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SEPARATION OF THE AROMATIC HYDROCARBONS, AND THE ISOLATION OF *n*-DODECANE, NAPHTHALENE, 1-METHYLNAPHTHALENE, AND 2-METHYLNAPHTHALENE, FROM THE KEROSENE FRACTION OF PETROLEUM[1]*

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ABSTRACT

This paper is the first report on the separation of the hydrocarbons in the kerosene fraction of petroleum, which investigation is being carried on as part of the work of the American Petroleum Institute Research Project 6. That part of the petroleum distilling between 114° and 144° C at a pressure of 56 mm Hg (corresponding approximately to 200° and 230° C at 760 mm Hg) was separated into a series of substantially constant-boiling fractions. From the material distilling between 127° and 133° C (at 56 mm Hg), *n*-dodecane was isolated by crystallization. All of the material except the isolated *n*-dodecane was then subjected to a systematic extraction with reflux in a two-solvent process in order to separate the aromatic hydrocarbons from the paraffins and naphthenes. The "clean-up" of the traces of aromatic hydrocarbons was accomplished by adsorption with silica gel. The aromatic fractions were then systematically distilled in fractionating columns of high efficiency. From the material boiling at 56 mm Hg between 127.0° and 127.5° C, 145° and 146.5° C, and 148.5° to 149.0° C, respectively, naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were isolated by fractional crystallization.

"Best" lots of each of the four hydrocarbons were prepared, with impurities estimated to be, in terms of mole fraction: *n*-dodecane, 0.0000 ±0.0006; naphthalene, 0.0006 ±0.0004; 1-methylnaphthalene, 0.0025 ±0.0011; 2-methylnaphthalene, 0.0000 ±0.0003. Values of certain physical properties of these four hydrocarbons, all extrapolated to material of 100 percent were determined as follows:

Hydrocarbon	*n*-Dodecane	Naphthalene	1-Methylnaphthalene	2-Methylnaphthalene
Boiling point at 760 mm Hg °C	216.26 ±0.03	217.96 ±0.03	244.78 ±0.10	241.14 ±0.05
Freezing point in air °C	−9.60 ±0.02	80.27 ±0.02	−30.77 ±0.06	34.44 ±0.02
Density at t° C g/ml	0.74512 ±0.00005	0.9752 ±0.0002	1.0163 ±0.0001	0.99045 ±0.00005
Refractive index at t° C n_D	1.41951 ±0.00010	1.5898 ±0.0002	1.61494 ±0.00010	1.60192 ±0.00010
Refractive dispersion at t° C n_F-n_C	0.00733 ±0.00010	0.0289 ±0.0002	0.02995 ±0.00010	0.02899 ±0.00010
Temperature of density, refractive-index, and dispersion measurements °C	25	85	25	40

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[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

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

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CONTENTS

I. INTRODUCTION

The work on the chemical constitution of petroleum being carried on at this Bureau by the American Petroleum Institute Research Project 6 was extended in July 1938 to the kerosene fraction. This paper constitutes the first report of this work on the kerosene fraction and describes the separation of the aromatic hydrocarbons from the paraffins and naphthenes and the isolation of *n*-dodecane, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene.

II. ORIGIN OF THE KEROSENE STOCK AND OUTLINE OF THE INVESTIGATION

The kerosene stock came from the lot (approximately 1,000 gallons) of crude petroleum already used in the investigation of the gasoline and lubricant fractions of petroleum by the American Petroleum Institute Research Project 6 [1].[3] This material was obtained in 1928 from the Brett No. 6 well in the Ponca City Field in Oklahoma. The crude petroleum was first separated in a semicommercial plant by the Sun Oil Co. into quantities which could be handled in the laboratory. The treatment of the kerosene fraction, after receipt at the laboratory, is shown schematically in figure 1. The first stage was a systematic distillation at a pressure of 56 mm Hg of all fractions which contained any material boiling in the range desired for this investigation, 114° to 144° C at 56 mm Hg (approximately 200° to 230° C at 760 mm Hg). The greater part of the *n*-dodecane was then removed by crystallization from the fractions which distilled between 127° and 133° C. The remainder of the distillation fractions and the mother liquors from the crystallization of the dodecane were separated by extraction with methyl cyanide and Marcol into two portions: (1) fractions of aromatic hydrocarbons and (2) raffinate fractions containing paraffins and naphthenes with about 2½ percent of aromatics. The aromatic hydrocarbons were removed

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[3] The numbers in brackets indicate the literature references at the end of this paper.

from the second portion by adsorption with silica gel, and the adsorbed portion was reextracted with the two solvents. The original petroleum distillate was thus separated into a series of fractions containing aromatic hydrocarbons and a series containing paraffins and naphthenes. The aromatic fractions were then systematically distilled in columns of high efficiency, and from the aromatic material boiling at 56 mm Hg in the ranges 127° to 127.5° C, 145° to 146.5° C, and 148.5° to 149.0° C, respectively, naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were isolated.

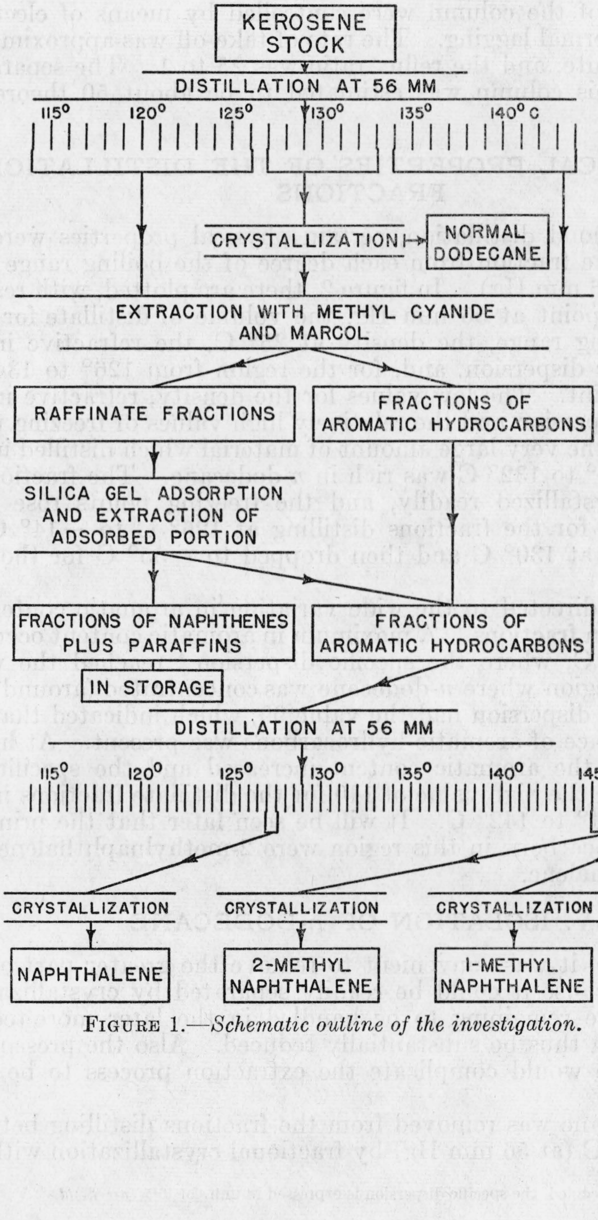

FIGURE 1.—*Schematic outline of the investigation.*

III. SYSTEMATIC DISTILLATION OF THE ORIGINAL DISTILLATE

The kerosene stock referred to in the preceding paragraph was systematically distilled twice at 56 mm Hg in a still which consisted of a 12-liter spherical Pyrex glass pot sealed to a Pyrex glass column 5 cm in diameter and 250 cm in length. This column was fitted with the type of reflux regulator recently described by Rossini and Glasgow [2] and was packed with single-turn helices (0.24 cm in diameter) made of No. 30 AWG stainless-steel wire. The temperatures of the three sections of the column were controlled by means of electrical heating and thermal lagging. The rate of take-off was approximately 1.5 ml per minute, and the reflux ratio was 25 to 1. The separating efficiency of this column was estimated to be about 50 theoretical plates [3].

