DEPARTMENT OF THE INTERIOR

UNITED STATES GEOLOGICAL SURVEY

GEORGE OTIS SMITH, DIRECTOR

BULLETIN 475

THE DIFFUSION OF CRUDE PETROLEUM THROUGH FULLER'S EARTH

WITH

NOTES ON ITS GEOLOGIC SIGNIFICANCE

BY

J. ELLIOTT GILPIN

AND

OSCAR E. BRANSKY

WASHINGTON

GOVERNMENT PRINTING OFFICE

1911

CONTENTS.

ILLUSTRATIONS.

THE DIFFUSION OF CRUDE PETROLEUM THROUGH FULLER'S EARTH.

By J. Elliott Gilpin and Oscar E. Bransky.[1]

INTRODUCTION.

It is well established that the petroleum obtained from the sandstones of the Upper Devonian and Mississippian epochs, generally known as Pennsylvania oil, differs markedly from the natural oil found in the Trenton limestone, usually designated Ohio oil and Trenton limestone oil. Both of these oils, in turn, are distinctly different from the petroleum occurring in the loose sands and soft shales of California. The unconsolidated Tertiary clays, sands, and gravels in the southern United States, particularly in Texas, yield still another variety of petroleum, characterized by properties more or less different from those of any of the other oils.

Not only do these differences exist in oils found in separate regions, but there are extreme variations in color and specific gravity, as well as in chemical composition, in many oils occurring in neighboring localities. On the other hand, close resemblances are often found between petroleums of widely separated regions. Some of the South American and many of the European oils, for instance, have been found to possess properties very similar to those of the oils of the southern United States, while the oil from the "Corniferous" limestone of Canada closely resembles the Ohio petroleum.

These variations in the oils of the United States and other countries have been carefully studied by many investigators. Warren, Storer, Mabery, Pelouze, Cahours, Schorlemmer, Beilstein, Markownikoff, Engler, and Kurbatoff have devoted their lives to the subject. The questions that naturally arise in connection with the variations are, Are these differences fundamental? Is the Pennsylvania petroleum as distinctly different from the Ohio oil as one chemical compound is from another? In answer to these questions, the following extract

[1] Dissertation submitted to the Johns Hopkins University by Oscar E. Bransky for the degree of doctor of philosophy. This research was aided by a grant received from the C. M. Warren committee of the American Academy of Arts and Sciences.

from a paper read by Mabery[1] in 1903 before the American Philosophical Society is of considerable importance:

> Now, after years of arduous labor, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of a simple definition—a mixture in variable proportions of a few series of hydrocarbons, the product of any particular field differing from that of any other only in the proportion of the series and the members of the series.

The evidence supporting this declaration has been and is accumulating constantly, and at the present time the view is generally accepted.

If petroleum, then, is everywhere one and the same substance, how can the extreme variations between the American oils be explained? Were the causes operating in the formation of the Pennsylvania oil, which is almost barren of sulphur and nitrogenous bodies, different from those acting in the production of the sulphur-bearing oils of Ohio or the heavy sulphur and nitrogenous oils of California?

To account for the formation of crude petroleum, two theories, the organic and inorganic, have been advanced. The Pennsylvania oil, according to these theories, may have been formed from either organic or inorganic substances, or from both. It is as yet impossible, however, to state conclusively from which of these sources the oil was derived. It is apparent, therefore, that the differences between the Pennsylvania and the Ohio, Texas, and California oils can not be explained on the assumption that the former was derived from organic remains and the latter from inorganic matter, or vice versa. If, however, the oils under discussion are organic in origin, they may have been formed either from vegetable or from animal remains. The following discussion is based on the assumption that these oils were derived from an organic source.

It has been suggested that the differences between these oils may be accounted for by assigning a vegetable origin to the Pennsylvania oil and an animal origin to the others. Mabery[1] states that—

> It would seem that the small proportion of these bodies [sulphur, nitrogen, and oxygen compounds] in the Pennsylvania oil, as compared with the larger proportions in the limestone oils and California oil, should be strong evidence in favor of a different origin, that the Pennsylvania oil came from organic vegetable remains, which should permit of the small amounts of sulphur and nitrogen compounds from this class of oils.

Newberry, Peckham, Orton, and other geologists also favor the view that the Pennsylvania oil is of vegetable origin and is derived from the organic matter of the bituminous shales of the Devonian period.

The association of this oil with a vegetable source has been compelled, it seems, first, by the fact that the oil is of a different character from the limestone oils of Ohio and those of Texas and California;

---

[1] Proc. Am. Philos. Soc., 1903.

second, by the fact that the Pennsylvania petroleum is found in strata that bear but few fossils; third, by the belief that the Chemung and immediately overlying formations are barren in animal organic remains; and fourth, by the existence of large quantities of microscopic fossils, whose origin many believe is vegetable, in the black shales of the Lower and Middle Devonian formations to which many investigators are inclined to refer the origin of the Pennsylvania oil.

Pennsylvania oil differs markedly from the Ohio, Texas, and California oils. Investigation has shown that it contains a much larger proportion of the paraffin hydrocarbons and a much smaller percentage of benzene, unsaturated hydrocarbons, sulphur, and nitrogenous bodies. It is further generally admitted that the Pennsylvania oil was not formed in place. These two facts aided strongly in assigning a vegetable origin to this oil.

To what strata should the source of the oil be referred? The great coal formations of Pennsylvania, lying above the Chemung, seem at first glance to offer a solution. It is a notable fact, however, that these formations have not, up to the present time, been connected, either chemically or geologically, with the Pennsylvania oil. The possibility exists that it may have been formed from vegetable remains in the Carboniferous formations above and reached its present position in the Chemung by downward diffusion. This view rests on the physical fact that a liquid diffuses by the force of capillarity in all directions, downward as well as upward. Little attention has been given to this possibility, but it seems to deserve a careful study. Owing, however, to the universal association of water under hydrostatic pressure with natural oil and gas, the migration of the latter is generally upward. This fact is attested by the accumulation of oil in anticlinal folds when water is present and by the existence of the remarkable gushing oil wells. That the Pennsylvania oil, if not formed in place, ascended to its present location seems, therefore, more probable.

In what strata below the Chemung, then, was the oil originally produced? It has been previously mentioned that a number of investigators refer the source of the oil to the black shales of the Lower and Middle Devonian. The organic matter of these shales is composed largely of microscopic sporangites, which suggest the existence, according to Orton, of masses of floating vegetation, or sargasso seas. According to this view the Pennsylvania oil is of vegetable origin and its primitive abode was in the shales of Devonian age lying below the Chemung formation, to which it ascended under the influence of natural agencies. A second view, which assigns an animal origin to the oil, is that it was formed in the fossil-bearing strata of Chemung age and diffused to the sandstone reservoirs in which it is now found, and that during such a diffusion its original character was changed.

Prof. C. K. Swartz, of Johns Hopkins University, who has made a critical study of the Chemung strata in Maryland, states that fossil remains exist in considerable abundance in the strata of this age in Maryland and adjoining areas. In Pennsylvania the corresponding strata have been found to bear many fossils. It is possible, therefore, that the oil may have formed in these strata and then diffused to strata barren of fossil remains, where it now exists.

