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THE FRACTIONATION OF CRUDE PETROLEUM BY CAPILLARY DIFFUSION

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UNDER THE SUPERVISION OF

DAVID T. DAY

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CONTENTS.

ILLUSTRATIONS.

THE FRACTIONATION OF CRUDE PETROLEUM BY CAPILLARY DIFFUSION.

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INTRODUCTION.

When, in process of refinement, black vaseline is filtered through warm, dry fuller's earth, the first product is an oil that is perfectly liquid at ordinary temperatures, but the succeeding portions are progressively more viscous until fairly hard vaseline is obtained. The observation that a fractional separation of oils in vaseline had been effected suggested to David T. Day that a like result might be obtained with crude petroleum. He applied this method to a sample of green crude petroleum from the "third sand" of Venango County, Pa., and found that light products, chiefly gasoline, first appeared when such crude oil was allowed to filter down through a long glass tube filled with granulated or powdered fuller's earth.[a]

This result was followed by experiments with a more elaborate system of specially constructed funnels similar to those used by the refiners of vaseline in testing the comparative value of various fuller's earths. The results from these experiments were briefly summarized in a paper on the ability of petroleum to migrate in the earth.[b] Engler later verified these results and showed that the separation was mechanical and that no oxidation was effected in the process. Day next used a large closed funnel of galvanized iron holding about 100 pounds of fuller's earth. When crude petroleum was dropped slowly and regularly into this funnel, rather light oils were obtained at first, followed by the usual succession of heavier oils. As it was evident from this work that much of the oil passed through crevices without any change, Day tried the effect of reversing the route of the oil and of allowing it to diffuse upward through a tube packed tightly with fuller's earth. In such a tube the lighter constituents rose much more rapidly than the more viscous oils, so that by separat-

[a] Proc. Am. Philos. Soc., vol. 36, No. 154, 1897. [b] Trans. Petroleum Congress (Paris), 1900.

ing the fuller's earth from different sections of the tube and displacing the oil by water, very different oils were obtained from the upper and lower parts of the tube.

By using several tubes and uniting oils of the same specific gravity oil of different grades can be collected in sufficient quantity to be fractionated again, and the process can be continued until oils result which are not altered by further passage through tubes filled with fuller's earth. At the suggestion and with the coöperation of Doctor Day we have taken up this problem with the results here stated.

DETAILED DESCRIPTION OF EXPERIMENTS.

FRACTIONATION IN TUBES.

The tubes used first were of glass, 3 feet long and 1⅛ inches in diameter. They were closed at the lower end with corks along whose sides six or seven grooves had been cut, the inner end of the cork being covered with a bit of cotton cloth to prevent the earth from sifting out through the grooves. Such tubes filled with fuller's earth were placed with their lower ends in an open dish of petroleum and the oil was allowed to rise.

At room temperatures (18° to 22° C.) and atmospheric pressure, the rate of rise of crude petroleum in a tube filled with fuller's earth was very slow. In seven days the oil ascended but 73 centimeters in one tube and 59 centimeters in another, and in a third tube ten days were required for it to rise 59 centimeters. To study the effect of heat, a glass tube about 3 feet long and 1⅓ inches in diameter was filled with earth and placed in a bottle holding about 2 liters of oil; and the whole was heated by an electric stove with which temperatures considerably above those of the room could be maintained day and night. The temperature of the tube was kept between 40° and 70° for three days, in which time the oil rose 54.7 centimeters in the tube; in another tube packed in all ways like the first, but held at room temperature (about 20°), the oil rose 46 centimeters in the same length of time. With two tubes in which the earth was packed much less compactly the time required for the oil to rise 54 centimeters was four days for the tube at room temperature and two days for the one at 50° to 80°. The rate of rise was evidently but little affected by heat, at least within this range of temperature, and higher temperatures could not be used without loss of the more volatile constituents of the oil.

The next attempt at increasing the rate of rise of the oil consisted in applying diminished pressure to the top of the tube, which reduced the time required for the oil to reach the top of a tube 5 feet long from several weeks to seventeen hours. If diminished pressure is continued after the oil has reached the top and if the oil is not exhausted in the reservoir at the bottom, oil will be drawn over from the top of the tube. The specific gravity of the oil thus collected steadily rises as it comes over. The samples so obtained, however, stand under very low pressures for some time, which may cause a loss of their more volatile constituents. This suggested applying increased pressure to the oil in the reservoir rather than diminished pressure to the top of the tube, and an iron bomb, like those used for the transportation of mercury, was fitted with an iron pipe 7 feet long to contain earth and a side arm at the bottom of the bomb to which a water column might be attached.

The bomb, which held about 2 liters, could be partly filled with petroleum and the pipe containing the earth screwed into the top. The side arm which opened into the bottom of the bomb could then be connected with the water pressure so that the lower part of the bomb was filled with water which drove the petroleum upward. The oil obtained at the top, however, was fractionated no further nor in any larger amounts than when the oil was not allowed to emerge from the top of the tube. The difficulty of setting up such a pressure apparatus with tight connections, as well as the range of pressure required—a column of water 7 feet high being too great when the oil was just started up the tube and a column 30 feet high being insufficient when it was near the top—made its use impracticable.

To use diminished pressure, the earth in the tubes must not be packed so hard that the air just above the oil can not be drawn through the earth above, nor must the earth be packed so loosely that the oil will rise as in a vacuum. The right degree of hardness is obtained by filling about 1 foot of the tube at a time and packing that much earth as hard as possible with a wooden rod tipped with a rubber stopper. If the tube when pounded on the floor rings in the hand, it indicates that the earth may be packed too closely. Tubes may be packed much more easily by filling several at once, with a separate ramrod for each. By allowing a few minutes to elapse between successive liftings of the ramrod, much labor is avoided. A bit of cotton waste below a rubber stopper at the top of the tube will prevent any earth from being drawn up when the air is exhausted.

The fuller's earth was first heated in shallow iron pans until it ceased to form geysers when stirred. The earth must be thoroughly cold before it is packed into tubes, or the contraction will be sufficient to allow the oil to run up the tube immediately when the air is exhausted.

Much trouble was experienced with the tubes first used on account of their breaking—not when in service, but soon afterward. This was thought to be due to the age of the tubing, but the same thing happened with new tubes 5 feet long and 1¼ inches in diameter. With the idea that the iron scraper used to remove the earth from the tubes might be the cause, a scraper entirely of wood was tried, but this did not decrease the breakage, it being nothing unusual on going to the laboratory in the morning to find that half of the tubes which had been emptied the day before were cracked.

It had been considered necessary to use tubes of glass in order that the height to which the oil had risen could be seen and that in removing the oil from the middle of the tube it might be scraped out to a sharp dividing line, as the level to which the oil has risen is the point from which should be made all measurements of sections into which the tube is to be divided. Tin tubes were used later to avoid the trouble experienced with glass tubes. These tin tubes were emptied by shaking the earth from the bottom into four 30-centimeter cylinders of the same diameter as the tube, these cylinders being made of two curved pieces of tin held together by a cap at one end and a ring at the other. The cylinders containing the contents of the tube could be opened lengthwise and the earth divided into any desired lengths. Two glass tubes 5 feet long and 1¼ inches in diameter were set up in the same dish of petroleum with ten or twenty tin tubes 5½ feet long and of the same diameter as the glass tubes, and when the oil stood at the top of the glass tubes the tin ones were also opened. Glass tubes, of course, can be emptied as well as tin tubes by shaking the contents from the bottom, and there was no more breakage after this method was adopted.

The level to which the oil will rise can be regulated by the amount of oil in which the tube is placed, and in the later work the adoption of this method did away with the use of glass tubes entirely. In a tube 1¼ inches in diameter and 5½ feet long 950 cubic centimeters of oil will rise within 20 to 35 centimeters of the top.

When the oily earth has been removed from the tube, the oil may be separated by adding water. In the first experiments enough water was added to form a very thin mud, which was thoroughly stirred by a small propeller driven by a water motor. The mixed earth, oil, and water were then poured into a large separating funnel and allowed to stand several minutes until the oil had collected at the top. The earth and water could then be drawn off and the pure oil left.

It was found later, however, that if less water is added to the earth as removed from the tubes, after standing a few minutes all the water will pass into the earth and this will be accompanied by the liberation of oil. Oil so liberated can then be poured off directly from the earth without the labor of churning. When water first begins to liberate oil, the earth is granular; but when more water has been added and the last of the oil recovered, the earth has the consistency of a thin paste that will flow when the dish is inclined, which it will not do when the oil begins to come off.

