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HYDROCARBONS IN THE FRACTION OF A MIDCONTINENT PETROLEUM DISTILLING BETWEEN 115 AND 124° C¹

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ABSTRACT

The distillate from a midcontinent petroleum which boiled between 115 and 124° C was distilled and crystallized systematically in order to identify or detect, if possible, all the constituent hydrocarbons. Large quantities of paraffinic constituent were found in the distillate between 116 and 118.5° C. Mixed melting points and photomicrographs showed that this material was an additional quantity of the hydrocarbon which had been isolated in earlier work on the fraction. The physical properties of the most concentrated sample indicate that it was probably 2-methylheptane.

Smaller quantities of naphthenic constituents distilling between 119.2 and 119.8° C; 119.8 and 120.4° C; 120.4 and 120.8° C; and 122 and 124° C were crystallized repeatedly and the physical properties, cooling curves, and photomicrographs were studied. The photomicrographs of synthetic samples of *p*- and *m*-dimethylcyclohexanes and their mixtures were also studied. The first three fractions contained additional quantities of two naphthenic hydrocarbons which had been isolated before. They were characterized by a six-sided type of crystal, which was definitely neither *m*- nor *p*-dimethylcyclohexane, and a long prismatic type tending to develop fronds, which was probably *m*-dimethylcyclohexane. The fourth naphthenic fraction showed the characteristic crystal behavior of the predominant constituent but also showed the presence of a small quantity of paraffinic hydrocarbon. The combustion analysis also indicated the presence of about 8 percent of paraffinic constituent. Physical properties of all the fractions were determined.

It was estimated that the petroleum contained about 0.5 percent of 2-methylheptane, 0.2 percent of the cyclohexanes distilling between 119.2 and 120.8° C, and 0.04 percent of the cyclohexane boiling at 123.4° C.

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I. INTRODUCTION

Previous papers describe the separation of *n*-octane,³ 2-methylheptane,⁴ and a dimethylcyclohexane fraction⁵ from the distillate of

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³ R. T. Leslie and S. T. Schickltanz, BS J. Research 6, 377 (1931) RP282.

⁴ R. T. Leslie, BS J. Research 10, 609 (1933) RP552.

⁵ R. T. Leslie, J. Research NBS 15, 41 (1935) RP808.

a midcontinent petroleum boiling between 115 and 126° C. These hydrocarbons represent the three types of compounds of which the distillate is constituted, and the isolation of each required the development of new methods of attack. While the methods are still somewhat tedious and difficult, they have solved most of the problems which arise in the crystallization of the hydrocarbons probably present in this distillate. This paper describes the study of the considerable material remaining after the work described above. The material was subjected to exhaustive distillation and crystallization until practically all of it was reduced to large-volume fractions of which the major constituents could be identified.

II. SEPARATION OF THE CONSTITUENTS BY DISTILLATION AND CRYSTALLIZATION

The outline of the work is shown concisely in figure 1. Chart 1 of figure 1 shows the results of careful distillation following the removal of about 2 liters of octonaphthene from the distillate between 119 and 120° C.⁶ The open circles and disks along the base line of this graph mark the approximate temperatures at which the known paraffinic and naphthenic compounds, respectively, are reported to boil.

Up to 119° C the low refractive indices indicated that the distillate was chiefly paraffinic. Cooling curves of the distillate in this range showed no arrests, and the material became glassy in appearance. Crystallization of the material which distilled between 116 and 118.5° C, by pouring a mixture of the oil with propane into liquid methane, resulted in the separation of a solid phase which yielded an oil with lower refractive index than that of the oil in the liquid phase. The distillate between 118.5 and 119.0° C gave only small amounts of solid phase in liquid methane.

Between 119 and 124° C the refractive indices of the fractions showed that they were highly naphthenic. The distillate which boiled at 119.8° gave a cooling curve with a slight arrest at -122°. Crystallization from methane of the distillate boiling between 119 and 124° C produced solid phases containing oil with higher index than that of the oil in the liquid phase. Above 124°, crystals with lower index than the liquid again resulted.

The two sections of distillate indicated by the cross-hatched areas were therefore crystallized separately, as shown by the diagram below chart 1. The areas in these diagrams are drawn on the same scale as the distillation charts and can be used for comparison of volumes. At this stage a total of about 9.5 liters of distillate in 200-ml lots was crystallized by mixing with propane and pouring into liquid methane.

The volumes of liquid and crystal fractions of the paraffinic distillate were in about the ratio of 2 to 3 and their refractive indices differed by 0.003. The crystal fraction was again crystallized as shown below chart 1 and was distilled carefully. The properties of the fractions from this distillate are shown in figure 2. The best fractions of the distillate were crystallized repeatedly until little improvement was observed in the shape of the cooling curve, and the properties of this final product are given in the table below chart 3 of figure 1.

⁶ See footnote 5.