IV. PHYSICAL PROPERTIES OF THE DISTILLATION FRACTIONS

After the second distillation, certain physical properties were determined on one fraction from each degree of the boiling range 114° to 144° C (at 56 mm Hg). In figure 2, there are plotted, with respect to the boiling point at 56 mm Hg, the volume of distillate for each degree of boiling range, the density at 25° C, the refractive index, n^{25}_{D}, the specific dispersion, and, for the region from 126° to 134° C, the freezing point. The low values for the density, refractive index, and specific dispersion and the relatively high values of freezing point indicated that the very large amount of material which distilled in the range from 128° to 132° C was rich in *n*-dodecane. The fractions in this region crystallized readily, and the freezing points rose from about −60° C for the fractions distilling at 126° C to −14° C for those distilling at 130° C and then dropped to −55° C for those at 133° C.

Attention is directed to the wide variation in aromatic content of these distillation fractions. A maximum in aromatic content occurred at about 119° C, where the specific dispersion [4] reached the value 129. In the region where *n*-dodecane was concentrated (around 130° C), the specific dispersion had the value 99, which indicated that not more than a trace of aromatic hydrocarbons was present. At higher boiling points, the aromatic content increased and the specific dispersion reached the high value of 140 for the distillate fractions in the region from 141° to 142° C. It will be seen later that the principal aromatic hydrocarbons in this region were 2-methylnaphthalene and 1-methylnaphthalene.

V. ISOLATION OF *n*-DODECANE

At this stage, it was convenient to remove the greater part of the *n*-dodecane because it could be readily separated by crystallization, and the volume remaining to be handled in the later more tedious processes would thus be substantially reduced. Also the presence of the *n*-dodecane would complicate the extraction process to be used later.

The *n*-dodecane was removed from the fractions distilling between 127° and 133° C (at 56 mm Hg) by fractional crystallization with the

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[4] Unless otherwise specified, the specific dispersion is expressed in units of $10^4 \times (n_f - n_c)/d$.

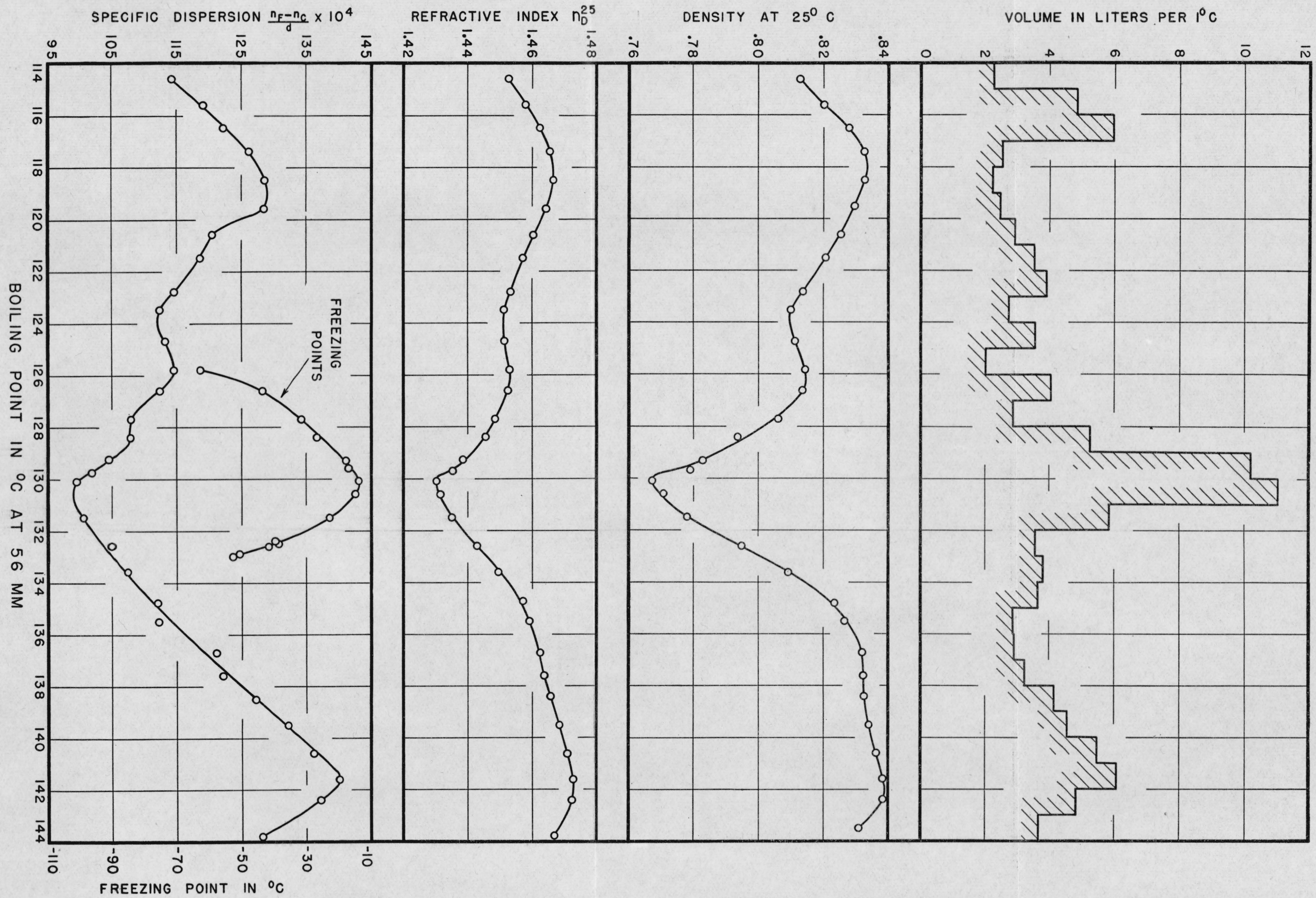

FIGURE 2.—*Properties and volume of the distillation fractions plotted with respect to the boiling range.*

low-temperature centrifuge described by Hicks-Bruun and Bruun [4]. The procedure used was to mix fractions with similar freezing points (determined approximately with a toluene-in-glass thermometer) and to repeat the crystallizations until the material was entirely separated into substantially pure *n*-dodecane and material so poor in dodecane that it yielded not more than a trace of crystals on cooling to −65° C. Certain physical properties, the volume, and the purity of the fractions of *n*-dodecane obtained by this process are recorded in table 1. The percentage of the total distillate, 114° to 144° C (at 56 mm Hg), constituted by the volume of *n*-dodecane isolated is recorded in table 9.

TABLE 1.—*Volume and properties of the various lots of crude n–dodecane actually isolated*

Lot	Volume	Refractive index at 25° C	Freezing point in air	Amount of impurity [a]
	ml	n_D	*°C*	*Mole fraction*
1	3, 340	1. 4199	−9. 83	0. 014 ±0. 003
2	3, 740	1. 4200	−9. 88	. 018 ±0. 004
3	3, 240	1. 4204	−10. 09	. 030 ±0. 006
4	2, 360	1. 4206	−10. 22	. 038 ±0. 008
5	2, 230	1. 4224	−11. 28	. 100 ±0. 020
Total	14, 910			

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, and using for the freezing point of pure *n*-dodecane the value −9.60 (see table 2) and for the heat of fusion the value 8,730 cal/mole [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at from 3 to 6 minutes from the start of supercooling. This would corespond to about 4 to 8 percent of the material frozen.

