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APPARATUS AND METHODS FOR INVESTIGATING THE CHEMICAL CONSTITUTION OF LUBRICATING OIL, AND PRELIMINARY FRACTIONATION OF THE LUBRICATING-OIL FRACTION OF A MIDCONTINENT PETROLEUM¹

By Beveridge J. Mair,² Sylvester T. Schickanz,² and Frank W. Rose, Jr.²

ABSTRACT

In the fall of 1933 work on American Petroleum Institute Research Project 6 at the National Bureau of Standards, which up to that time had been confined to the naphtha fraction of petroleum, was extended to include the lubricating oil fraction. This paper gives the first report on the apparatus and methods developed for investigating the chemical constitution of lubricating oil and describes the preliminary separation of the lubricant fraction of a midcontinent petroleum into "wax", "extract", and "water-white" fractions by dewaxing with ethylene chloride, extracting with sulphur dioxide, and filtering through silica gel. The results of the first four stages of distillation of the water-white oil are given.

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I. INTRODUCTION

Researches on the chemical constitution of the lubricant fraction of petroleum have been going on for more than 30 years. In these investigations usually one, or at the most two, methods of fractionation have been used, and these not exhaustively. The available information indicates that the average molecular formulas of fractions of lubricating oils range from about C_nH_{2n} to about C_nH_{2n-20} . In some cases fractions even poorer in hydrogen have been obtained.

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 Associates at the National Bureau of Standards, representing the American Petroleum Institute.

The low ratio of hydrogen to carbon in these oils is attributed not to unsaturation, as in olefinic hydrocarbons, but rather to the existence in the molecule of one or more naphthenic (saturated) ring nuclei, as in cyclopentane and cyclohexane, or aromatic ring nuclei as in naphthalene and anthracene, etc. The extent of our present actual knowledge of the chemical constituents of lubricating oil may be summed up in the statement that from it not one pure hydrocarbon has ever been isolated.

Modern demands in the automotive field for lubricants having good lubricity or oiliness, high resistance to oxidation and decomposition, a low temperature coefficient of viscosity, and a low congealing temperature have made it very desirable that something definite be learned about the hydrocarbon constituents of lubricating oil. Consequently, the work on American Petroleum Institute Research Project 6 at the National Bureau of Standards, which up to the fall of 1933 had been confined to the naphtha fraction of petroleum, was extended to include the lubricating oil fraction. The purpose of the present investigation is to separate the lubricant fraction exhaustively by all feasible physical processes, such as distillation, crystallization, solvent extraction, and selective adsorption, in the hope that there may be isolated individual hydrocarbons, or at least hydrocarbons of a single type and nearly equal molecular weights.

This paper presents a description of the apparatus and methods used, and the results of the preliminary separation of a midcontinent petroleum into wax, extract, and water-white fractions, together with the results of the first four stages of the distillation of the last.

II. SOURCE OF THE LUBRICATING-OIL FRACTIONS

The lubricating oil came from the same 1,000-gallon lot of crude petroleum from well no. 6 of the South Ponca Field, Kay County, Okla., as did the naphtha distillate which is under investigation in this laboratory.^{3 4} Before receipt at this Bureau, the portion of the crude petroleum containing the lubricating oil was fractionally distilled in "vacuo" by the Sun Oil Co., at Philadelphia. The fractions (of about 1¼ to 1½ gallons each) were shipped in tightly sealed metal containers, from which the air had been displaced by nitrogen. Sixteen of these fractions (designated as cuts 23 to 38), with a total weight of about 67 kg and representing 10 percent of the crude oil, had a sufficiently high viscosity to be of interest in this investigation.

III. EXTRACTION WITH LIQUID SULPHUR DIOXIDE

The first steps in the preparation of an oil free from wax, and from asphaltic and resinous materials, were crystallization from ethylene chloride to remove the wax and extraction with liquid sulphur dioxide to remove asphaltic and resinous materials. Cuts 23 to 29, inclusive, were extracted before dewaxing. Because of the high-melting nature of the waxes in cuts 30 to 38, it was found preferable to dewax them before extracting with sulphur dioxide.

Four extractions were performed on each cut. In the first extraction the ratio by weight of sulphur dioxide to oil was 7 to 9, while

³ See figure 1, Leslie and White [1].

⁴ The figure in brackets in footnote 3 and elsewhere in this paper refer to the numbered literature references given on page 573.

in the last three the ratio was 5 to 9. The apparatus used for this extraction is shown in figure 1. It consisted essentially of the metal cylinder A, in which the mixing of the lubricating oil with sulphur dioxide took place, the liter distilling flask E, into which the extract first flowed from the mixing cylinder, a second flask G (5-liter capacity), into which the extract was then forced, and from which the sulphur dioxide was distilled through the drying tower D into the condenser J, into which the extract was then forced, and from which the sulphur dioxide was distilled through the drying tower D into the condenser J,

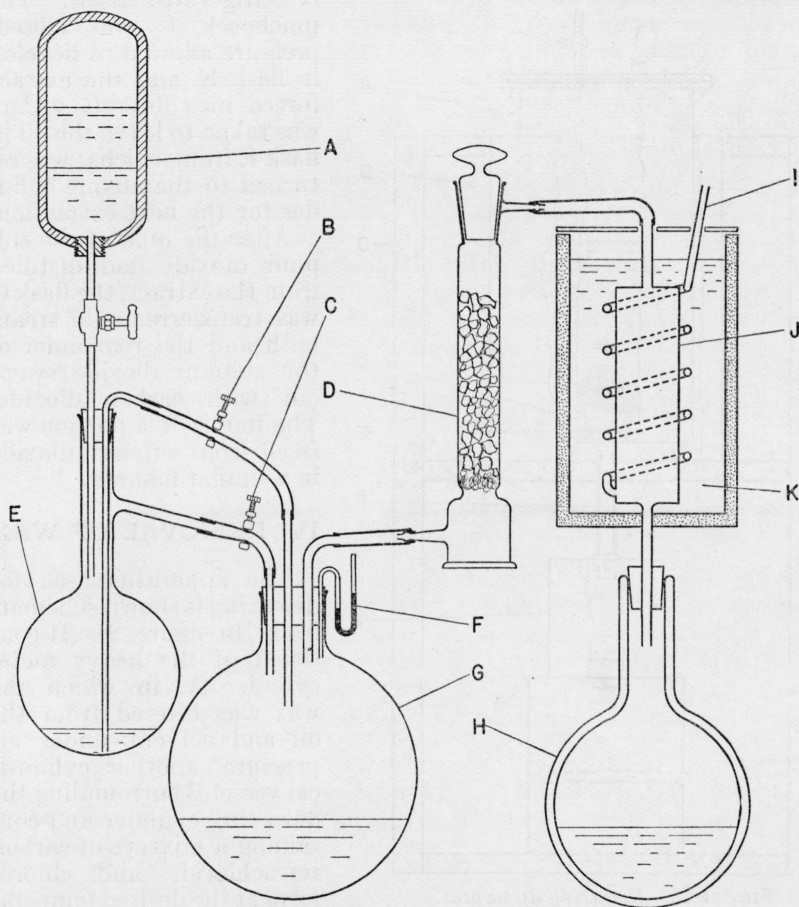


FIGURE 1.—Extraction apparatus.

