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ISOLATION OF AN ISONONANE FROM PETROLEUM—ITS FRACTIONATION FROM NAPHTHENES BY DISTILLA- TION WITH ACETIC ACID ¹

By Joseph D. White ² and Frank W. Rose, Jr. ²

ABSTRACT

A nonane boiling at 135.2° C, probably a dimethylheptane, has been isolated from Oklahoma petroleum. It was found closely associated with naphthenic hydrocarbons in a distillation fraction boiling normally between 135 and 136° C from which aromatic hydrocarbons had already been removed. Separation of the mixture by distillation with glacial acetic acid yielded a fraction highly concentrated in the nonane from which the compound was finally isolated by crystallization from solution in liquid dichlorodifluoromethane. It constitutes about 0.1 percent of the crude petroleum.

The physical constants of the nonane have been determined and compared with those of nonanes known to boil near 135° C. It has properties similar to those of 2, 6-dimethylheptane, but the agreement is not sufficient, in the absence of knowledge concerning other possible isomers, to identify the compound completely.

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I. INTRODUCTION

In the first systematic examination of American petroleum, Pelouse and Cahours [1]³ obtained, upon treating a distillate "boiling within close limits" with concentrated sulphuric acid and redistilling the residual oil, a fraction which boiled between 136 and 138° C. On the basis of its vapor density they called the material *hydrure de nonyle*. It was characterized by them as having an odor faintly like that of lemons. Twenty years later, Lemoine [2], in a similar investigation obtained a fraction boiling within the range 135 to 137° C, which he designated as α -nonane. The exact source of the petroleum used in

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

³ Figures in brackets throughout the text indicate references listed at the end of the paper.

each investigation was not recorded. Most likely it came from eastern Canada or from the Appalachian fields. On the other hand, contemporaneously with Pelouse and Cahours, Warren, in a more carefully conducted examination of Pennsylvania petroleum, found no nonane which boiled near 135° C [3]. No other investigation of the composition of petroleum has revealed the presence of such a nonane.

Neither of the nonane fractions obtained by the above investigators closely resembled a pure aliphatic hydrocarbon in physical properties. This is not at all surprising since the nonane, whose separation from a midcontinent petroleum is described below, was found mixed with a naphthene hydrocarbon in an approximately constant-boiling distillate. An exhaustive distillation did not separate the nonane completely and only by subsequent crystallization could the compound be isolated in a nearly pure state.

II. PRELIMINARY DISTILLATION

In the course of separating the hydrocarbon constituents in an Oklahoma petroleum,⁴ a 35-liter fraction was obtained which distilled between 130 and 140° C. After extracting the aromatic constituents [4], a redistillation of the residual oil at reduced pressure yielded a 9-liter fraction, boiling in the narrow range of 93 to 94° C at 215 mm (around 136° C at 760 mm), which was composed of a mixture of paraffin and naphthene hydrocarbons. Its refractive index⁵ of 1.418, when compared with those for paraffin and naphthene hydrocarbons boiling near 136° C (1.400 and 1.430, respectively) showed that it was somewhat enriched in the naphthene constituents. In an effort to resolve the fraction into its components, it was again systematically distilled—this time at atmospheric pressure and through more efficient columns packed with brass locket chain. With a reflux ratio of approximately 15:1, the distillation proceeded at a rate of 0.5 to 1 ml a minute. The distillate was collected in 50-ml cuts which were sorted and combined according to boiling point and refractive index and redistilled in the same manner.

To guard against decomposition of the material at its elevated temperature of boiling, the distillation was carried out in the presence of carbon dioxide. Even so, the still residues, in which the naphthene was concentrated, were partially decomposed when distillation was carried too far. To minimize this, a large portion of a charge—frequently a third—was generally left undistilled.⁶

At the end of four distillations, the fractionation had proceeded as far as was feasible. Figure 1 shows the relation of the volume and refractive index of the resulting distillate to its boiling range. The lower step-wise line indicates the volumes of combined fractions which boiled within half-degree ranges. The upper line represents their refractive indices. The smooth curve imposed upon the upper line represents, without indicating the individual points, the refractive indices plotted against the boiling points of the 50-ml distillation cuts before pouring them together. The marked slope of the curve, as

⁴ A description of the oil is given in BS J. Research 2, 469, table 1 (1929) RP45, and in J. Research NBS 15, 212 (1935) RP824.

