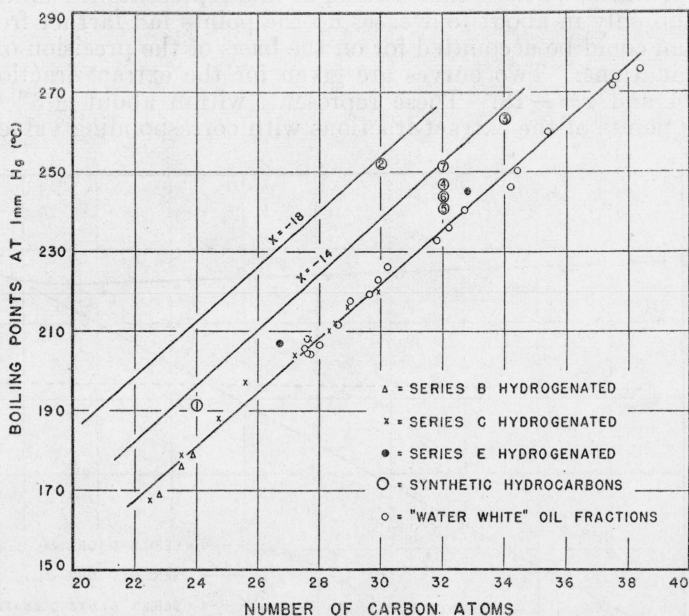


FIGURE 22.—Boiling points of petroleum fractions and synthetic hydrocarbons with respect to the carbon atoms per molecule.

The numbers represent values for the hydrocarbons as follows:

1. 1-Phenyl-octadecane
2. 1-(*p*-diphenyl)-octadecane
3. 5-(*p*-diphenyl)-docosene-5
4. 5-(7-tetrahydronaphthyl)-docosene-5
5. 5-(7-tetrahydronaphthyl)-docosane
6. 5-(2-decahydronaphthyl)-docosane
7. *n*-Dotriacontane

#### IV. CONCLUSION

As a result of the work on the water-white oil and on the extract material, it is possible to obtain an approximate estimate of the quantities of the various types of hydrocarbons in the lubricant fraction of this midcontinent petroleum. Excluding the wax and the asphaltic portions, the oil contains (1) about 60 percent of naphthenes with from 1 to 3 rings per molecule—a very small amount of material containing 4 naphthenic rings per molecule is probably present also; (2) about 15 percent of material with 1 aromatic ring and with from 1 to 3 naphthenic rings per molecule and with this material is associated a small amount of sulfur and oxygen compounds; (3) about 14 percent of material with 2 aromatic rings (linked through two common carbon

atoms) together with about 2 naphthenic rings per molecule, and with this material is associated a small amount of sulfur and oxygen compounds; (4) about 11 percent of material with more than 2 aromatic rings per molecule (each probably linked through two common carbon atoms) together with 1 or 2 naphthenic rings per molecule, and with this material is associated some sulfur, nitrogen, and oxygen compounds.

The authors desire to express their gratitude for the advice and encouragement of F. D. Rossini.

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