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SEPARATION OF A DIMETHYLCYCLOHEXANE FRACTION FROM A MIDCONTINENT PETROLEUM [1]

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ABSTRACT

A practically constant-boiling and constant-freezing material with an empirical formula of a monocyclic naphthene hydrocarbon was isolated from a fraction of a midcontinent petroleum boiling at approximately 119 to 121° C. For the purpose of identifying the material derived from petroleum, pure *m*- and *p*-xylene were hydrogenated and the constituents of the resulting mixtures were partially separated (probably *cis*- and *trans*- forms of the corresponding naphthenes) by fractional crystallization. The change of the refractive indices and freezing points of the hydrogenated products on repeated fractional crystallizations indicated that the naphthene from petroleum was probably chiefly *m*-dimethylcyclohexane. The infrared spectrogram of the product from petroleum showed a similarity to the spectrograms of both hydrogenated *m*- and *p*-xylenes

Photomicrographs showed distinct eutectic structures with excesses of one crystalline form in both synthetic products. The material from petroleum showed the presence of at least two crystalline forms, one of which melted at a higher temperature than the other. The cooling curves also indicated the presence of more than one crystal form. It is possible that the material isolated was a eutectic of isomers with a slight excess of one.

It is estimated that the octonaphthene was present in the original crude oil to the extent of not less than 0.15 percent by volume.

CONTENTS

I. INTRODUCTION

Analyses of petroleum by distillation generally indicate the presence of a considerable quantity of material boiling between 116 and 121° C. This is not surprising in view of the fact that the boiling points of at least four isomeric octanes, cycloheptane, and the *cis*- and *trans*- forms of two dimethylcyclohexanes are reported to lie

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[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

within this range. The general nature of the constituents of this fraction of petroleum has been indicated by a number of investigators. Thus, Beilstein and Kurbatow[3] demonstrated the presence of both cyclic and paraffin series in American petroleum distillates of this boiling range by the action of nitric acid on the material. Evidence advanced by a number of investigators to show the presence of isomeric octanes, cycloheptane, and the dimethylcyclohexanes in oils from various sources is cited by Engler and Höfer.[4] Mabery,[5] working on Ohio, and Warren,[6] on Pennsylvania oils, found that the molecular weight of the fractions boiling at about 118 to 120° C. corresponded closely to octane hydrocarbons, but the carbon-hydrogen ratio showed the presence of a small amount of compounds with less hydrogen than is required for paraffins.

The actual identification of these compounds by comparison of their physical constants with those of synthetic materials is somewhat uncertain because of the contradictory values for the constants to be found in the literature. The confused state of these data is doubtless caused by the difficulty of preparing the pure synthetic compounds. Previous investigators have generally preferred to classify the compounds in this fraction of petroleum as isooctanes and octonaphthenes, and to base their opinions as to structure on the similarity of the petroleum fractions and impure synthetic materials, as indicated by their chemical behavior.

The object of the present work has been to isolate the material from petroleum in as pure condition as possible and to identify it tentatively, leaving the conclusions open to revision when subsequent investigations on the structure and properties of the synthetic substances make this possible.

The determination of the naphthene-hydrocarbon content of petroleum is of interest because of the part which these compounds play in the "knocking" characteristics of gasoline and the lubricating qualities of higher-boiling fractions. It appears also that there is much to be learned about the chemistry and the physical properties of this class of compounds. The fact that they resemble the paraffin hydrocarbons in their chemical inertness and knocking behavior in internal-combustion engines, but can be more or less readily dehydrogenated to aromatic hydrocarbons with quite different properties in these respects, makes their investigation important.

II. HISTORY OF THE MATERIAL AND INDICATIONS OF THE PRESENCE OF NAPHTHENES

The unshaded line C in the lower chart of figure 1 is the distillation curve between 100 and 129° C of the midcontinent oil[7] upon which the work of Project 6 of the American Petroleum Institute has concentrated, before the isolation of any material. This distribution resulted after an initial distillation in a refinery and four systematic fractional distillations in the laboratory. The shaded line D in the same chart shows the distribution of volumes after the removal of

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[3] F. Beilstein and A. Kurbatow, Ber. deut. chem. Ges. **13**, 2028 (1880).

[4] C. Engler and H. v. Höfer. Die Chemie und Physik des Erdöls, S. Hirzel, Leipzig (1913).

[5] C. F. Mabery, Proc. Am. Acad. Sci. **31**, 1 (1895).

[6] C. M. Warren, Proc. Am. Acad. Sci. **27**, 78 (1891).