⁵ All refractive indices in this paper are for n_D^{25} , unless otherwise noted.

⁶ Redistillation of the combined naphthenic residues resulted in pronounced decomposition, as evidenced by the brown color and unpleasant pungent odor of the still residue. If, however, the residues were first filtered through a small amount of silica gel, the colored and odorous material could be adsorbed and the filtered oil largely stabilized towards decomposition upon subsequent distillation.

well as its minimum for material boiling near 135° C., indicates that the distillation had partially separated the original mixture into its component hydrocarbons. Comparing the volumes of distillate with the refractive indices reveals that a fraction, more paraffinic than the others, was obtained which boiled between 135 and 135.5° C. A smaller and lower-boiling fraction obviously contained a naphthene, and a larger fraction, boiling higher, contained another naphthene as

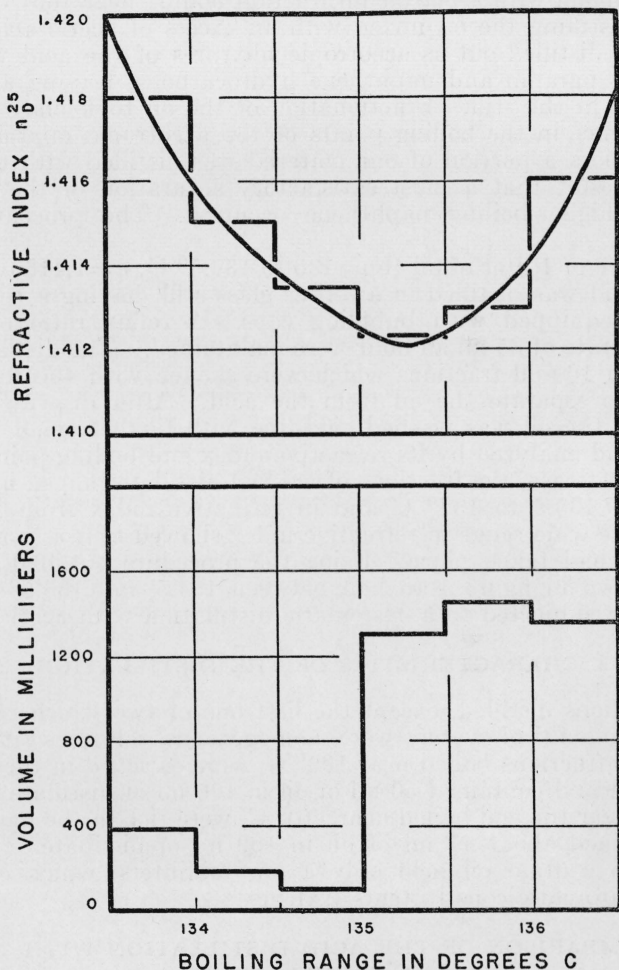


FIGURE 1.—Volumes and refractive indices of petroleum fractions, boiling between 133.5 and 136.5° C., after being distilled through chain-packed columns.

Lower graph, volume distribution; upper graph, refractive indices; upper curve, change in refractive index with boiling point.

its chief constituent. The isolation from this petroleum of the two naphthenes, ethylcyclohexane and a nonanaphthene, has already been reported [5].

The paraffinic fraction ($n=1.4123$) still contained a large amount of naphthene. While it could be crystallized from solution in liquid propane and methane, it could not be fractionated by crystallization, probably because it was nearly eutectic in composition.

III. CONCENTRATION OF THE PARAFFINIC CONSTITUENT BY DISTILLATION WITH ACETIC ACID

1. METHOD

A relatively large fraction, composed chiefly of the paraffin constituent, was obtained by redistilling the material with glacial acetic acid. S. T. Schicktanz [6], while working in this laboratory on a similar problem with a petroleum fraction boiling near 165° C, found that, by distilling the oil mixed with an excess of acetic acid, all of it could be distilled out as azeotropic mixtures of the acid with the constituent paraffin and naphthene hydrocarbons, leaving a residue of the acid in the still. Fractionation of the oil took place because of a difference in the boiling points of the azeotropic mixtures. At his suggestion, a portion of our material was distilled with the acid, with the result that a most satisfactory separation of the paraffin from the higher-boiling naphthene occurred. The procedure was as follows:

A mixture of 1 liter of oil (bp=136 to 136.5° C; $n=1.4160$) and 1.5 liters of acid was distilled in a 3-liter glass still, having a column of 30 plates equipped with bubbling caps. A reflux ratio of about 20:1 and a rate of 35 ml an hour were maintained. The distillate was collected in 100-ml fractions which were shaken with 400 to 500 ml of water to separate the oil from the acid. After drawing off the acid layer, the oil was washed acid-free with further small portions of water and analyzed by its refractive index and boiling point.

In the test case, the fractions of washed distillate ranged in boiling point from 135.5 to 137° C and in refractive index from 1.408 to 1.427. The wide range in refractive index showed that a pronounced separation had taken place. Using the procedure outlined, the 4.2 liters—shown in figure 1 to boil between 134.5 and 136.5° C—was accordingly subjected to a systematic distillation with acetic acid.

2. CHARACTERISTICS OF THE DISTILLATION

All fractions distilled, except the first one or two which contained a small amount of water, were homogeneous solutions at 25° C. The initial fractions boiled near 109° C, were enriched in the paraffin constituent and contained 50 ml of oil in 100 ml of distillate. Those distilling near the end boiled near 110° C, were rich in the naphthene, and contained about 47 ml of oil in 100 ml of distillate. The last fraction to contain oil held only a few milliliters, which consisted chiefly of aromatic constituents (xylenes).⁷

3. COMPARISON OF THE ACID DISTILLATION WITH THE OIL DISTILLATION

In order to point out more clearly the effectiveness of the acid distillation in separating the paraffin-naphthene mixture, the results of distilling certain fractions of the oil through columns packed with

⁷ This discovery led to our developing a method, which we expect to publish later, for separating the aromatic from aliphatic and naphthenic hydrocarbons in the petroleum fraction boiling between 155 and 160° C. A solution of isopropylbenzene (boiling point 153.5° C) and acetic acid was found to distill several degrees higher than the azeotropic mixtures of the acid with the paraffins and naphthenes boiling near 155° C. Similar facts account for the ease with which the xylene constituents are separated from a mixture of petroleum hydrocarbons boiling near 136° C when it is distilled with acetic acid. Lecat found the boiling point of the azeotrope of acetic acid-*m*-xylene to be 115.38° C. See Int. Crit. Tables 3, 319 (McGraw-Hill Book Co., New York, N. Y., 1928.)

locket chain are compared in figure 2 with those obtained by distilling similar fractions with acetic acid, through columns equipped with bubble-cap plates. In the figure, the refractive indices of selected