The evidence accumulated in this investigation seems to show that it is not necessary to assign a vegetable origin to the Pennsylvania oil to explain the differences between it and the oils of Ohio and California. It is clear from the results of this and other investigations that when such oils as those of Ohio, California, and Texas, which seem to be animal in origin, are allowed to diffuse through such porous media as fuller's earth, they yield oils very similar to those of Pennsylvania. By assuming, therefore, that the Pennsylvania oil migrated from some primitive source, in which it may have been formed from animal remains, through shales, limestones, and sandstones, its peculiar character can be understood.

Wherever the original home of the oil may have been, it seems probable that it migrated to its present location from below. It is with the changes occurring in crude petroleum as a result of such a migration through porous strata that the present investigation is primarily concerned.

In 1897 David T. Day,[1] on his own observations and those of John N. MacGonigle, proposed the view that the Pennsylvania oil, at some past time, possessed properties very similar to those of the Ohio oil, but that in its migration to its present abode from strata below its character was changed. Guided by this view, Day conducted, in the laboratories of the United States Geological Survey, an investigation into the changes occurring in crude petroleum when allowed to diffuse through porous media, such as fuller's earth. He demonstrated clearly that an oil resembling the light Pennsylvania oil could be readily produced in the laboratory from the heavier crude Ohio oil. Glass tubes were packed firmly with the dry earth, through which the crude oil diffused by its own force of capillarity. From the earth of the upper sections of the tubes very light, even colorless, oils were liberated by treatment with water; from the earth of the lower sections of the tubes much darker and heavier oils were obtained.

The fractionation, it will be observed, is effected entirely by capillarity; oils with different surface tensions rise with different velocities through the capillary openings, such as the fine interstices and minute pores of the fuller's earth. A separation of the various constituents making up the complex of any one oil is thus brought

[1] Proc. Am. Philos. Soc., 1897.

about. The view once held that this phenomenon is chemical was clearly disproved by Engler and Albrecht[1] in 1901, and later by other investigators.

Any medium, therefore, sufficiently fine grained and porous to afford capillary spaces, causes a separation of the constituents of any mixture, provided they possess different surface tensions. The compact sandstones, shales, and limestones that recur in many cycles throughout the earth's crust present an excellent medium for the separation of the constituents of so complex a mixture as petroleum. The force of capillarity, assisted by the hydrostatic pressure of the water occurring in the interior of the earth, acting over vast periods of time, is, it seems safe to state, sufficiently powerful to transport the oil from the lower strata to those above. That the conditions, therefore, to cause such a migration, with the consequent fractionation of the original oil, are abundantly present appears extremely probable.

The members composing the natural oil may be grouped under the following general heads: Paraffin; aromatic, unsaturated hydrocarbons; and sulphur, nitrogen, and oxygen compounds. The behavior of the paraffin and unsaturated hydrocarbons when subjected to fractionation will be considered first.

Day early observed that the unsaturated hydrocarbons are less diffusible than the paraffin hydrocarbons. Later, Gilpin and Cram[2] demonstrated that when petroleum is allowed to diffuse through tubes packed with fuller's earth, the unsaturated hydrocarbons collect in the earth of lower sections of the tubes, while the paraffins tend to accumulate in the lightest fraction at the top of the tube. In the present investigation these results have been fully confirmed. On pages 44–45 are given the bromine absorption values and the percentages by volume absorbed by concentrated sulphuric acid of the various oils obtained from definite sections of a tube. These figures indicate conclusively that the amount of unsaturated hydrocarbons is much greater in the oils from the lower sections of the tube than in the lightest fractions at the top of the tube. Furthermore, the bromine absorption values for the oils of similar fractions of the first, second, and third fractionation, given on page 46, show that in the progress of the fractionation more and more of the unsaturated hydrocarbons are removed. Herr,[3] in Russia, has likewise observed that these hydrocarbons are less diffusible than the paraffins.

An interesting confirmation of these experiments in nature has been recently presented by Clifford Richardson and K. G. MacKenzie.[4] They found that a colorless natural naphtha from the Province of

[1] Zeitschr. angew. Chemie, 1901, p. 889.
[2] Bull. U. S. Geol. Survey No. 365, 1908.
[3] Petroleum, August, 1909.
[4] Am. Jour. Sci., May, 1910.

Santa Clara, Cuba, contained practically no unsaturated hydrocarbons but was almost entirely a mixture of naphthenes and paraffins. Concentrated sulphuric acid absorbed but 0.76 per cent by volume, while fuming sulphuric acid absorbed only 1.8 per cent. With the naphtha were obtained water and an emulsion of water, oil, and clay. These investigators are of the opinion that the naphtha was "undoubtedly formed by the upward filtration of heavy petroleum through the clay stratum, similar to the fuller's earth filtrations of Gilpin and Cram, and the light naphtha in the upper part of the stratum was afterwards partly liberated by saline waters, the oil remaining in the clay forming, with water, the emulsion."

A comparison of the proportions of the unsaturated hydrocarbons in the Ohio and Pennsylvania oils shows that the latter contain a much smaller percentage of these hydrocarbons. By assuming that the Pennsylvania oil diffused upward through such porous media as shales and limestones to its present location in the sandstones, it is possible to account for the smaller amounts of the olefines in it on the basis of the experimental work described above. In its passage through the capillary interstices of the clays, limestones, and sandstones, a fractionation, resulting in the removal of the unsaturated hydrocarbons, probably occurred. It is reasonable to conclude, therefore, that the variation in the content of unsaturated hydrocarbons between the Ohio, Texas, and California oils, on the one hand, and the Pennsylvania oil, on the other, can probably be accounted for by assuming that the Pennsylvania oil was subjected to capillary diffusion at some time in its career. That the light-colored naphthas occurring in different parts of the world were originally darker and heavier oils, and that their primitive character was changed by diffusion through media possessing the power of fractionation seems very probable.

The behavior of the aromatic hydrocarbons, in particular benzene, in passing through fuller's earth constitutes one of the subjects of this investigation. The results of this study, given in detail on pages 15–28, indicate clearly that benzene, like the olefines, tends to collect in the lower sections of a tube of fuller's earth through which the benzene, in solution, is allowed to diffuse. That the aromatic hydrocarbons in the natural oil behave in a similar manner has not yet been decided. The proportion of these hydrocarbons in the Illinois oil investigated was too small to enable us to determine accurately their amounts in the fractions obtained by the capillary diffusion of the crude oil. The ordinary methods, such as nitration with the mixture of nitric and sulphuric acids, and sulphonation, employed for the quantitative determination of the aromatic hydrocarbons, could not be used in this work, owing to the fact that these reagents readily affect the unsaturated hydrocarbons as well. A study of the conduct of the aromatic hydrocarbons in the natural oil containing large amounts of them will be undertaken in the near future. It is probable, however, that the benzene and homologous compounds in crude petroleum behave like the unsaturated hydrocarbons.

The presence of larger amounts of aromatic hydrocarbons in the Ohio than in the Pennsylvania petroleum, and of still larger amounts in the California and Texas oils, seems to afford further evidence in favor of the view that the Pennsylvania oil has undergone much greater diffusion, and consequently greater fractionation, than any of the other oils.

The conduct of the sulphur compounds in petroleum in the process of diffusion is similar to that of the unsaturated hydrocarbons. On page 46 the percentages of sulphur present in the oils from different parts of the tube and different stages of fractionation are tabulated. One series of figures will be given here to show the behavior of the sulphur compounds.

Behavior of sulphur compounds in fractionation.