[7] Taken from well no. 6 of the South Ponca Field, Kay County, Okla.

toluene [8] from the material boiling below 110°, 2-methylheptane [9] boiling at 116 to 117°, and *n*-octane [10] at 123 to 126° C. It is to be observed that the original mountainous concentration of material boiling between 119 and 127° has been separated into two peaks by the removal of a large quantity of *n*-octane by crystallization and subsequent fractional distillations. Curve A, in the upper part of figure 1, shows the change in the refractive index with the boiling point of the fractions shown in curve D. Since the material was free from aromatic hydrocarbons, the abrupt rise in this curve between 120 and 123° indicated the probable presence of naphthenic compounds, as suspected by other investigators. Before the removal of the *n*-octane and 2-methylheptane there was no indication of the presence of a component which was in sufficient concentration to crystallize. When the status of separation depicted by curve D was reached, however, freezing halts in the cooling curves of some of the samples became detectable. Curve B, figure 1, shows the tempera-

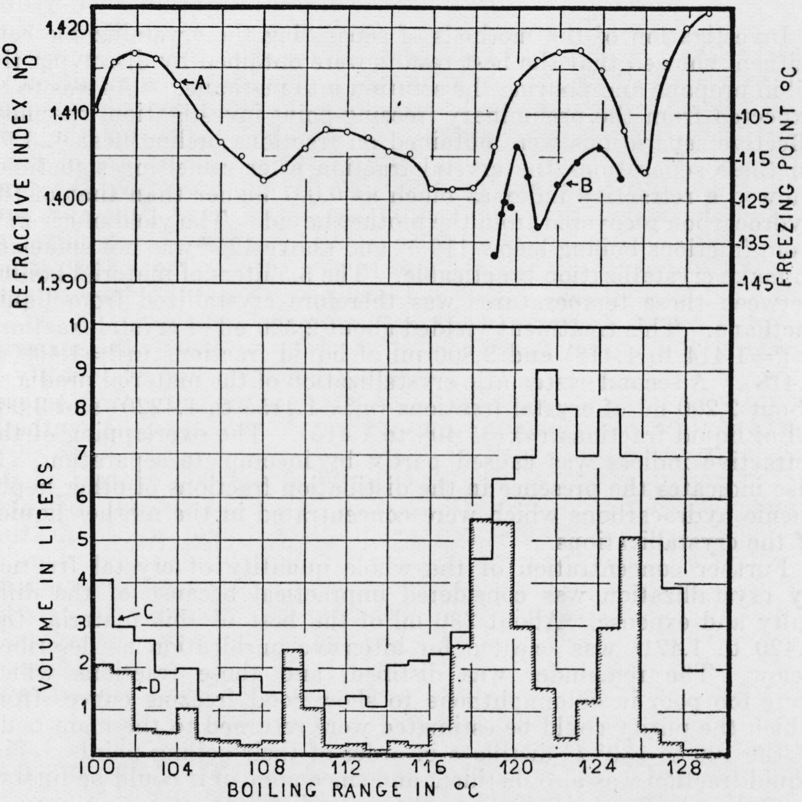

FIGURE 1.—*Volumes and properties of distillation fractions boiling between 100 and 129° C.*

A, Refractive indices; B, initial freezing halts; C, volumes before removal of any constituents; D, volumes after removal of toluene, isooctane, and *n*-octane and fifteen subsequent fractional distillations.

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[8] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research **6**, 377 (1931) RP280.

[9] R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.

[10] R. T. Leslie and S. T. Schicktanz, BS J. Research **6**, 377 (1931) RP282.

ture of the initial observed halts in the cooling curves of samples selected at intervals over the boiling range from which crystals could be obtained. It is apparent that the maximum concentration of crystallizable material occurred at approximately 120.5° C. Even at this temperature the concentration was small, as indicated by the low congealing temperature compared with the freezing points of the naphthenic compounds reported in this boiling range.

III. SEPARATION OF OCTONAPHTHENE FROM PETROLEUM

Investigation of the methods of separating the crystallizable constituent showed that the best results were obtained by dissolving the oil in propane and pouring the solution into methane.[11] As was to be expected from the preliminary freezing-point investigation, the most effective separations were obtained on fractions boiling near 120.5°. In these separations the crystal fraction after remelting sometimes showed a refractive index as much as 0.007 higher than that of the hydrocarbon recovered from the mother liquid. The yield of crystals from fractions boiling below 119.5° and above 121° was not sufficient to make crystallization practicable. The 5.5 liters of material boiling between these temperatures was therefore crystallized from liquid methane. This treatment yielded about 2,500 ml of crystal fractions (n_D^{20}=1.414 to 1.418) and 2,800 ml of liquid fractions (n_D^{20}=1.408 to 1.418). A second systematic crystallization of the material produced about 2,200 ml of crystal fractions (n_D^{20}=1.4155 to 1.4220) and 3,000 ml of liquid fractions (n_D^{20}=1.408 to 1.416). The overlapping of the refractive indices was caused partly by incomplete separation. It also indicates the presence in the distillation fractions of other naphthenic hydrocarbons which were concentrated in the mother liquids of the crystallizations.