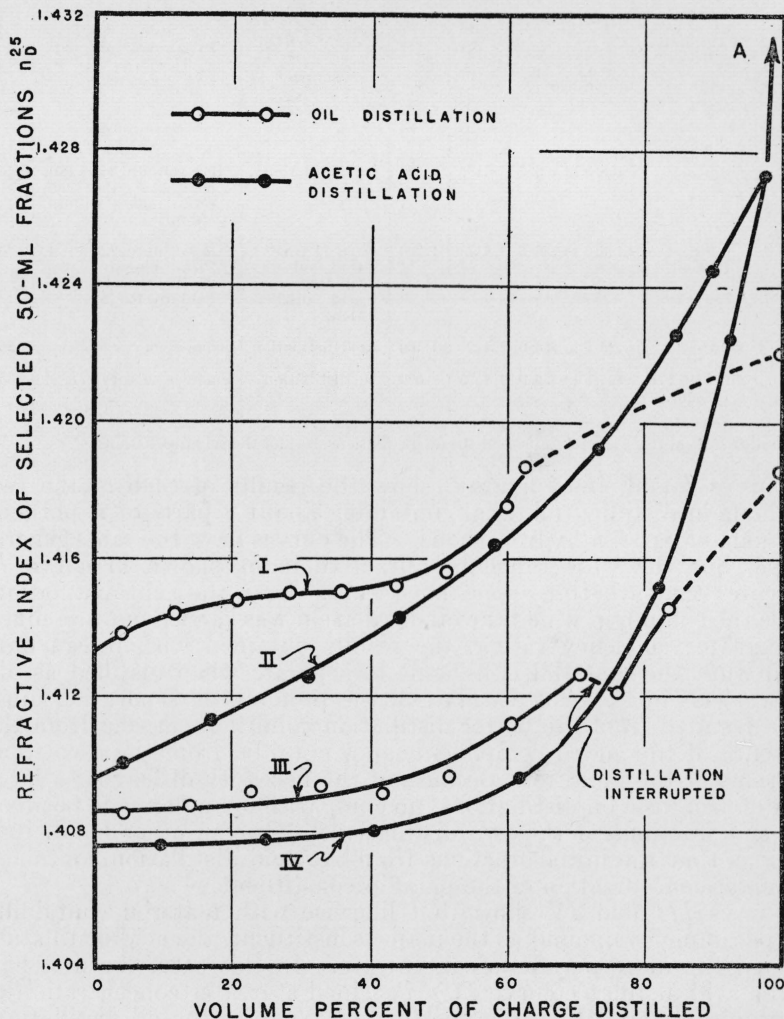


FIGURE 2.—Curves comparing the distillation of petroleum fractions, boiling between 135.5 and 136.5 C alone and with glacial acetic acid

Curves I and II show the progressive change in composition (refractive index) of the distillate during distillation of material enriched in naphthene. Curves III and IV show the same for material enriched in paraffin. For properties of the material distilled, see table 1.

50-ml fractions of distilled oil are plotted against the percentage of the original charge distilled. The properties of the material used, and the conditions under which its distillation was carried out, are given in table 1.

TABLE 1.—*Properties of the oil, and distillation conditions used to obtain the curves shown in figure 2*

Curve	Type of distillation	Oil used for distillation				Type of column used	Total amount of distillate per hr. ¹
		Boiling range	Refractive index, n_D^{20}	Amount	Source		
<i>I</i>	Oil.....	°C 136.0 to 136.5	1.418	ml 1,320	Oil distillation..	Glass column, 2.5 m tall, chain-packed; 60 theoretical plates; hold-up, 160 ml.	ml 46
<i>II</i>	Oil with acetic acid.	136.0 to 136.5	1.4175	1,200	Equal parts from oil distillation and acid distillation.	Glass column, 2.5 m tall, 30 bubble-cap plates; 25 theoretical plates; hold-up, 160 ml.	36
<i>III</i>	Oil.....	135.5 to 136.0	1.412	1,100	Acid distillation..	Same as for curve <i>I</i>	20.5
<i>IV</i>	Oil with acetic acid.	135.5 to 136.0	1.4125	990	Oil distillation..	Same as for curve <i>II</i>	35

¹ A reflux ratio of 15:1 was maintained for the oil distillations; 20:1 for the acid distillations.

Curves *I* and *II* of figure 2 show the results of each of the two methods in distilling material containing about 2 parts of naphthene to 1 part of paraffin hydrocarbons. The curves have the same general shape, but the wide range in refractive index shown in curve *II* indicates that a better separation resulted from the acid distillation. Since the column in which the oil distillation was carried out had much the greater efficiency rating, the results obtained with it can only mean that the material is difficult to separate when distilled as oil. Conversely, in the acid distillation, the pronounced separation must have resulted from the better distillation conditions arising from the presence of the added component, and, notably, from the azeotropic relations of the mixture. Because of the necessity of leaving a large residue from the oil distillations, no comparison can be made between the end fractions of the two distillations. On the other hand, it is obvious that the initial fractions from the acid distillation contained a greater concentration of the paraffin constituent.

Curves *III* and *IV* show that likewise with material containing the paraffinic compound as the major constituent, the acid distillation yielded the more paraffinic concentrate. In this case, the first half of the acid distillate (curve *IV*) contained a greater concentration of paraffinic material than did the first 50 ml from the oil distillation.

In addition to effecting a better separation of the naphthene and paraffin constituents, the distillation with acetic acid had the advantage of permitting smaller initial quantities of oil to be distilled without leaving a residue of oil. This permitted the systematic distillation to be carried well towards completion. A further advantage was the readiness with which any aromatic material present could be separated from the other classes of hydrocarbons. This is illustrated in curve *IV* of figure 2 by the arrow and the letter *A*, which represents the last 2.5 percent of distillate. The average refractive index for this small fraction was 1.450, which indicates that about a third of it was aromatic hydrocarbon. Finally, in the acid distilla-

tion, no thermal decomposition of the oil occurred as it did from prolonged heating of the still residues in the oil distillation.