	Per cent of sulphur.
First fractionation (lot 6):	
Fraction A	0.04
Fraction B	.05
Fraction D	.09
Fraction E	.16
Second fractionation: Fraction A	.04
Third fractionation: Fraction A	.003

It is clear from these figures that the sulphur compounds, like the unsaturated hydrocarbons, tend to collect in the lower sections of a layer of fuller's earth through which petroleum is allowed to diffuse.

In 1902 Clifford Richardson and E. C. Wallace,[1] in an investigation on the occurrence of free sulphur in Beaumont petroleum, passed the oil upward through a fuller's earth filter similar to one described by Day at the petroleum congress in Paris in 1900, and obtained distinct fractionation. The percentages of sulphur in the crude oil and in the oils obtained by this fractionation were determined. The results are given in the following table:

Percentages of sulphur in crude oil and after fractionation.

	Specific gravity $\frac{25^\circ}{25^\circ}$	Per cent of sulphur.
Crude oil	0.9140	1.75
First fraction	.8775	.80
Second fraction	.8986	.91
Third fraction	.9038	1.04

[1] Jour. Soc. Chem. Ind., March, 1902.

It seems reasonable to assume from these results that the variations in the sulphur content between the Pennsylvania and Ohio oils may be satisfactorily explained by the view that the former oil, as previously stated, diffused from other strata to its present location, and in its migration a large part of its original content of sulphur was removed. Further work on this point will be undertaken in the Johns Hopkins University laboratory.

No careful study of the behavior of the nitrogen and oxygen compounds in petroleum diffusing through a porous medium has yet been undertaken, but such an investigation will be pursued in the same laboratory later. It is probable that such an investigation will show that the nitrogen compounds act like the sulphur and unsaturated compounds.

OBJECT OF THIS INVESTIGATION.

The present investigation was undertaken for the immediate purpose of studying the changes occurring in the crude Illinois oil when allowed to diffuse through fuller's earth. The more distant but more fundamental object was to gain further insight into the causes of the variations among the oils of this country.

PRELIMINARY EXPERIMENTS.

RELATIVE AMOUNTS OF OIL LOST IN HEATED AND UNHEATED FULLER'S EARTH.

Before the actual investigation of the Illinois oil was undertaken, experiments were made to determine the relative amounts of oil lost in heated and unheated fuller's earth.[1] In the work of Gilpin and Cram the earth was always heated until geysers ceased to form and then allowed to cool for several hours. The purpose of heating the earth was to obtain larger yields of oil, but toward the close of their investigation it became apparent that the amount of oil lost in unheated fuller's earth was not as large as they had supposed it to be. As much time and labor is consumed in the process of heating and then cooling the earth, it seemed advisable to settle this point at the outset.

The apparatus employed for the present investigation was essentially the same as that used by Gilpin and Cram. Figure 1 shows the arrangement of the diffusion tubes. A, A, A, A are tin reservoirs made to hold somewhat more than a liter. The tin tubes B, B, B, B, 5½ feet long and 1¼ inch in diameter, rest upon narrow tin supports placed upon the bottom of the reservoirs, and are connected with the branched glass tube F by suction tubing fitted with pinchcocks at

[1] The fuller's earth employed in this work was generously supplied by the Atlantic Refining Co., of Philadelphia.

E, E, E, E. The branched glass tube is connected with the large tank C, which serves to maintain fairly constant pressures; C is in turn joined by the glass tube D to a manometer, and the latter is connected with the Chapman pump. Any number of tubes may be set up in series under the same diminished pressure.

After the tubes are closed at their lower ends with grooved corks covered with muslin to prevent the earth from sifting out, they are packed to the desired firmness with the fuller's earth. Each tube is then placed in its own reservoir, containing the oil to be fractionated. When they are connected to the branched tube F, the pressure in the system of tubes is reduced by the suction pump. The oil rises at first rapidly; then its diffusion gradually diminishes in power. When the reservoirs are almost exhausted, the tubes are disconnected and

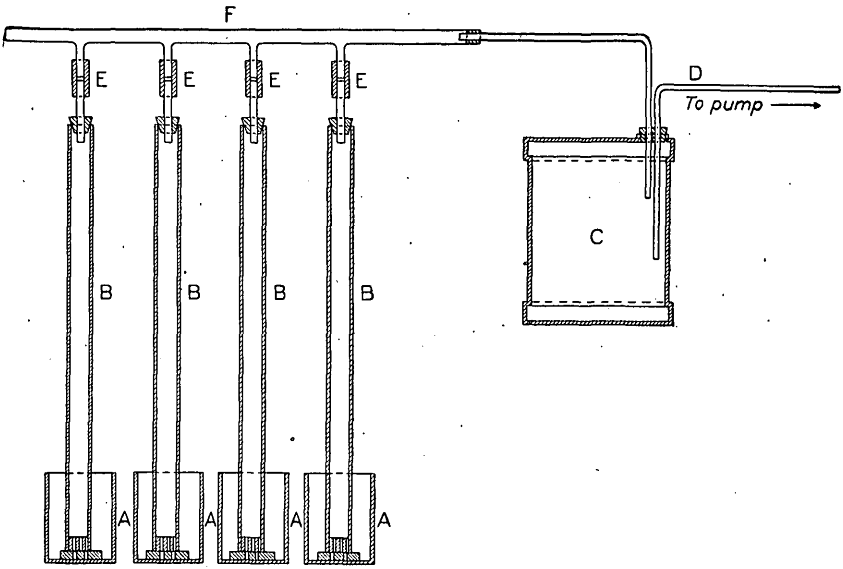

FIGURE 1.—Arrangement of diffusion tubes. See text for explanation.

clamped with the bottom ends up above shorter tubes of the same diameter, into which the oil-laden earth is allowed to slide. These shorter tubes are made of two curved pieces, joined at the bottom by a cap and held together at the top by a ring. The cylinders are opened by slipping off the ring and cap and removing one of the curved pieces, and the earth is divided into the desired sections. When water is added in portions to the earth and the two mixed thoroughly, the oil is displaced and is drawn off in separate portions.

Six tubes packed with heated fuller's earth were set up alternately with six tubes filled with the unheated earth. Each tube was placed in its own reservoir containing 950 cubic centimeters of crude oil. The oil was allowed to diffuse upward through the tubes under diminished pressure. The oil in the reservoirs was not exhausted until

16 hours had elapsed. As the tubes did not rest directly upon the bottoms of the reservoirs, a small amount of oil remained in each; the volumes were subtracted from the volumes originally supplied. The earth from each tube was shaken into a bucket, and the oil was recovered by displacement with water, as described above. The results of these experiments are arranged in the following table:

Pennsylvania oil lost on heated and unheated fuller's earth.

Heated fuller's earth.

Tube.	Weight of fuller's earth (grams).	Oil absorbed by earth (cubic centimeters).	Oil recovered (cubic centimeters).	Oil lost. Cubic centimeters.	Oil lost. Per cent.
1	1,005	850	450	390	46
3	1,000	792	460	332	41
5	1,035	850	500	350	41
7	1,070	865	450	415	48
9	1,035	813	430	383	47
11	1,045	885	530	355	41
	....	5,055	2,830	2,225	44

Unheated fuller's earth.

Tube.	Weight of fuller's earth (grams).	Oil absorbed by earth (cubic centimeters).	Oil recovered (cubic centimeters).	Oil lost. Cubic centimeters.	Oil lost. Per cent.
2	1,075	917	585	332	36
4	1,095	853	562	291	34
6	1,065	840	500	340	42
8	1,045	814	435	379	46
10	1,035	873	510	363	41
12	1,055	850	485	365	41
	....	5,147	3,077	2,070	40

The petroleum employed in the above-described experiments was a dark-green oil from Venango County, Pa., possessing a specific gravity of 0.810. As the Illinois oil which was used in the fractionation proper, described later, differs materially from the Pennsylvania petroleum, further experiments were undertaken to determine the relative amounts of this oil retained by heated and unheated earth.