To obtain a pure sample of *n*-dodecane, some of lot 1, described in table 1, was diluted with an equal volume of diethyl ether, and was crystallized and centrifuged. The crystal portion was again dissolved in an equal volume of ether, crystallized, and centrifuged. The solvent was removed by refluxing at 56 mm Hg. The time-temperature cooling curve for this best lot of *n*-dodecane is shown in figure 3. On the basis of this curve, the amount of impurity in this best lot was estimated [6] to be 0.0000 ±0.0006 mole fraction.

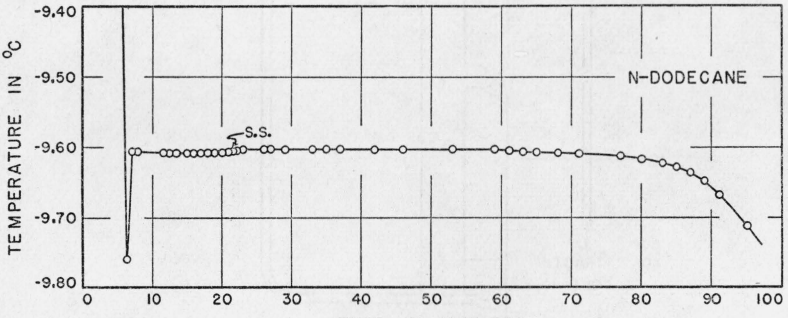

FIGURE 3.—*Time-temperature cooling curve for n-dodecane.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

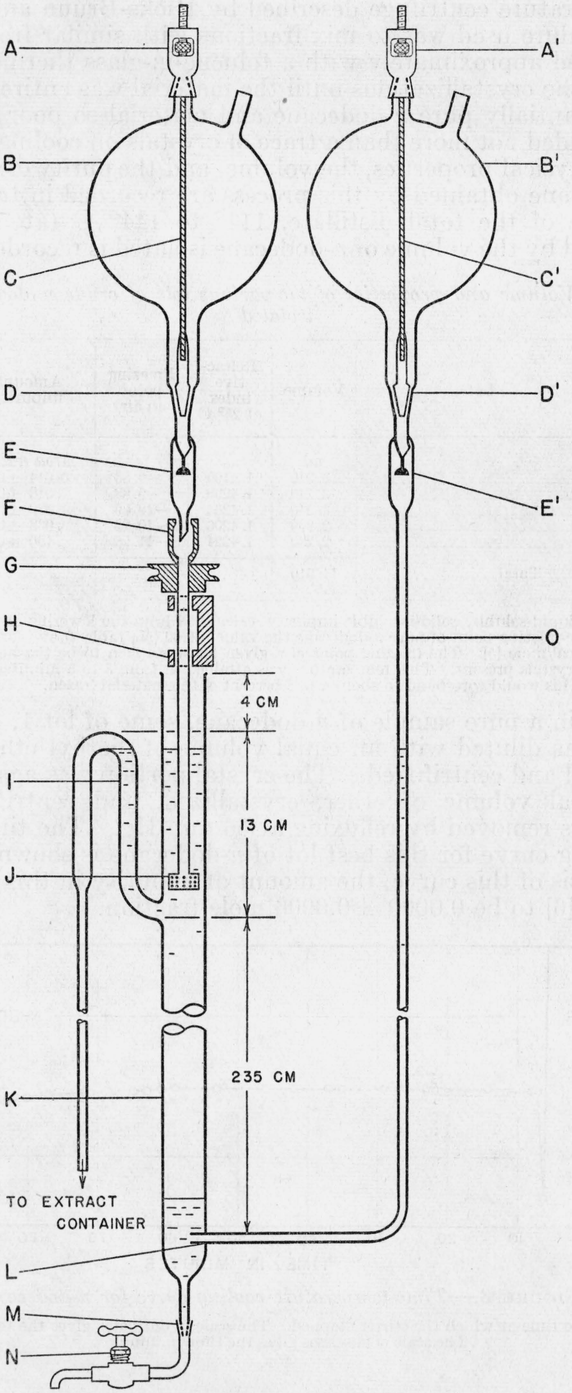

FIGURE 4.—*Extraction apparatus.*

The properties of the best *n*-dodecane from this petroleum are given in table 2, together with values previously determined for this substance by Shepard, Henne, and Midgley [7] and by Mair [8].

TABLE 2.—*Properties of n-dodecane*

Material	From petroleum, Mair and Streiff		Shepard, Henne, and Midgley [7]	Mair [8]
	(*A*) Actual "best" lot[a]	(*B*) Extrapolated to a purity of 100 percent		
Boiling point at 760 mm, °C	[b]216.26 ±0.03	216.26 ±0.03	216.23	--------
Boiling point at 57.78 mm, °C	[b]131.33 ±0.05	131.33 ± .05	--------	--------
Freezing point in air, °C	−9.60 ±0.01	−9.60 ±0.02	−9.73	−9.61
Density at 20°C, g/ml	[c](0.7486) ±0.0001	(0.7486) ±0.0001	--------	--------
Density at 25°C, g/ml	[d].74512 ±0.00002	.74512 ±0.00005	0.74542	--------
Refractive index at 20°C, n_D	[c](1.4217) ±0.0001	(1.4217) ±0.0001	1.42188	--------
Refractive index at 25°C, n_C	[e]1.41736 ±0.00010	1.41736 ±0.00010	1.41752	--------
Refractive index at 25°C, n_D	[e]1.41951 ±0.00010	1.41951 ±0.00010	1.41967	1.41952
Refractive index at 25°C, n_F	[e]1.42469 ±0.00010	1.42469 ±0.00010	1.42501	--------
Refractive dispersion at 25°C, $n_F - n_C$	0.00733 ±0.00010	0.00733 ±0.00010	0.00749	--------
Specific dispersion at 25°C, $(n_F - n_C)/d$	0.00984 ±0.00010	0.00984 ±0.00010	0.0100	--------

[a] Amount of impurity estimated to be 0.0000 ±0.0006 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] These values were estimated from the values observed at 25° C.
[d] Determined by the Capacity and Density Section of this Bureau.
[e] Determined by L. W. Tilton of the Optical Instruments Section, of this Bureau.

VI. PROCESS OF EXTRACTION

1. METHOD

The next step in the separation of the kerosene stock was to subject it to an efficient process of extraction with solvents to separate the aromatic hydrocarbons from the paraffins and naphthenes. There was used for this purpose a system of two solvents, methyl cyanide[5] and Marcol, which is a commercial aromatic-free mixture of paraffins and naphthenes having an initial boiling point of about 230° C at 56 mm Hg. The methyl cyanide served to separate the kerosene stock into a "raffinate" portion, which consisted of a mixture of paraffins and naphthenes with about 2½ percent of aromatic hydrocarbons, and an "extract" portion, which consisted mainly of aromatic hydrocarbons but had an appreciable amount of paraffins and naphthenes. The "extract" portion, including the solvent, methyl cyanide, was then treated with Marcol to produce an aromatic portion substantially free from paraffins and naphthenes and an unresolved portion containing all three types of hydrocarbons. The unresolved portion was then reprocessed.

2. APPARATUS

The apparatus used in the extraction process is shown diagrammatically in figure 4. Referring to this figure, kerosene is contained in reservoir *B* and is allowed to flow at a controlled rate through glass valve *D* to the top of rotating shaft *F*. It then flows down the hollow shaft to the enlargement in the distributor *J* and is there

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[5] For this material, methyl cyanide appears to have about the same selectivity for aromatic hydrocarbons as does sulfur dioxide. Furthermore, the methyl cyanide can be used at room temperature in apparatus not closed to the atmosphere. The methyl cyanide used was purified by distillation.

forced through small holes and dispersed in the form of small globules in the solvent contained in the column, *K*.[6] These globules fall to the bottom of the column and form a layer which is withdrawn intermittently through the valve, *N*. The solvent is contained in reservoir *B′* and is admitted at a controlled rate through glass valve *D′*, and tube *O* to the bottom of the column. The extract portion flows through tube *I* (where small globules of oil have an opportunity to settle out and return to the column) to a collecting bottle.