All the oil from one section of a tube is of the same color irrespective of whether it is the first or the last oil to come off when water is added. It was assumed at first that all the oil which came from one section of earth had the same specific gravity, but this was found later not to be the case. The first oil to be collected, if taken in sufficiently small volume, say about 20 cubic centimeters, is slightly heavier than the next portion. If as much as 100 cubic centimeters is included in the first sample, however, this will not be true. Beginning with the second sample the successive portions of oil steadily increase in specific gravity, the gradual addition of water affording another means of fractionation in addition to the separating power of the earth. Both of these methods of separation have been combined in this investigation. The earth must be thoroughly mixed after each addition of water to prevent a layer of water-wet earth from isolating earth that contains oil from the water added.

The petroleum used was a dark-green oil from Venango County, Pa., of specific gravity 0.810. When 950 cubic centimeters of this oil was drawn upward in a tin tube 5½ feet long, the following separation was obtained:

TABLE 1.—*Fractionation of crude petroleum in single tubes.*

	1.		2.		3.	
Time required, in hours	23.5		17.5		17.5	
Distance from top of tube to oil when opened, in centimeters	31		28		28	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A, 8 centimeters at top	0.796	42	0.8012	30	0.8022	18
B, next 8 centimeters	.808	45	.804	37	.803	35
C, next 18 centimeters	.8125	75	.807	47	.8075	66
	.8137	24	.809	22	.810	25
D, next 30 centimeters	.815	130	.8125	148	.812	140
E, next 35 centimeters	.818	170	.8185	190	.8175	145
F, rest	.8205	125	.823	100	.821	105
		611		574		534

The oil in grade C was collected in two portions, the second being obtained by the addition of more water after the first lot of oil was poured off. Although 950 cubic centimeters of crude petroleum were used in each experiment, it will be noticed that the oil recovered measures much less than that. When several tubes were worked up together, in one test 9,070 cubic centimeters of crude petroleum yielded 5,951 cubic centimeters of oil and in another 8,915 cubic centimeters gave 5,415 cubic centimeters.

TABLE 2.—*First fractionation of crude petroleum.*

	4.		5.		6.		7.		8.		9.	
Tubes	2 glass, 8 tin		2 glass, 7 tin		2 glass, 8 tin		2 glass, 7 tin		2 glass, 7 tin		2 glass, 7 tin.	
Distance from level of oil to top of tube, in centimeters.[a]	Glass, 0, 15; tin, 40, 15, 24, 22, 28, 19, 24, 32.		Glass, 0, 6.5; tin, 26, 28, 18, 15, 28, 12, 24.		Glass, 0, 12; tin, 30, 28, 22, 30, 13, 12.[b]		Glass, 0, 7; tin, 25, 26, 23, 26, 28, 20, 28.		Glass, 0, 5; tin, 16, 34, 28, 15, 18, 23, 10.		Glass, 8.5, 15; tin, 58, 31, 60, 40, 16, 53, 16.	
Time required, in hours	54.		24.		54.		84.		48.		117.	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8015	50	0.804	100	0.805	65	0.800	200	0.798	130	0.8025	175
	.8005	350	.8055	190	.805	200	.802	115	.801	130	.8037	120
B	.807	260	.8085	220	.807	140	.8042	200	.803	155	.8042	180
	.810	190	.811	120	.8097	125	.8048	200	.8045	230	.8078	215
C	.809	100	.8097	430	.810	390	.808	330	.8072	430	.809	300
	.809	400	.8122	300	.8135	380	.8078	430	.808	275	.8095	440
	.810	225					.811	95	.808	225	.8127	100
	.8115	260										
D	.815	425	.813	530	.8133	610	.812	425	.8117	420	.812	390
	.8145	625	.8135	600	.816	325	.812	625	.812	580	.8137	400
	.8175	460	.816	200	.8175	435	.814	360	.822	[c] 250	.8145	300
					.825	125			.8145	300	.8155	200
									.8177	42		
E	.816	440	.8162	480	.816	850	.8172	240	.8135	390	.818	340
	.815	400	.8162	725	.8195	260	.816	650	.814	560	.8197	240
	.821	830	.819	390	.821	330	.8162	660	.8248	[c] 390	.818	290
					.827	325	.8195	300	.817	230	.818	350
									.821	42		

[a] The glass tubes are 5 feet long, the tin tubes 5½ feet. Both are 1¼ inches in diameter.
[b] Record of distance lost for two of the tin tubes.
[c] These fractions stood uncovered on top of the earth overnight, and consequently were exposed to considerable evaporation.

TABLE 2.—*First fractionation of crude petroleum*—Continued.

	10.		11.[a]		12.[b]		13.[c]		14.		15.	
Tubes	2 glass, 9 tin		2 glass, 8 tin		2 glass, 6 tin		2 glass, 9 tin		2 glass, 9 tin		2 glass, 9 tin.	
Distance from level of oil to top of tube, in centimeters.[d]	Glass, 0, 8.5; tin, 40, 32, 36, 26, 27, 20, 27, 25, 18.		Glass, 0, 4; tin, 0, 0, 0, 0, 20, 17, 7, 5.		Glass, 7, 13; tin, 32, 19, 32, 35, 48, 29.		Glass, 2, 2.5; tin, 17, 10, 11, 22, 16, 29, 8, 5, 5.5, 14.		Glass, 0, 0; tin, 20, 20.5, 13.5, 15, 14.5, 19, 8, 12, 14.		Glass, 0, 10; tin, 32, 31, 23, 23, 24, 26, 9, 16, 14.	
Time required in hours	84.		39.		60.		20.		16.5.		16.75.	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.7995	200	0.799	80	0.798	150	0.8015	110	0.798	225	0.800	300
	.8037	160	.802	180	.801	140	.8055	40	.8005	110	.805	95
	.806	23					.8028	125	.8015	80		
							.8033	100				
B	.8085	125	.807	200	.8022	160	.802	230	.8015	210	.802	300
	.810	275	.8115	140	.806	105	.8072	60	.804	150	.808	90
	.8112	23			.8072	20	.8085	50	.8058	120	.8055	120
							.8070	75				
C	.810	350	.810	300	.807	400	.806	340	.8048	500	.8065	800
	.812	525	.811	490	.809	200	.808	220	.8065	385	.810	350
	.8135	150	.8145	175	.8115	60	.8072	320	.8075	225		
							.8097	150				
D	.8148	440	.8133	450	.811	400	.809	400	.810	500	.8112	600
	.8175	700	.8133	530	.8097	420	.8135	250	.810	660	.8142	525
	.817	370	.816	290	.811	290	.8115	680	.810	650	.8122	680
	.817	200	.8142	250	.815	60	.812	650	.812	260	.8155	200
E	.8197	315	.8172	400	.815	260	.813	400	.8135	470	.8145	740
	.8215	720	.818	520	.8148	510	.818	285	.8155	530	.820	400
	.8223	570	.819	405	.815	400	.8167	700	.8155	700	.818	400
	.821	215	.8175	370	.817	100	.8167	805	.8162	680	.817	820

[a] During the night, oil was drawn entirely through and out at the top of five tubes and so was lost.
[b] Three other tubes were set up with these, but when opened the oil in them was 81, 81, and 90 centimeters from the top, so they were discarded. This unevenness between the tubes was probably caused by using in some of them earth which was not entirely cold.
[c] Beginning with lot 13 the pump was run continuously day and night.
[d] The glass tubes are 5 feet long, the tin tubes 5½ feet. Both are 1¼ inches in diameter.

TABLE 2.—*First fractionation of crude petroleum*—Continued.

	16.		17.		18.[a]		19.[a]	
Tubes	2 glass, 9 tin		1 glass, 9 tin		2 glass, 9 tin	2 glass, 9 tin	2 glass, 9 tin	2 glass, 9 tin.
Distance from level of oil to top of tube, in centimeters.[b]	Glass, 0, 0.5; tin, 24, 19, 16, 15, 17, 23, 17, 4, 2.		Glass, 14; tin, 8, 27, 13, 6, 8, 0, 0, 0, 0.		Glass, 8, 5; tin, 17, 2, 15, 19, 12, 33, 21, 0, 0.	Glass, 14, 17; tin, 30, 42, 39, 28, 35, 33, 42, 30, 42.	Glass, 0, 0; tin, 17, 11, 5, 18, 12, 15, 13, 18, 11.	Glass, 0, 9; tin, 13, 12, 23, 15, 19, 11, 13, 26.
Time required, in hours	16.5.		17.		21.5.		23.	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.800	125	0.804	240	0.8005	425	0.806	200
	.8025	200	.8055	120	.8005	225	.804	300
	.8028	80	.8085	23	.8015	190	.8085	180
B					.803	320	.8055	290
	.8042	245	.812	220	.803	320	.8072	175
	.8065	100	.812	155	.8042	200	.809	175
	.810	110	.8127	45	.8055	75	.807	200
C					.8078	475		
	.8085	230	.814	500	.8078	680	.809	570
	.8085	600	.8125	450	.808	500	.8097	930
	.8115	210	.815	40	.8085	200	.8135	140
					.8095	170	.813	100
					.8105	150		
D	.8117	435	.814	540	0.8117 420	0.8122 500	0.8128 560	0.8128 475
	.8135	650	.814	670	.8117 680	.8125 500	.813 725	.813 740
	.8137	370	.8145	350	.813 660	.814 350	.815 400	.8185 180
	.8184	350			.8155 90	.817 40		
E	See below.		.817	740	.8158	1,450	.816	930
			.8172	750	.8158	1,000	.816	930
					.8165	420	.8165	460
					.8175	350	.8185	400
					.8187	500	.8185	520
							.820	200

[a] Two reservoirs of crude oil were used in each of lots 18 and 19, but the earth from all 22 tubes was worked up together. Section D from all 22 tubes was first united and then, for convenience in working, divided into two portions.