Further concentration of the whole quantity of crystal fraction by crystallization was considered impractical because of the difficulty and expense. About 330 ml of the best of this material (n_D^{20} 1.420 to 1.421) was selected for intensive purification as described below. The remainder was distilled, and those fractions which were too poor in octonaphthene to show good freezing curves from which the purity could be estimated were returned to the main body of the 100 to 130° C distillate in order of their boiling points. The liquid fraction was also distilled, and since none of it could be further crystallized, it was returned to the main distillate.

The 330 ml of best material was carefully distilled through a spiral carborundum-coated column.[12] The results of this distillation are shown in figure 2. Fractions amounting to about 75 percent distilled within 0.2° C. The middle fractions amounting to 60 percent showed practically constant boiling points, refractive indices, and freezing points. This constant-distilling material was further purified by two crystallizations from methane and two without solvents. The last crystallization raised the freezing point by about 0.1° and caused little improvement in the shape of the curve. The cooling curve of the best sample is shown in figure 3, and its properties are given in table 1, together with those of the other concentrated material.

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[11] R. T. Leslie, BS J. Research, 10, 609 (1933) RP552.
[12] Designed by S. T. Schicktanz.

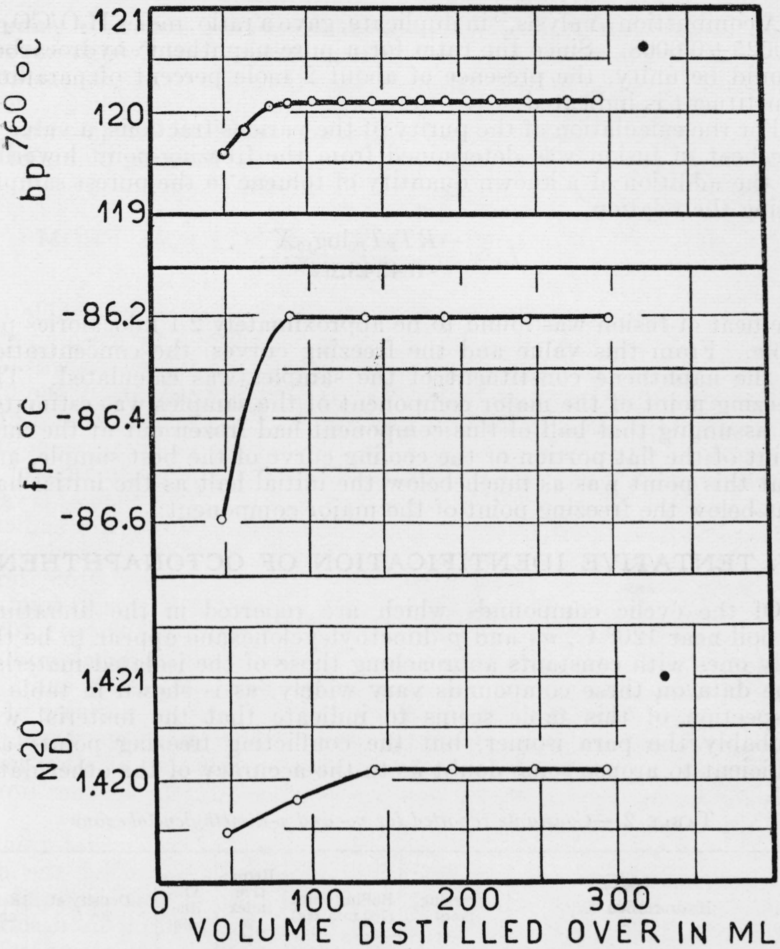

FIGURE 2.—*Properties of best 330-*ml *fraction of octonaphthene crystallized from petroleum after a distillation, but before final purification.*

The solid disks represent properties of the residue from the distillation.