Some details of the extractor may be added. The rate of flow of kerosene or solvent was adjusted by means of screws *AA′* attached through tungsten rods *CC′* to the solid ground glass stoppers which fit in sockets *DD′*. These devices have been described by Rossini and Glasgow [2], and a detailed drawing of them is given in figure 4 of their paper. The rate of flow may be computed from the number of drops leaving glass hemispheres *EE′*. The distributor, rotating in bearing *H*, was operated at a speed of 500 rpm. The enlargement in distributor *J* contains 30 holes in each of the three rows, each hole being 0.035 cm in diameter. Valve *N* is a small brass needle valve which is attached to the bottom of the column through copper tubing and through the ground and tapered brass-to-glass joint *M*. This joint is tightly sealed with soft solder [9]. The reservoirs are of 1-liter capacity. The diameter of the column is 3 cm. Other dimensions of the column may be obtained from figure 4.

3. PROCEDURE

The extraction procedure is illustrated schematically in figure 5. Extractors 1 and 2 were operated in series. In extractor 1 partially extracted kerosene from extractor 2 was reextracted with fresh methyl cyanide and yielded kerosene raffinate fractions with values for the specific dispersion of about 100, which indicated the presence of about 2.5 percent of aromatic hydrocarbons. The methyl cyanide extract from extractor 1 was used as solvent in extractor 2 with the original kerosene. In extractor 3 the methyl cyanide extract was reextracted with Marcol and yielded a methyl cyanide extract substantially free from naphthenes and paraffins. The Marcol, however, dissolved some aromatic hydrocarbons in addition to the naphthene and paraffin hydrocarbons, so that it was necessary to separate these kerosene hydrocarbons from the Marcol by distillation and recycle them as shown in figure 5.

The rate of flow of methyl cyanide was from 3 to 4 ml per minute; of kerosene from 0.6 to 0.9 ml per minute; and of Marcol about 0.4 ml per minute. Beginning at the low end of the boiling range, charges of kerosene distillation fractions covering a range of 1° C (except for the dodecane mother liquors which covered a 6° C range)

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[6] In preliminary experiments, kerosene was allowed to flow through an auxiliary tube into an open rotating basket. We are indebted to C. B. Willingham for suggesting the use of a hollow shaft.

were fed successively to the extractors. The extract and raffinate fractions were collected according to the boiling range of the charge from which they came, although, owing to the "hold-up" of the columns, a precise demarcation of material from successive charges was not possible.

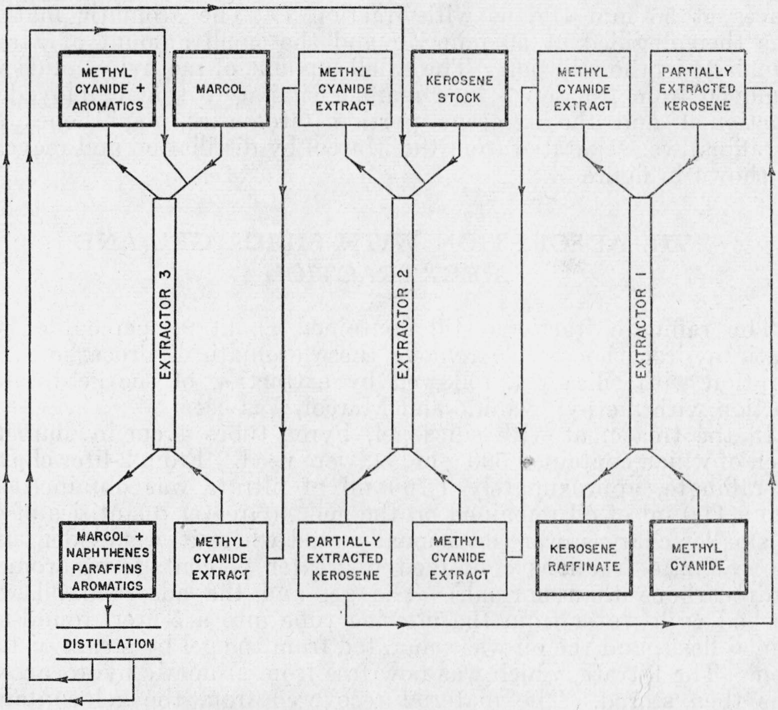

FIGURE 5.—*Schematic diagram of the extraction process.*

It will be seen that as a result of this process there were obtained from the extractors the following three fractions:

1. A raffinate portion from extractor 1 which contained naphthenes and paraffins with about 2.5 percent of aromatic hydrocarbons and a small quantity of methyl cyanide.
2. An extract portion from extractor 3 which contained the greater part of the methyl cyanide and the aromatic hydrocarbons, with substantially no naphthenes or paraffins. In addition, this portion contained a small quantity of Marcol.

3. An unresolved portion which contained the Marcol and the naphthenes and paraffins and aromatics from extractor 3. This portion contained also a small amount of methyl cyanide.

Three stills with rectifying sections 90 cm long packed with stainless steel helices were used in the further treatment of these fractions. Fraction 1 (the raffinate portion) was refluxed in one of these stills at 56 mm Hg and the small amount of methyl cyanide which it contained was caught in a trap maintained at the temperature of solid carbon dioxide. After cooling the fraction, it was siphoned from the still pot. The greater part of the methyl cyanide was removed from fraction 2 by distillation at atmospheric pressure and the last traces at 56 mm Hg, as with fraction 1. The aromatic material was then distilled at 56 mm Hg and the small amount of Marcol remained in the still pot. The small amount of methyl cyanide was removed from fraction 3 in a manner similar to that employed for fraction 1 and the kerosene portion (aromatics, naphthenes and paraffins) was separated from the Marcol by distillation and recycled, as shown in figure 5.

VII. ADSORPTION WITH SILICA GEL AND REEXTRACTION

The raffinate fractions still contained about 2½ percent of aromatic hydrocarbons. To remove these aromatic hydrocarbons, adsorption with silica gel, followed by extraction of the gel-retained portion with methyl cyanide and Marcol, was used.

In the treatment with silica gel, Pyrex tubes 4 cm in diameter, each of which contained 500 g of gel, were used. From 2-liter charges of raffinate, approximately 1,700 ml of filtrate was obtained and about 300 ml of oil remained on the gel. (Greater quantities of gel, or smaller charges, were occasionally used where it was evident that the raffinate fractions contained a greater percentage of aromatic hydrocarbons than normal.) The gel and the adsorbed oil were flushed with water from the filtering tube into a 5-liter, round-bottomed flask, and the oil was separated from the gel by steam distillation. The filtrate, which was now free from aromatic hydrocarbons, was then stored. The material recovered from the gel contained about 20 percent of aromatic hydrocarbons, and was separated as before, by extraction with methyl cyanide and Marcol, into a raffinate portion and a portion consisting substantially of aromatic hydrocarbons. This raffinate, of much smaller volume than the original, was further separated by adsorption into a filtrate and an adsorbed portion, and the adsorbed portion again separated by extraction into a raffinate and an aromatic portion. This process was repeated until all the oil was resolved into filtrate fractions consisting of naphthenes plus paraffins and extract fractions consisting substantially of aromatic hydrocarbons.