[b] The glass tubes are 5 feet long, the tin tubes 5½ feet. Both are 1¼ inches in diameter.

To collect a sufficient quantity of oil, several tubes were placed in the same container of petroleum, two of the tubes being of glass and the rest of tin. When the oil had reached the top of the glass tubes all the tubes were opened, and the earth from the same level in all the tubes was mixed in tin pails. The oil was then liberated in several successive fractions by the addition of successive amounts of water. If the earth had been thoroughly mixed after each addition of water, the various oils from the same lot of earth would have increased regularly in specific gravity, instead of showing the variations which they did. For example, the first oil to be displaced by water in grades D and E of lot 4 (Table 2), with so large a volume, would not have been heavier than the succeeding oils if the water and earth had been thoroughly mixed before the oil was poured off. If we were to repeat the work, instead of using one common reservoir for all the tubes, we should use a separate reservoir for each tube, and open the tube when the oil in the reservoir was exhausted. This would do away entirely with the use of glass tubes, besides insuring that the level of the oil in each tube when opened would be practically the same. If a common reservoir is to be used, the tubes should all be packed with practically the same degree of hardness if the oil is to ascend in all with equal rapidity, as the ascent in all tubes is checked at the same time—that is, when the oil in the reservoir is exhausted.

Diminished pressure was obtained by the use of a Chapman water pump, which reduced the pressure to 5 to 12 centimeters Hg., when connected with a system of tubes. In the earlier work the pump was not run through the night, which accounts for the much longer time required for these lots of tubes.

The earth from a tube was divided into six sections, the level to which the oil had ascended in the tube being taken as the point to be measured from. A, the top section, included the 8 centimeters next the top; B, the next 8 centimeters; C, the next 18; D, the next 30; E, the next 35; and F what earth was left. F varied, of course, depending on the height to which the oil had risen. In fractionating the crude petroleum in bulk, F was usually discarded, as it was so viscous that it was deemed impossible to pass it through earth again. Records from several lots of tubes are given in Table 2. The specific gravity was measured with a Westphal balance, the temperature of the oil being in every case exactly 20° C. Although the fourth decimal place is not to be taken as strictly accurate, yet it is considered worth while to record it as giving a nearer approach to the truth than would result from the use of only three decimal places.

To study further the fractionation on addition of water, the oil of grade E from lot 16 was collected in fourteen fractions. The weight of the earth impregnated with oil before any water had been added was 13.5 pounds, and the weight of the earth containing all the water added, but minus the oil, was 17.5 pounds. The earth was placed in a galvanized-iron garbage pail and the water stirred in with an iron paddle. When the first portion of oil was liberated, the mass was of the consistency of bran, but as more water was added it turned to a fluid paste. When water was added and the pail inclined, oil would continue to drain out for half an hour or longer before the addition of more water became necessary. The oil which was liberated by one lot of water, therefore, could be collected in several portions, and this was done to see whether the oil which comes off immediately after the addition of water is the same as that which drains out later. The letters I, II, etc., indicate that the fractions included were liberated by one addition of water.

TABLE 3.—*Fractionation of oil of grade E, lot 16, Table 2.*

	Specific gravity.	Cubic centimeters.		Specific gravity.	Cubic centimeters.
I	0.821	25	IV	0.8208	575
				.8222	55
II	.818	70	V	.824	170
	.818	70		.828	16
	.8193	250			
III	.818	395	VI	.827	95
	.818	350		.830	45
	.818	460			
	.820	60			

The first fraction is regularly of higher specific gravity than those immediately following if only enough water is added to liberate a first fraction of small volume, say about 20 cubic centimeters. As the fraction first obtained becomes larger in volume, it approaches nearer to the second fraction in specific gravity, and will even fall below that fraction if the volume is made too large.

The range of specific gravity covered by this first fractionation of the crude petroleum of specific gravity 0.810 was from 0.800 to 0.830. Fractions of the same specific gravity and of the same grade were united and the products chilled and filtered to remove all the dissolved paraffin possible. This was done out of doors toward the last of December, when the thermometer stood at about 4° to 8° C. Lower temperatures would not only throw paraffin out of solution, but cause the whole oil to thicken. The oils were filtered through large plaited filters of drying paper, twenty-four hours or more being required for many of the filters to empty completely. The lighter oils in sections A and B deposited no paraffin. Some of the heavier grades deposited as much as 10 per cent of their weight, accompanied in many cases by a slight change in specific gravity.

When these oils were filtered through earth again they behaved as shown in Table 4. As before, 950 cubic centimeters of each oil was used and the tube was divided into five sections, A being the top 8 centimeters, B the next 8, C the next 18, D the next 30, and EF the rest.

TABLE 4.—*Second fractionation.*

[NOTE.—Nine hundred and fifty cubic centimeters were needed for each tube, and for many tubes this amount was available of the same grade (A, B, C, etc.) and of the same specific gravity. For some tubes, however, it was necessary to unite oils of the same grade which differed slightly in specific gravity. No such samples differed by more than 0.0015 and all are marked with an asterisk (*) in the table.]

	20 (A, 0.8015).		21 (A, 0.806).		*22 (B, 0.805).		23 (B, 0.8055).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8012	36	0.8038	45	0.7997	50	0.8005	45
B	.800	44	.8035	48	.802	50	.8033	48
C	.8012	68	.8035	78	.8055	108	.805	115
	.8027	35	.8052	28				
D	.8022	170	.805	160	.8063	175	.8063	180
EF	.8047	330	.807	320	.808	260	.8085	260
		683		679		643		648

	24 (B, 0.8065).		25 (B, 0.809).		*26 (B, 0.8105).		*27 (B, 0.812).	
A	0.8077	38	0.8013	45	0.8075	38	0.8105	42
B	.807	50	.805	50	.8085	50	.8105	42
C	.808	80	.807	75	.8105	100	.8085	73
			.810	30	....	....	.810	22
D	.8092	160	.8095	180	.8125	160	.8115	140
EF	.8115	300	.8115	350	.8133	275	.8145	250
		628		730		523		569

	28 (C, 0.8095).		29 (C, 0.810).		30 (C, 0.811).		*31 (C, 0.811).	
A	0.805	52	0.8035	40	0.8005	50	0.803	50
B	.8065	52	.808	40	.809	38	.808	55
C	.8085	70	.810	75	.812	115	.813	105
	.811	28	.8115	30				
D	.811	160	.8115	140	.813	175	.8135	180
			.8135	40				
EF	.813	350	.813	350	.8145	310	.8155	300
		712		715		688		690

	32 (C, 0.8115).		33 (C, 0.813).		*34 (C, 0.8135).		*35 (C, 0.8135).	
A	0.806	45	0.8072	20	0.803	42	0.8025	35
B	.807	35	.811	35	.810	53	.8077	35
C	.810	60	.812	70	.813	100	.8135	100
	.812	33	.813	25				
D	.812	70	.8145	90	.815	150	.8145	160
	.813	97	.815	80				
EF	.813	103	.8155	200	.817	300	.817	325
	.8135	105	.8155	125				
	.813	50	.818	35				
	.813	47						
		a 63						
		708		680		645		655

	36 (C, 0.815).		*37 (C, 0.8155).		*38 (C, 0.8155).		*39 (C, 0.8165).	
A	0.805	43	0.8053	50	0.808	40	0.808	50
B	.8105	40	.812	45	.8095	50	.8145	50
C	.814	98	.816	103	.8135	100	.816	82
D	.815	155	.8175	160	.817	165	.8175	125
EF	.817	280	.819	310	.819	290	.820	310
		616		668		645		617

a Unused.

TABLE 4.—*Second fractionation*—Continued.