CHART 1-DISTILLATION OF LIQUID FRACTION AFTER REMOVAL OF M - DIMETHYLCYCLOHEXANE

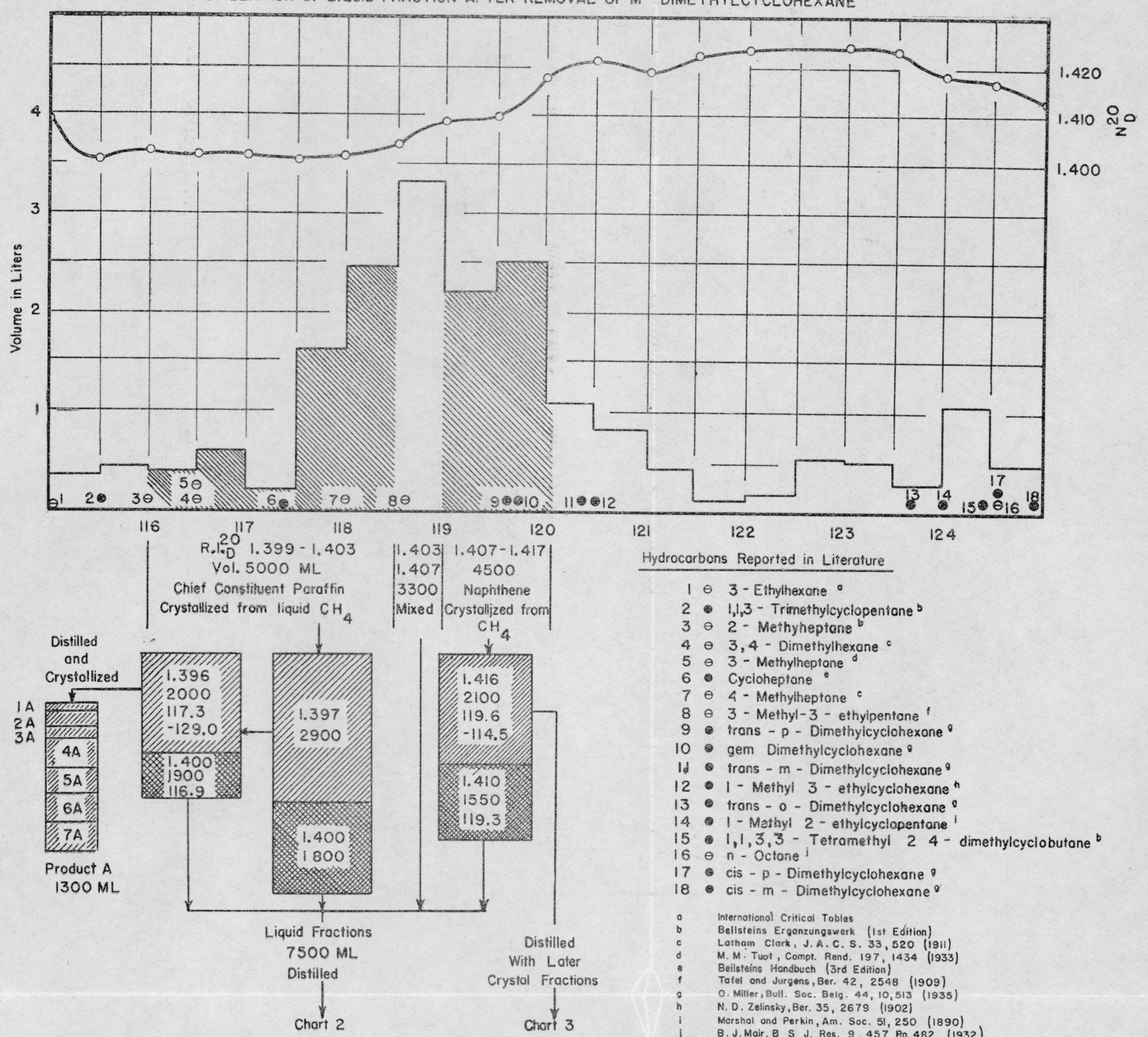


CHART 2-DISTILLATION OF LIQUID FRACTION

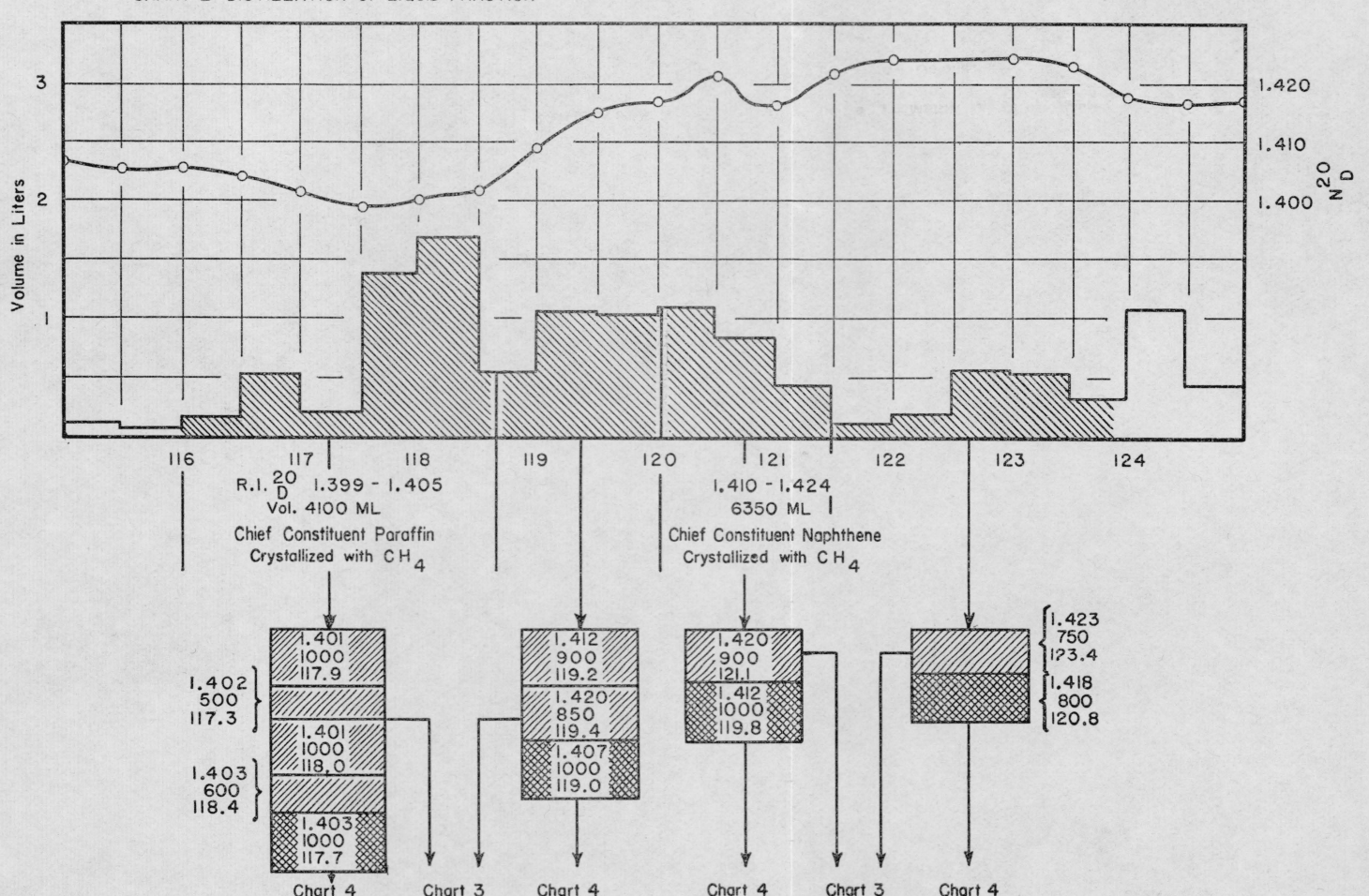


CHART 3-DISTILLATION OF CRYSTAL FRACTIONS

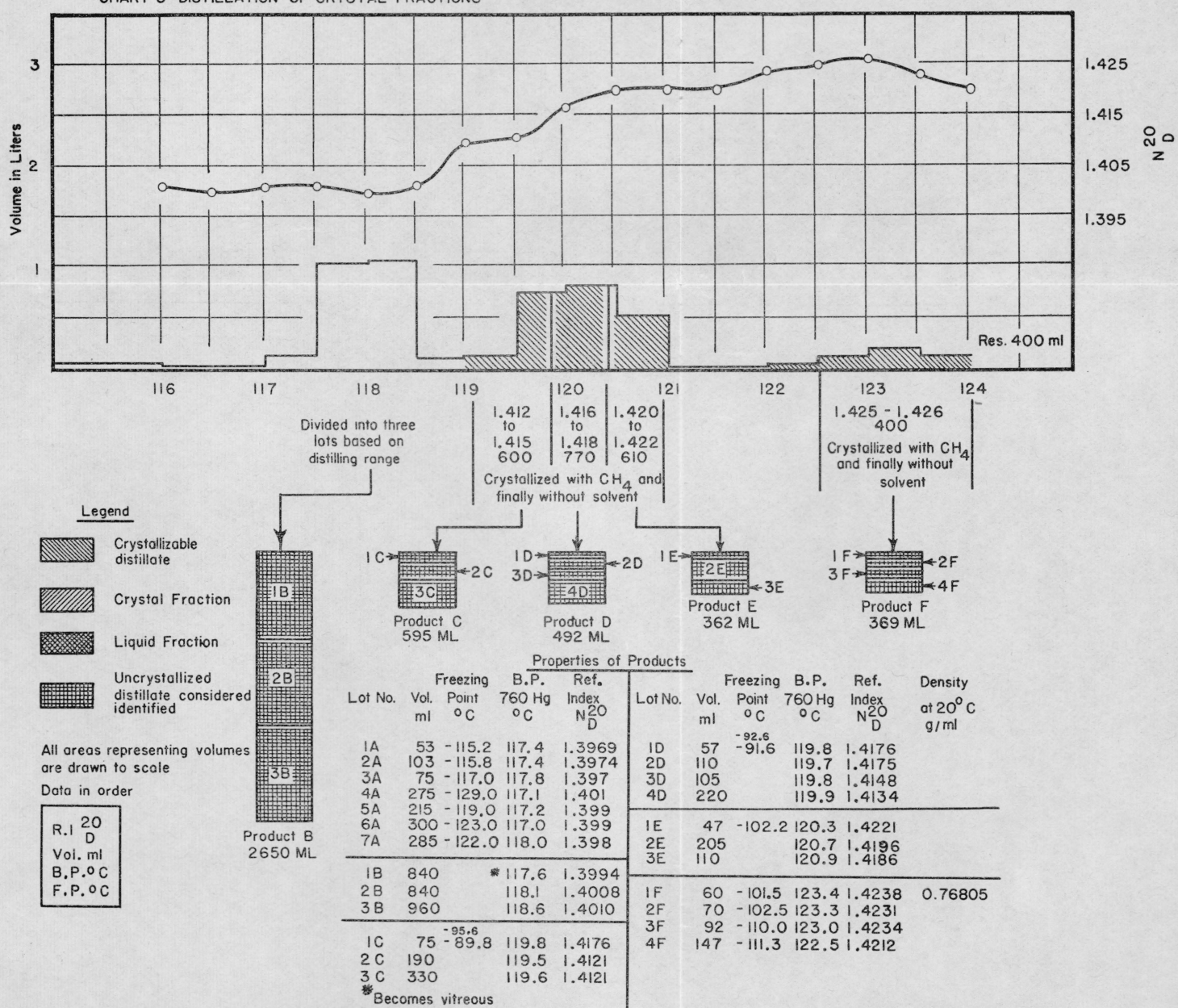


CHART 4-DISTILLATION OF LIQUID FRACTIONS

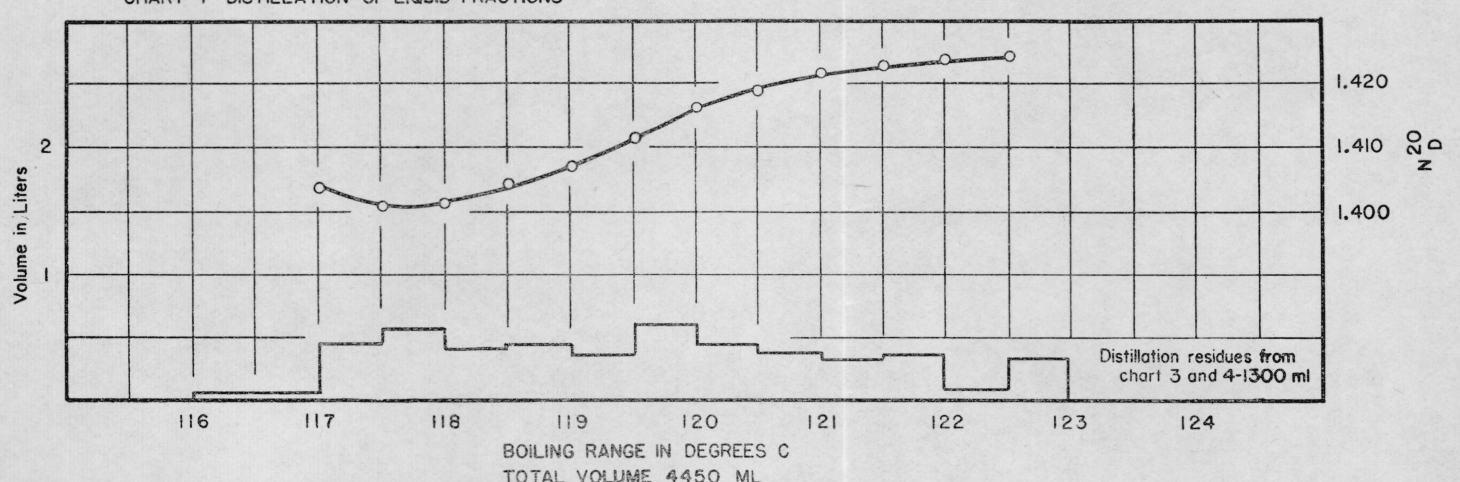


FIGURE 1.—Flow-sheet of distillations and crystallizations performed in the isolation and detection of the constituent hydrocarbons of a petroleum distillate boiling between 115 and 124° C.

Physical properties of the products (below chart 3). See legend and key to order and units in which properties are given.

The ratio of the volumes of the liquid and crystal fractions of the naphthenic distillate was about 3 to 4 and the refractive indices differed by 0.006. The crystal fraction was distilled and combined with the distillate shown in chart 3.

All the liquid fractions, together with the part of the distillate of chart 1 which was not crystallized (118.5 to 119° C, and 120.2 and 124° C) were redistilled, and the results are shown by chart 2. This distillate was again divided into sections for crystallization. From the distillate between 116 and 118.6° C paraffinic crystals were again

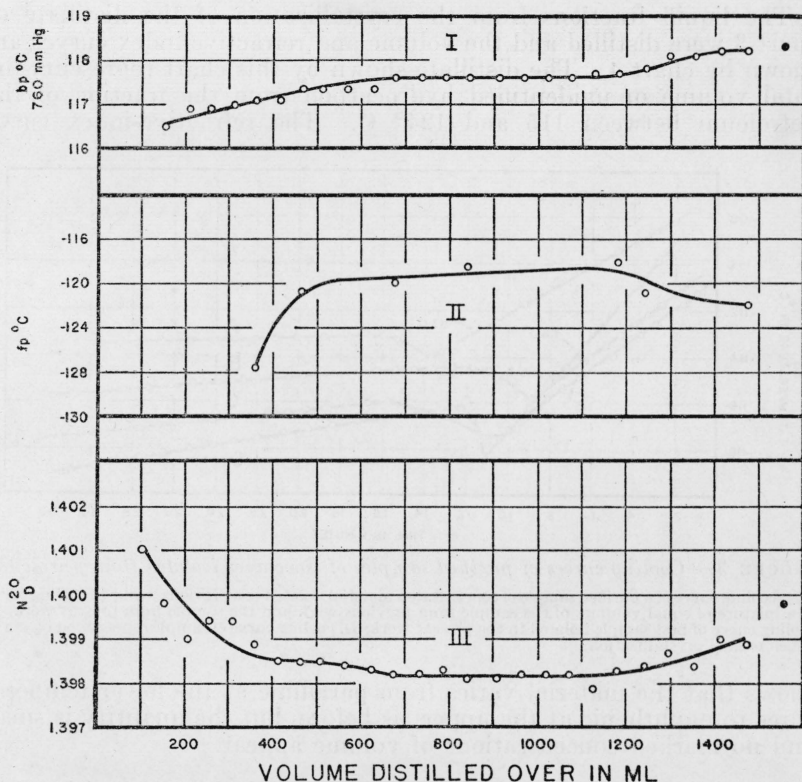


FIGURE 2.—Properties of a fraction containing an isooctane crystallized from the petroleum after distillation, but before preparation of a final pure sample.

Properties are plotted on the ordinates for each fraction of distillate against the total volume over on the abscissa.