The chief disadvantage of the acid distillation was the necessary washing of the distillate to free the oil from acid.

4. RESULTS OF THE ACID DISTILLATION

The results of systematically distilling the petroleum fraction with acetic acid are given in figure 3. The lines and curves have the same

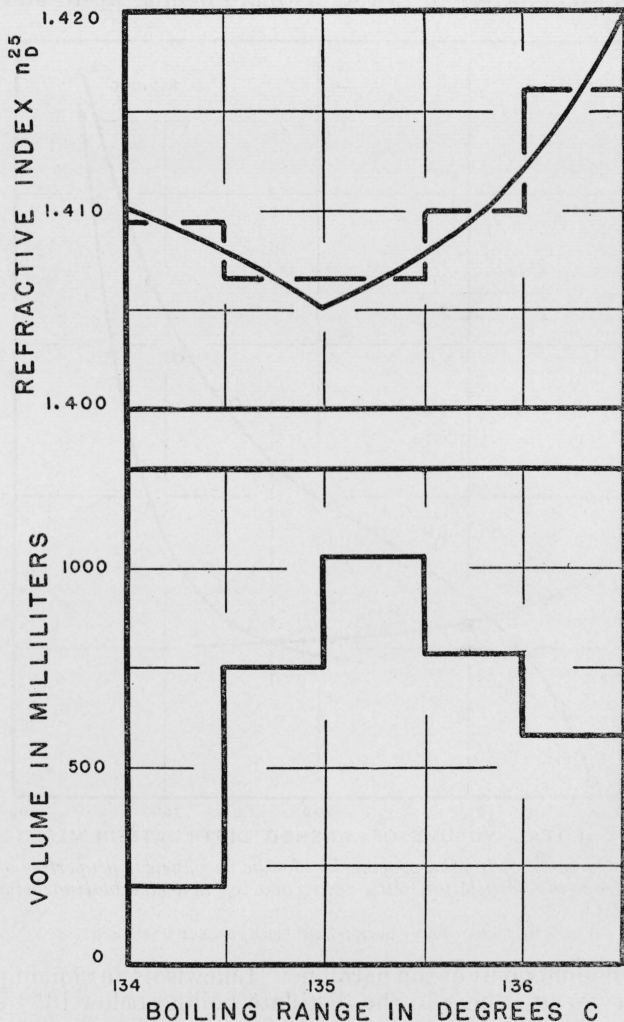


FIGURE 3.—Volumes and refractive indices of petroleum fractions boiling between 134 and 136.5° C after distillation with acetic acid.
The graphs and curve have the same significance as in figure 1.

significance as in figure 1. A liter of the nonaphthene (bp=136.7°C) was removed, which left about 2.5 liters of paraffin concentrate boiling between 134.5 and 136.0° C. The largest single fraction boiled between 135 and 135.5° C, which indicated that the boiling point of the paraffin hydrocarbon lay within these limits.

Towards the end of the distillation, further concentration of the paraffin constituent became slow, the separation being complicated by the presence of some ethylcyclohexane. In the refractive index curve of figure 3, it is observed that the distillate boiling at 135.0°C had the lowest value, 1.405, and therefore contained the least amount of naphthene. That some naphthene remained in this fraction was later verified from the refractive index, 1.399, of the pure paraffin. Probably as a result of the azeotropic conditions, a small amount of ethylcyclohexane persisted in the distillate boiling up to and slightly