and collected in the dewar flask H. To avoid the blowing out of stoppers, the pressure in G, observed on the manometer F, was not allowed to exceed about 2 cm of mercury. I is a vent from the bottom of the condenser to the atmosphere. K is an insulated metal container. It held the refrigerant, a mixture of chloroform and carbon tetrachloride chilled with solid carbon dioxide.

For extraction, the mixing cylinder containing a weighed quantity of oil was chilled with solid carbon dioxide and the required amount of sulphur dioxide introduced. The outlet valve was replaced in the cylinder and the cylinder warmed to about 45° C and shaken vigor-

ously. The cylinder was placed in position above the distilling flask E and the valve opened slightly. The pressure exerted by the sulphur dioxide forced the extract out rapidly. Oil was always observed floating on the surface of the extract in the distilling flask. Some of this oil came through the valve before the operator could observe the change in phase of the liquid and close the valve. Most of it was probably due to precipitation of constituents of the extract as

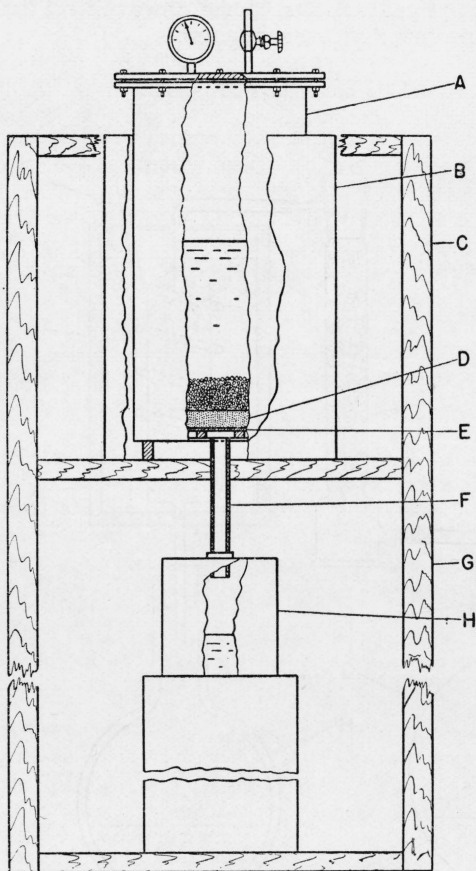


FIGURE 2.—Dewaxing apparatus.

it refrigerated itself. The pinchcock C was closed, pressure allowed to develop in flask E, and the extract forced into flask G. Care was taken to leave the oil in flask E from which it was returned to the mixing cylinder for the next extraction.

After the bulk of the sulphur dioxide had distilled from the extract, the flask G was transferred to a steam bath and the remainder of the sulphur dioxide swept out with carbon dioxide. The immiscible portion was freed from sulphur dioxide in a similar manner.

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IV. REMOVAL OF WAX

The apparatus used for dewaxing is shown schematically in figure 2. It consisted of the heavy metal cylinder A, in which the wax was filtered from the oil and solvent under air pressure, another cylindrical vessel B surrounding the dewaxing cylinder and containing a mixture of carbon tetrachloride and chloroform at the desired temperature, an insulated wooden

box C, which was raised from the floor on legs G and which held the dewaxing cylinder. F is a tube which was soldered to the bottom of the dewaxing cylinder and through which oil and solvent flowed to the receiving vessel H. The lid of the dewaxing cylinder contained a pressure gage and a valve through which pressure was applied to the cylinder. When filtering, the lid was bolted to a flange on the upper periphery of the cylinder and sealed tightly with a leather gasket. Fitting snugly inside the filtering cylinder and supported on short legs about 1 cm from the bottom was the perforated circular brass plate E. Over this, fitting the walls of the cylinder tightly, was placed the disk of felt D, about 2 cm thick, which served as a filtering medium.

In dewaxing, the oil, mixed with four times its volume of ethylene chloride, was warmed to dissolve the wax, then cooled slowly to -18°C and the wax removed by filtration under air pressure of 50 lb/in.² The wax was then recrystallized from ethylene chloride and filtered again under pressure. The bulk of ethylene chloride was distilled from the mother liquors. The last of the solvent was removed from both the oil and wax by sweeping it out at 110°C with a strong stream of carbon dioxide gas. Tests of the dewaxed oil for chlorides indicated that chlorination had been negligible.

V. FILTRATION THROUGH SILICA GEL

The raffinate from the sulphur dioxide extraction contained sulphur compounds and was unstable with respect to color when exposed to light and air. A sample of this oil, containing 0.14 percent of sulphur, was filtered through silica gel at 90°C in an attempt to reduce the sulphur content. A water-white filtrate, which was stable with respect to color and which contained less than 0.01 percent of sulphur⁵, was obtained.

To ascertain whether the silica gel cracked or polymerized, or in any other manner attacked the constituents of the lubricating oil fraction, an experiment was performed in which the filtrate and adsorbed material were recombined. The results of this experiment which are given in table 1, show that the physical characteristics of the combined fractions agree with those of the original sample within the experimental error. The recovery was 99.9 percent.

It also appears from table 1 that the silica gel does more than remove sulphur compounds. Material with the higher refractive index and higher density, greater viscosity, and greater temperature coefficient of viscosity tended to be adsorbed.