obtained by freezing from solvents. The large volume distilling between 118.6 and 121.5° C was divided into two sections because it was suspected that there might be more than one naphthenic compound present in it. The section from 122.5 to 124° C definitely contained a naphthene not previously detected. The results of crystallizing the distillate from these sections are shown by the diagram below chart 2. About 10.5 liters of hydrocarbon was crystallized from methane in the second stage.

The crystal fractions from these crystallizations were distilled with the results shown by chart 3. The paraffinic crystal fraction again

concentrated between 117 and 118.5° C. This distillate was divided into three sections and was considered as identifiable without further treatment. The distillate between 119 and 121° C was divided into three parts, as shown by the cross-hatched areas, and crystallized repeatedly until the cooling curves of the best fractions did not improve rapidly with successive crystallizations. In the same way the distillate between 122.5 and 124° C was crystallized to obtain a fraction whose physical properties could be obtained for identification. The properties of all the products are given in the table below chart 3.

The liquid fractions from the crystallization of the distillate of chart 3 were distilled and the volume and refractive index curves are shown by chart 4. The distillate shown by this chart represents the total volume of unidentified hydrocarbon from the fraction of the petroleum between 115 and 124° C. The refractive-index curve

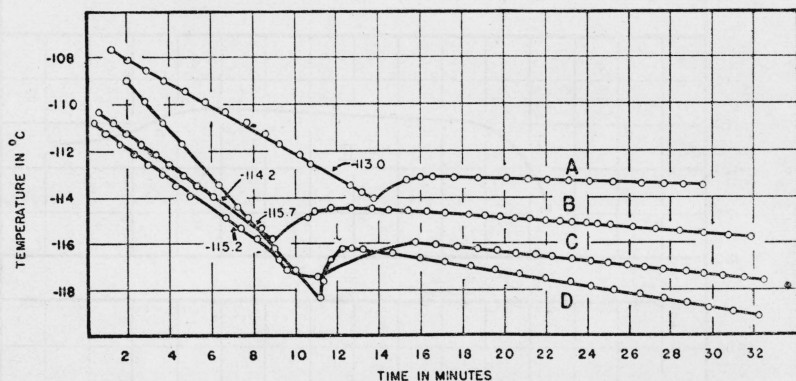


FIGURE 3.—Cooling curves of purified samples of isooctanes isolated from petroleum.