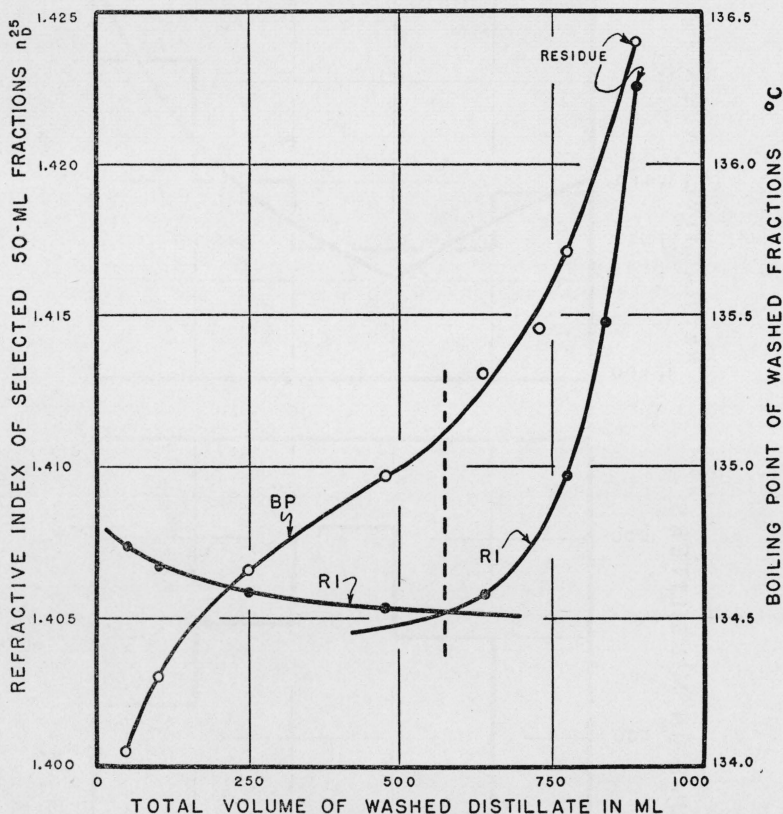


FIGURE 4.—Curves showing the progressive change in physical properties of fractions resulting from the distillation with acetic acid of material boiling between 134.8 and 135.2°C .

White circles represent boiling points; black circles, refractive indices.

above the boiling point of the paraffin.⁸ Likewise, the nonanaphthene, in turn, began to appear in the distillate boiling below 135°C . The situation is illustrated by the curves in figure 4 which show the change in boiling point and refractive index of material boiling between 134.8 and 135.2°C when distilled with acetic acid. The minimum for the refractive-index curve seems to correspond with material boiling at 135.1°C .

⁸ This was found to be the case when a redistillation of material boiling immediately above that temperature, and from which a portion of the paraffin had been removed by crystallization, yielded fractions containing ethylcyclohexane.

The inability to obtain a fraction of nearly pure paraffin hydrocarbon by distilling the material described above with acetic acid is explained in part by the data given in table 2, which show that the minimum boiling points of the constituent hydrocarbons with acetic acid are closer together than the boiling points of the constituents themselves.

TABLE 2.—Boiling points of three hydrocarbons compared with the boiling points of their acetic acid azeotropes

Hydrocarbon	Boiling point 760 mm	Azeotropic boiling point (approx.) 760 mm
	°C	°C
Ethylcyclohexane.....	131.8	107.9
Isononane.....	135.2	* 108.8
Nonanaphthene.....	136.7	109.6

* For a fraction of the nonane having boiling point = 135.5° C; n_D^{25} = 1.4045. All other values in this table were obtained with the best samples of the hydrocarbons isolated from petroleum. See table 4 and reference [5].

Although distillation with acetic acid resulted in a decided separation of the petroleum fraction herein discussed, it is not to be concluded that every mixture consisting of paraffin and naphthene hydrocarbons, and boiling in a narrow temperature range, can be so separated. Mixtures of this kind exist in which the azeotropic relations cause both classes of hydrocarbons to distill at the same temperature with acetic acid.

IV. ISOLATION OF THE PARAFFIN CONSTITUENT BY CRYSTALLIZATION FROM SOLUTION

When various fractions of the paraffinic material obtained from the acid distillation were cooled they could not be induced to form crystals but they would suddenly become viscous at -115° C. The sudden change in viscosity⁹ seemed to indicate that the oil was tending to crystallize at this temperature. When diluted with an equal volume of liquid dichlorodifluoromethane, all of the distillate boiling within the range 134.7 to 135.7° C and having a refractive index less than 1.408 crystallized readily and yielded, on fractionation of the partially frozen material, a solid phase in which the paraffin was more concentrated. Systematic crystallization of a liter of material, which boiled between 135.3 and 135.8° C and ranged in refractive index from 1.4055 to 1.409, finally produced a nearly pure sample of an isononane. The progress of the separation of the compound is outlined in table 3.