TABLE 1.—*Nature of adsorption with silica gel*

[Oil passed through 102 g of silica gel at 90 to 100°C]

Material	Weight	Refractive index, n_D^{65}	Density at—		Kinematic viscosity at—	
			150° F	210° F	150° F	210° F
Original.....	g 311.58	1.4710	g/ml 0.846	g/ml 0.824	Stoke 0.1360	Stoke 0.0565
Filtrate.....	246.44	1.4663	.838	.815	.1245	.0540
Adsorbed material ¹	64.83	1.4899	.875	.851	.1710	.0653
Recombination of filtrate with adsorbed material.....	311.27	1.4710	.846	.825	.1361	.0565 ⁷

¹ Recovered from the gel by washing with ethylene chloride and acetone.

It has been shown in this laboratory [2] that aromatic hydrocarbons may be completely removed from the naphtha distillate of petroleum by adsorption on silica gel. It seems probable that aromatic hydrocarbons also were adsorbed from the lubricating oil, and possibly to a small extent naphthenes.

Since it had been determined in the preceding experiments that treatment with silica gel removed sulphur compounds and gave a water-white oil which did not darken on exposure to light and air, and also that the gel itself did not harm the oil appreciably, it was

⁵ The sulphur determinations were made by C. E. Waters of this Bureau.

decided to remove sulphur compounds from all the fractions by means of silica gel and obtain a stable oil for further work.

Glass tubes mounted vertically served to hold the gel. These tubes were 150 cm long and 2 cm in internal diameter and held about 280 g of gel. Silica gel of grade "150-F-850" (40 to 200 sieve), obtained from the Silica Gel Corporation, of Baltimore, was used. The procedure finally adopted was to mix the oil with from 1 to 3 times its volume of petroleum ether, depending on its viscosity, pour it onto the gel, and allow it to filter at room temperature under gravity.

The first portion of the filtrate was water-white, and then yellow and darker fractions came through. Oil was added to the top of the column and allowed to filter until the color of the filtrate was almost

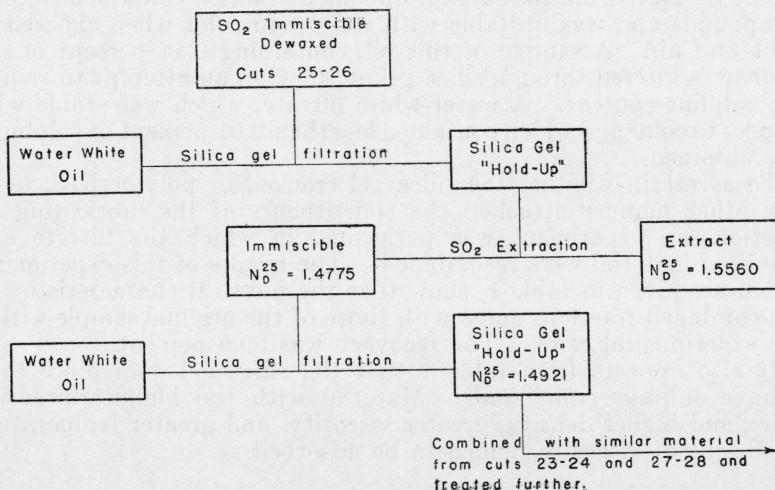


FIGURE 3.—Interlocking of extraction with adsorption.

as dark as that of the oil added. The water-white filtrate was stored separately, the colored fractions were poured onto fresh columns of gel in order of their color, and further water-white fractions were obtained. The oil held on the gel was washed off by adding ethylene chloride to the top of the column, allowing it to filter through, and draining it with suction. This treatment was repeated several times. Finally, a small amount of material which was not readily removed with ethylene chloride was washed off with acetone. The bulk of the solvents was distilled off on the steam bath, and the remainder swept out by passage of a rapid stream of carbon dioxide gas. The oil recovered from the gel with ethylene chloride and acetone contained not only that portion of the oil actually adsorbed by the gel but also a portion of the oil which was retained between the particles by surface tension, much of which could be rendered water-white. To obtain from the material held on the gel a further quantity of water-white oil, an interlocking process of extraction with sulphur dioxide and adsorption with silica gel was employed. The first steps of this interlocking process are shown schematically in figure 3 for cuts 25-26.

When the quantity of silica gel "hold up" from cuts 25-26 became too small to be handled satisfactorily, it was mixed with the corresponding hold up from cuts 27-28, and 23-24, and the treatment continued.

TABLE 2.—Physical properties of original oil, wax, sulphur dioxide extract, and water-white oil

Cut	Original oil				Wax (total weight 20.25 kg)				Sulphur dioxide extract (total weight 17.93 kg)				Water-white oil (total weight 19.78 kg)					
	Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Refractive index n_D^{25}	Weight
	150° F	210° F	g/ml	g/ml	150° F	210° F	150° F	210° F	100° F	210° F	100° F	210° F	100° F	210° F	100° F	210° F		
23	<i>Stoke</i> 0.094	<i>Stoke</i> 0.0460	g/ml 0.854	g/ml 0.835	<i>Stoke</i> 0.0615	<i>Stoke</i> 0.0330	g/ml 0.783	g/ml 0.761	<i>Stoke</i> 1.89	<i>Stoke</i> 0.0807	g/ml 0.989	g/ml 0.948	} 0.214	} 0.0422	} 0.849	} 0.804	} 1.4684	} 3,134
24	.103	.0452	.856	.836	.0705	.0354	.794	.773	1.72	.0828	.987	.963						
25	.113	.0480	.858	.837	.0735	.0379	.799	.779	2.60	.0915	.983	.956	} .300	} .0498	} .850	} .809	} 1.4709	} 2,944
26	.119	.0523	.859	.839	.0825	.0400	.800	.780	2.72	.0942	.983	.956						
27	.128	.0536	.860	.840	.0822	.0410	.800	.781	4.12	.113	.992	.958	} .409	} .0604	} .857	} .831	} 1.4739	} 2,214
28	.138	.0575	.862	.842	.0803	.0473	.805	.784	4.57	.125	.991	.955						
29	.138	.0583	.863	.843	.0902	.0518	.805	.786	6.79	.137	1.013	.982	} .409	} .0604	} .857	} .831	} 1.4739	} 2,214
30	.143	.0588	.859	.839	.0925	.0457	.804	.783	3.37	.118	.971	.932						
31	.176	.0687	.865	.844	.104	.0498	.813	.792	} 191	} .359	} 1.067	} .990	} .409	} .0604	} .857	} .831	} 1.4739	} 2,214
32	.213	.0828	.870	.850	.118	.0555	.812	.792										
33	.256	.104	.873	.856	.131	.0777	.819	.799	} 64.7	} .383	} 1.007	} .960	} .757	} .0882	} .860	} .825	} 1.4771	} 958
34	.311	.108	.877	.857	.173	.0736	.826	.806										
35	.329	.114	.879	.859	.187	.0785	.829	.810	} 6.60	} .122	} .972	} .955	} .605	} .0715	} .878	} .841	} 1.4909	} 1,423
36	.446	.146	.884	.865	-----	-----	-----	.807										
37	.557	.160	.886	.867	-----	-----	-----	.817	} 8.78	} .255	} .949	} .912	} 1.13	} .1096	} .873	} .845	} 1.4861	} 1,693
38	.648	.187	.891	.870	-----	-----	-----	.818										
a ¹	-----	-----	-----	-----	-----	-----	-----	-----	2.80	.122	.972	.955	.605	.0715	.878	.841	1.4909	1,423
b ¹	-----	-----	-----	-----	-----	-----	-----	-----	6.60	.187	.967	.936	.584	.0769	.866	.826	1.4815	595
c ¹	-----	-----	-----	-----	-----	-----	-----	-----	8.78	.255	.949	.912	1.13	.1096	.873	.845	1.4861	1,693