A, cooling curve of a purified sample of concentrated material isolated in a previous work; B, cooling curve of a mixture of equal volumes of the sample from previous work and the sample from present work; C, cooling curve of best sample isolated in the present work; D, cooling curve of sample represented by curve C before final crystallization.

shows that the material varies from paraffinic at the lower temperatures to naphthenic at the upper, as before, but the quantity is small and no marked concentrations of volume appear.

III. IDENTIFICATION OF THE HYDROCARBON ISOLATED FROM THE DISTILLATE BOILING BETWEEN 116 AND 118.5° C

The physical properties of the paraffin hydrocarbon (sample 1A) are not greatly different from those of the hydrocarbon isolated in a previous work⁷ and identified as 2-methylheptane. As in the previous work, none of the constants agree exactly with those of L. Clark,⁸ but, in the absence of a sample of synthetic material with which to compare the properties, it has been assumed that the differences are due to differences in purity or to the methods of measuring the constants. This is not surprising when it is observed that the material isolated in this work has somewhat different constants from that

⁷ R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.

⁸ J. Am. Chem. Soc. **31**, 107 (1909).



FIGURE 4.—*Photomicrograph of crystals from best sample of the isooctane isolated in present work.*

Crystallization induced by seeding with material precipitated from methane.

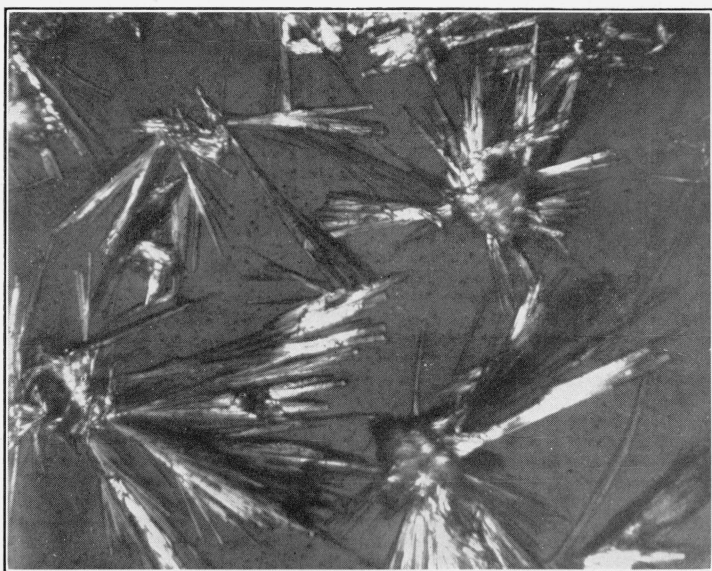


FIGURE 5.—*Photomicrograph of crystals of isooctane isolated in previous work.*

Crystallization induced as described in figure 4.

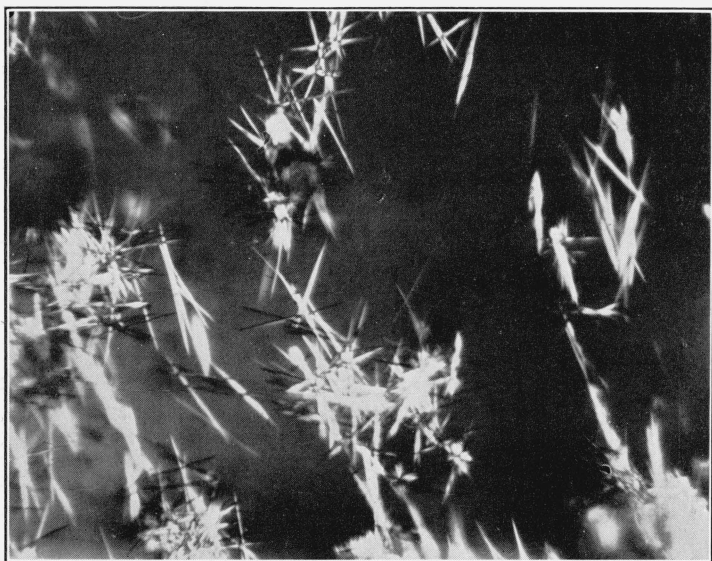


FIGURE 6.—*Crystals from a mixture of equal volumes of the hydrocarbons shown in figures 4 and 5.*

Note the similarity in the appearance of the crystals of all three samples.

previously obtained. To make certain that the differences were not due to the methods of observation, one of the less pure samples from the previous work was further concentrated, and its constants were found to be: boiling point 116.9°C (760 mm of Hg), refractive index, 1.3968^{20} , freezing point, -113.0°C . This boiling point is lower and the freezing point higher than those of sample 1A. In figure 3 are shown the cooling curves of sample 1A, of the purified sample from the previous work, and of a mixture of equal volumes of the two. Since the cooling curve of the mixture lies between the

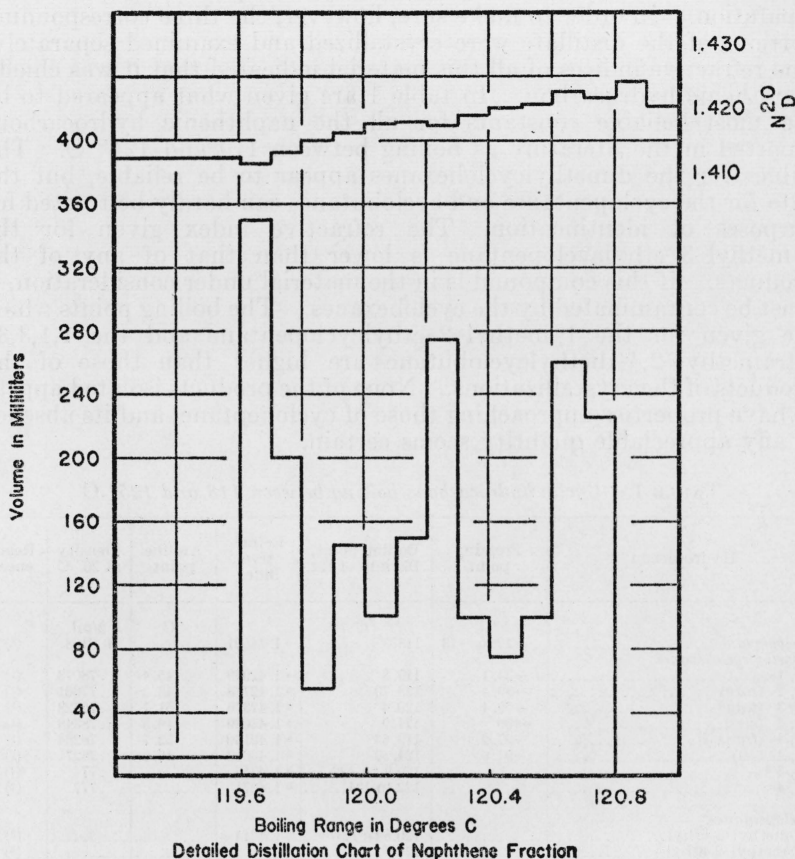


FIGURE 7.—Chart of the distillation of the fraction from petroleum boiling between 119.2 and 120.8°C .

These are the same data given in chart 3 of figure 1 but plotted at 0.1°C intervals instead of 0.5°C intervals.

other two it appears that the chief constituents of both samples are identical or that they form solid solutions.