In the first filtration of raffinate through silica gel, a sufficient quantity of material was available to prepare charges and store filtrate fractions with distillation ranges of only one or two degrees. However, in the subsequent resolution of the adsorbed material into fractions consisting of naphthenes plus paraffins and fractions consisting of aromatic hydrocarbons, the material was treated in two ranges: one distilling from 114° to 134° C, the other from 134° to 144° C.

VIII. SYSTEMATIC DISTILLATION OF THE AROMATIC MATERIAL

The aromatic material obtained from the process of extraction with solvents was systematically distilled at a pressure of 56 mm Hg in a column which had a rectifying section 2.5 by 280 cm and a separating efficiency corresponding to about 100 theoretical plates [10]. The reflux ratio was about 30 to 1, and the distillate was removed at the rate of about 0.2 ml per minute and collected in fractions of 50 ml.

Figure 6 gives the distribution of the aromatic material by volume with respect to the boiling point at a pressure of 56 mm Hg. Of the several pronounced peaks which may be observed in the volume curve in figure 6, attention is particularly directed to those occurring at 127.0° to 127.5° C, 145.0° to 146.5° C, and 148.5° to 149.0° C, from which material naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene, respectively, were isolated later.

IX. ISOLATION OF NAPHTHALENE

During the distillation of the aromatic material which was separated from the original petroleum distillate boiling at 118° to 120° C, crystals formed in the condenser of the distilling column and in the tubes leading to the receiver. The boiling point of this material was near that to be expected for naphthalene at 56 mm Hg; namely, about 127° C. The undistilled residue from this charge had a volume of about 400 ml, it crystallized to a solid mass at room temperature, and obviously was rich in naphthalene. Additional residues of 144 and 100 ml of substantially the same material were obtained from the distillation of the aromatic material separated from the original petroleum distillate boiling at 120° to 121° C, and at 121° and 123° C. These residues, rich in naphthalene, are represented by the shaded block at the temperature 127.0° to 127.5° C in figure 6.

It is apparent that the bulk of the naphthalene is found in those fractions of the original petroleum distillate which, at 56 mm Hg, distil at about 120° C, that is, 7° C below the boiling point of pure naphthalene at this pressure. For the alkylbenzenes occurring in this region, no marked displacement of boiling point was observed, though a small displacement of one or two degrees may exist. This difference in behavior of alkylbenzenes and naphthalene helps to explain the highly concentrated naphthalene residues which were obtained by distillation alone. That is, the aromatic material separated from the original petroleum distillate boiling at 118° to 120° C contained alkylbenzenes boiling at about 119° to 122° C and naphthalene boiling at 127° C. The naphthalene may readily be separated by distillation from the mononuclear aromatics associated with it. As shown in figure 6, the additional aromatic material which was found to distil in the neighborhood of 127° C came principally from kerosene which distilled at or slightly above this temperature, and its refractive index, $n_D^{25}=1.50$ to 1.51, indicated that this was substantially mononuclear aromatic material.

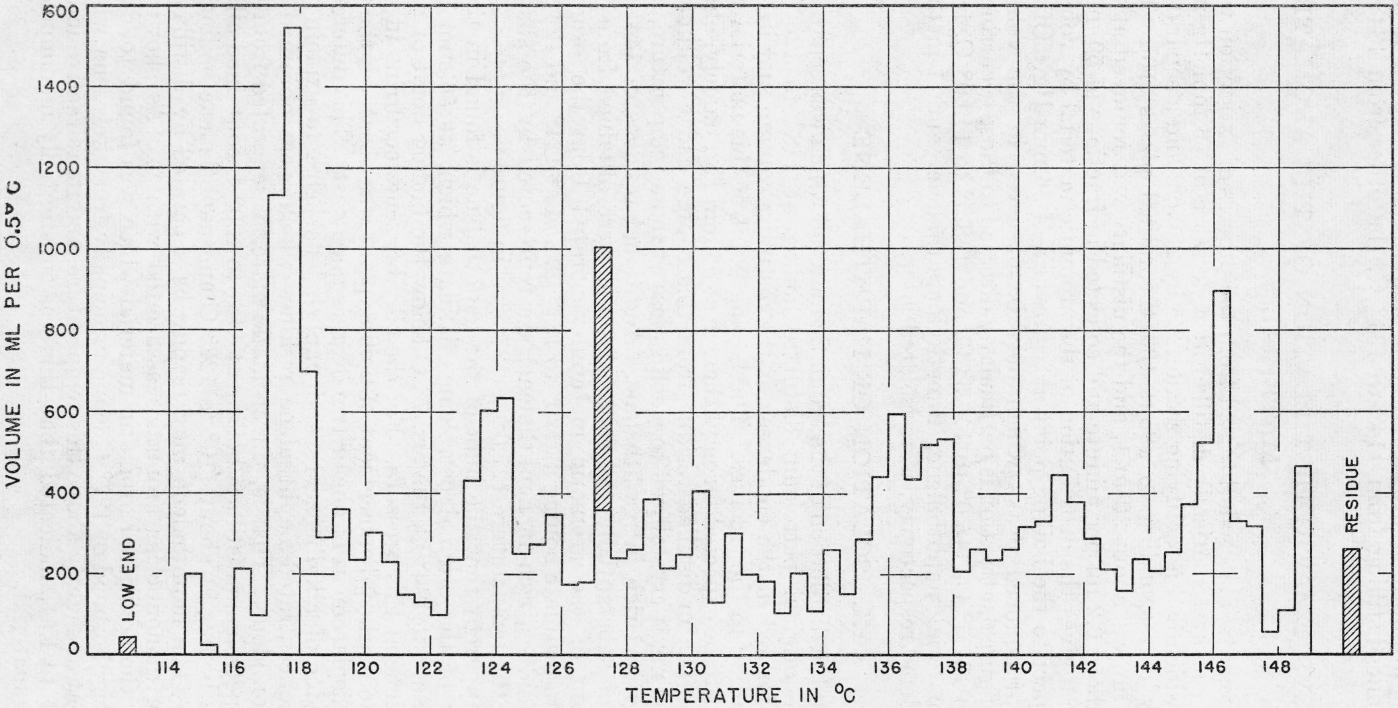

FIGURE 6.—*Distribution of the aromatic distillate by volume with respect to the boiling point.*

The scale of ordinates gives the volume in ml for each 0.5° C fraction. The scale of abscissas gives the boiling point of these fractions in °C at a pressure of 56 mm Hg.

The naphthalene was purified by systematic crystallization from ethyl alcohol. The residues rich in naphthalene were dissolved in a minimum of hot alcohol, the solution was cooled to about 10° C, and the crystals were removed by filtration with suction. Second crops of crystals were obtained by distilling off a portion of the alcohol in a fractionating column and again cooling and filtering with suction. The original naphthalene residues from the still pot were highly colored, and this color was used as a basis for blending fractions and for following the process of purification. Oil was recovered from the final alcoholic solution of mother liquors by distilling off the greater part of the alcohol, then diluting the solution with water and separating the oil phase. Before determining the freezing point, the naphthalene was first distilled at 56 mm Hg to remove all traces of solvent. The volumes, percentages of impurities, and certain physical properties of the various lots of crude naphthalene are recorded in table 3. As is evident from the low refractive index, the recovered oil contained little naphthalene. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the volume of naphthalene actually isolated, is recorded in table 9.