TABLE 1.—*Physical properties of dimethylcyclohexane fractions from petroleum*

Lot	Volume	Freezing point [b]	Boiling point [c] (760 mm Hg)	Refractive index n_D^{20}	Concentration
	ml	*Degrees* C	*Degrees* C		*Mole percent*
I [a]	48	-84.8_8	120.0	1.4199_5	98.5
II	100	−86.4	119.9	1.4198	94.7
III	55	−87.0	119.8	1.4190	92.9
IV	420	−88.5	119.8	1.4162	88.7
V	125	−89.0	119.8	1.4167	87.3
VI	175	−92.4	119.6	1.4143	78.2
VII	230	−92.8	119.5	1.4131	77.2
VIII	100	−95.8	119.1	1.4120	69.8
IX	230	−96,0	120.0	1.4180	69.3
X	100	−97.0	119.8	1.4187	66.6

[a] The density of lot I, as determined by the Weights and Measures Division of the National Bureau of Standards, was 0.76492 ±0.00002 g/ml at 20° C.

[b] Value for lot I is the initial extrapolated freezing point. The values for the other lots are the initial observed points.

[c] The boiling points were determined in a Cottrell boiling-point apparatus.

A combustion analysis,[13] in duplicate, gave a ratio, moles $H_2O/CO_2 = 1.0025 \pm 0.0008$. Since the ratio for a pure naphthenic hydrocarbon should be unity, the presence of about 2 mole percent of paraffinic constituent is indicated.

For the calculation of the purity of the various fractions, a value of the heat of fusion was determined from the freezing-point lowering on the addition of a known quantity of toluene to the purest sample. Using the relation,

$$L_F = \frac{-RT_F T_{F0} \log_{10} X}{0.4343 \Delta t_F},$$

the heat of fusion was found to be approximately 2.1 kilocalories per mole. From this value and the freezing curves, the concentration of the naphthene constituent of the samples was calculated. The freezing point of the major component of the samples was estimated by assuming that half of this component had frozen out at the midpoint of the flat portion of the cooling curve of the best sample, and that this point was as much below the initial halt as the initial halt was below the freezing point of the major component.

IV. TENTATIVE IDENTIFICATION OF OCTONAPHTHENE

Of the cyclic compounds which are reported in the literature, to boil near 120° C, *m*- and *p*-dimethylcyclohexane appear to be the only ones with constants approaching those of the isolated material. The data on these compounds vary widely, as is shown in table 2. Inspection of this table seems to indicate that the material was probably the para isomer, but the conflicting freezing points are sufficient to arouse some doubt as to the accuracy of the other data.

TABLE 2.—*Constants reported for m- and p-dimethylcyclohexane*

Hydrocarbon	Freezing point	Boiling point (760 mm Hg)	Refractive index n^{20}_D	Aniline point	Density at 20° C	Reference
	°C	°C		°C	g/ml	
m-Dimethylcyclohexane	Below −75	121.6±1	1.4255	47.8	[a] $0.7723^{20/4}$	1
cis-m-Dimethylcyclohexane	Below −75	121.0	1.4238		[a] $.7735^{20\ \mathrm{vac}}$	2
trans-m-Dimethylcyclohexane		119^{756}	1.4226			2
m-Dimethylcyclohexane		120^{744}	1.4234		[a] $.7736^{18/4}$	3
Do	−85	123.7	1.425		.771	4
Do		120.9 to 122.5	1.4253		.774	5
p-Dimethylcyclohexane	−59	121.7±1	1.4253	47.8	.7727	1
cis-p-Dimethylcyclohexane		$120._5{}^{755}$	1.4206		.7671	2
trans-p-Dimethylcyclohexane		119^{760}	1.4183		.7655	2
p-Dimethylcyclohexane	−86	120.5	1.421		.769	4
Do		122 to 124	1.4271		.777	5

[a] Specific gravity.

1. E. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18**, 107, 751 (1932).
2. F. Eisenlohr, Fortsch. Chem. **18**, 9, 521 (1925).
3. C. Engler and H. v. Höfer, Die Chemie und Physik des Erdöls.
4. Int. Critical Tables, **1**, p. 222 (1926).
5. F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55**, 3326 (1933).

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[13] The author is indebted to J. D. White for this determination.

In order to decide between the various values, synthetic samples of sufficient purity to distinguish definitely between the properties of the compounds were prepared. Samples of very pure *m*-xylene (freezing point, −49.9° C; $n_D^{25.2}$, 1.4945) and *p*-xylene (freezing point, +13.3° C; $n_D^{25.2}$, 1.4931), kindly made available by F. W. Rose, Jr.,[14] were hydrogenated by passing a mixture of hydrogen and hydrocarbon vapors over a nickel-aluminum catalyst [15] at the temperature of boiling toluidine. After treatment with nitrating mixture to remove the unhydrogenated aromatics, washing with alkali and distilling from sodium, 55 ml of hydrogenated *m*-xylene (boiling point, 121.3° C; n_D^{25}, 1.4230; freezing point, about −92.5) and 48 ml of hydrogenated *p*-xylene (boiling point, 121.3° C; n_D^{25}, 1.4220; eutectic halt, −94° C) were obtained. The cooling curves of both these samples indicated that they were far from pure substances. Evidently mixtures of *cis*- and *trans*- forms result on hydrogenation of these substances in the manner described.[16] The hydrogenated *p*-xylene was purified by a crystallization without the use of solvent, after which the cooling curve shown in figure 3 was obtained on the material. The initial freezing point (−44.7° C) is so high that the