Photomicrographs of the crystals from the three samples are shown in figures 4, 5, and 6. All three show needle-like crystals which are similar in appearance.⁹

⁹ All photomicrographs in this paper were taken with an especially constructed microscope which will be described later. Magnification about $80\times$. Compare the photomicrographs of these hydrocarbons with those from paraffin waxes: C. C. Bachler and G. D. Graves, *Ind. Eng. Chem.* **19**, 718 (1927); S. W. Ferris, N. C. Cowles, Jr., and L. M. Henderson, *Ind. Eng. Chem.* **23**, 681 (1931); G. D. Graves, *Ind. Eng. Chem.* **23**, 762 (1931).

IV. STUDY OF THE CONSTITUENTS OF THE LARGE-VOLUME FRACTION DISTILLING BETWEEN 119.2 AND 120.8° C.

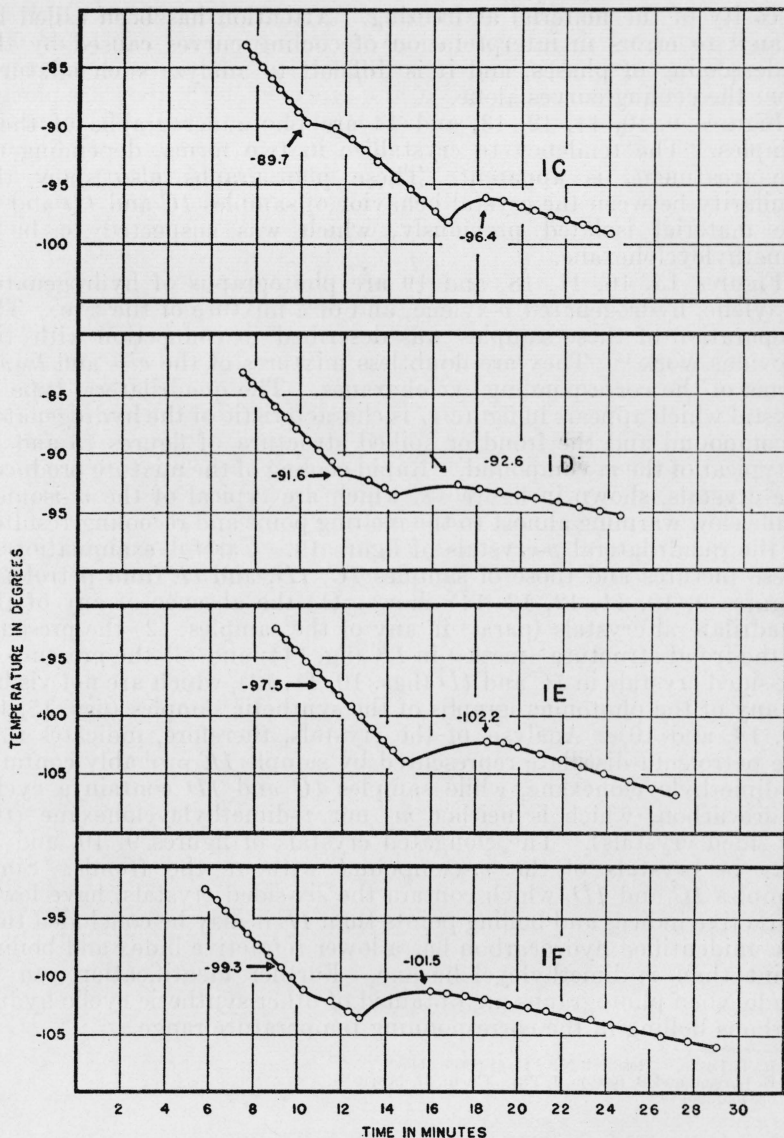
In figure 7 is shown a distillation chart of this fraction in which the volumes and refractive indices are plotted for 0.1° instead of 0.5° intervals as they are in chart 3 of figure 1. Three distinct concentrations of volume appear within the range when the data are plotted in this way. This may have been fortuitous, since it is doubtful whether the distillation was precise enough to produce such a sharp separation. In order to make sure, however, the three corresponding portions of the distillate were crystallized and examined separately. The refractive indices of all this material indicated that it was chiefly naphthenic hydrocarbon. In table 1 are given what appeared to be the most reliable constants for all the naphthenic hydrocarbons reported in the literature as boiling between 119 and 124° C. The values for the dimethylcyclohexanes appear to be reliable, but the data for the cyclopentanes and cyclobutanes can hardly be trusted for purposes of identification. The refractive index given for the 1-methyl-3-ethylcyclopentane is lower than that of any of the products. If this compound is in the material under consideration, it must be contaminated by the cyclohexanes. The boiling points which are given for the 1-methyl-2-ethylcyclopentane and the 1,1,3,3-tetramethyl-2,4-diethylcyclobutane are higher than those of the products of the crystallizations. None of the products isolated appear to have properties approaching those of cycloheptane, and its absence in any appreciable quantity seems certain.

TABLE 1.—*Cyclic hydrocarbons boiling between 118 and 125° C*

Hydrocarbon	Freezing point	Boiling point, 760 mm of Hg	Refractive index	Aniline point	Density at 20° C	References
	°C	°C		°C	g/ml	
<i>Cycloheptane</i>	-12 to -13	118 ⁷²⁶	<i>n</i> 1.44521	-----	0.8108	(⁹)
<i>Dimethylcyclohexanes:</i>						
1, 1-.....	-34.1	119.8	<i>n</i> 1.42959	45.4	.78073	(1)
1, 2- (<i>trans</i> -).....	-89.4	123.70	<i>n</i> 1.42768	48.3	.77601	(1)
1, 3- (<i>trans</i> -).....	-79.4	120.4	<i>n</i> 1.42376	51.7	.76628	(1)
1, 3- (<i>cis</i> -).....	-100	124.9	<i>n</i> 1.43099	46.3	.78348	(1)
1, 4- (<i>trans</i> -).....	-37.2	119.63	<i>n</i> 1.42160	52.7	.76264	(1)
1, 4- (<i>cis</i> -).....	-91.6	124.59	<i>n</i> 1.43029	46.9	.78271	(1)
1, 3-.....	-----	120.9 to 122.5	<i>n</i> 1.4253	-----	.774	(2)
1, 4-.....	-----	122 to 124	<i>n</i> 1.4271	-----	.777	(2)
<i>Cyclopentanes:</i>						
1-methyl-3-ethyl.....	-----	120.5 to 121 ⁷³⁶	<i>n</i> 1.4214	-----	-----	(3)
1-methyl-2-ethyl.....	-----	124 ⁷⁶⁰	-----	-----	-----	(4)
<i>Cyclobutanes:</i>						
1,1,3,3-tetramethyl 2,4-diethyl- cyclobutane.....	-----	124 to 125 ⁷⁶⁰	-----	-----	-----	(4)

¹ O. Miller, *Bul. soc. chim. Belg.* **44**, 10, 513 (1935).² F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.* **55**, 3326 (1933).³ N. D. Zelinsky, *Ber. deut. chem. Ges.* **35**, 2679 (1902).⁴ Marshall and Perkin, *J. Chem. Soc. Trans.* **57**, 250 (1890).⁵ Beilsteins *Ergänzungsband* 5, 25 (Wedekind and Miller, *Ber. deut. chem. Ges.* **44**, 3286).⁶ Beilsteins *Handbuch* 5, 29, 4th ed. (Willstätter, Kametaka, *Ber. deut. chem. Ges.* **41**, 1483).⁷²⁶ n_{D}^{20} ; ⁷³⁶ n_{D}^{20} ; ⁷⁶⁰ n_{D}^{20} .