	*40 (D, 0.8135).		41 (D, 0.814).		42 (D, 0.814).		43 (D, 0.814).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8095	45	0.8045	30	0.806	32	0.806	25
B	.8085	45	.8115	45	.811	45	.8097	30
C	.811	95	.8135	75	.813	92	.814	50
			.8165	28				
D	.8155	165	.818	140	.8175	140	.8157	145
EF	.817	320	.821	300	.8195	310	.8175	400
		670		618		619		650

	44 (D, 0.814).		45 (D, 0.814).		46 (D, 0.8145).		47 (D, 0.815).	
A	0.8008	45	0.800	50	0.808	45	0.800	42
B	.8077	50	.8065	55	.8115	40	.807	47
C	.814	103	.8125	100	.8135	65	.814	110
					.8155	30		
D	.8175	160	.816	160	.817	105	.816	150
					.818	58		
EF	.819	310	.817	300	.8195	180	.819	330
					.8202	120		
					.821	53		
		668		665		696		679

	48 (D, 0.815).		49 (D, 0.8155).		50 (D, 0.8155).		51 (D, 0.8155).	
A	0.810	37	0.8045	40	0.8105	45	0.8058	40
B	.805	47	.811	48	.8148	47	.810	40
C	.812	105	.815	98	.810	100	.8132	60
							.8145	50
D	.817	160	.8185	160	.815	140	.8172	75
							.8188	55
							.8188	38
EF	.819	300	.820	310	.819	400	.820	38
							.819	100
							.8208	30
							.8208	45
							.8208	30
							.8208	95
								[a] 40
		649		656		732		736

	52 (D, 0.816).		*53 (D, 0.816).		54 (D, 0.8165).		55 (D, 0.8165).	
A	0.806	38	0.803	43	0.806	47	0.8095	42
B	.8115	42	.8105	30	.811	48	.8135	40
C	.814	70	.815	100	.815	98	.8145	77
	.8175	25						
D	.8185	125	.8185	175	.8188	150	.8188	150
EF	.821	300	.820	290	.8208	300	.821	295
		700		638		643		604

	*56 (D, 0.8165).		*57 (D, 0.817).		*58 (D, 0.818).		59 (D, 0.8187).	
A	0.806	45	0.8075	40	0.808	45	0.811	40
B	.810	45	.8115	40	.8135	45	.812	45
C	.8145	95	.815	100	.817	105	.814	92
D	.8185	160	.818	130	.820	150	.819	150
EF	.821	295	.821	330	.822	300	.823	305
		640		640		645		632

[a] Unused.

TABLE 4.—*Second fractionation*—Continued.

	*60 (D, 0.8205).		61 (E, 0.814).		*62 (E, 0.8163).		*63 (E, 0.817).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8045	45	0.8075	33	0.8155	42	0.804	45
B	.813	45	.810	35	.808	50	.8075	50
C	.8175	90	.8125	80	.8095	70	.8145	102
					.812	25		
D	.822	170	.818	125	.8175	105	.8205	150
					.8182	32		
EF	.823	270	.8245	300	.823	250	.8245	300
		[a]70			.8255	41		
		692		573		615		647

	*64 (E, 0.817).		*65 (E, 0.818).[a]		*66 (E, 0.818).		67 (E, 0.818).	
A	0.805	42	0.8065	90	0.805	38	0.805	40
			.809	20				
B	.810	42	.810	110	.811	38	.811	45
C	.8145	75	.8155	186	.8135	104	.8145	85
			.817	50				
D	.820	135	.8205	385	.819	175	.8185	125
			.8205	75				
EF	.8255	235	.8255	650	.8235	240	.824	325
			.8255	260				
		529		1,826		695		620

	*68 (E, 0.8185).		69 (E, 0.819).		70 (E, 0.819).		*71 (E, 0.819).	
A	0.8205	15	0.804	24	0.8115	21	0.8095	23
B	.8043	35	.808	40	.814	31	.8085	34
C	.810	60	.8145	85	.815	90	.814	80
	.812	30						
D	.817	160	.8195	140	.8165	120	.820	160
EF	.8225	300	.824	330	.824	330	.824	280
		590		589		592		577

	*72 (E, 0.8195).		*73 (E, 0.8195).		74 (E, 0.8195).		75 (E, 0.8197).	
A	0.8145	30	0.8055	34	0.816	40	0.8025	40
B	.8105	42	.811	45	.8135	42	.8105	38
C	.8135	103	.8155	80	.809	65	.816	90
					.814	34		
D	.8195	160	.820	120	.8185	160	.822	150
EF	.824	285	.824	290	.824	260	.8255	300
					.827	30		
		620		569		631		618

	*76 (E, 0.820).		*77 (E, 0.8205).		78 (E, 0.8215).		*79 (E, 0.822).	
A	0.8045	48	0.806	32	0.8045	28	0.8105	32
B	.812	40	.8125	45	.8135	36	.8145	42
C	.817	91	.8175	90	.8185	78	.819	77
D	.822	155	.823	100	.823	150	.8225	155
EF	.826	260	.8245	330	.8275	300	.827	280
		594		597		592		586

[a] Three tubes.

TABLE 4.—*Second fractionation*—Continued.

	80 (E, 0.822).		81 (E, 0.822).		82 (E, 0.824).		*83 (A-B, 0.804).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.817	30	0.8083	26	0.8125	48	0.803	32
B	.810	40	.814	40	.8127	48	.8035	25
C	.8153	46	.8185	92	.818	53	.8035	63
	.8163	42			.819	50		
D	.8225	160	.824	140	.8245	175	.804	140
EF	.8265	295	.8265	270	.828	200	.806	275
					.830	90		
						[a] 50		
		613		568		714		535

	*84 (A-B, 0.8065).		*85 (A-B, 0.808).		*86 (B-C-D, 0.8125).		*87 (B-C-D, 0.8125).[b]	
A	0.8035	40	0.8085	30	0.805	32	0.805	80
B	.8055	40	.807	30	.808	42	.8085	73
C	.809	80	.8065	92	.813	85	.812	118
							.813	75
D	.8085	155	.8085	115	.815	175	.815	285
EF	.811	300	.8115	330	.820	280	.8175	520
		615		597		614		1,151

	*88 (C-D-F, 0.813).		*89 (C-D-E, 0.813).[c]		*90 (B-C-D, 0.8145).[c]		*91 (D-E, 0.815).[d]	
A	0.8035	40	0.8035	130	0.8065	130	0.801	165
			.807	20	.808	27	.8025	176
B	.808	40	.8077	160	.809	137	.8075	206
					.8115	20	.8085	156
C	.8115	73	.8125	330	.813	305	.812	330
	.813	30	.813	60	.815	40	.812	512
D	.8155	160	.815	550	.815	560	.817	340
			.8175	90	.8175	75	.817	800
							.817	150
EF	.8195	290	.8175	830	.8175	775	.8215	2,733
			.818	425	.818	410	etc.	
		633		2,595		2,479		5,568

	*92 (D-E, 0.8163).[e]		93 (F, 0.822).		94 (F, 0.822).			
A	0.805	84	0.8107	35	0.804	28		
	.8075	20						
B	.807	100	.810	43	.808	37		
	.8115	20						
C	.815	205	.814	70	.8165	63		
	.816	45	.816	25	.817	30		
D	.820	350	.8215	156	.8218	146		
	.820	102						
EF	.8225	500	.8285	250	.831	255		
	.8225	480	.831	60				
		1,906		639		559		

[a] Left.
[b] Two tubes.
[c] Four tubes.
[d] Nine tubes.
[e] Three tubes.

To chill and filter these products of two fractionations would have entailed too much loss. As it was, much uniting of samples which differed but slightly from one another was necessary to obtain sufficient oil for further fractionation. A list of the unions which were made is given in Table 5.

TABLE 5.—*Products of two fractionations united for the third fractionation.*

Lot.	Specific gravity.	Fractions united.								
		Grade.	Specific gravity.	Cubic centimeters.	Grade.	Specific gravity.	Cubic centimeters.	Grade.	Specfic gravity.	Cubic centimeters.
95....	0.805	B	0.8033	48	A	0.8035	240	B	0.8035	25
		C	.8035	63	A	.804	65	D	.804	140
		A	.8045	150	A	.805	360	B	.805	95
		C	.805	115						
										1,251
96....	.807	A	.8058	40	A	.806	235	EF	.806	275
		A	.8065	240	B	.8065	100	D	.8063	180
		A	.807	53	C	.807	75	C	.8065	92
										1,290
97....	.8085	B	.808	767	C	.808	80	A	.8083	26
		A	.809	20	C	.809	210	A	.8085	118
										1,221
98....	.8085	A	.8072	20	A	.8075	290	D	.8075	270
		A	.8077	38	B	.8075	480			
										1,098
99....	.8105	A	.8105	70	A	.8115	21	B	.811	580
		C	.811	115	A	.811	40	C	.8115	73
		C	.8105	270	B	.8115	308			
										1,477
100...	.8115	EF	.8113	300	EF	.8115	920			
							1,220			
101...	.8125	C	.8123	520	D	.8125	160	EF	.8125	820
										1,500
103...	.8135	B	.8125	180	B	.813	45	C	.8132	60
		B	.8135	106	C	.8135	925			
										1,316
104...	.814	D	.8135	370	EF	.8135	715			
							1,085			
106...	.8145	D	.814	500	C	.8145	910			
							1,410			
112...	.8175	C	.8165	258	D	.817	425	D	.8172	75
		C	.8175	200						
										958
115...	.819	D	.8175	305	D	.818	990			
							1,295			
116...	.819	EF	.8185	845	EF	.819	683			
							1,528			
120...	.820	D	.8195	475	D	.820	600			
							1,075			
123...	.822	EF	.8215	700	D	.8218	460	EF	.822	300
										1,460
126...	.824	D	.823	250	EF	.8235	860	D	.824	140
										1,250

No uniting was necessary for lots 102, 105, 107–111, 113, 114, 117–119, 121, 122, 124, 125, and 127. In the third fractionation, 950 cubic centimeters of each of these lots was filtered through earth again, with the results shown in Table 6.