Ten tubes, of which five were packed as uniformly as possible with fuller's earth that had been heated until geysers ceased to form and the other five with unheated earth, were placed in reservoirs, each containing 950 cubic centimeters of Illinois oil, having a specific gravity of 0.8375. When the oil was entirely absorbed, the tubes were taken down, the oil-laden earth was shaken into two breakable cylinders, and divided into six sections—A, 10 centimeters in length, measured downward from the level to which the oil had ascended; B, the next 15 centimeters; C, 20 centimeters; D, 30 centimeters; E, 35 centimeters; F, the remainder of the earth to the bottom of the tube. Section F was entirely discarded.

The earth was then treated with separate portions of water. The oils displaced by the successive additions of water were collected separately and are designated in the table below as A^1, A^2, B^1, B^2, and so on; A^1 is the oil first displaced, A^2 the oil next expelled by further additions of water. The volumes and specific gravities of the recovered oils were determined. The results are expressed in the following table:

Fractions of Illinois oil recovered after diffusion through fuller's earth.

Fraction.	Heated fuller's earth.		Unheated fuller's earth.	
	Specific gravity.	Volume (cubic centimeters).	Specific gravity.	Volume (cubic centimeters).
A^1	0.8287	100	0.8320	72
A^2	....	....	.8352	22
B^1	.8390	157	.8405	184
B^2	.8485	35	.8451	124
C^1	.8441	280	.8443	270
C^2	.8507	67	.8495	147
D^1	.8450	393	.8483	368
D^2	.8490	132	.8517	210
E^1	.8537	339	.8500	360
E^2	.8564	174	.8569	185
		1,701		1,942

In these experiments the percentage of oil lost in the unheated earth is less than the percentage of oil lost in the heated earth. Gilpin and Cram, employing heated earth, recovered in one test 5,951 cubic centimeters from 9,070 cubic centimeters, and in another 5,415 cubic centimeters from 8,915 cubic centimeters, the amount of oil lost in the earth in the first test corresponding to 34 per cent and in the second to 39 per cent. It is clear, therefore, that there is not sufficient compensation, if any, for the time and labor spent in heating the earth. In the investigations that followed the unheated fuller's earth was always used.

THE DIFFUSION OF BENZENE IN SOLUTION THROUGH FULLER'S EARTH.

In order to deal more intelligently with the fractionation of the crude Illinois petroleum, it seemed advisable to study the behavior of the individual aromatic hydrocarbons, especially benzene, both alone and mixed with paraffin hydrocarbons, when allowed to diffuse upward through fuller's earth. Gilpin and Cram established the fact that the paraffin hydrocarbons tend to collect in the lightest fractions at the top of the tube. Their method consisted in distilling by heat six samples of oils of different specific gravities, each 300 cubic centimeters in volume, and collecting 10 fractions between definite intervals. Five of these samples consisted of oil partly fractionated by fuller's earth and the other sample consisted of the crude oil. The specific gravity and viscosity of each fraction were determined; then to 30 cubic centimeters, or to all there was where the amount was less than 30 cubic centimeters, an equal volume of concentrated sulphuric acid (specific gravity 1.84) was added, and the two were shaken by a machine for half an hour or longer. The volume of the oil unaffected by the acid was measured, and by subtraction the volume of oil absorbed was calculated. This latter volume represents only approximately the percentage of unsaturated hydrocarbons present in the oil, because sulphuric acid of this strength readily dissolves benzene when the two are thoroughly shaken.

In this investigation various solutions of benzene and a refined paraffin oil, boiling between 160° and 240° and only slightly attacked by sulphuric acid, were made up and allowed to rise in tubes packed with unheated fuller's earth. The pressure in the system was reduced very little, because the liquid, under a greatly diminished pressure, rose too rapidly. About 24 hours elapsed before the oil in the reservoirs was exhausted.

The earth in each tube was shaken out and divided into six sections. Beginning at the uppermost point to which the oil had ascended grade A consisted of the first 8 centimeters, grade B of the next 8 centimeters, grade C of 18 centimeters, grade D of 30 centimeters, grade E of 35 centimeters, and grade F of the remainder of the earth, depending on the height to which the oil had ascended. This division is the same as that used by Gilpin and Cram. The oil in the earth was displaced by water and drawn off.

The specific gravity of each fraction was determined by means of the Mohr-Westphal balance at exactly 20° C. The fourth decimal place is not to be considered as strictly accurate, but gives a closer approximation to the truth than if it were entirely discarded.

The viscosity was determined by means of the viscosmeter described by Ostwald and Luther and modified by Jones and Veazey.[1] The time taken for measured volumes of the oils to drain from the small bulb, whose capacity was 4.5 cubic centimeters, was compared with the time required for a similar amount of water to run through. These values were substituted in the equation—

$$y=y_0\frac{TS}{T_0S_0}$$

in which—

y_0 =coefficient of viscosity of water. For this, 0.01002, the value obtained by Thorpe and Rodger,[2] was used.
T =time of flow of liquid under examination.
S =specific gravity, measured at 20° C., of liquid under examination.
T_0 =time of flow of water.
S_0 =specific gravity of water. Since the balance was calibrated for water 20° C., the value for S is unity.
y =coefficient of viscosity of oil under examination.

---

[1] Zeitschr. physikal. Chemie, vol. 61, p. 651.
[2] Philos. Trans., vol. 185A, 1894, p. 397.

The amount of benzene present in each fraction was determined by shaking the oil with an excess of ordinary concentrated sulphuric acid (specific gravity 1.84) for periods of time varying from 30 to 60 minutes, until there was no further diminution in the volume of the oil.

The results of the experiments tabulated below demonstrate the power of this acid to dissolve benzene, forming benzene-sulphonic acid:

Action of concentrated sulphuric acid (specific gravity 1.84) on benzene when shaken by machine.

Benzene taken (cubic centimeters).	Acid taken (cubic centimeters).	Time shaken (minutes).	Benzene dissolved.	
			Cubic centimeters.	Per cent.
25	25	30	7	28
25	50	30	18	72
25	75	30	25	100

The reagents usually employed for removing benzene are a mixture of fuming nitric and concentrated sulphuric acid. The work of Worstall,[1] Francis and Young,[2] and others shows that such a mixture readily attacks the paraffin hydrocarbons, especially at higher temperatures, forming nitro-derivatives and also oxidizing them to a considerable extent. Furthermore, in working with this mixture the oil must be kept at a low temperature to prevent a violent reaction, which results usually in the decomposition of the oil. In this work, therefore, in order to avoid the danger of attacking the paraffin hydrocarbons and for the sake of convenience concentrated sulphuric acid was used.