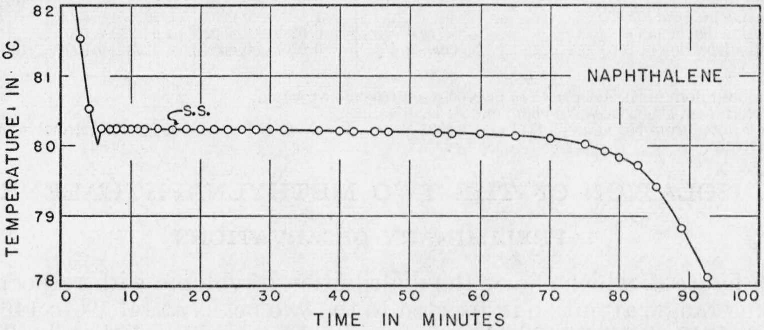

FIGURE 7.—*Time-temperature cooling curve for naphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

TABLE 3.—*Volumes and properties of the various lots of crude naphthalene actually isolated*

Lot	Volume	Refractive index at 85° C	Refractive index at 25° C	Freezing point in air	Amount of impurity [a]
	ml	n_D	n_D	*°C*	*Mole fraction*
1. Crystals I	395	1.5898		80.24	0.0006 ±0.0004
2. Crystals II	40	1.5749		72.0	.12 ±0.02
3. Oil	132		1.5383		

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using 80.27° C (see table 4) for the freezing point of pure naphthalene and 4,610 cal/mole as its heat of fusion [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained for lot 1 about 1 minute from the start of supercooling. This would correspond to about 1.5 percent of the material frozen.

The time-temperature cooling curve of the best lot of naphthalene (lot 1 in table 3) is shown in figure 7, which gives an initial freezing point of 80.24° C. On the basis of this curve, the amount of impurity in this best lot of naphthalene was estimated [6] to be 0.0006±0.0004 mole fraction, and the freezing point of pure naphthalene was estimated to be 80.27° C. A recrystallization of this best lot from alcohol, followed by a distillation at 56 mm Hg, failed to improve the purity, the freezing point of the material being unchanged within the experimental error (actually lower by 0.003° C).

The properties of the best naphthalene from petroleum are given in table 4, together with values of other investigators.

TABLE 4.—*Properties of naphthalene*

Material	From petroleum, Mair and Streiff		Auwers and Fruhling [11]
	(*A*) Actual "best" lot [a]	(*B*) Extrapolated to a purity of 100 percent	
Boiling point at 760 mm °C	[b]217.96 ±0.03	217.96 ±0.03	----------
Boiling point at 57.78 mm °C	[b]128.51 ±0.10	128.51 ±0.10	----------
Freezing point in air °C	80.24 ±0.01	80.27 ±0.02	----------
Density at 85° C g/ml	0.9752 ±0.0002	0.9752 ±0.0002	[c](0.9751)
Refractive index at 85° C n_D	1.5898 ±0.0002	1.5898 ±0.0002	[c](1.5900)
Refractive dispersion at 85° C n_F-n_C	0.0289 ±0.0002	0.0289 ±0.0002	----------
Specific dispersion at 85° C $(n_F-n_C)/d$	0.0297 ±0.0002	0.0297 ±0.0002	(0.0298)

[a] Amount of impurity estimated to be 0.0006 ±0.0004 mole fraction.

[b] Determined by C. B. Willingham and F. D. Rossini.

[c] Computed from the values 0.9641 and 1.5827 observed at 99.6° C for the density and refractive index, respectively.

X. ISOLATION OF THE TWO METHYLNAPHTHALENES

1. PRELIMINARY OBSERVATIONS

In figure 6, which shows the distribution of volume with respect to boiling range, attention is directed to the two peaks at 145.0° to 146.5° C and 148.5° to 149.0° C. A considerable number of the distillate fractions in the region from 145.0° to 146.5° C were solid at room temperature, and a few, boiling at 146.4° C, had freezing points of 31° to 32° C and refractive indices, $n_D^{40}=1.601$. Judging from these properties, this material was principally 2-methylnaphthalene. As the boiling point of the fractions increased from 146.4° to 148.3° C, the freezing point decreased to −47° C; then as the boiling point increased from 148.3° to 148.9° C, the freezing point increased, and a distillate fraction with freezing point equal to −31.9° C and $n_D^{25}=1.6142$ was obtained. This fraction was obviously rich in 1-methylnaphthalene.

As with naphthalene, the 1- and 2-methylnaphthalenes were obtained from fractions of the original petroleum distillate boiling approximately 6° or 7° C below the boiling points of the respective methylnaphthalenes. The boiling point ranges of the material from which these two hydrocarbons were obtained overlapped, and it was principally from charges of aromatic material extracted from the original kerosene boiling in the range 139° to 140° C that aromatic distillate fractions solid at room temperature and very concentrated in 2-methylnaphthalene were obtained. Charges of aromatic material extracted from the original kerosene boiling at 141° to 144° C yielded some fractions which distilled at about 146.5° C, and contained, in addition to 2-methylnaphthalene, a considerable amount of 1-methylnaphthalene. These fractions were not solid at room temperature. Higher-boiling fractions from these same charges were of course richer in 1-methylnaphthalene. Before proceeding with the isolation of these compounds by fractional crystallization, some of the material was concentrated further by a second distillation. All fractions which distilled from 142° to 146° C and had freezing points below 22° C were combined for one distillation. An additional volume of material rich in 2-methylnaphthalene was thus obtained. The residue from this distillation, together with all fractions which distilled from 146° to 148.5° C and which had freezing points below 22° C, were combined for a second distillation. This second distillation yielded fractions in the region from 146° to 146.5° C which were rich in 2-methylnaphthalene, and fractions in the region from 148.5° to 149.0° C with freezing points which indicated they were on the 1-methylnaphthalene side of the eutectic of 2-methylnaphthalene and 1-methylnaphthalene.

2. ISOLATION OF 2-METHYLNAPHTHALENE

The 2-methylnaphthalene was isolated by systematic crystallization, using an equal volume of ethyl alcohol as solvent and centrifuging the crystals. The freezing point of the fractions served as a basis for mixing various fractions for crystallization and for following the process of purification. The fractions were refluxed at 56 mm Hg to remove solvent before determining their physical properties. The volumes, certain physical properties, and the amounts of impurities of the various lots of crude 2-methylnaphthalene actually isolated are shown in table 5. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the 2-methylnaphthalene actually isolated, is recorded in table 9.

TABLE 5.—*Volumes and properties of the various lots of 2-methylnaphthalene actually isolated*

Lot	Volume	Refractive index at 40° C	Freezing point in air	Amount of impurity [a]
	ml	n_D	°*C*	*Mole fraction*
1. Crystal I	962	1.6015	33.81	0.009±0.002
2. Crystal II	470	1.5988	31.25	.023±0.005
3. Mother liquors	535	1.5566	−24	----------

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using 34.44° C (see table 6) for the freezing point of pure 2-methylnaphthalene and 2,850 cal/mole as its heat of fusion [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at about 5 minutes from the start of supercooling. This would correspond to about 7 percent of the material frozen.

To obtain a best lot of 2-methylnaphthalene, some of the material described as lot 1 in table 5 was recrystallized twice from an equal volume of ethyl alcohol and the crystals were separated by centrifuging. After removal of the solvent, the "crystal" portion of this material had an initial freezing point of 34.415° C. The process of purification was repeated on this last portion, and a best lot was obtained which had an initial freezing point of 34.437° C. The time-temperature cooling curve of the best lot is shown in figure 8. On the basis of this curve, the amount of impurity in the best lot of 2-methylnaphthalene was estimated [6] to be 0.0000 ±0.0003 mole fraction.

The properties of the best 2-methylnaphthalene from petroleum are given in table 6, together with values of other investigators.