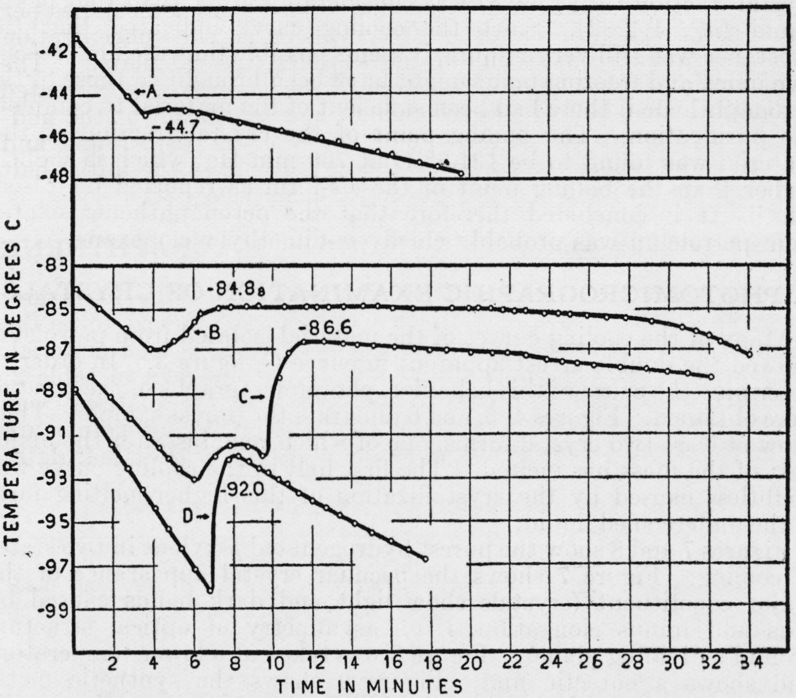

Figure 3.—*Cooling curves of hydrogenated m- and p-xylenes and of octonaphthene fractions from petroleum.*

A, Hydrogenated *p*-xylene; B, best sample from petroleum; C, mother liquid from crystallization of best sample; D, hydrogenated *m*-xylene.

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[14] Prepared by the method of J. D. White and F. W. Rose, Jr., BS J. Research **9**, 711 (1932).

[15] N. Zelinsky and W. Kommarewsky, Ber. deut. chem. Ges. **57**, 667 (1924).

[16] G. Chavanne and E. Bode, J. Am. Chem. Soc. **52**, 1609 (1930).

particular stereoisomer of *p*-dimethylcyclohexane which was present in excess of the eutectic in the synthetic product cannot be identical with the major constituent of the isolated product. The other stereoisomer of *p*-dimethylcyclohexane is also eliminated by the fact that the refractive index of the mother liquid from the crystallization was too high (n_D^{25}, 1.4232, as compared to 1.4199_5 for the octonaphthene). The boiling point of the crystal fraction was found to be 121.0° C at 760 mm Hg.

The hydrogenated *m*-xylene was crystallized once without solvent and twice with methane. The final freezing curve (freezing point, about −92° C) is shown in figure 3. The final refractive index of the crystal fraction (n_D^{25}, 1.4228) was considerably lower than that of the liquid (n_D^{25}, 1.4232). Since the cooling curve indicated that the substance was still very impure, it seems possible that the final refractive index and freezing point might have been brought to those of the octonaphthene if there had been sufficient of the material to complete the purification. The boiling point of the crystal fraction of this material was found to be 121.3° C at 760 mm Hg, which is slightly higher than the boiling point of the *cis*-form as reported by Eisenlohr.[17] It is concluded therefore that the octonaphthene isolated from petroleum was probably chiefly *m*-dimethylcyclohexane.

V. PHOTOMICROGRAPHIC EXAMINATION OF CRYSTALS[18]

Many of the cooling curves of the material isolated from petroleum showed the double arrest apparent in curve C, figure 3. In order to determine the cause of this behavior, photomicrographs of the crystals were obtained. Figures 4, 5, and 6 illustrate the purest sample. They show at least two crystal forms, one of which remains after the major part of the mass has melted. The first halt in the cooling curve was doubtless caused by the crystallization of this higher-melting form in the undercooled liquid.