TABLE 3.—Progress of the fractional crystallization of the paraffin concentrate

Stage	Volume	Refractive index, un- corrected	Initial freezing point, un- corrected
	ml	n_{25}^D	°C
Start.....	1,000	1.4070	Glass at -115
1st.....	540	1.4054	-114
2d.....	270	1.4038	-----
3d.....	170	1.4013	-107
4th.....	102	1.4000	-103.8
5th.....	50	1.3990	-103.0

⁹ More recently we have observed the same phenomenon with the petroleum fraction boiling near 143° C, which contains the methyloctanes.

V. PROPERTIES OF THE ISONONANE

The 50-ml sample obtained after five crystallizations was refluxed over sodium to remove traces of solvent and then distilled. The time-temperature cooling curve of the distillate is recorded in figure 5. The curve shows that the sample had a freezing range of only 0.25°C , which indicates that the material, while not of the highest purity, was composed almost entirely of a single substance. Its nearly pure state was also indicated by the difference between its boiling point and condensation point. The small interval of 0.033°C was measured by M. Wojciechowski in a Swietoslowski ebulliometer of standard dimensions [7]. Further information concerning the sample's composition was obtained by determining its carbon-hydrogen ratio. From two determinations, the average ratio, moles H_2O /moles CO_2 , was found to be 1.1082 ± 0.0004 . (The experimental values were, respectively, 1.1086 and 1.1078.) Compared with the calculated value, 1.1111 for a nonane C_9H_{20} , and 1.0000 for a naphthene C_nH_{2n} , the value found

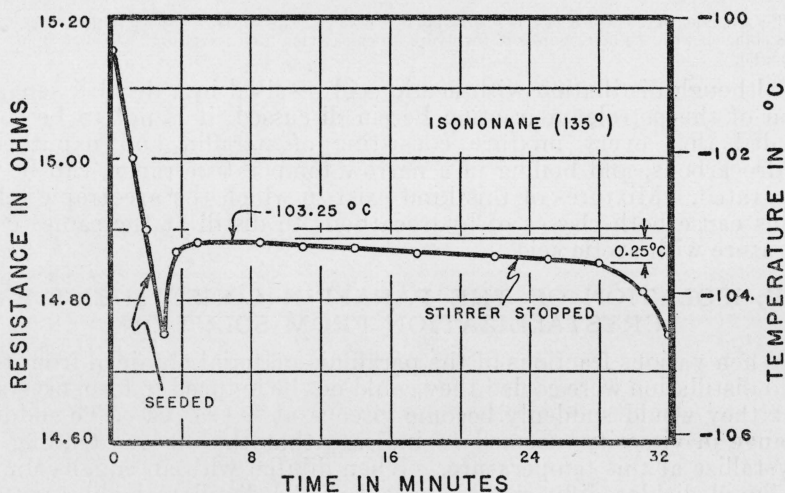


FIGURE 5.—Time-temperature cooling curve of the nonane isolated from petroleum.

indicated that the sample contained over 97 mole percent of the nonane.

The compound was found by H. S. Isbell of the Polarimetry Section of this Bureau to be optically inactive. It is further characterized by a very pleasant odor, but, unlike the fraction obtained by Pelouse and Cahours many years ago, it scarcely smells like lemons.

The physical constants of the isolated sample are listed in table 4.

TABLE 4.—Physical constants of the isononane from Oklahoma petroleum

Normal boiling point, $^{\circ}\text{C}$	135.21 ± 0.02 . ^a
Difference between boiling and condensation, $^{\circ}\text{C}$	0.033 . ^a
Freezing point, $^{\circ}\text{C}$	-103.25 ± 0.05 .
Specific gravity, d_{20}^{20}	0.70963 ± 0.00002 . ^b
Temperature coefficient, $\Delta d/\Delta t$	-0.00079 (20 to 25°C).
Refractive index, n_D^{20}	1.40115 ± 0.00005 .
Temperature coefficient, $\Delta n/\Delta t$	-0.00049 (20 to 25°C).
Critical solution temperature in aniline, $^{\circ}\text{C}$	81.2 ± 0.5 . ^c
Carbon-hydrogen composition, $\frac{\text{moles H}_2\text{O}}{\text{moles CO}_2}$	1.1082 ± 0.0004 .