¹ a, b, and c are from silica gel hold up of cuts 23-28, 29-32, and 33-38, respectively. (See text and fig. 3.)

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In table 2 are shown certain physical characteristics of the original oil, wax, sulphur dioxide extract, and water-white oil fractions obtained by the processes just described. A total of 19.78 kg of water-white oil was obtained. Most of this oil had a viscosity-temperature relationship similar to that of a refined Pennsylvania oil. The viscosity indices [3] for the various fractions ranged as follows: Original oil, about 75 to 90; wax, about 125 to 150; extract, about -150 to -300; water-white, about 100 to 120.

VI. DISTILLING EQUIPMENT

The design of distilling equipment is limited by the low vapor pressures of these oils at any temperature below that at which thermal decomposition begins. Two types of stills were used: Short fractionating columns for the more volatile portion of the oil and molecular stills for the less volatile portion.

1. FRACTIONATING COLUMNS

One of the fractionating columns is shown in figure 4. It consisted of a Pyrex flask E, which served as a still pot into which the oil was charged through the side tube I. The still was sealed to a tube 120 cm long and 2 cm in inside diameter which served as the column. At the top of the column was sealed a bulb A, which served as a condenser and from which the distillate passed through the tube B to the receiver. This receiver was so designed that fractions could be withdrawn without breaking the vacuum in the still proper.

The high-vacuum line was sealed to B and led to the liquid-air trap F and to the McLeod gage and mercury-diffusion pump. Surrounding the column itself, and concentric with it, was a large glass tube D equipped for electrical heating and insulated with about 1 cm of asbestos. The still pot, placed in a metal container, was insulated with asbestos and heated electrically. Since the pressure in the pot E, and consequently the temperature, depend on the resistance to flow encountered by the vapors in their passage from E to A, the only packing used in this column was a spiral of no. 8 copper wire. This spiral fitted the walls of the column closely and, although offering little resistance to passage of the vapors, retarded the return of the reflux and spread it more uniformly over the entire surface of the column. All stoppers and stopcocks were lubricated with tetraethylene glycol citrate resin. With this excellent lubricant [4] which is insoluble in oils, little difficulty was experienced with leaks, the stopcock seals remained good during many charges of the still.

The still was operated with a large reflux in comparison to the amount of distillate. Heat was applied to the column so that the amount of reflux appeared to be about the same throughout its length. The rate of distillation was about 0.5 ml per minute. To avoid thermal decomposition of the oil, the use of this type of column was confined to oils which could be distilled without the still-pot temperature rising above 250° C. Temperatures in the still pot of 250° C were reached in the distillation of oils having a viscosity of about 0.6 stoke (about 280 Saybolt) at 100° F. The temperatures in the still head ranged from about 160 to 190° C. A pressure of 10^{-4} mm of Hg or lower (observed on the McLeod gage) was readily maintained throughout the distillations without the continuous use of the fore

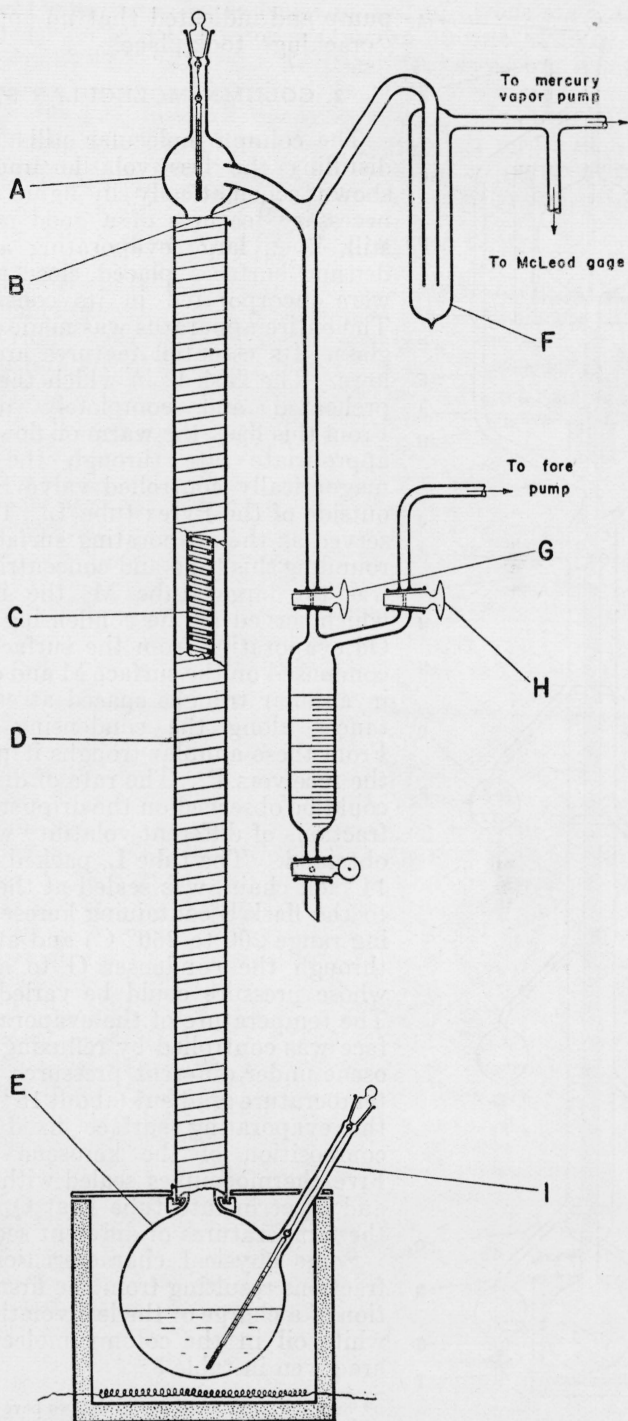


FIGURE 4.—Vacuum fractionating column.