It seems advisable, at this point, to call attention to the fact that the power of ordinary concentrated sulphuric acid to remove benzene and homologous hydrocarbons has been generally overlooked. In order to determine the percentages of these hydrocarbons it is customary to shake the oils to be analyzed with concentrated sulphuric acid and then to nitrate the unaffected oil. It is assumed that the acid removes such substances as the unsaturated hydrocarbons and does not attack the aromatic hydrocarbons. Thus, P. Poni,[3] in determining the presence and percentage of aromatic hydrocarbons in Roumanian petroleum, collected fractions between 35° and 70° C., distilled under diminished pressure. These were purified by shaking with sulphuric acid, and each was nitrated with a mixture of 1 part

[1] Am. Chem. Jour., vol. 20, p. 202; vol. 21, p. 210.
[2] Jour. Chem. Soc., 1898, p. 928.
[3] Annales sci. Univ. Jassy, 1907, pp. 192–202. (Abstracted in Jour. Chem. Soc., vol. 92, 1907.)

of nitric acid (specific gravity, 1.52) and 2 parts sulphuric acid (specific gravity, 1.8). The recovered oils were assumed to be paraffins and naphthenes, while the proportions of benzene and unsaturated hydrocarbons were calculated from the nitro-products obtained. It is obvious from the results obtained in the present work that some of the benzene was removed in the process of purifying the fractions. The amount dissolved depended on the vigor of the shaking and its duration, as well as the strength of the sulphuric acid. It is highly probable, therefore, that Poni's percentage of benzene is too low.

In the study of the mixture of benzene and paraffin hydrocarbons 25 cubic centimeters of each fraction, or all there was when the amount was less, was shaken vigorously with three times the volume of concentrated sulphuric acid for 30 minutes. The amount unabsorbed was measured over the acid in a burette, after sufficient time had been allowed for most of the oil mechanically held in suspension to rise. The oil was then reshaken with a little more acid for 15 minutes and the volume again read. When the benzene was present in small quantities one shaking was sufficient; when larger amounts were present shaking was repeated.

The paraffin oil employed (specific gravity, 0.797) was shaken several times with fresh portions of concentrated sulphuric acid until the coloration of the acid disappeared, and only a slight diminution in volume occurred when a small sample of the oil was thoroughly shaken by machine for some time with the acid. The oil was then washed with water and sodium hydroxide and dried over calcium chloride. The specific gravity decreased to 0.792.

When this oil was mixed with benzene in various proportions and allowed to diffuse upward through fuller's earth the following results, arranged in series, were obtained:

Results of diffusion of benzene and paraffin hydrocarbons through fuller's earth.

Series 1, oil alone.

[Specific gravity, 0.792. Level of oil, 28 centimeters.]

Grade.	Volume of oil (cubic centimeters).	Specific gravity.	Viscosity.	Per cent of benzene.
A	11	0.789		(a)
B	17	.792		
C	60	.7912	0.0154	
D	100	.7915	.0140	
E	150	.7913	.0134	
F	139	.7915	.0134	
	477			
Original volume b	778			

a In this series the percentages of benzene are not given, because the paraffin oil alone was used.

b The original volumes of solution vary with each series, owing to the fact that more or less always remained behind in the reservoir below the level of the tin support. In series 1, 2, 3, and 4, 950 cubic centimeters was supplied to each reservoir; in the rest of the series each reservoir contained originally 1,000 cubic centimeters.

Results of diffusion of benzene and paraffin hydrocarbons through fuller's earth—Contd.

Series 2, 90 per cent oil (0.792), 10 per cent benzene (0.8775).

[Specific gravity, 0.7983. Level of oil, 22 centimeters.]

Grade.	Volume of oil (cubic centimeters).	Specific gravity.	Viscosity.	Per cent of benzene.
A	11	0.787	....	10.0
B	16	.7923	....	13.3
C	56	.7935	0.0131	11.6
D	109	.7943	.0123	14.8
E	145	.7957	.0120	14.4
F	245	.7955	.0116	14.8
	582			
Original volume	872			

Series 3, 80 per cent oil (0.792), 20 per cent benzene (0.8775).

[Specific gravity, 0.806. Level of oil, 25 centimeters.]

A	25	0.7948	0.0147	15.3
B	35	.7981	.0130	16
C	78	.8017	.0117	22.4
D	128	.8005	.0105	21.6
E	166	.801	.0107	22.4
F	146	.798	.0110	20.8
	576			
Original volume	892			

Series 4, 75 per cent oil (0.792), 25 per cent benzene (0.8775).

[Specific gravity, 0.810. Level of oil, 33 centimeters.]

A	16	0.800	(a)	22
B	35	.803	0.0129	23.3
C	74	.8077	.0126	24
D	128	.805	.0114	24
E	152	.8068	.0102	26
F	120	.8065	.0105	28
	525			
Original volume	655			

Series 5, 75 per cent oil (0.794 [b]), 25 per cent benzene (0.8775).

[Specific gravity, 0.8115. Level of oil, 24 centimeters.]

A	25	0.7942	0.0123	14
B	28	.8048	.0104	21.2
C	70	.8105	.0094	31.2
D	140	.8100	.0094	27.6
E	172	.8100	.0094	32
F	144	.8093	.0095	27.6
	579			
Original volume	875			

[a] The viscosities of grades A and B in a few of the tables are not given, because in these series, the first made, the decision to determine the viscosities was reached only after the fractions had been treated with acid. As A and B were small in amount, all the oil was used in this treatment.

[b] As the quantity of oil of specific gravity 0.792 was not sufficient for all the series, a second quantity with the specific gravity 0.794 was prepared. This oil was used in series 5, 8, 9, and 10.

Results of diffusion of benzene and paraffin hydrocarbons through fuller's earth—Contd.

Series 6, 75 per cent oil (0.792), 25 per cent benzene (0.8775).

[Specific gravity, 0.8083. Level of oil, 27 centimeters.]

Grade.	Volume of oil (cubic centimeters).	Specific gravity.	Viscosity.	Per cent of benzene.
A	22	0.7995	0.0106	17.5
B	32	.8055	.0099	24.4
C	82	.8052	.0100	24
D	155	.8085	.0093	28.8
E	190	.8085	.0093	31.2
F	93	.8063	.0096	28.8
	574			
Original volume	923			

Series 7, 59.5 per cent oil (0.792), 40.5 per cent benzene (0.8775).

[Specific gravity, 0.8223. Level of oil, 9 centimeters.]

A	a 9	....	....	....
B	15	0.8069	....	14
C	48	.816	0.0103	22.4
D	96	.8182	.0086	31.2
E	160	.820	.0082	31.6
F	255	.8185	.0083	29.6
	583			
Original volume	922			

Series 8, 50 per cent oil (0.794), 50 per cent benzene (0.8775).

[Specific gravity, 0.8295. Level of oil, 17 centimeters.]

A	22	0.8122	....	24.5
B	32	.819	....	28.4
C	78	.8287	0.0077	44.8
D	111	.8275	.0077	47.6
E	155	.827	.0077	39.2
F	192	.8256	.0079	36.4
	590			
Original volume	960			

Series 9, 50 per cent oil (0.794), 50 per cent benzene (0.8775).

[Specific gravity, 0.8315. Level of oil, 18 centimeters.]

A	18	0.816	0.0091	26
B	24	.8210	.0085	34.5
C	76	.8275	.0078	47.6
D	136	.8283	.0077	50
E	174	.8293	.0076	49.2
F	144	.8277	.0078	40
	572			
Original volume	923			

Series 10, 50 per cent oil (0.794), 50 per cent benzene (0.8775).

[Specific gravity, 0.8295. Level of oil, 16 centimeters.]

A	31	0.8135	0.0097	31.6
B	45	.8251	.0081	43.6
C	85	.8290	.0076	46.4
D	140	.8280	.0077	47.6
E	175	.8285	.0076	49.6
F	137	.8272	.0076	50
	613			
Original volume	972			

a In series 7 the volume of grade A recovered was so small that no measurements could be made.