TABLE 6.—*Third fractionation.*

	95 (A-D, 0.805).		96 (A-EF, 0.807).		97 (A-C, 0.8085).		98 (A-D, 0.8085).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8065	33	0.8045	37	0.806	40	0.8047	38
B	.805	33	.806	38	.8068	40	.8052	38
C	.804	62	.8065	65	.807	58	.808	70
	.805	40	.8083	25	.8095	18	.8093	30
D	.8055	150	.808	142	.8093	154	.8095	132
EF	.808	315	.8095	250	.812	295	.811	335
		633		557		605		643
	99 (A-C, 0.8105).		100 (EF, 0.8115).		101 (C-EF, 0.8125).		102 (C, 0.813).	
A	0.8105	33	0.8065	30	0.808	33	0.806	26
B	.810	36	.809	36	.8085	34	.8105	33
C	.8075	71	.810	60	.811	54	.8105	50
	.8085	17	.812	20	.8145	22	.813	17
D	.811	115	.812	136	.8145	162	.813	136
EF	.814	300	.815	315	.817	295	.8157	365
		572		597		600		627
	103 (B-C, 0.8135).		104 (D-EF, 0.814).		105 (C, 0.814).		106 (C-D, 0.8145).	
A	0.8065	28	0.8042	35	0.804	40	0.803	33
B	.810	33	.8115	36	.810	40	.810	40
C	.8135	60	.8125	60	.8142	58	.8145	54
	.8165	18	.8147	28	.816	25	.816	22
D	.815	150	.815	175	.8163	270	.816	150
EF	.817	325	.819	230	.8185	280	.8185	260
		614		564		713		559
	107 (D, 0.815).		108 (EF, 0.8155).		109 (D, 0.8163).		110 (D, 0.817).	
A	0.8035	45	0.809	52	0.810	33	0.8065	35
B	.8115	47	.811	47	.8105	45	.8125	40
C	.815	85	.815	55	.8132	55	.817	68
	.8177	30	.815	40	.8145	33	.818	30
D	.8175	156	.8165	170	.8185	140	.8195	145
EF	.8195	300	.8185	255	.8215	275	.821	290
		663		619		531		608
	111 (EF, 0.817).		112 (C-D, 0.8175).		113 (EF, 0.8175).		114 (EF, 0.8187).	
A	0.8043	30	0.8145	35	0.8065	35	0.817	30
B	.8105	32	.811	32	.812	48	.8065	25
C	.8152	65	.8165	60	.8155	75	.8122	30
	.816	43	.818	30	.8175	18	.813	15
D	.8182	160	.819	150	.8185	150	.8175	150
EF	.8205	290	.822	245	.8225	283	.822	340
		620		552		609		590
	115 (D, 0.819).		116 (EF, 0.819).		117 (D, 0.819).		118 (EF, 0.819).	
A	0.8055	16	0.8032	30	0.8045	33	0.805	30
B	.807	Lost.	.8115	36	.813	38	.813	30
C	.816	43	.816	52	.8175	60	.8165	60
	.817	30	.820	21	.8175	34		10
D	.820	130	.8205	160	.8215	150	.821	154
EF	.8225	300	.8235	240	.8235	325	.8243	295
		....		539		640		579

TABLE 6.—*Third fractionation*—Continued.

	119 (EF, 0.8195).		120 (D, 0.820).		121 (EF, 0.821).		122 (EF, 0.8215).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.805	23	0.805	33	0.8075	33	0.803	41
B	.814	35	.811	35	.814	41	.811	43
C	.8165	58	.817	53	.8182	63	.8165	60
	.8175	32	.8175	35	.819	18	.818	23
D	.8205	152	.822	165	.822	150	.8225	182
EF	.823	300	.825	310	.8245	273	.828	270
		600		633		578		629

	123 (D-EF, 0.822).		124 (EF, 0.8225).		125 (EF, 0.8235).		126 (D-EF, 0.824).		127 (EF, 0.8255).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.808	34	0.807	31	0.804	35	0.805	35	0.8055	45
B	.813	35	.8095	27	.813	40	.814	35	.8155	40
C	.8178	52	.8175	65	.8185	70	.820	60	.821	75
	.8192	42	.8185	17	.8195	21	.821	20	.823	25
D	.8233	155	.8232	150	.8252	144	.8253	170	.8275	170
EF	.8265	260	.8275	300	.829	280	.828	300	.830	280
		578		590		590		620		635

Sufficient oil of five grades for the fourth fractionation was obtained by uniting fractions from the third, as shown in Table 7.

TABLE 7.—*Products of three fractionations united for the fourth fractionation.*

Lot.	Specific gravity.	Fractions united.							
		Lot.	Grade.	Specific gravity.	Cubic centimeters.	Lot.	Grade.	Specific gravity.	Cubic centimeters.
128	0.815	99	EF	0.814	300	100	EF	0.815	315
		101	C	.8145	22	101	D	.8145	162
		103	D	.815	150	104	C	.8147	28
		104	D	.815	175	105	C	.8142	58
		106	C	.8145	54	107	C	.815	85
		108	C	.815	55	108	C	.815	40
		109	C	.8145	33	111	C	.8152	65
									1,542
129	.8163	101	EF	.817	295	105	D	.8163	270
		102	EF	.8157	365	106	D	.816	150
		103	EF	.817	325	108	D	.8165	170
									1,575
130	.819	104	EF	.819	230	108	EF	.8185	255
		105	EF	.8185	280	113	D	.8185	150
		106	EF	.8185	260	109	D	.8185	140
									1,315
131	.8205	107	EF	.8195	300	115	D	.820	130
		110	D	.8195	145	116	D	.8205	160
		111	EF	.8205	290	118	D	.821	154
		119	EF	.8205	152				
									1,467
132	.823	113	EF	.8225	283	120	D	.822	165
		115	EF	.8225	300	121	D	.822	150
		119	EF	.823	300	122	D	.8225	182
									1,380

The results of the fourth fractionation are stated in Table 8.

TABLE 8.—*Fourth fractionation.*

	228 (C-EF, 0.815).		129 (D-EF, 0.8168).		130 (D-EF, 0.819).		131 (D-EF, 0.8205).		132 (D-EF, 0.823).	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8135	19	0.812	30	0.8115	24	0.8095	18	0.8092	35
B	.815	27	.8122	42	.8127	35	.813	26	Lost.	35
C	.8118	50	.8165	55	.8173	60	.819	45	.8195	60
	.813	15	.818	25	.8185	22	.8195	17	.8213	25
D	.8147	140	.818	160	.820	160	.8215	130	.8235	150
EF	.8175	360	.8195	305	.8215	310	.824	340	.826	280
		611		617		611		576		585

To better compare the oils of different specific gravities that were obtained by the process just described each of six 300 cubic centimeter samples (five of partly refined oil and one of crude petroleum) was separated by distillation into ten fractions. Each sample was distilled in the same 500 cubic centimeter distilling bulb, which was heated by an electric stove that entirely surrounded it. The oil was first heated to 200° under atmospheric pressure and then to 360° under a pressure of 50 millimeters. The diminished pressure was obtained with a large Chapman water pump and kept constant by the use of a valve which automatically admitted air to the evacuated system whenever the pressure fell below 50 millimeters. This valve was constructed from a piece of iron pipe 1 inch in diameter and 5 feet long. The lower end was closed with a cap and the pipe filled with mercury to a depth of 76 centimeters. The upper end of the pipe was closed with a two-hole rubber stopper. In one hole was a long glass tube with the lower end beveled, which reached to the bottom of the mercury and could be raised or lowered as the barometer varied from day to day. In the other hole was a tube which passed just through the stopper and was connected on the outside with the apparatus to be exhausted. To prevent mercury from being drawn up and over into the apparatus by the air admitted, the end of the tube inside the stopper was drawn out and bent at a right angle and over this was slipped a cap made of larger tubing closed at the bottom, but having a fine opening in the side for air. This cap was about 6 centimeters long and extended about 3 centimeters below the end of the tube inside. If any mercury passed through this first fine opening into the cap, it would fall to the bottom without being drawn over into the apparatus or clogging the fine opening in the tube leading thereto. With this valve there was no difficulty in keeping a pressure of 50 millimeters constant within 1 millimeter.