The cooling curves of the samples from the three large fractions after repeated crystallization are shown by curves *1C*, *1D*, and *1E* of figure 8. Curves *1C* and *1D* show a peculiar double halt



COOLING CURVES OF OCTONAPHTHENE FRACTIONS FROM PETROLEUM DISTILLING BETWEEN 119° AND 124°

FIGURE 8.—Cooling curves of best samples isolated from distillate between 119.2 and 124° C

1C, cooling curve of best sample from distillate between 119.2 and 119.8° C; *1D* best sample from distillate between 119.8 and 120.4° C; *1E*, best sample from distillate between 120.4 and 120.8° C; *1F*, best sample from distillate between 122 and 124° C.

similar to those in some of the curves obtained on a naphthene previously separated at about this temperature.¹⁰ Curve *1E* does not exhibit this behavior. The double arrests may indicate eutectics, transitions in crystal forms, or metastable states due to the viscosity of the material at freezing. Attention has been called by Skau¹¹ to errors in interpretation of cooling curves caused by the undercooling of phases, and it is difficult to analyze such mixtures from the cooling curves alone.

Figures 9, 10, 11, 12, 13, and 14 are photomicrographs of these samples. The tendency to crystallize in two forms, depending on the treatment, is apparent. These photographs also show the similarity between the crystal behavior of samples *1C* and *1D* and of the material isolated previously, which was suspected to be a dimethylcyclohexane.

Figures 15, 16, 17, 18, and 19 are photographs of hydrogenated *m*-xylene, hydrogenated *p*-xylene, and of a mixture of the two. The preparation of these samples was described in connection with the previous work.¹² They are doubtless mixtures of the *cis*- and *trans*-forms of the corresponding cyclohexanes. The quadrilateral type of crystal which appears in figure 17 is characteristic of the hydrogenated *p*-compound and the frond or spiked structure of figures 15 and 16 is typical of the *m*-compound. Rapid cooling of the mixture produced the crystals, shown in figure 18, which are typical of the *m*-isomer, while slow warming almost to the melting point and recooling resulted in the quadrilateral *p*-crystals of figure 19. Careful examination of these pictures and those of samples *1C*, *1D*, and *1E* from petroleum (figures 9, 10, 11, 12, 13, 14) shows: (1) the absence of any of the quadrilateral crystals (para-) in any of the samples; (2) the presence of the frond structure (meta-) in *1E* (fig. 14); and (3) the presence of six-sided crystals in *1C* and *1D* (figs. 10, 11, 12), which are not visible in any of the photomicrographs of the synthetic samples (figs. 15, 16, 17, 18, and 19). Analysis of the crystals, therefore, indicates that the petroleum distillate represented by sample *1E* probably contains *m*-dimethylcyclohexane, while samples *1C* and *1D* contain a cyclic hydrocarbon, which is neither *m*- nor *p*-dimethylcyclohexane (the six-sided crystals). The elongated crystals of figures 9, 10, and 13 may be crystals of the *m*-compound without the fronds. Since samples *1C* and *1D*, which contain the six-sided crystals, have lower refractive indices and boiling points than *1E* it may be concluded that the unidentified hydrocarbon has a lower refractive index and boiling point than *m*-dimethylcyclohexane. Further identification can be made when photographs are obtained of other synthetic cyclic hydrocarbons boiling in the corresponding temperature range.

¹⁰ R. T. Leslie, J. Research NBS **15**, 41 (1935) RP808.

¹¹ E. L. Skau and B. Saxton, J. Phys. Chem. **37**, 183 (1933).

¹² See footnote 10.

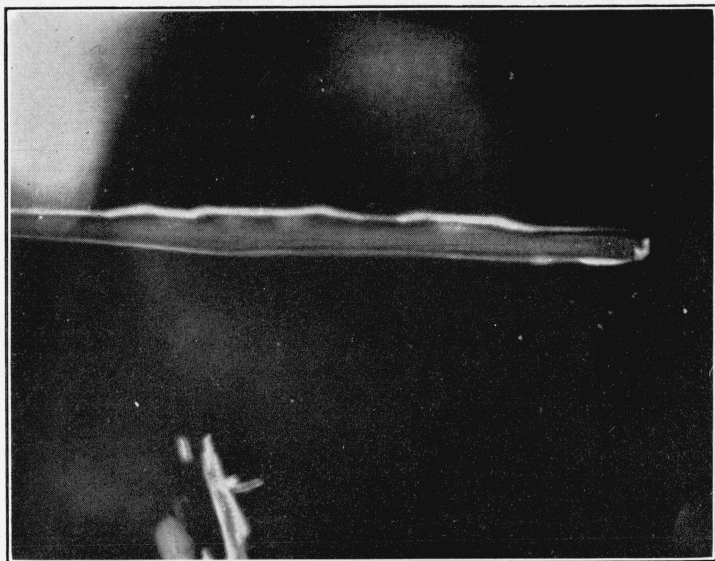


FIGURE 9.—*Long platelike crystal form of sample 1C.*

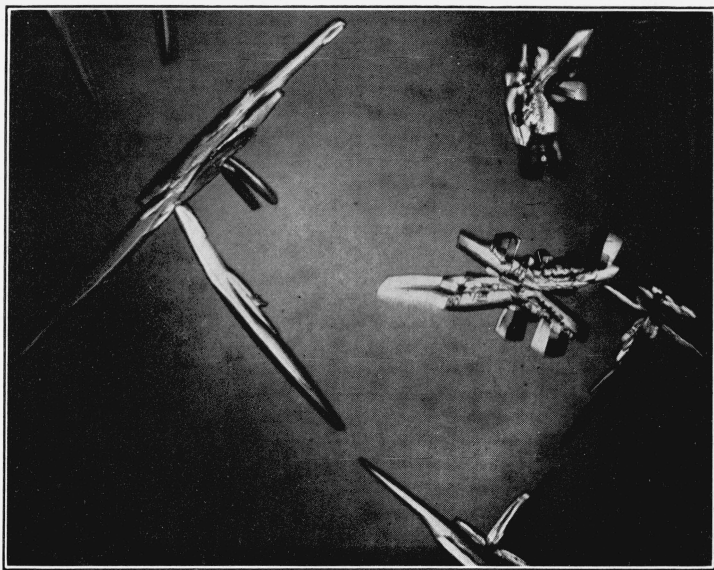


FIGURE 10.—*Crystals of sample 1C showing long plates with six-sided crystals attached.*

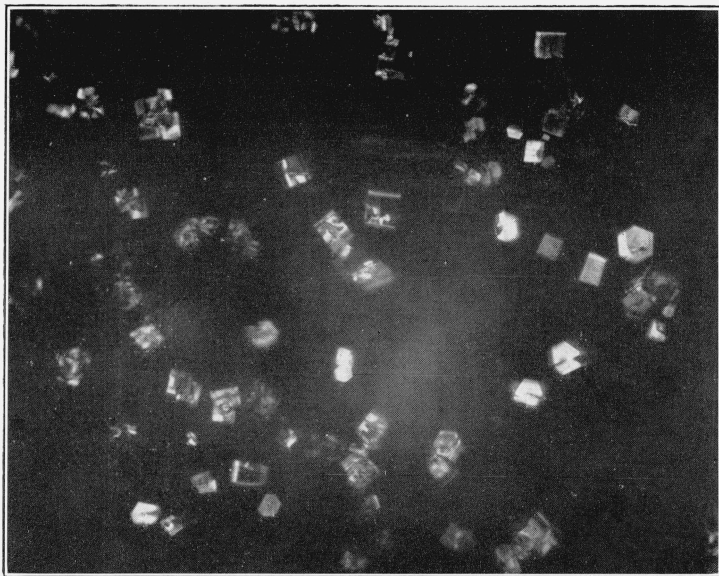


FIGURE 11.—Crystals from sample 1C, showing only the six-sided forms.

These were obtained by cooling the material below its initial freezing point until a dense matrix of crystals was visible, warming till almost all of the crystals melted, and recooling gradually.