Results of diffusion of benzene and paraffin hydrocarbons through fuller's earth—Contd.

Series 11, 75 per cent crude oil (0.810), 25 per cent benzene (0.8775).

[Specific gravity, 0.8312. Level of oil, 18 centimeters.]

Grade.	Volume of oil (cubic centimeters).	Specific gravity.	Viscosity.	Per cent of benzene.
A	12	0.8255	0.0445	(a)
B	22	.8268	.0423	
C	52	.8280	.0300	
D	76	.8290	.0298	
E	140	.8300	.0263	
F	186	.8320	.0276	
	488			
Original volume	890			

Series 12, benzene alone.

[Specific gravity, 0.8775. Level of oil, 33 centimeters.]

Grade.	Volume of oil (cubic centimeters).	Specific gravity.	Viscosity.	Per cent of benzene.
A	16	0.8765		
B	15	.877		
C	68	.878	0.0066	
D	128	.8778	.0066	
E	157	.8775	.0066	
F	89	.8771	.0066	
	473			
Original volume	888			

[a] The percentages of benzene in series 11, in which crude oil was employed, are not recorded, because, owing to the formation of heavy black emulsions, the loss in volume could not be determined with any degree of accuracy.

The results tabulated for series 2 to 10 are expressed diagrammatically in the curves shown in figures 2 to 6. The ordinates represent the different grades of oil, and the abscissas the percentages of benzene and the specific gravities. The curves in figure 7 represent as a whole the results of the experimental work on the diffusion of benzene in solution through fuller's earth. The ordinates of these curves represent the percentages of benzene, and the abscissas the various mixtures of benzene and oil that were allowed to diffuse through the earth.

An examination of these shows conclusively that benzene tends to collect in the lower portions of the tube. The specific gravities and viscosities confirm the results obtained by determining the percentages of benzene present by removing the benzene with concentrated sulphuric acid. The specific gravities of grades F to C run very close together and are all much greater than those of grades A and B. As benzene possesses a high specific gravity—in this work the specimen had a specific gravity of 0.8775—the larger values for the lower grades indicate the presence of larger amounts of benzene. The specific gravity of the paraffin oil was only 0.792, showing that the higher specific gravities were due to larger percentages of benzene. Moreover, as the viscosity of the benzene used was 0.0066 and that of the paraffin oil about 0.0150, the viscosities of the fractions containing higher percentages of benzene ought to be much smaller than those of the fractions containing less benzene. The results show that the viscosities of grades F to C are much smaller than those of A and B.

It will be observed that the maximum in specific gravity is not at F, as may be expected in the fractionation of the crude oil, but

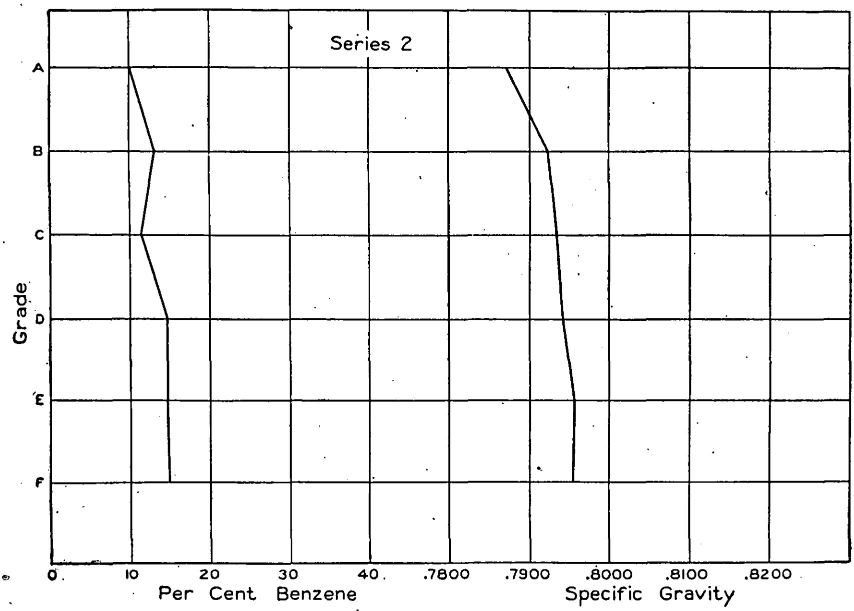

FIGURE 2.—Curve showing results of diffusion of benzene and paraffin oil through fuller's earth, series 2.

between C and D. Between B and C there is a marked decrease. This sudden break is found also in the viscosities and in the percentages of benzene. While the sharp breaks in the curves represent the marked change in the proportion of benzene and the height to which it rises in the tube, no satisfactory explanation has yet been obtained as to why it should occur at these points. This action will be studied more carefully later.

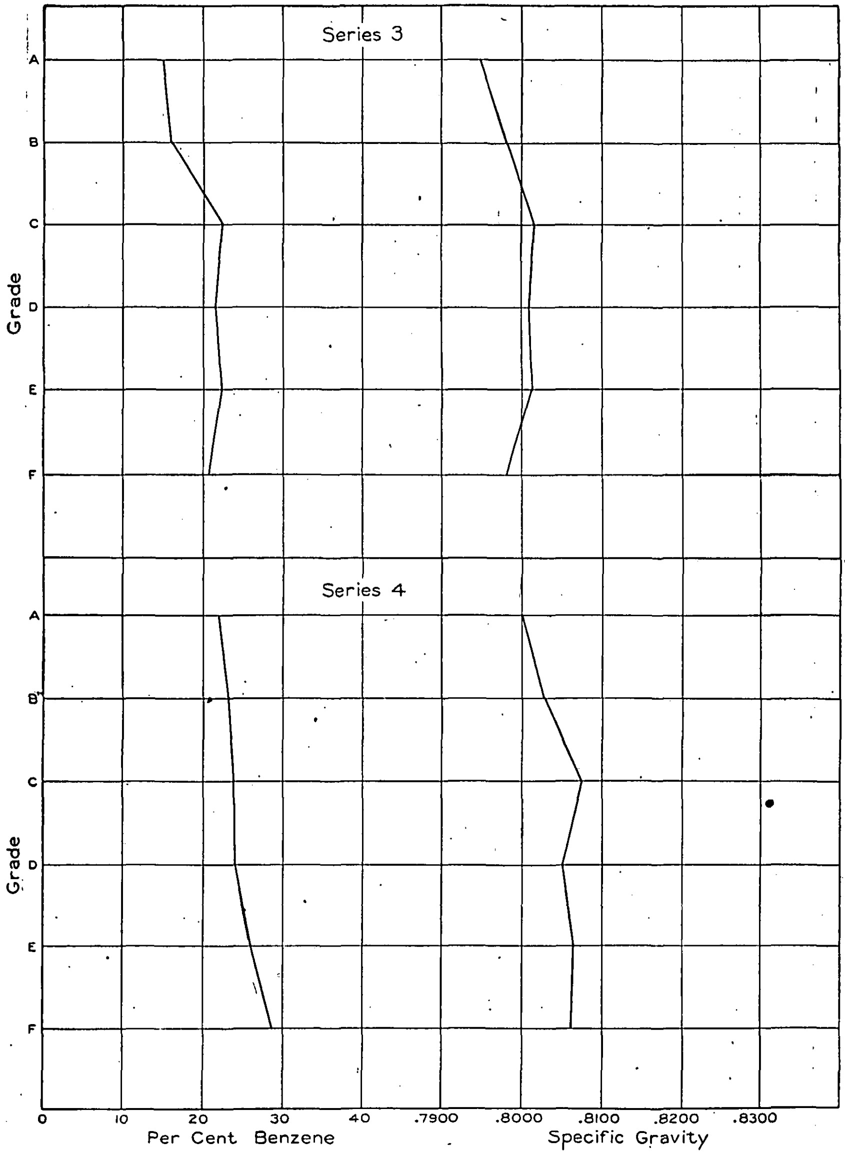

FIGURE 3.—Curves showing results of diffusion of benzene and paraffin oil through fuller's earth, series 3 and 4.