Each distillate of sufficient volume, which was not too viscous or partly solid, was tested as to specific gravity, viscosity, and percentage absorbed when treated with concentrated sulphuric acid (specific gravity 1.84).

TABLE 9.—*Fractionation of six samples by distillation.*

		1.	2.	3.	4.	5.	6.
Specific gravity		0.801	0.808	0.815	0 8195	0.824	0.810
Viscosity		0.0404	0.0555	0.0589	....	0.0657	0.0441
Tubes passed through		1	3	3	4	4	Crude oil.
Normal pressure:							
Below 150°	Amount, cubic centimeters	36	1	13	5	2	45
	Specific gravity	0.720	....	0.737	....	....	0.714
	Viscosity	0.0052	....	0.0059	....	....	0.0047
	Acid treatment: Per cent absorbed	4.4	....	....	....	....	8.6
	Acid treatment: Specific gravity	0.722	....	0.7365	....	....	0.712
150°-200°	Amount, cubic centimeters	47	61	52	60	60	43
	Specific gravity	0.749	0.7465	0.756	0.757	0.759	0.759
	Viscosity	0.0075	0.0073	0.0075	0.0073	0.0072	0.0076
	Acid treatment: Per cent absorbed	3.4	4.4	8.2	11.3	12.0	9.3
	Acid treatment: Specific gravity	0.749	0.7469	0.750	0.749	0.750	0.752
50 mm. pressure:							
Below 140°	Amount, cubic centimeters	10	9	3	6	10	19
	Specific gravity	....	....	....	....	....	0.7805
	Viscosity	....	....	....	....	....	0.0112
	Acid treatment: Per cent absorbed	....	....	....	....	....	11.9
	Acid treatment: Specific gravity	....	....	....	....	....	0.7735
140°-200°	Amount, cubic centimeters	69	75	80	80	73	48
	Specific gravity	0.790	0.790	0.797	0.800	0.8015	0.804
	Viscosity	0.0212	0.0185	0.0211	0.0216	0.0196	0.0254
	Acid treatment: Per cent absorbed	3.4	4.4	8.9	9.6	14.8	11.0
	Acid treatment: Specific gravity	0.790	0.7885	0.7915	0.795	0.7915	0.799
200°-230°	Amount, cubic centimeters	25	30	23	25	30	21
	Specific gravity	0.813	0.8135	0.818	0.8225	0.822	0.823
	Viscosity	0.0556	0.0594	0.0573	0.0661	0.0505	0.0593
	Acid treatment: Per cent absorbed	....	4.3	11.0	8.4	10.5	8.7
	Acid treatment: Specific gravity	0.813	0.8125	0.816	0.8217	0.818	0.8175
230°-260°	Amount, cubic centimeters	23	27	23	20	24	22
	Specific gravity	0.8255	0.826	0.830	0.833	0.838	0.8355
	Viscosity	0.1106	0.1150	0.1116	0.1168	0.1259	0.1284
	Acid treatment: Per cent absorbed	3.4	8.5	7.0	8.8	7.6	12.6
	Acid treatment: Specific gravity	0.8255	0.8255	0.828	0.832	0.833	0.830
260°-300°	Amount, cubic centimeters	20	22	23	24	20	17
	Specific gravity	0.8395	0.838	Fluid.	Fluid.	Fluid.	Fluid.
	Viscosity	0.2520	....	....	....	....	....
300°-340°	Amount, cubic centimeters	25	[a] 30	27	30	26	25
	Specific gravity	0.847	0.849	Solid.	Solid.	Solid.	Solid.
340°-360°	Amount, cubic centimeters	21	[a] 26	22	....	19	20
	Specific gravity	Fluid.	Fluid.	Fluid.	....	Fluid.	Fluid.
Residue	Amount, cubic centimeters	22	17	30	45	35	32
	Specific gravity	Fluid.	Fluid.	Fluid.	Fluid.	Fluid.	Fluid.
Total volume, cubic centimeters		298	298	296	295	299	292

[a] To 355°.

Viscosity was measured by taking the time of flow of a measured volume of oil through a capillary, the viscometer used being the one described by Ostwald and Luther as modified by Jones and Veazey.[a] The capacity of the small bulb was 4.5 cubic centimeters and the diameter of the capillary such as to require from five to eight minutes for that amount of oil to flow through it, and 1 minute 2.6 seconds for the same amount of water. The viscosity as well as the specific gravity was always measured at a temperature of 20° C. Viscosities have been calculated from the formula $\eta = \eta_0 \frac{TS}{T_0S_0}$ in which η_0 is the coef-

[a] Zeitschr. physikal. Chemie, vol. 61, p. 651.

ficient of viscosity for water, S_0 is the specific gravity of water, and T_0 the time of flow of water through any given capillary at a given temperature; η is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as unity at any given temperature, and T is the time of flow of the given solution at that temperature. The value for pure water at 20° was taken from the work of Thorpe and Rodger.[a]

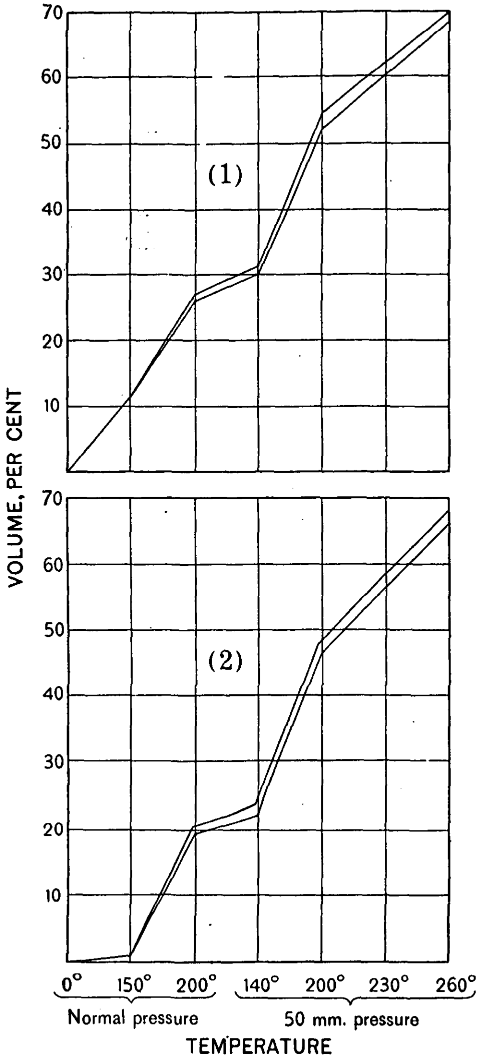

FIG. 1.—Curves showing proportion of hydrocarbons soluble in sulphuric acid, oils 1 and 2.

Thirty cubic centimeters of each of these distillates where that much oil was available, or all the oil there was where the volume was less than 30 cubic centimeters was mixed with an equal volume of concentrated sulphuric acid (specific gravity 1.84) and shaken for half an hour or longer in a shaking machine. The oil and acid were then poured into a separating funnel and the acid drawn off. The oil was then washed twice with water, once with aqueous NaOH, again with water, and then with this last wash water poured into a burette and allowed to settle. After standing overnight the volume was read.

The oils boiling below 200° (at 50 millimeters pressure) separated clear, but the heavy distillates were milky from water. The volume of these milky oils was read, their specific gravity was taken, and then the milkiness was removed by shaking and heating to about 60° with $CaCl_2$. The specific gravity of the clear oil was then taken and the proper correction made to the milky volume. In no case,

[a]Phil. Trans., vol. 185A, 1894, p. 397.

however, was this correction large, and only for the three or four heaviest oils did it exceed one-half of 1 per cent, the largest correction of all being 2.6 per cent for the distillate between 230° and 260° of the oil of specific gravity 0.824. An attempt to treat with acid the oils selected to be distilled resulted in so much loss from the formation of emulsions that the loss in volume and change in specific gravity could not be determined with any degree of accuracy.

The results of the distillation of these samples are summarized in Table 9.

"Fluid" means that the oil at 20° was partly solid, but would flow when the bottle was inclined; "solid" means that the oil would not change its shape when the bottle was turned upside down.

It was hoped that sulphuric acid of the strength used would dissolve only unsaturated hydrocarbons and leave untouched the paraffins and benzene. By long-continued shaking at ordinary temperatures, however, with acid of this strength benzene is dissolved, provided that the acid is in large excess. On being shaken for four hours 100 cubic centimeters of benzene was completely dissolved in 434 cubic centimeters of acid.