Figures 7 and 8 show the purest hydrogenated *p*-xylene in two states of cooling. Figure 7 shows the peculiar crystal appearance of the major constituent (crystals show light and dark bands caused by plus and minus elongation, i. e., asymmetry of optical structure around a dividing plane). Figure 8 was taken at a lower temperature and shows a eutectic mat. Figure 9 shows the synthetic meta-compound with both the excess constituent and the eutectic.

Comparison of the crystal forms of the synthetic samples with the best petroleum sample shows that all three products are alike in containing more than one crystal form. The angles and twinned structure of the higher-melting crystal form of the petroleum sample resemble those of the excess constituent which appears in the hydrogenated *p*-xylene.

To test the possibility that they were identical, some of the twinned crystals were isolated from the petroleum sample by cooling under the microscope and draining off the excess liquid. Hydrogenated *p*-xylene was then allowed to crystallize around them. On warming the

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[17] F. Eisenlohr, Fortsch. Chem. Phys. Chem. **18**, 521 (1925).

[18] All photomicrographic work was done by C. P. Saylor. The photographs were made between crossed nicols and under a magnification of 71 ×. See W. H. Smith, C. P. Saylor, and H. J. Wing, BS J. Research **10**, 479 (1933) RP544, for description of apparatus. For the work here described no acetone was used in the refrigerating dewar tube. The hydrocarbon was placed between small cover glasses in the bottom of the dewar tube in the optical path.

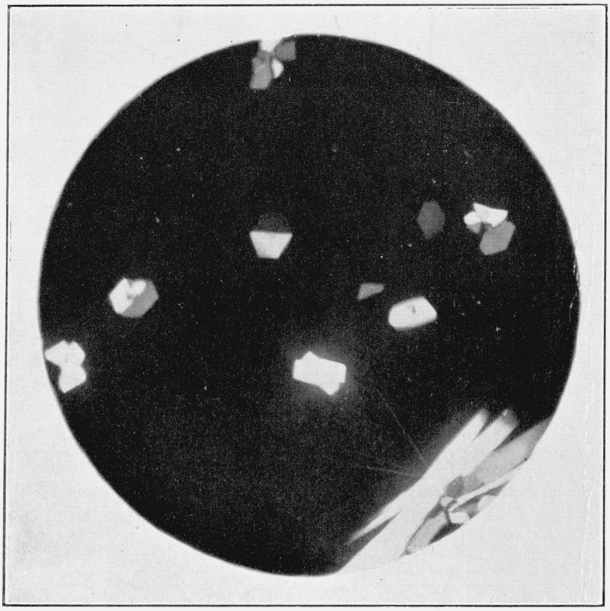

FIGURE 4.—*Best octonaphthene undercooled, warmed until only seeds remained, and cooled gradually.*