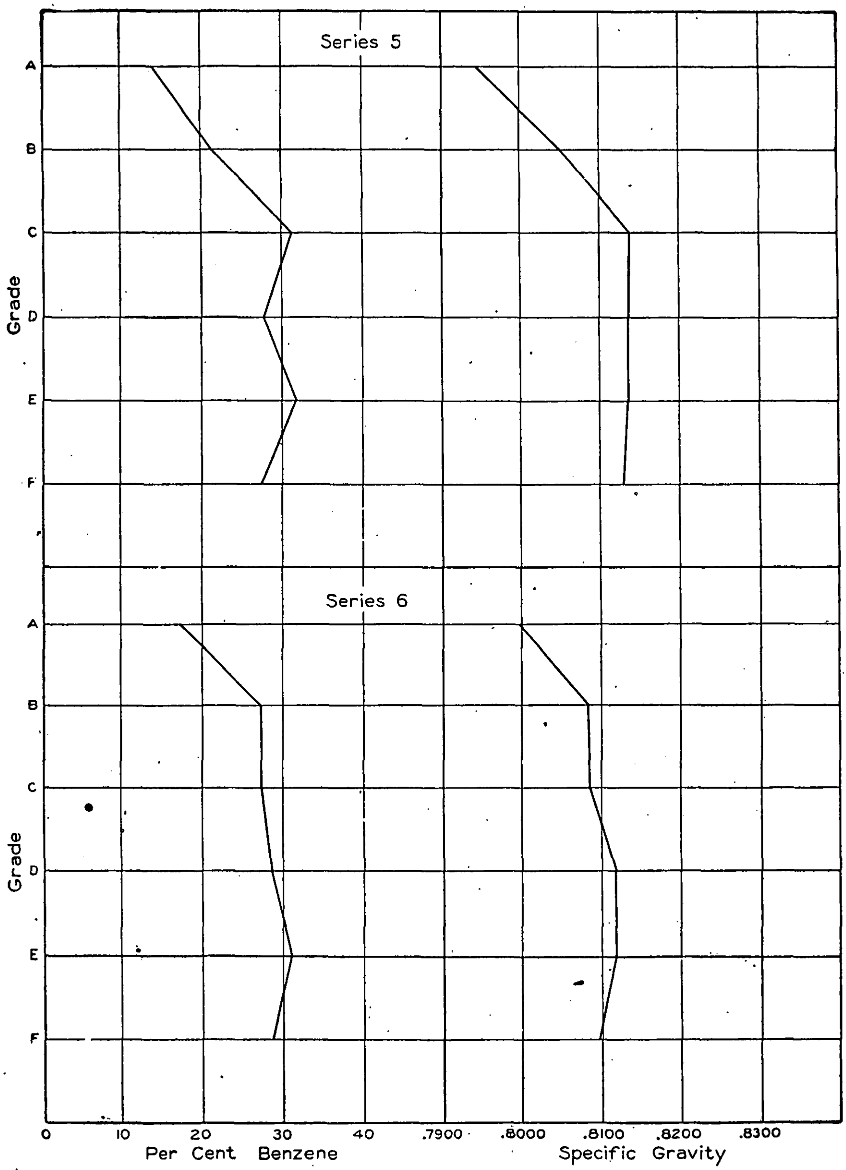

FIGURE 4.—Curves showing results of diffusion of benzene and paraffin oil through fuller's earth, series 5 and 6.

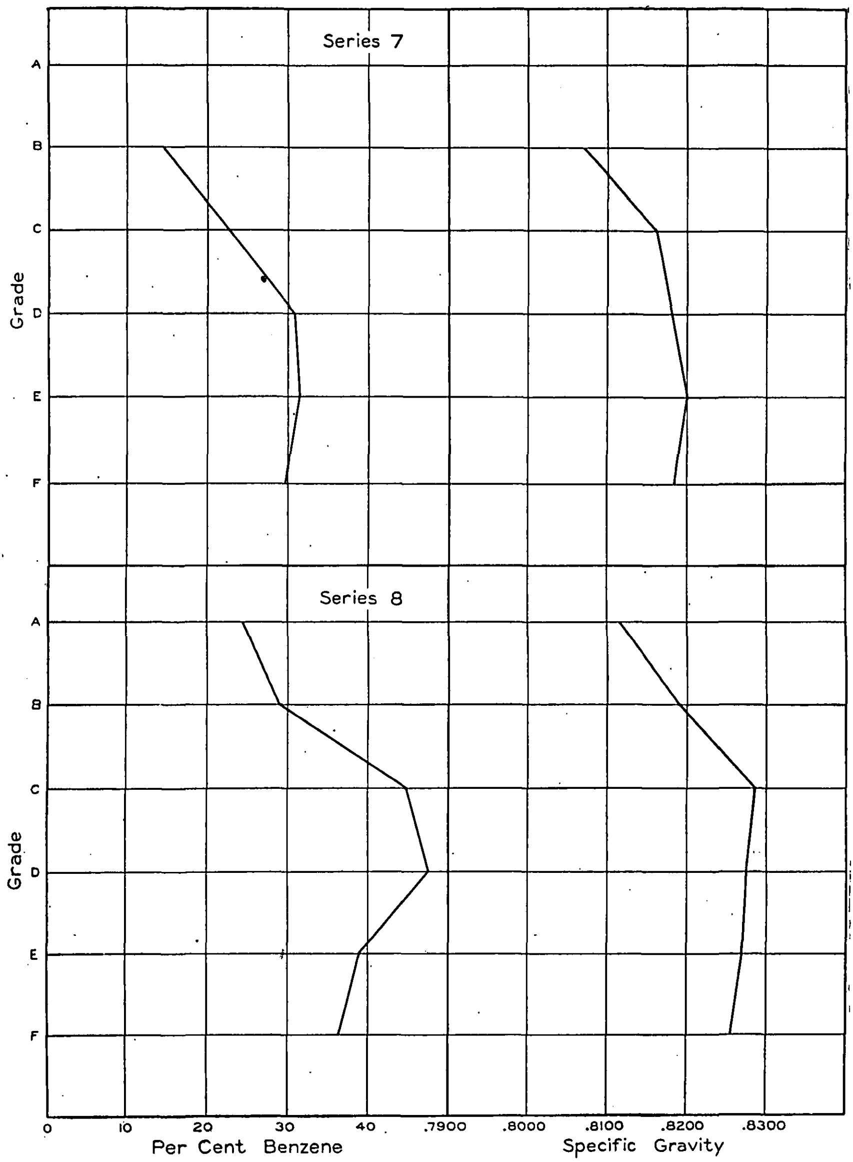

FIGURE 5.—Curves showing results of diffusion of benzene and paraffin oil through fuller's earth, series 7 and 8.