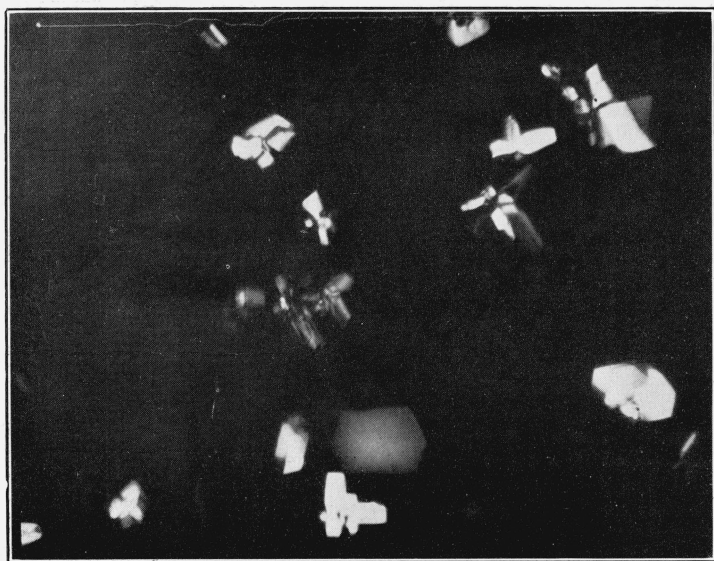


FIGURE 12.—Crystals from sample 1D, showing six-sided types.

These were obtained as described under figure 11.

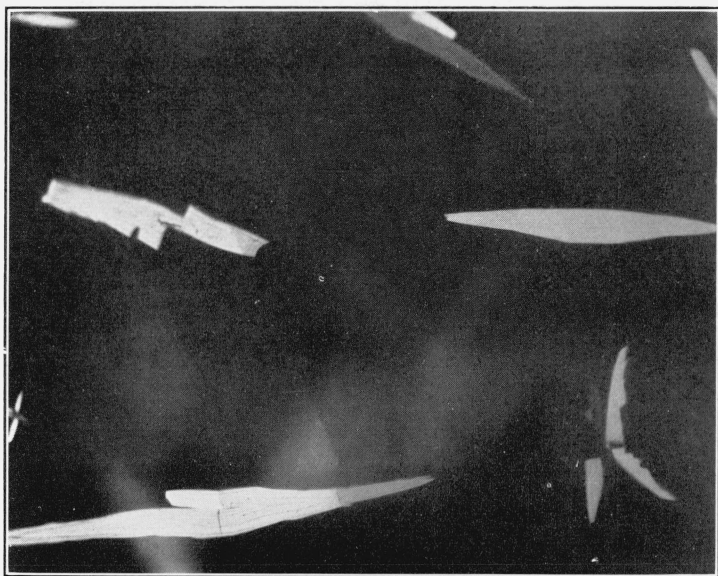


FIGURE 13.—Crystals from sample 1D, showing long platelike crystals.
Compare with figure 10.



FIGURE 14.—Crystals from sample 1E, showing long, platelike crystals with tendencies to grow fronds.

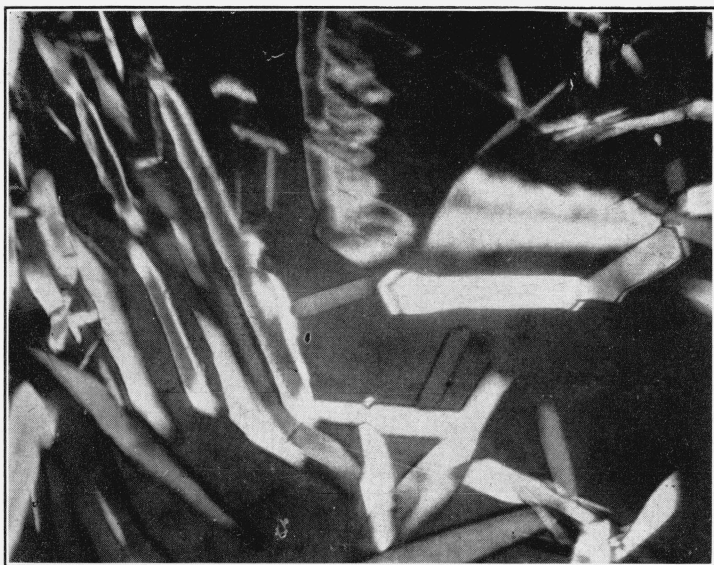


FIGURE 15.—Crystals of hydrogenated *m*-xylene, showing long platelike crystals with tendencies to grow fronds.
Compare with figure 14.

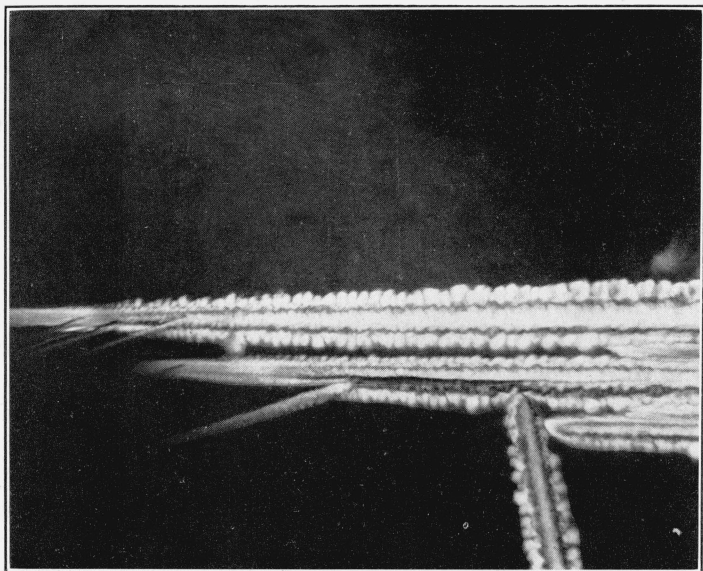


FIGURE 16.—Another example of the frondlike growth characteristic of the hydrogenated *m*-xylene.
Compare with figure 14.

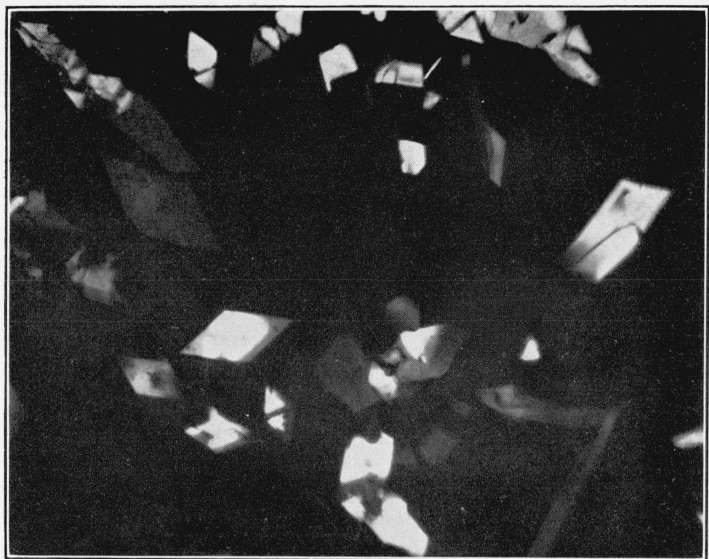


FIGURE 17.—Crystals from hydrogenated *p*-xylene, showing the characteristic quadrilateral type of crystal.

Observe absence of such crystals in figures 9, 10, 11, 12, and 13.

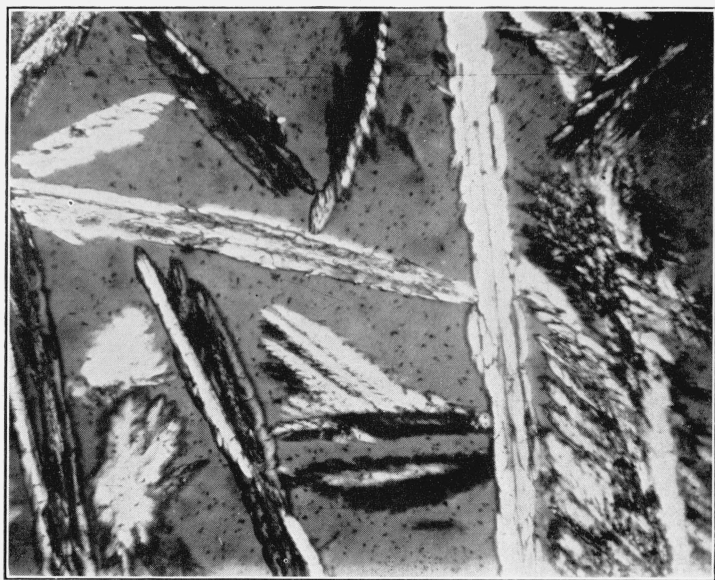


FIGURE 18.—Crystals formed in a mixture of equal volumes of the hydrogenated *m*- and *p*-xylene, showing fronds of the *m*-isomer.