TABLE 6.—*Properties of 2-methylnaphthalene*

Material	From petroleum, Mair and Streiff: (*A*) Actual "best" lot [a]	From petroleum, Mair and Streiff: (*B*) Extrapolated to a purity of 100 percent	Evans [12]	Auwers and Fruhling [11]
Boiling point at 760 mm °C	[b] 241.14 ±0.05	241.14 ±0.05	----------	----------
Boiling point at 57.78 mm °C	[b] 148.07 ±0.05	148.07 ±0.05	----------	----------
Freezing point in air °C	34.44 ±0.01	34.44 ±0.02	34.5	31.5 to 32.5
Density at 40° C g/ml	[c] 0.99045 ±0.00002	0.99045 ±0.00005	1.008	0.9939
Refractive index at 40 °C n_C	[d] 1.59407 ±0.00010	1.59407 ±0.00010	1.6015	1.59444
Refractive index at 40 °C n_D	[d] 1.60192 ±0.00010	1.60192 ±0.00010		1.60258
Refractive index at 40 °C n_F	[d] 1.62306 ±0.00010	1.62306 ±0.00010		1.62390
Refractive dispersion at 40° C n_F-n_C	[d] 0.02899 ±0.00010	0.02899 ±0.00010	----------	0.02946
Specific dispersion at 40° C $(n_F-n_C)/d$	0.02927 ±0.00010	0.02927 ±0.00010	----------	0.0297

[a] Amount of impurity estimated to be 0.0000 ±0.0003 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] Determined by the Capacity and Density Section of this Bureau.
[d] Determined by L. W. Tilton of the Optical Instrument Section, of this Bureau.

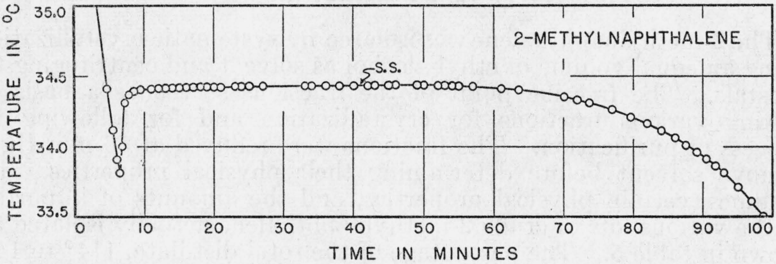

FIGURE 8.—*Time-temperature cooling curve for 2-methylnaphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

3. ISOLATION OF 1-METHYLNAPHTHALENE

For the isolation of 1-methylnaphthalene, all fractions on the 1-methylnaphthalene side of the eutectic of 1-methyl- and 2-methyl naphthalene were used, together with two distillation residues which, judging from their lower refractive indices, $n_D^{25}=1.594$ and 1.608, contained some mononuclear aromatics as impurities. This material was crystallized from alcohol and centrifuged in a manner similar to that employed with 2-methylnaphthalene. The volumes of the fractions obtained, percentages of impurities, and certain physical properties of the various lots of 1-methylnaphthalene are recorded in table 7. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the volume of 1-methylnaphthalene actually isolated, is recorded in table 9.

TABLE 7.—*Volumes and properties of the various lots of 1-methylnaphthalene actually isolated*

Lot	Volume	Refractive index at 25° C.	Freezing point in air	Amount of impurity [a]
	ml	n_D	*° C*	*Mole fraction*
1. Crystal I	90	1.6146	−31.02	0.0048±0.0011
2. Crystal II	100	1.6131	−33.5	.05 ±0.01
3. Crystal III	135	1.6113	−36.5	.11 ±0.02
4. Mother liquor	230	1.6016	−43.	----------

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using −30.77° C. (see table 8) as the freezing point of pure 1-methylnaphthalene and 2,250 cal/mole as its heat of fusion. This latter value was estimated by assuming the entropy of crystallization of 1-methylnaphthalene to be the same as that for 2-methylnaphthalene. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at about 5 to 8 minutes from the start of supercooling. This would correspond to about 6 to 10 percent of the material frozen.

To obtain a best lot of 1-methylnaphthalene, the material labelled as lot 1 in table 7 was recrystallized twice from alcohol. The time-temperature freezing curve for the best 1-methylnaphthalene is shown in figure 9. On the basis of this curve, the amount of impurity in this best lot of 1-methylnaphthalene was estimated [6] to be 0.0025 ±0.0011 mole fraction, and the freezing point of pure 1-methylnaphthalene was estimated to be −30.77 ±0.06° C.

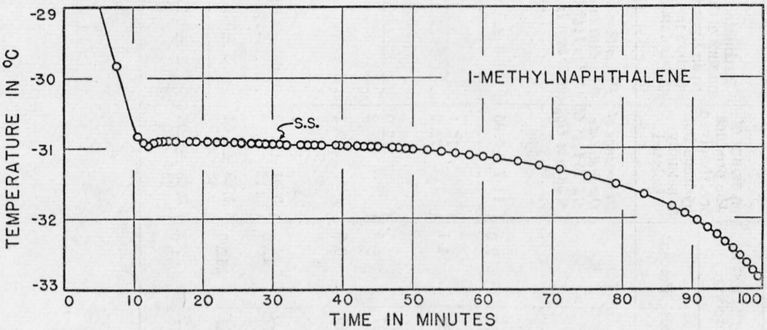

FIGURE 9.—*Time-temperature cooling curve for 1-methylnaphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in ° C. The scale of abscissas gives the time in minutes.

The properties of the best 1-methynaphthalene from petroleum are given in table 8, together with values previously determined for this substance.

TABLE 8.—*Properties of 1-methylnaphthalene*

Material	From petroleum, Mair and Streiff		Evans [12]	Auwers and Fruhling [11]
	(*A*) Actual "best" lot [b]	(*B*) Extrapolated to a purity of 100 percent		
Boiling point at 760 mm, °C	[c] 244.78 ±0.10	244.78 ±0.10	244.4	----------
Boiling point at 57.8 mm, °C	[c] 151.3 ±0.2	151.3 ±0.2	----------	----------
Freezing point in air, °C	−30.90 ±0.01	−30.77 ±0.06	−31	----------
Density [a] at 20° C, g/ml	(1.0200) ±0.0002	(1.0200) ±0.0002	1.020	(1.0201)
Density [a] at 25° C, g/ml	1.0163 ±0.0001	1.0163 ±0.0001	(1.016)	(1.016)
Refractive index [a] at 20° C, n_D	(1.6175) ±0.0002	(1.6175) ±0.0002	1.6172	(1.6180)
Refractive index [a] at 25° C, n_C	[d] 1.60677 ±0.00010	1.60677 ±0.00010	----------	----------
Refractive index [a] at 25° C, n_D	[d] 1.61494 ±0.00010	1.61494 ±0.00010	1.6145	----------
Refractive index [a] at 25° C, n_F	[d] 1.63672 ±0.00010	1.63672 ±0.00010	----------	----------
Refractive dispersion at 25° C, $n_F - n_C$	0.02995 ±0.00010	0.02995 ±0.00010	----------	(0.0300)
Specific dispersion at 25° C, $(n_F - n_C)/d$	0.02947 ±0.00010	0.02947 ±0.00010	----------	(0.0295)

[a] Values in parentheses were obtained by extrapolation, using for dn_D/dt and dD/dt the values 0.00051 and 0.00074, respectively. In the case of the data of Auwers and Fruhling, the extrapolation was made from 13.6° C.

[b] Amount of impurity (presumably 2-methylnaphthalene) estimated to be 0.0025 ±0.0011 mole fraction.

[c] Determined by C. B. Willingham and F. D. Rossini.

[d] Determined by L. W. Tilton of the Optical Instruments Section, of this Bureau.

XI. SUMMARY OF AMOUNTS OF MATERIAL PROCESSED, LOSSES DUE TO PROCESSING, AND AMOUNTS OF HYDROCARBONS ISOLATED

In table 9 there is given a summary of the material processed, the losses due to processing, the amounts of the hydrocarbons actually isolated, and estimates of the total amounts of these hydrocarbons in the petroleum. Columns 1, 2, and 3 identify the material processed and give the volume.