^a Determined in a Swietoslowski ebulliometer by M. Wojciechowski. For method, see reference [7.]

^b Determined by the Division of Weights and Measures of this Bureau.

^c Determined by Wilson Heuer.

VI. RELATION OF THE ISOLATED NONANE TO THOSE KNOWN TO BOIL NEAR 135° C

A comparison of properties of the nonane from petroleum with those for a certain few of the synthetic nonanes is made in table 5. The properties of the isolated compound are the nearest like those of 2,6-dimethylheptane prepared by Konowalow, but are noticeably different from the properties of the same compound synthesized by Escourrou. This discrepancy prevents an accurate identification of the nonane from petroleum. Possibly it is 2,6-dimethylheptane. On the other hand, it is possible that the prototype of the isolated nonane has not yet been synthesized. Sixteen of the 35 structurally isomeric nonanes have been made. Of these, only those listed in table 5 boil near 135° C. It is quite likely that a few of the 19 unknown nonanes, especially other dimethylheptanes or some of the trimethylhexanes, boil in this region. The nonane from petroleum may be one of these. It follows, however, from its optical inactivity that the compound either contains no asymmetric carbon atom or is the *dl* mixture of its optical isomers.

TABLE 5.—Comparison of properties of the isolated nonane with those of certain known nonanes

Nonane C ₉ H ₂₀	Boiling point 760 mm	d_4^{20}	n_D^{20}
From Oklahoma petroleum:			
White and Rose	135.21	0.7096	1.4011
From "American petroleum":			
Pelouse and Cahours, Compt. Rend. 56 , 505 (1863)	136 to 138	α . 737	
Lemoine, Bul. soc. chim., Paris (1) 41 , 164 (1884)	135 to 137	α . 736	
2,6-Dimethylheptane:			
Escourrou, Bul. soc. chim., France (4) 43 , 1112 (1928)	134 to 135 α	α . 714	α 1.402
Konowalow, Chem. centra. 77 (11), 313 (1906)	134.5 to 135.5 α	α . 711	α 1.4007
2,5-Dimethylheptane:			
Clarke and Beggs, J. Am. Chem. Soc. 34 , 54 (1912)	135.6 to 135.9	b . 7198	1.4045
Levene and Marker, J. Biol. Chem. 91 , 418 (1931)	135	α . 716	
Levene and Marker, J. Biol. Chem. 95 , 13 (1932)	134	α . 719	
Tuot, Compt. Rend. 197 , 1434 (1933)	134 α	α . 713	1.4033
2,4-Dimethylheptane:			
Clarke and Beggs, J. Am. Chem. Soc. 34 , 60 (1912)	133.3 α	b . 7158	α 1.4040
Tuot, Compt. Rend. 197 , 1434 (1933)	130.5 α	α . 711	1.4023
3,3-Dimethylheptane:			
Noller, J. Am. Chem. Soc. 51 , 598 (1929)	137 to 138	.7304	1.4095

α Constants are reported values corrected to 760 mm or to 20° C. For $\Delta t_B/\Delta P$, see Int. Crit. Tables **3**, 246 (McGraw-Hill Book Co., New York, N. Y., 1928). $\Delta d/\Delta t = -0.0008$; $\Delta n/\Delta t = -0.0005$.

b Richards and Shipley, J. Am. Chem. Soc. **38**, 996 (1916).

VII. CONTENT OF THE ISONONANE IN THE PETROLEUM

All fractions from the acetic acid distillation which boiled between 133.5° and 136.5° C contained the isolated nonane. No other paraffin hydrocarbon was present in a detectable amount. Further fractionation of the distillate, by distillation and crystallization, yielded 2.5 liters of assorted fractions in which the nonane was the chief constituent. The fractions ranged in boiling point from 135.0° to 136.0° C and in refractive index from 1.400 to 1.410.

The amount of isononane in this material as estimated from the refractive index was approximately 1.8 liters. The total quantity originally present, counting losses, was more than 2 liters, which, based on an original 2,300 liters of crude, amounts to about 0.1 per cent of the petroleum.

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