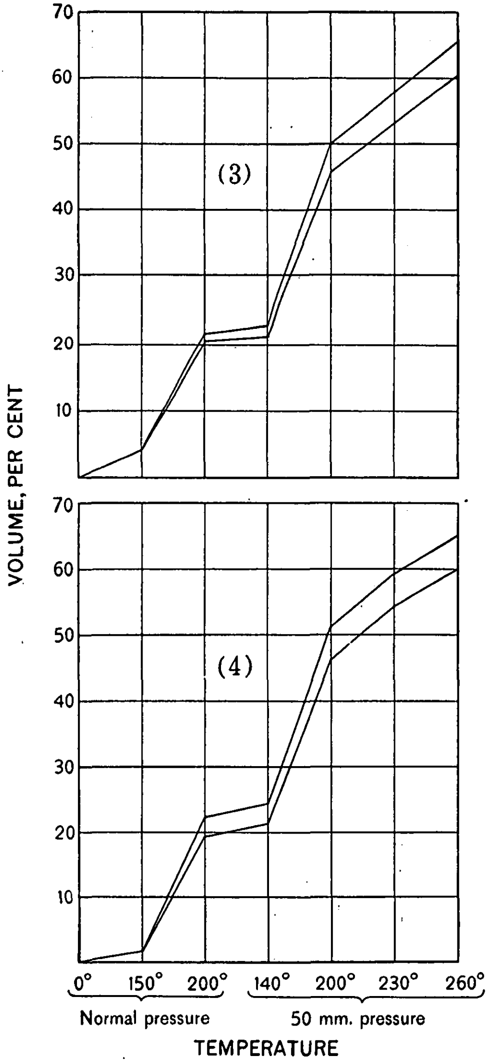

FIG. 2.—Curves showing proportion of hydrocarbons soluble in sulphuric acid, oils 3 and 4.

Three of the distillates which had been shaken with acid showed no action when treated with a mixture of equal parts of concentrated sulphuric acid and fuming nitric acid, whereas this nitrating mixture did act on distillates which had not been previously shaken with sulphuric acid. The action of the sulphuric acid, therefore, appears to have been complete.

The results of the acid treatment showed that over 90 per cent of the oil used consisted of paraffin hydrocarbons, and that in the filtration through earth the paraffin hydrocarbons tended to collect at the top of the tube and the unsaturated hydrocarbons at the bottom.

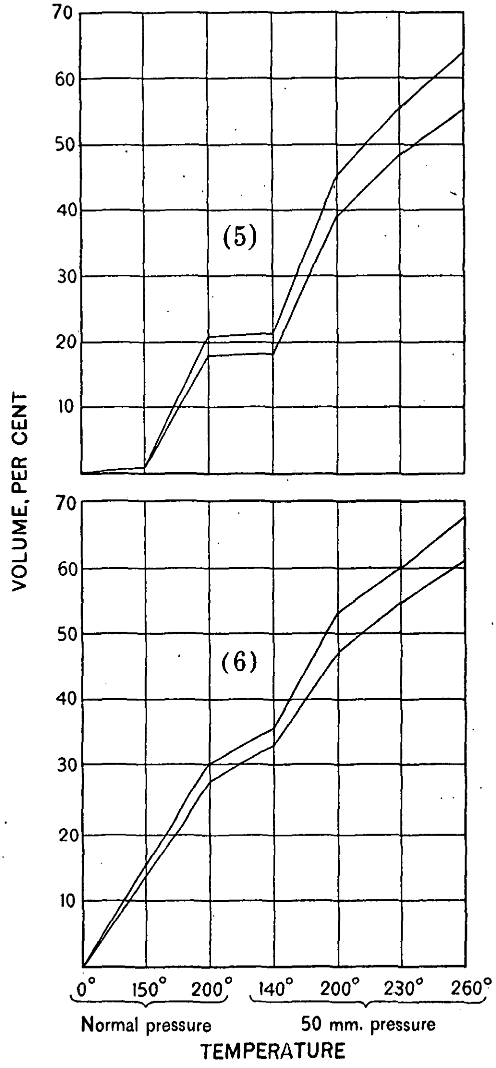

FIG. 3.—Curves showing proportion of hydrocarbons soluble in sulphuric acid, oils 5 and 6.

The increasing amount dissolved by sulphuric acid in the heavier oils may be seen in the curves shown in figs. 1 to 3. The abscissas represent temperatures and the ordinates volumes. The same distance on the x axis is taken to represent a distillate, whatever be the number of degrees over which it may have been collected. The upper curve represents the percentage of the total volume that distilled between given temperatures; the lower curve the percentage of the total volume recovered that was not absorbed by sulphuric acid (that is, the paraffin hydrocarbons). For the upper curve the ordinates are obtained by dividing the number of cubic centimeters in the distillate by the total volume of oil recovered. For the lower curve the ordinates are obtained by dividing the number of cubic centimeters in the distillate not absorbed by sulphuric acid by the total volume of oil recovered. The area between the two curves represents the proportion of hydrocarbons soluble in sulphuric acid. It will be seen that this is greatest for the oils of highest specific gravity.

Tables 4 and 6 show that in several tubes the specific gravity of the oil of grade A was greater than that of the grade B oil and in some tubes than that of the grade C oil. This irregularity was marked in tubes 48, 62, 68, 72, 74, and 80 of Table 4 and 112 and 114 of Table 6. A slight irregularity appears in tubes 20, 21, 24, 27, 40, 71, and 85 of Table 4 and tube 99 of Table 6. Of the oils in these tubes that were not colorless the color was strongest where the specific gravity was greatest, so that although the oil of grade A had passed through the most earth it was yet more strongly colored than that of grade B or C.

No reason for this variation has been established. It should be remembered, however, that the different oils rise in the earth with differing velocities, not because they differ from one another in specific gravity, but because they differ in surface tension. A rough attempt was made to determine relative surface tensions by measuring the height to which different oils rise in the same capillary tube, but although a kathetometer was used and the level of the oil in the capillary brought to the same spot each time the work sufficed only to show that the difference in the surface tension of the oils was so slight as to require very careful measurement to obtain results of any value.

That the viscosity shows the same irregularity in these oils as color and specific gravity appears from the following measurements:

TABLE 10.—*Specific gravity and viscosity of fractions from tubes 62 and 68.*

	62.		68.	
	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.
A	0.8155	0.0539	0.8205	0.0626
B	.808	.0469	.8043	.0469
C	.8095 .812	.0509 .0555	.810 .812	.0520 .0554
D	.8175 .8182	.0525 .0535	.817	.0524
E F	.823	.0612	.8225	.0606

Tube 50 (Table 4) showed an irregularity in grade B, which is also found in the viscosity:

TABLE 11.—*Specific gravity and viscosity of fractions from tube 50.*

	Specific gravity.	Viscosity.
A	0.8105	0.0532
B	.8148	.0559
C	.810	.0526
D	.815	.0526
EF	.819	.0552

The oils obtained by one fractionation of the crude petroleum (see Table 1) had the following viscosities:

TABLE 12.—*Specific gravity and viscosity of fractions from tubes 1 to 3.*

	1.		2.		3.	
	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.
A	0.796	0.0376	0.8012	0.0408	0.8022	0.0401
B	.808	.0529	.804	.0485	.803	.0470
C	.8125	.0501	.807	.0443	.8075	.0453
	.8137	.0529	.809	.0476	.810	.0471
D	.815	.0504	.8125	.0460	.812	.0472
E	.818	.0521	.8185	.0537	.8175	.0529
F	.8205		.823		.821	

That the viscosity does not increase with the specific gravity, particularly in the higher fractions, is apparent in two of the three series just given. The same is also shown in four tubes whose records are given in Table 4.

TABLE 13.—*Specific gravity and viscosity of fractions from tubes 21, 22, 47, and 53.*

	21.		22.		47.		53.	
	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.	Specific gravity.	Viscosity.
A	0.8038	0.0465	0.7997	0.0421	0.800	0.0453	0.803	0.0515
B	.8035	.0456	.802	.0485	.807	.0538	.8105	.0563
C	.8035	.0456	.8055	.0502	.814	.0542	.815	.0684
	.8052	.0485						
D	.805	.0479	.8063	.0496	.816	.0528	.8185	.0570
EF	.807	.0480	.808	.0510	.819	.0556	.820	.0559

This drop in viscosity which occurs at the bottom of the tube appears to be a regular occurrence in the dozen or so oils which have been tested. Further investigation of this point is intended.

WATER FRACTIONATION.

To test the effectiveness of water fractionation alone, 1,000 cubic centimeters of crude petroleum, previously chilled and filtered, of specific gravity 0.807, was mixed with 1,000 grams of earth and allowed to stand for twenty-four hours. Water was then added in small amounts and the oil collected. The results are stated below.