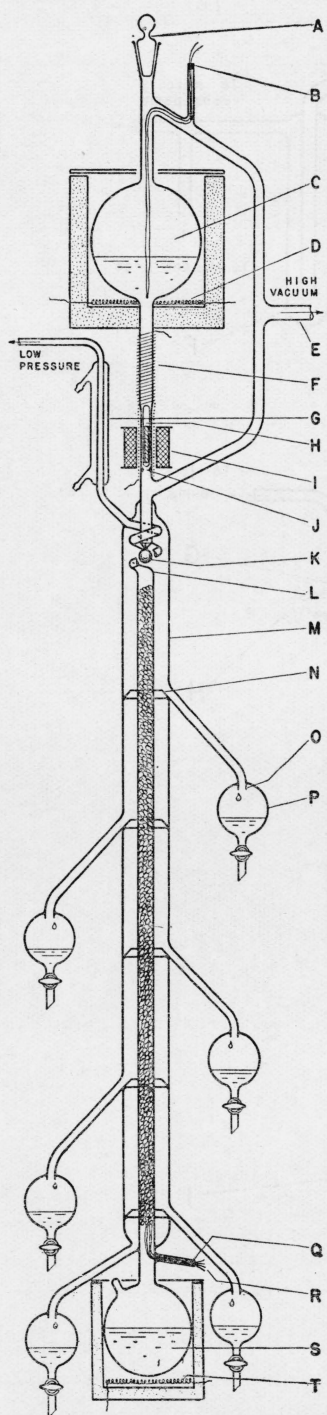


FIG. 5.—Column molecular still.

pump and indicated that no appreciable "cracking" took place.

2. COLUMN MOLECULAR STILL

The column molecular still⁶ used for distilling the less volatile fractions is shown schematically in figure 5. The necessary features of a good molecular still, i. e., large evaporating and condensing surfaces placed close together, were incorporated in its construction. The entire apparatus was made of Pyrex glass. Its essential features are as follows. The flask C in which the oil was preheated and completely degassed. From this flask the warm oil flowed at an appropriate rate through the electromagnetically controlled valve H to the outside of the Pyrex tube L. This tube served as the evaporating surface. Surrounding this tube and concentric with it was the larger tube M, the inside of which served as the condensing surface. Oil evaporating from the surface L was condensed on the surface M and collected in annular troughs spaced at equal distances along the condensing surface. From these annular troughs it passed to the receivers P. The rate of distillation could be observed on the drippers O. Six fractions of different volatility were thus obtained. The tube L, packed with no. 14 jack chain, was sealed at the bottom to the flask S containing kerosene (boiling range 200 to 250° C) and at the top through the condenser G to a system whose pressure could be varied at will. The temperature of the evaporating surface was controlled by refluxing the kerosene under different pressures, and the temperature gradient (about 15° C) along the evaporating surface fixed by the composition of the kerosene mixture. Five thermocouples sealed with litharge and glycerin into tube L at Q recorded the temperatures of different sections.

Some physical characteristics of the fractions resulting from the first distillation of a charge of the less volatile water-white oil in the column molecular still are given in table 3.

⁶ Since the construction of this still we have learned that similar stills have been used for some time by W. H. Bahlke, of the Standard Oil Co., of Ind.

TABLE 3.—Properties of fractions resulting from distillation of a charge of water-white oil in column molecular still

Fraction	Weight	Kinematic viscosity at—		Refractive index n_D^{25}	Temperature of section of still
		100° F	210° F		
Original.....	g 900	Stoke 1.134	Stoke 0.1096	1.4861	°C
1.....	219	.650	.0747	1.4840	214
2.....	202	.966	.0967	1.4852	214
3.....	150	1.321	.1171	1.4860	214
4.....	117	1.650	.1351	1.4867	218
5.....	84	1.987	.1537	1.4875	228
Residue.....	127	3.067	.2165	1.4901	

3. SIMPLE MOLECULAR STILL

Simple molecular stills were also useful for distilling the less volatile fractions. The best type of simple molecular still tried is the one depicted in figure 6. This still⁷ consisted of the large Pyrex-glass cylinder E sealed at the bottom, and drawn down and sealed at the top to the smaller tube A used for introducing the charge and withdrawing the residue. Attachment to the high-vacuum system was also made through this tube. The distillate which condensed on the surface B was caught in the annular trough C and flowed through the side arm D to a multiple receiver. A small funnel with iron core, operated electromagnetically, was used to direct the distillate as desired into each of the six small receivers which constituted the multiple receiver. The vacuum was not broken during the distillation of the charge. Molecular stills of this type were made with a diameter up to about 12 cm and a capacity of about 1,500 ml.

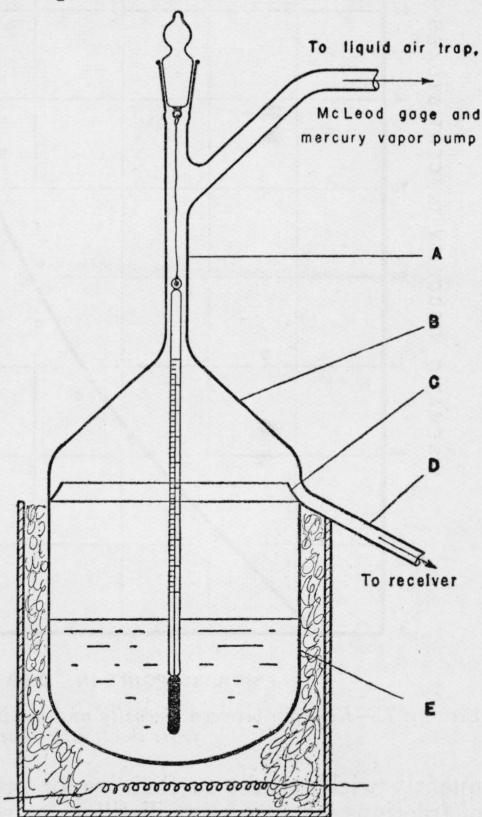


FIGURE 6.—Simple molecular still.