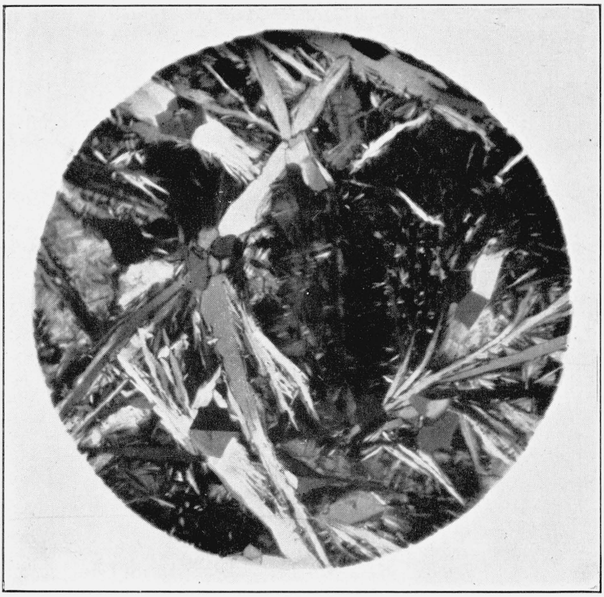

FIGURE 5.—*Same field shown in figure 4 on further gradual cooling.*

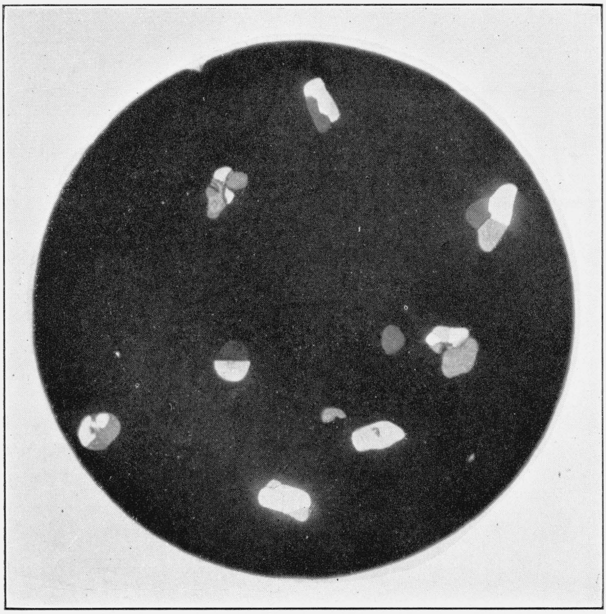

FIGURE 6.—*Field shown in figure 5 on gradual warming.*

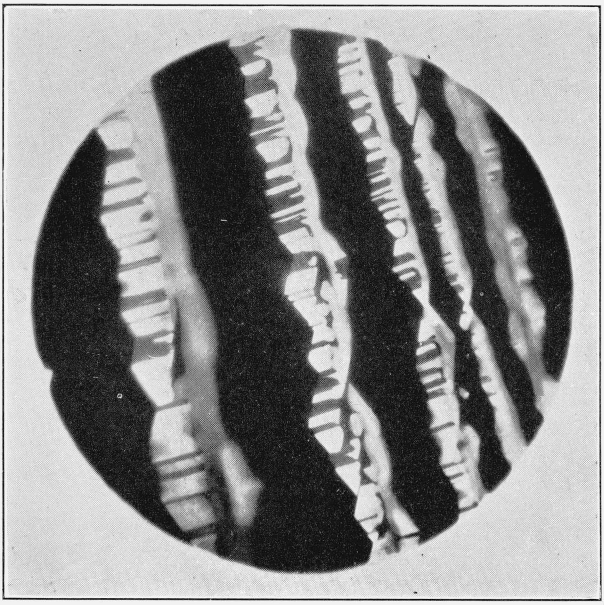

FIGURE 7.—*Hydrogenated p-xylene undercooled, warmed until only seeds remained, and cooled gradually to allow the first crystal phase to grow.*

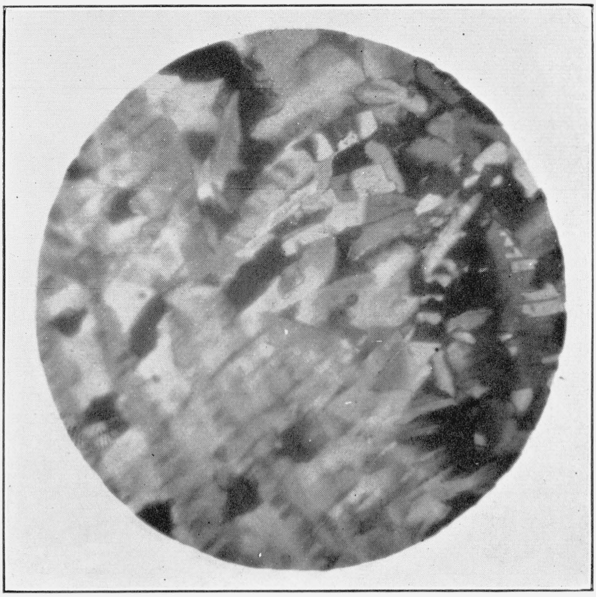

FIGURE 8.—*Same field shown in figure 7 on further gradual cooling.*

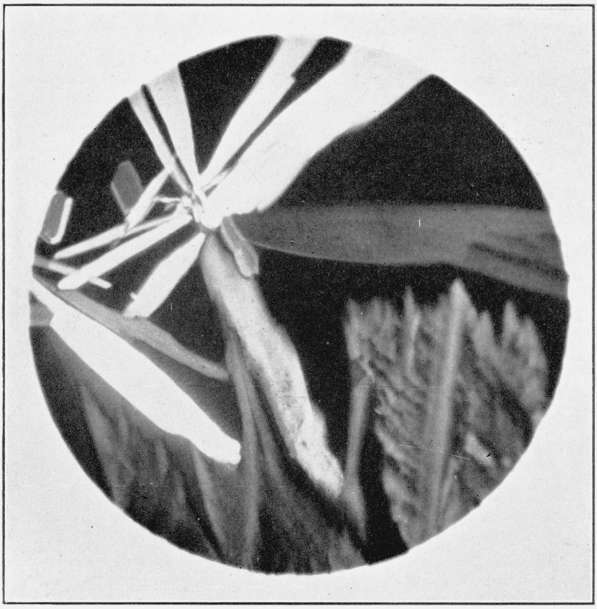

FIGURE 9.—*Hydrogenated m-xylene on gradual cooling.*
Both eutectic and excess constituent visible.

mass, the twinned crystals seemed to disappear before the remainder. This behavior indicated that the twinned crystals appearing in the petroleum sample were not the higher-melting crystal constituent from the synthetic *p*-dimethylcyclohexane. Additional evidence for this conclusion was obtained by growing crystals from the synthetic *p*-compound, draining off the excess liquid, and adding octonaphthene which was undercooled below the melting point of its twinned crystals. The crystals dissolved, which showed that they were not in equilibrium with the octonaphthene.