TABLE 14.—*Fractionation of crude petroleum with water.*

	Specific gravity.	Cubic centimeters.	Total water present (cubic centimeters).
A	0.8148	44	500
B	.8139	278	650
C	.816	211	800
D	.820	84	950
E	.8225	28	1,400
F	.8245	28	2,750
		673	

The fractions of large enough volume were then mixed with earth again and the oil replaced with water. One gram of earth was used for each cubic centimeter of oil, the earth having been heated and allowed to cool. Table 15 shows the results.

TABLE 15.—*Second fractionation of petroleum with water.*

	B.			C.			D.		
Specific gravity..	0.8139			0.816			0.820		
Cubic centimeters.	278			211			84		
Time (hrs.)	1.5			6			2.5		
	Specific gravity.	Cubic centimeters.	Water (cubic centimeters).	Specific gravity.	Cubic centimeters.	Water (cubic centimeters).	Specific gravity.	Cubic centimeters.	Water (cubic centimeters).
1..........	0.8185	10	70	0.820	10	80	0.822	32	76
2..........	.818	10	110	.820	20	125	.823	20	207
3..........	.818	21	164	.8195	72	250			
4..........	.818	20	....	.820	30	410			
5..........	.817	42	....	.820	10	588			
6..........	.819	10	216						
7..........	.820	44	277						
8..........	.820	16	428						
9..........	.8215	20	686						
		193			142			52	

It is apparent that while petroleum is fractionated by simply mixing the oil with fuller's earth and then displacing the oil from the earth with water, the fractionation is much more complete when tubes are used, as previously described.

It will be noticed that although fractions C and D of Table 14 are separated hardly at all by further treatment with earth and water (Table 15), yet the specific gravity of all the oil recovered is higher than that of the oil used; for example, fraction C (specific gravity 0.816) yields nothing lighter than 0.8195, and D (specific gravity 0.820) nothing lighter than 0.822.

To determine whether the specific gravity of the oil recovered will continue to rise after the oil is fractionated no further by repeated treatment, 330 cubic centimeters of specific gravity 0.819, obtained by uniting several products of one fractionation of the crude petroleum, were mixed with 330 grams of earth, and water was added, as shown in Table 16.

TABLE 16.—*Second fractionation of petroleum (combined sample) with water.*

	Specific gravity.	Cubic centimeters.	Total water present (cubic centimeters).
A..........	....	6	64
B..........	0.8215	50	....
C..........	....	12	214
D..........	.821	60	270
E..........	.821	82	413
F..........	.8225	26	613
		236	

When 75 cubic centimeters of fraction E (specific gravity 0.821) was next mixed with 75 grams of earth and 150 cubic centimeters of water was added, 51 cubic centimeters of oil whose specific gravity was unchanged, but whose color was reduced, was obtained. Fifty cubic centimeters of this oil when treated with earth and water, returned 34 cubic centimeters of oil with the color considerably lighter, but with the specific gravity still 0.821.

Although only two-thirds of the oil used is recovered when oil is mixed with earth and then displaced with water, yet this loss does not seem to affect the specific gravity of the oil obtained except in the first one or two treatments after the oil ceases to be fractionated. After these first treatments the oil recovered has the same specific gravity as the oil used.

OIL LOST IN THE FULLER'S EARTH.

The sum of the fractions of oil displaced from the earth is as a rule only about two-thirds of the volume of the oil used. A pressure of approximately 200 tons per square inch on the earth from which water has displaced all oil that it will results in the liberation of considerable water but very little oil. When earth which has been pressed is heated to 165° for three hours, considerable water distills over, but much less oil than would be expected; for example, from 75 grams of earth which should contain 25 cubic centimeters of oil only 4 cubic centimeters of oil was obtained. The earth was removed once from the flask and pulverized, and when the heat was discontinued the earth was thoroughly dry. On extraction with ether in a Soxlet extractor the earth gave a solution having the color of the original petroleum. The extraction was continued until the extract was colorless. On evaporation of the ether there remained about 8 cubic centimeters of a heavy oil with the color of the natural petroleum. Pressure, heat, and extraction with ether together gave about half the amount of oil which the earth must have contained.

Earth that had been used once was allowed to dry for several weeks at room temperature until it had lost all appearance of containing moisture. It was then pulverized, sifted, and 720 grams used in a tube with 740 cubic centimeters of the crude petroleum of specific gravity 0.810, with the following results:

TABLE 17.—*Fractionation of crude petroleum with earth that had been used once.*

	Specific gravity.	Cubic centimeters.
8 centimeters at top	....	0
Next 8 centimeters	0.8284	10
Next 18 centimeters	.8225	45
Next 30 centimeters	{ .8143	60
	{ .8155	80
Rest	{ .8175	83
	{ .819	114
		392

The first oil up the tube is evidently absorbed by heavy material in the earth; the first oil recovered dissolves material from the earth, which increases its specific gravity beyond that of the next fraction.

To see how much of the weight of the earth used the second time was due to material which it had retained from its first use, 300 grams of earth was mixed with 300 cubic centimeters of crude petroleum and the oil displaced by water. The oil recovered measured 205 cubic centimeters, and the weight of the earth after drying for several weeks at room temperatures was 347.5 grams. Fully 15 per cent, therefore, of the weight of the earth used the second time was solid matter which it had retained from its first use.

In all tests the earth was heated before it was used because it was believed that heating decreased the amount of oil lost in the earth. The earth was heated usually in iron pans on a gas stove until it ceased to form geysers when stirred. A tube 5 feet long and 1¼ inches in diameter, packed with 948 grams of earth that had not been heated, gave results as follows with 930 cubic centimeters of crude petroleum of specific gravity 0.810, after standing for twenty hours at diminished pressure:

TABLE 18.—*Fractionation of crude petroleum with earth that had not been heated.*

	Specific gravity.	Cubic centimeters.
Top 8 centimeters	0.803	30
Next 8 centimeters	.8045	38
Next 18 centimeters	.8103	85
Rest		440
		593

In a test of water fractionation alone with unheated earth but 242 cubic centimeters of oil was recovered from 500 cubic centimeters of crude petroleum.

The results obtained toward the close of our work indicate that the loss of oil when unheated earth is used is much less than we had supposed it to be. The gain from heating the earth may not pay for the trouble of heating it, and this point should be investigated before any very extensive experiments are again undertaken.

Earth after heating must become thoroughly cold before it is used to pack tubes. The earth holds its heat for several hours, and if it is used the same day on which it is heated, there is apt to be sufficient contraction in the tube to allow the oil to run up the side as it would in a vacuum.

The length of the tubes used was 5½ feet. A tube 9 feet long was connected to the same vacuum pump with several 5½-foot tubes and held for two days with a constant diminished pressure of about 10 centimeters Hg. The oil was drawn to the top of the shorter tubes; these were removed and a second lot substituted, and these also were fully impregnated with oil before the long tube was opened. When it was opened the oil had ascended but 45 centimeters, showing that the diminished pressure had not penetrated the 9 feet of earth and reached the bottom of the tube.

A shorter tube in which the earth was packed very much harder, so that it rang like an iron rod when pounded on the floor, was connected with a vacuum pump at one end and a manometer at the other, and showed diminished pressure on the manometer when the column of earth was 2 feet long but not when it was 2 feet 4 inches.

FRACTIONATING POWER OF SUBSTANCES OTHER THAN FULLER'S EARTH.

A clay from Topsham, Me., showed in tubes a power of fractionating as well as of decolorizing the higher fractions. Tubes 5 feet long and 1¼ inches in diameter were used, with petroleum of specific gravity 0.806. Compared with fuller's earth, the action was as follows:

TABLE 19.—*Fractionation of crude petroleum with clay from Topsham, Me., and with fuller's earth.*

	Clay.	Fuller's earth.
8 centimeters at top ... specific gravity	0.799	0.793
Next 8 centimeters ... do	.804	.800
Next 8 centimeters ... do	.810	.806
Next 10 centimeters ... do	.810	.807
Next 30 centimeters ... do	.812	.8092
Next 45 centimeters ... do	.812	.8112
Time required ... hours	69	76

Neither powdered brick made from the same clay nor powdered feldspar showed any power of fractionation.

Another similar clay (from Mere Point, Brunswick, Me.) showed a power of water fractionation, but its behavior in a tube was not tested. Four hundred grams of this clay, previously sifted and heated, was mixed with 170 cubic centimeters of crude petroleum of specific gravity 0.806 and allowed to stand for fourteen hours. Water was then added and the following fractions were obtained:

TABLE 20.—*Fractionation of crude petroleum with clay from Brunswick, Me.*

	Specific gravity.	Cubic centimeters.	Total water present (cubic centimeters).
A	0.8165	24	104
B	.817	60	133
C	.8188	20	234
D	....	6	374
		110	

The color was scarcely changed at all.

SUMMARY.

1. When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom.

2. When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterward, when more water is added.

3. When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffin hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom.

4. When oil is mixed with fuller's earth and then displaced with water, about one-third of the oil remains in the earth.