VIII. SYSTEMATIC FRACTIONAL DISTILLATION

The combining of fractions for successive distillations is usually based on the property of boiling point. However, other physical properties may be used if it can be shown that they are continuous

⁷ Stills similar to this have been described by Hickman and Sanford [5].

functions of the boiling point. Owing to the low vapor pressure of these fractions, the accurate determination of their boiling points is a time-consuming process, and blending on the basis of some property more easily determinable is desirable. There was a continuous increase in the viscosity of the fractions of water-white oil with respect to the order in which they were removed from the still and conse-

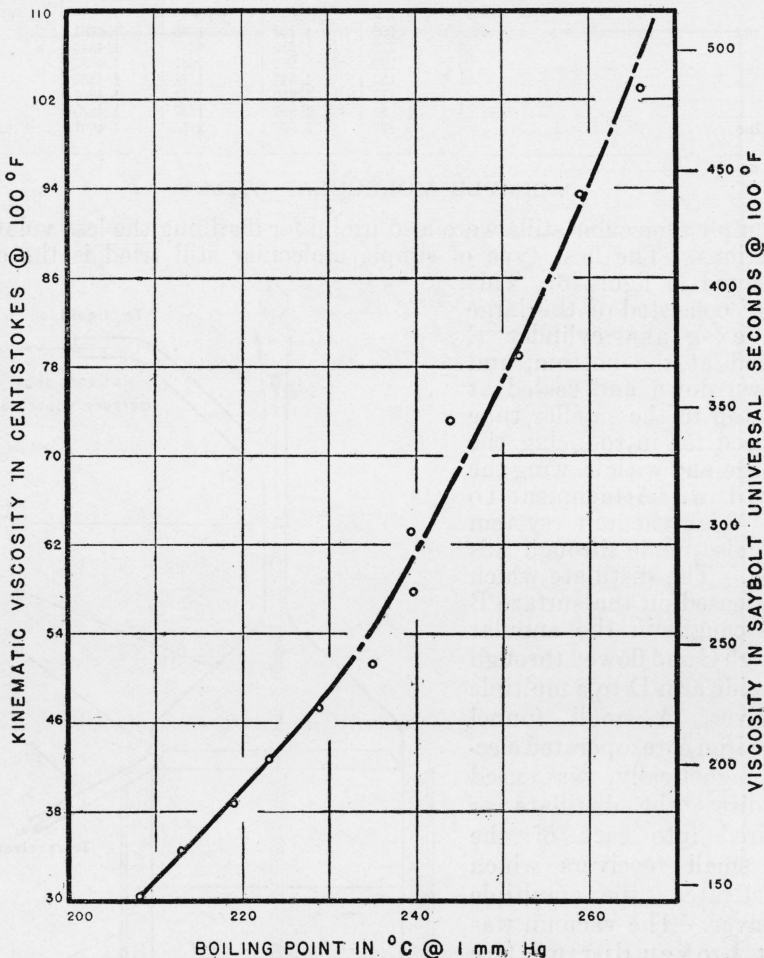


FIGURE 7.—Relation between viscosity and boiling point of water-white oil fractions from the fourth distillation.

quently with respect to their vapor pressures. Therefore, blending of fractions for successive distillations was accomplished on the basis of viscosity (instead of boiling point). In figure 7 is shown a plot of the viscosity with respect to the boiling point⁸ at 1-mm pressure obtained on some of the fractions resulting from the fourth distillation. It is apparent that the viscosity increases continuously with increase in boiling point. This relationship between viscosity and boiling

⁸ The apparatus used for the boiling-point determinations has been described by Schickantz [6].

point may be expected to break down if one type of hydrocarbon is concentrated within a narrow boiling range during distillation. However, there is no evidence that any such concentration has occurred at this stage of the distillation.

What has been accomplished by the systematic fractional distillation of the more volatile portion of water-white oil is shown in figure 8, in which are plotted the viscosities of the fractions with respect to

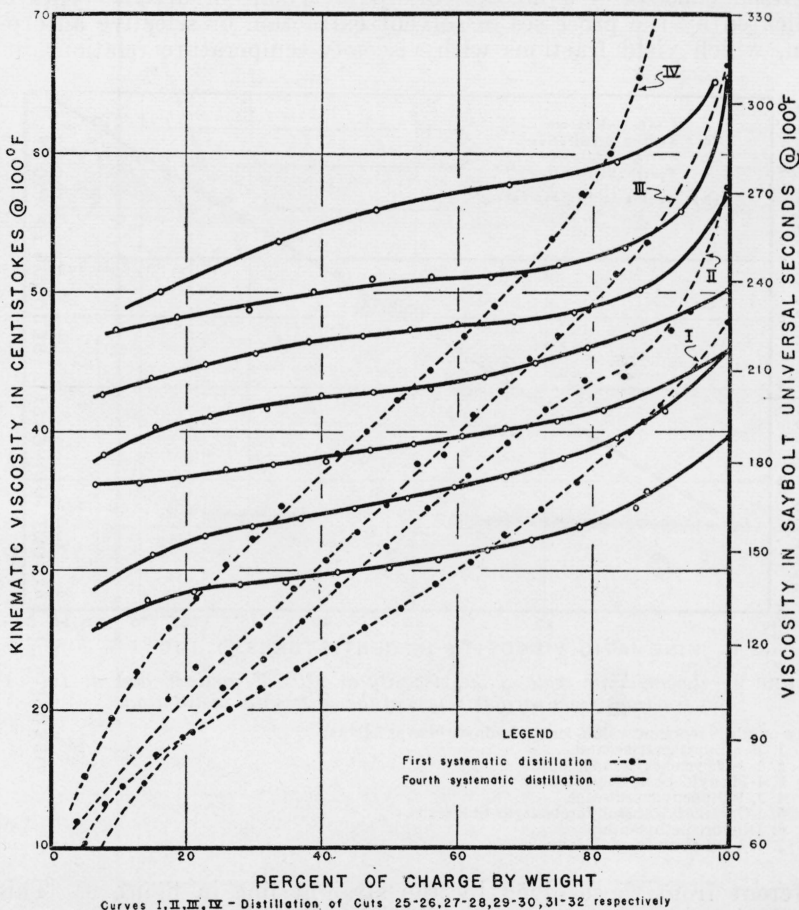


FIGURE 8.—Result of four stages of systematic distillation of the water-white oil.

the percentage by weight of the charge. The fractions resulting from the first distillation of the original cuts (represented by broken lines) cover a wide range in viscosity and overlap markedly, while the fractions resulting from the fourth distillation (represented by solid lines) cover a much smaller range in viscosity and show comparatively little overlapping.