TABLE 9.—*Summary of the material processed, losses due to processing, and amounts of hydrocarbons isolated*[a]

No.	Material		Process	Product		Material lost in process		Amount of the product or of the given hydrocarbon actually isolated	Estimated amount of the given hydrocarbon not yet isolated	Total amount of the given hydrocarbon in the petroleum
	Name	Volume		Name	Volume	Volume	Percent			
		Liters			*Liters*	*Liters*	%	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*
I	Original distillate 114° to 144° C.	130.06								
II	Original distillate 127° to 133° C (from I).	38.81	Crystallization	*n*-Dodecane Mother liquors	14.91 23.14	0.76	2.0	11.7 ±0.05	1.9 ±0.8	13.6 ±0.8
III	Original distillate less *n*-dodecane removed (from II).	114.39	Extraction	Aromatic hydrocarbons Raffinate	21.11 87.96	5.32	4.7	17.1 71.2		
IV	Raffinate from extraction (from III).	87.96	Alternate adsorption plus extraction.	Aromatic hydrocarbons Naphthenes plus paraffins	2.40 82.59	2.97	3.4	2.0 69.2		
V	Aromatic hydrocarbons from extraction (from III and IV).	23.51	Distillation	Aromatic distillate fractions.	23.32	0.19	0.8	19.1		
VI	Stock used for naphthalene (from V).	0.644	Crystallization	Naphthalene Mother liquors	0.435 .132	.077	12.0	0.41 ±0.02 .12	0.05 ±0.03	0.46 ±0.04
VII	Stock used for 2-methylnaphthalene (from V).	2.150	Crystallization	2-Methylnaphthalene Mother liquors	1.432 0.535	.183	12.0	1.28 ±0.04 0.48	.5 ±0.2	1.78 ±0.21
VIII	Stock used for 1-methylnaphthalene (from V).	0.730	Crystallization	1-Methylnaphthalene Mother liquors	0.325 .230	.175	24.0	0.35 ±0.05 .25	.3 ±0.15	0.65 ±0.16

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[a] See text for explanation.

Column 4 gives the fractionating process to which the material was subjected. Columns 5 and 6 give the name and volume of the products of the fractionating process. Columns 7 and 8 give the volume and percentage of the material lost in the given fractionating process. Column 9 gives the amount of the given hydrocarbon actually isolated, in percentage, based on the original distillate 114° to 144° C at 56 mm Hg as 100 percent. There are included in the values given in column 9 only those materials listed in tables 1, 3, 5, and 7 which had a purity better than 0.90 mole fraction. Column 10 gives an estimate of the amount of the given hydrocarbon not yet isolated, including material remaining in the mother liquors and in some of the distillation fractions which were not rich enough in the given hydrocarbon to crystallize profitably. Column 11 gives an estimate of the total amount of the given hydrocarbon in the petroleum, based on the original distillate, 114° to 144° C at 56 mm Hg, as 100 percent. The values given in columns 9, 10, and 11 were calculated in the following way. The volume of the original distillate, 130.06 liters, was taken as 100 percent at the start. The losses occurring in each process of fractionation were charged equally on a fractional basis to the products obtained from the given process. The losses were carried throughout in this cumulative way, so that at any given time the total volume of all the material on hand, including hydrocarbons isolated, remained 100 percent. In this way, the total material actually on hand, regardless of the losses which occurred, represented the original distillate, 114° to 144° C at 56 mm Hg.

XII. REVIEW OF EARLIER INVESTIGATIONS

Several earlier investigators established the presence in petroleum of the hydrocarbons whose isolation is described in the present paper. In some cases, these previous workers isolated the hydrocarbons by chemical means, but none obtained material of high purity by purely physical methods of separation, such as those used in the present work.

Shepard, Henne, and Midgley [7] prepared pure *n*-dodecane from a special fraction of petroleum extraordinarily high in normal paraffin hydrocarbons, by distillation, chemical treatment with chlorosulfonic acid, and redistillation.

Mabery and Hudson [13] found some Californian petroleums so rich in aromatic hydrocarbons that distillate fractions of the range 220° to 222° C at atmospheric pressure solidified on cooling to room temperature, because of the high concentration of naphthalene.

Jones and Wootton [14] established the presence in a Borneo petroleum of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. The fractions distilling above 210° C at atmospheric pressure were treated with picric acid to obtain picrates. These picrates were separated and the hydrocarbon material was regenerated and recovered by steam distillation. The recovered hydrocarbon material was distilled, and naphthalene and the two methylnaphthalenes were recognized in the distillate fractions.

Birch and Norris [15] obtained naphthalene and 2-methylnaphthalene from a Persian petroleum. They used as a starting material the sulfur dioxide extract of the kerosene fraction, treated this with picric acid, separated the picrates, and regenerated and fractionally distilled the hydrocarbon material. Crystalline naphthalene separated from the fractions boiling at 215° to 230° C, and 2-methylnaphthalene was obtained from the fractions distilling at 237° to 245° C by cooling to −21° C. Both of these hydrocarbons were purified by crystallization from alcohol. Their attempts to separate the picrate of 1-methylnaphthalene were not successful.

Tasaki and Yamamoto [16] likewise obtained naphthalene and 2-methylnaphthalene. They steam-distilled the sulfuric acid sludge from a Shukkoko kerosene, and fractionally distilled the oil obtained. On cooling the fractions, naphthalene and 2-methylnaphthalene crystallized from some of them.

Cosciug [17], using the picric acid method with a Rumanian petroleum, obtained picrates which he identified as those of naphthalene and 2-methylnaphthalene. By fractional crystallization of the picrates from ethyl alcohol, followed by distillation of the regenerated hydrocarbons, he was able to obtain pure 2-methylnaphthalene but not pure 1-methylnaphthalene.

XIII. REFERENCES

[1] F. D. Rossini, Proc. Am. Petroleum Inst. **18** (III), 36–59 (1937); Oil Gas J. **36,** No. 26, 193–222 (1937); Refiner Natural Gasoline Mfg. **16,** No. 11, 545 (1937).

[2] F. D. Rossini and A. R. Glasgow, Jr., J. Research NBS **23,** 509 (1939) RP1249.

[3] M. R. Fenske, S. Lawroski, and C. O. Tongberg, Ing. Eng. Chem. **30,** 297 (1938).

[4] M. M. Hicks-Bruun and J. H. Bruun, BS J. Research **8,** 528 (1932) RP432.

[5] G. S. Parks and H. N. Huffman, Ind. Eng. Chem. **23,** 1138 (1931).

[6] W. P. White, J. Phys. Chem. **24,** 393 (1920).

[7] A. F. Shepard, A. L. Henne, and T. Midgley, Jr., J. Am. Chem. Soc. **53,** 1948 (1931).

[8] B. J. Mair, BS J. Research **9,** 457 (1932) RP482.

[9] C. H. Meyers, J. Am. Chem. Soc. **45,** 2135 (1923).

[10] F. D. Rossini and C. B. Willingham (Unpublished).

[11] K. v. Auwers and A. Fruhling, Ann. Chem. Liebig **422,** 192 (1921).

[12] E. B. Evans, J. Inst. Pet. Tech. **24,** 537 (1938).

[13] C. F. Mabery and E. J. Hudson, J. Soc. Chem. Ind. **19,** 502 (1900).

[14] H. O. Jones and H. A. Wootton, J. Chem. Soc. **91,** 1149 (1907).

[15] S. F. Birch and W. S. G. P. Norris, J. Chem. Soc. **1926,** 2545.

[16] S. Tasaki and J. Yamamoto, J. Chem. Ind. (Japan) **34,** 247 (1931).

[17] T. Cosciug, Petroleum Z. **31,** No. 41, 5 (1935); **34,** No. 16, 3 (1938).

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