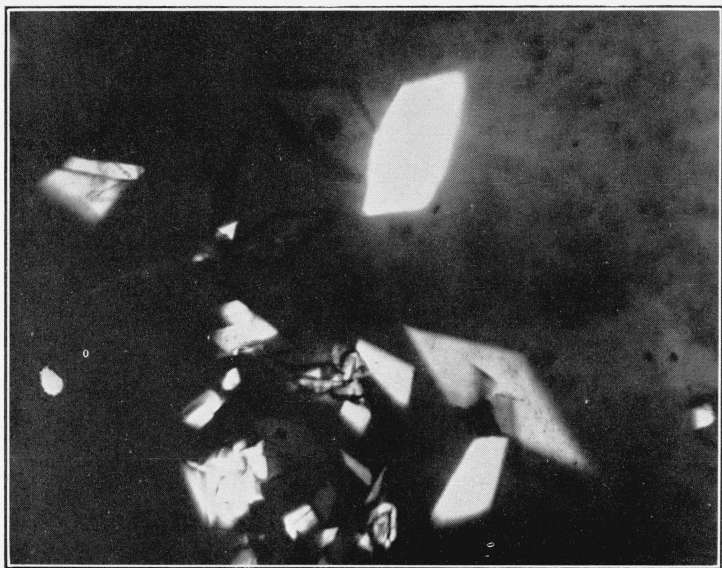


FIGURE 19.—Crystals from same mixture as figure 18, but warmed almost to melting point and recooled slowly.

Quadrilateral crystals of the *p*-isomer visible. Compare figures 18 and 19 with figures 9, 10, 11, 12, and 13. Difference in crystal behavior is to be noted.

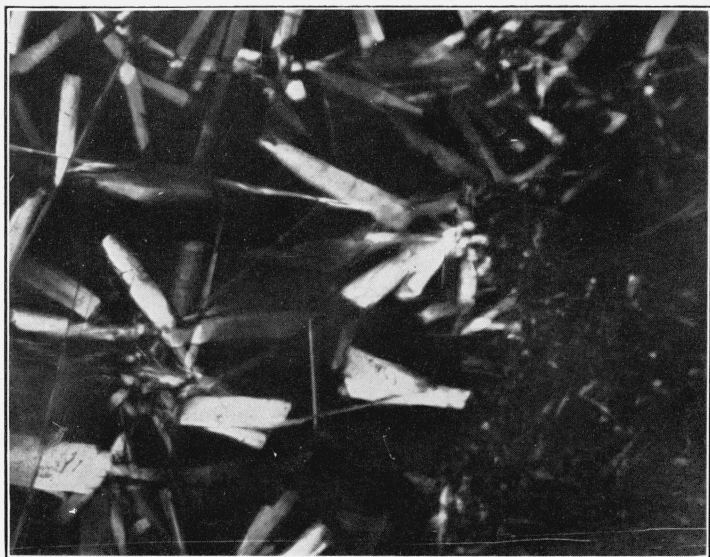


FIGURE 20.—Crystals from sample 1F, showing presence of needles which is probably a paraffinic constituent.

This mat of crystals appears from the melt on undercooling.

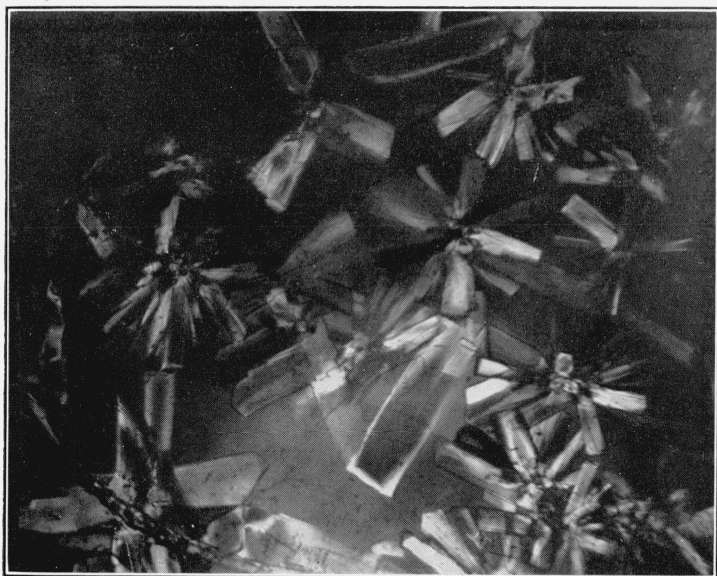


FIGURE 21.—Crystals from sample 1F, showing platelike crystals characteristic of the octonaphthene.

These crystals were obtained by warming the mat shown in figure 20 almost to the melting point and recooling gradually.

V. TENTATIVE IDENTIFICATION OF THE HYDROCARBON ISOLATED FROM THE DISTILLATE BOILING BETWEEN 122 AND 124° C.

At the beginning of the work on the petroleum, the large volumes of *n*-octane masked the presence of any cyclic hydrocarbons in this boiling range,¹³ and it is possible that quantities of cycloparaffins were contained in the residual paraffin distillate boiling above this temperature. The product as represented by sample 1*F* was still contaminated with *n*- or iso-paraffin constituent, as shown by the prismatic needles which are visible in figure 20. The cooling curve shown by 1*F* of figure 8 also suggests the presence of another constituent. Three combustion analyses gave an average value of 1.0108, with an average deviation of 0.0021, for the ratio of H₂O to CO₂. This indicates the presence of 8.6 ± 1.6 percent of paraffinic constituent. Careful warming of the crystals shown in figure 20 almost to the melting point and recooling developed the crystals shown by figure 21. These crystals are definitely angular plates with angles differing from those observed in samples 1*C*, 1*D*, and 1*E*. The constants for the sample 1*F* are given in the table below chart 3 of figure 1. The density was determined by the Division of Weights and Measures at the National Bureau of Standards and was estimated to be correct within 0.00005. The critical-solution temperature in aniline was found to be 52° C. Examination of table 1 shows that the material may be *trans*-*o*-dimethylcyclohexane containing enough paraffinic constituent to lower its refractive index and density.

VI. ESTIMATE OF THE RELATIVE QUANTITIES OF THE CONSTITUENTS

It must be emphasized that estimates of percentages in this work are only indications of the relative amounts of the constituents present. In all estimates made by the author the volumes, in liters, actually isolated have been doubled to compensate for losses and this quantity has been divided by 2,270 liters (the original volume of the crude petroleum from which the gasoline fraction was obtained). On this basis the estimated quantity of isooctane which boils at about 117° C should be increased from 0.15 percent (as given previously)¹⁴ to 0.5 percent, the quantity of cyclohexanes from the distillate between 119.2 and 120.8° C should be increased from 0.15 percent¹⁵ to 0.2 percent, and the quantity of cycloparaffin boiling at 123.4° can be placed at 0.04 percent.

The author acknowledges the assistance of W. W. Hewer in the crystallization and the photographic work, and for the determination of the critical solution temperatures in aniline.

WASHINGTON, August 12, 1936.

¹³ R. T. Leslie and S. T. Schiektanz, BS J. Research **6**, 377 (1931) RP282.

¹⁴ R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.

¹⁵ R. T. Leslie, BS J. Research **15**, 41 (1935) RP808.