At the end of the fourth distillation the total quantity of water-white oil in the region under investigation (viscosity, 140 to 500 Saybolt seconds) was 10.7 kg, of which about 6.5 kg lay in the region from 140 to 280 Saybolt seconds.

In figure 9 a plot on a logarithmic scale of the viscosity at 210° F with respect to that at 100° F for a large number of distillation fractions is shown together with values for the viscosities of several synthetic hydrocarbons.⁹ The data for successive distillations may be reproduced within the experimental error by a straight line. This is taken to indicate that no appreciable concentration of hydrocarbons by type has resulted from fractional distillation. That the oil itself consists of a mixture of hydrocarbons of diverse types is indicated by the processes of solvent extraction or selective adsorption, which yield fractions with viscosity-temperature relationships

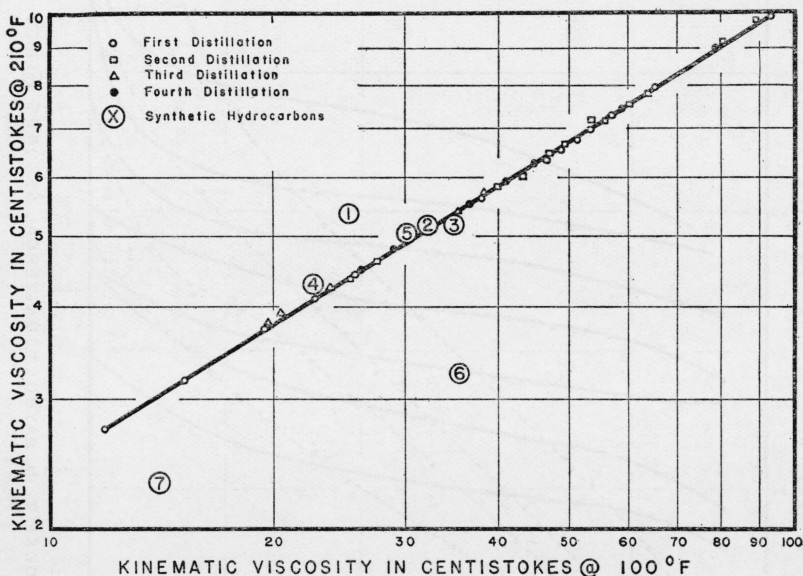


FIGURE 9.—*Logarithmic scale of the viscosity at 210° F against that at 100° F for fractions from various stages of the systematic distillation.*

The numbers represent values for the hydrocarbons as follows:

1. 16-*n*-Butylhentriacontane.
2. 1, 1-Dicyclohexylhexadecane.
3. 1-Phenyl-2-benzylheptadecane.
4. 1, 1-Diphenylhexadecane.
5. 1-Cyclohexyl-2-hexahydrobenzylheptadecane.
6. Dihydrodiethylantracene.
7. 1, 4-Diisobutyl-naphthalene.

different from those given by the straight line in figure 9. This separation into fractions with different viscosity-temperature relationships by solvent extraction is shown by the data in table 4, in which are recorded certain physical properties of fractions resulting from extraction of a distillation fraction with acetone. Similarly certain physical properties of fractions resulting from adsorption of a distillation fraction on silica gel are recorded in table 5. It is evident that here also a separation with respect to type has occurred.

⁹ The values for the synthetic hydrocarbons were obtained by interpolation or extrapolation with the aid of Cragoe's [7] equation from the original data, which extended from approximately 20 to nearly 100° C, of Suida and Planckh [8] for 16-*n*-butylhentriacontane, Landa and Cech [9] for 1, 1-dicyclohexylhexadecane, 1-phenyl-2-benzylheptadecane, 1, 1-diphenylhexadecane, 1-cyclohexyl-2-hexahydrobenzylheptadecane, Lerer [10] for dihydrodiethylantracene, and 1, 4-diisobutyl-naphthalene.

TABLE 4.—*Extraction, with acetone, of a water-white distillation fraction*

Fraction	Weight	Refractive index n_D^{25}	Kinematic viscosity at—		Saybolt universal viscosity ¹ at—		Viscosity index
			100° F	210° F	100° F	210° F	
	<i>Percent</i>		<i>Stoke</i>	<i>Stoke</i>	<i>sec</i>	<i>sec</i>	
Original.....	100	1.4728	0.3693	0.0546	172.1	43.4	93
First extract.....	12.17	1.4764	.4174	.0582	194.1	44.5	87
Second extract.....	12.42	1.4746	.4027	.0578	187.5	44.3	93
Third extract.....	27.85	1.4722	.3766	.0557	175.5	43.7	94
Fourth extract.....	27.51	1.4705	.3596	.0548	167.7	43.4	97
Raffinate.....	20.05	1.4682	.3343	.0546	156.3	43.4	111

¹ The conversion from kinematic viscosity to Saybolt universal viscosity here and in the rest of this paper was made with the aid of the conversion data of McCluer and Fenske [11].