Crystals of the higher-melting material from the synthetic meta-compound, obtained by drawing off the mother liquid as described above, remained in equilibrium with the cold octonaphthene. The presence of the seed crystals from the synthetic product also appeared to decrease the proportion of twinned crystals which formed. From the last experiment it appears that the lower-melting constituent in the octonaphthene from petroleum was identical with the higher-melting crystal constituent in the hydrogenated *m*-xylene.

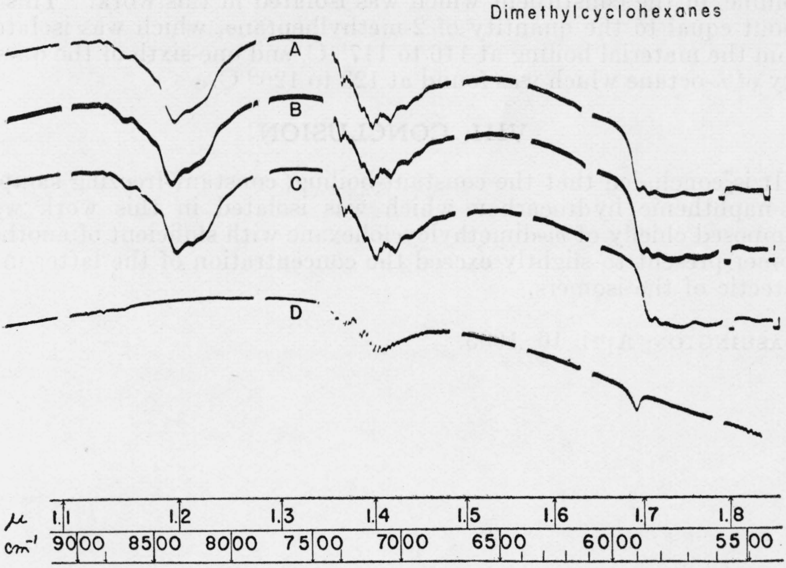

FIGURE 10.—*Infrared-absorption curves of dimethylcyclohexanes.*

Record of the transmission in the near infrared through 10 cm of solution of synthetic samples of dimethylcyclohexane and of the octonaphthene from petroleum in purified carbon tetrachloride. The concentrations were 0.0609, 0.0590, and 0.0589 molal for curves A, B, and C, respectively.

A, Hydrogenated *m*-xylene; *B*, octonaphthene fraction from petroleum; C, hydrogenated *p*-xylene; D, carbon tetrachloride.

VI. INFRARED-ABSORPTION SPECTRA OF DIMETHYLCYCLOHEXANES[19]

Comparison, figure 10, of the infrared-absorption spectrograms of the hydrogenated *p*- and *m*-xylene with that of the material isolated from petroleum shows that the latter is probably composed of deriva-

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[19] The author is indebted to U. Liddel and O. R. Wulf, of the U. S. Bureau of Chemistry and Soils, for recording these spectrograms and interpreting the results.

tives of cyclohexane. Inspection also shows that the spectrogram of the naphthene from petroleum more nearly resembles that of hydrogenated *m*-xylene than that of the *p*-xylene, but is not identical with either. This lends further credence to the belief that the material was chiefly *m*-dimethylcyclohexane with some other constituent or more than one isomeric form present.

VII. ESTIMATION OF THE QUANTITY OF THE DIMETHYLCYCLOHEXANE FRACTION IN THE CRUDE PETROLEUM

In the approximately 2,200 liters of the original crude oil it is estimated that there were at least 3 liters, or about 0.15 percent by volume, of the constituent which was isolated in this work. This is about equal to the quantity of 2-methylheptane, which was isolated from the material boiling at 116 to 117° C, and one-sixth of the quantity of *n*-octane which was found at 123 to 126° C.

VIII. CONCLUSION

It is concluded that the constant-boiling, constant-freezing sample of naphthenic hydrocarbon which was isolated in this work was composed chiefly of *m*-dimethylcyclohexane with sufficient of another isomer present to slightly exceed the concentration of the latter in a eutectic of the isomers.

WASHINGTON, April 16, 1935.