TABLE 5.—*Adsorption, with silica gel, of a water-white distillation fraction*

[100 ml oil, plus 150 ml petroleum ether, passed through a column containing 150 g silica gel at room temperature]

Fraction	Weight	Refractive index n_D^{25}	Kinematic viscosity at—		Saybolt universal viscosity		Viscosity index
			100° F	210° F	100° F	210° F	
	<i>g</i>		<i>Stoke</i>	<i>Stoke</i>	<i>sec</i>	<i>sec</i>	
Original.....	15.65	1.4734	0.3917	0.0577	182.5	44.3	95
First.....	11.60	1.4702	.3565	.0564	166.3	43.9	107
Second.....	13.44	1.4717	.3823	.0569	178.1	44.1	98
Third.....	13.73	1.4718	.3868	.0571	180.2	44.1	96
Fourth.....	10.47	1.4718	.3862	.0572	180.0	44.2	97
Fifth.....	13.29	1.4720	.3871	.0573	180.4	44.2	97
Silica gel hold up.....	13.29	1.4819	.4732	.0622	219.2	45.7	84

IX. VISCOSITY DETERMINATIONS

A knowledge of the viscosity of oil fractions and of their change in viscosity with temperature is essential in any investigation of the hydrocarbon constitution of lubricating oil. Mention has already been made of their use in connection with the systematic distillation in which blending of the oil fractions for successive distillations was done on the basis of viscosity. The temperature coefficient of viscosity is equally important, since with its aid the course of fractionation with respect to type (as accomplished by extraction with a solvent or by selective adsorption) can be followed. Consequently, the determination of viscosity after every fractionating process is an established procedure in this laboratory. Viscosities are usually determined at 100 and 210° F. Where the nature of the material makes this impossible (as with the waxes and original cuts), determinations were made with 150° F as the lower temperature.

The essentials embodied in the design of the viscosity apparatus are that (a) the viscosity should be obtainable in fundamental units of kinematic viscosity with an accuracy of about ± 1 percent and a precision of about ± 0.2 percent; (b) the sample should not exceed 10 ml and should be readily recoverable; (c) the determination of viscosity should be a routine matter with about 40 determinations per day; and (d) it should be possible to determine the density in the same apparatus.

The above conditions were fulfilled by the assembly of a series of pipettes with capillaries of different dimensions mounted vertically in

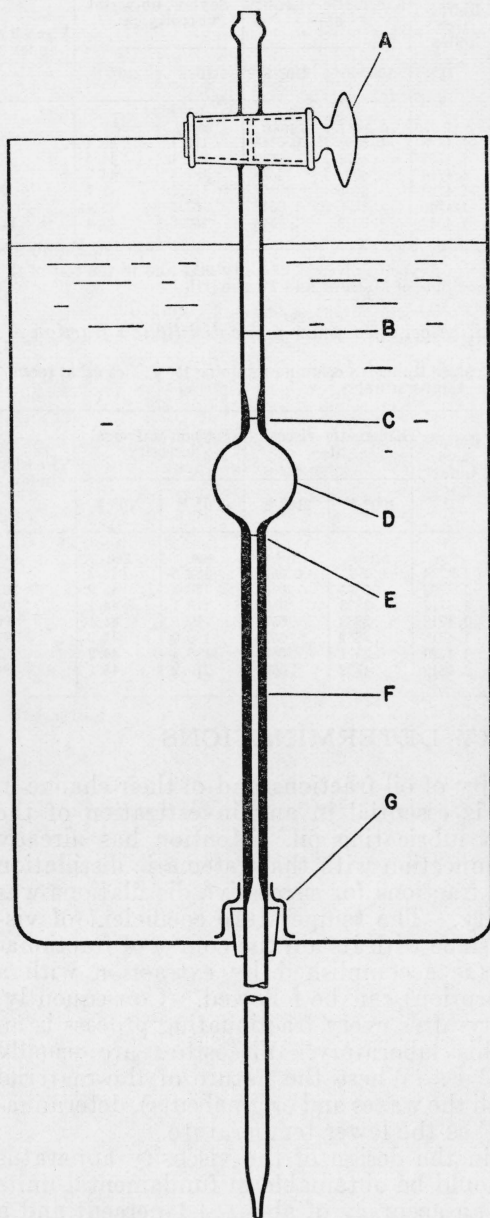


FIGURE 10.—*Viscosity pipette.*

oil baths thermostatically controlled to $\pm 0.05^\circ$ F. One of these pipettes mounted in the large Pyrex jar which served as a bath is shown schematically in figure 10. The bulb D and capillary F are entirely within the oil bath. The lower portion of the pipette extended through the bottom of the bath¹⁰ into an insulated double-walled air bath regulated to $\pm 2^\circ$ F. Viscosity determinations were made by drawing the sample of oil into the pipette, allowing it to come to the temperature of the bath, and noting the time of efflux from C to E. The effluent oil was collected in its original container. The pipettes were washed in situ with benzene or toluene and dried with a current of air.

Standard samples of oil, whose viscosities were considered accurate to ± 0.5 percent, were obtained from the Heat Division of this Bureau and used to calibrate the pipettes. Each pipette was calibrated with several of these standard samples, whose viscosities covered the range for which the pipette was designed. In table 6 are given the calibration data for one pipette. The values for the viscometer constant agreed within ± 0.5 percent.

¹⁰ This was accomplished in the case of the bath operating at 210° F by ground-glass joints, and in the case of the bath operating at the lower temperature, 100° F, by rubber stoppers fitted with glass protectors (G, fig. 10) and painted with the condensation product of polyvinyl alcohol and butyraldehyde, a resin developed by T. P. Sager, of this Bureau, which gives a flexible film highly resistant to oil.

TABLE 6.—Calibration of pipette no. 2 used in 100° F measurements

Sample	Temperature ¹	Time of efflux	Kinematic viscosity, KV	Viscometer constant, $C = \frac{KV^2}{t}$
	°C	sec	Stoke	
SVS 1A.....	25.0 ₀	64.5	0.2878	4.462×10 ⁻³
SVS 3A.....	21.9 ₀	171.5	.7697	4.489
SVS 4.....	21.9 ₀	382.7	1.715	4.481
SVS 6G.....	21.9 ₀	1,961.3	8.731	4.452
Average.....				4.471×10 ⁻³

¹ Tests at the operating temperature of the bath, 100° F, gave the same viscometer constant (within the limits of accuracy) for a given pipette.

Densities and viscosities could be determined with one filling of the pipette. In the density determinations, oil from a weighed erlenmeyer flask was drawn up to mark B; the flask was weighed again; and the weight of oil in the pipette obtained by difference. The volume of the pipette was determined by calibration in a similar manner with oil of known density. With care a precision of about ±0.2 percent is obtainable with this method. However, the precision obtained in the routine determination of density was in some cases not better than ±1 percent.

X. CONCLUSION

From what has been accomplished so far it appears likely that the oil may be separated by distillation into substantially constant-boiling fractions, and that these fractions may be separated into hydrocarbons of different types by one of the other physical methods.

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XI. LITERATURE REFERENCES

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