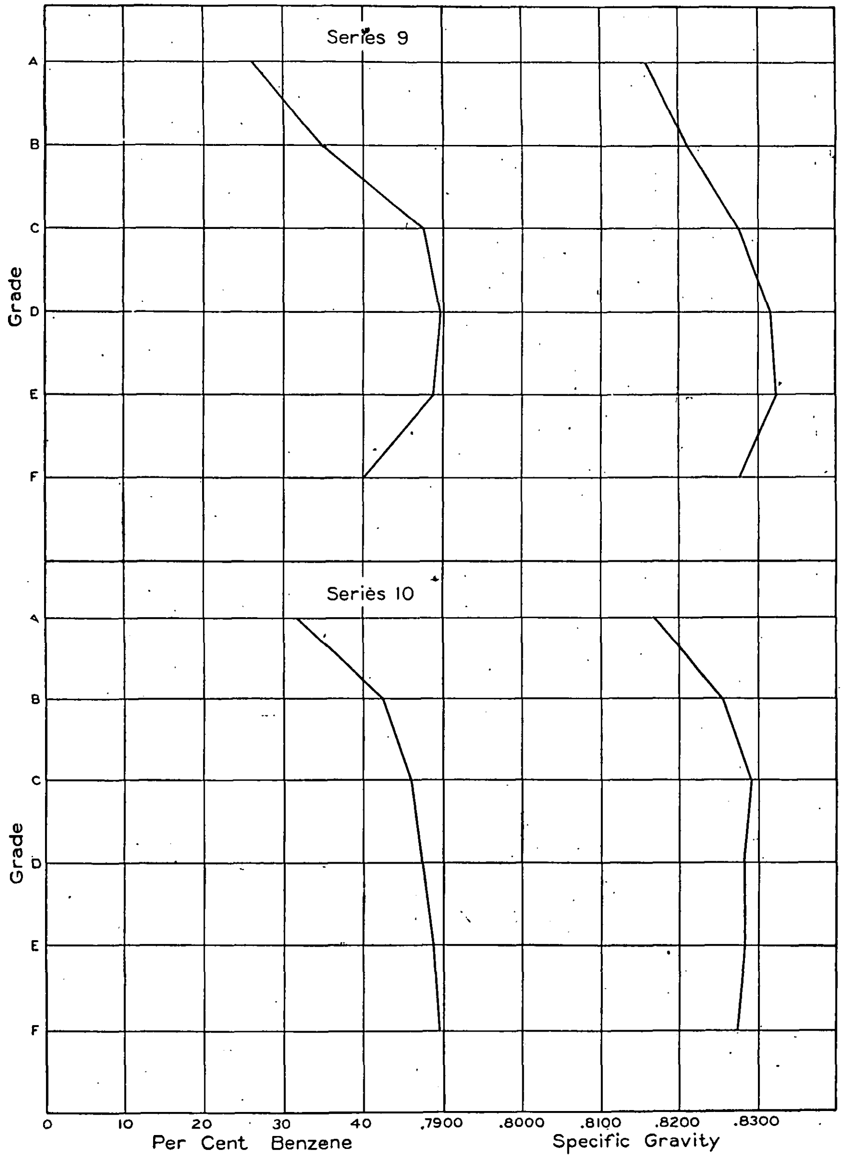

FIGURE 6.—Curves showing results of diffusion of benzene and paraffin oil through fuller's earth, series 9 and 10.

In order to determine the degree of exactness of the percentages of benzene obtained, known amounts of benzene were added to the

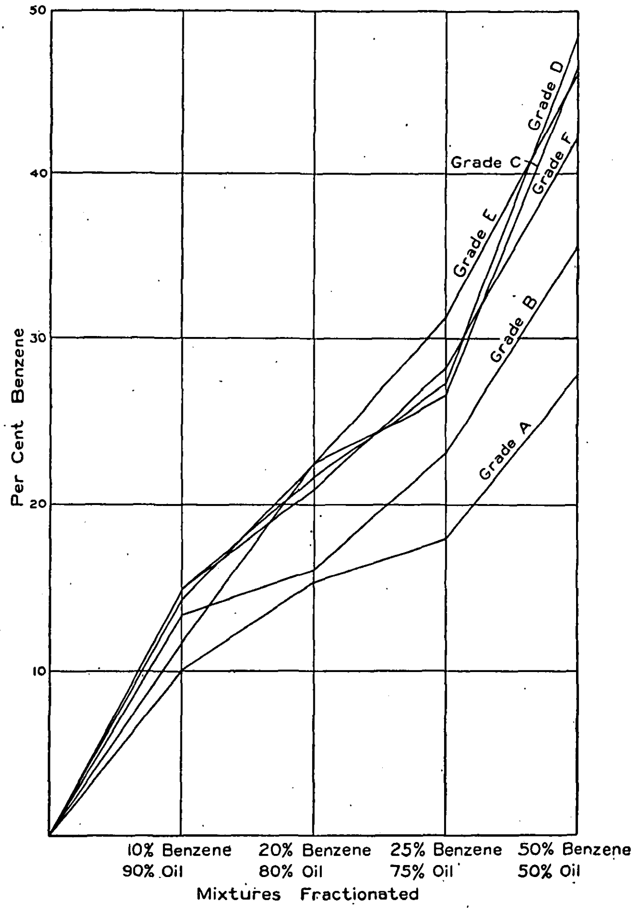

FIGURE 7.—Curves showing results of diffusion of benzene and paraffin oil through fuller's earth.

oil until the specific gravity corresponded closely to that obtained by fractionation.

The amount of benzene thus added and the amount actually removed by the acid agree very closely, as the following results show:

Results of tests to determine accuracy of benzene percentages.

Benzene in 25 cubic centimeters of mixture.		Benzene found in series 8.	
Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.
7.3	0.8143	Grade A, 7.9	0.8135
9.4	.8213	Grade B, 10.9	.8251
11.1	.8274	Grade F, 12.5	.8272
11.3	.8287	Grade E, 12.4	.8287
11.9	.8293	Grade C, 11.6	.8290

The variations in the specific gravities of the prepared mixtures and those of grades A to F are due to the fact that in the latter some fractionation had taken place in the paraffin oils, while in the mixtures the same paraffin oil was used each time. The paraffins found in grades A to F, therefore, exhibited slight gradations not common to the unfractionated paraffin oil used in preparing the mixtures.

FRACTIONATION OF PETROLEUM.

FIRST FRACTIONATION—CRUDE PETROLEUM.

The petroleum employed for the fractionation was an oil obtained by the United States Geological Survey from the E. E. Newlin farm, 2½ miles west of Robinson, Crawford County, Ill. The specific gravity of the oil was 0.8375 at 20° C.; its color was dark brown.

The fractionation of the oil was effected by upward diffusion through tubes packed with fuller's earth. In order to shorten the time required for the oil to diffuse by capillarity to the upper parts of the tube, the fine interstices and pores of the earth were evacuated by applying diminished pressure at the top of the tube. By this aid the time required for the oil to reach the top of a tube was reduced from several weeks to one or two days.

The apparatus employed is the same as that described on page 12.

The tin tubes, 5½ feet long and 1¼ inches in diameter, were packed as uniformly as possible by introducing definite amounts of earth and ramming solidly with rods tipped with rubber stoppers. The degree of compactness depended on the kind of oil to be used. For the crude oil about 1½ feet of the tube was filled at a time, and the earth packed as firmly as possible; for the lighter oils, 1 foot of the tube was filled at a time; for the oils heavier than the crude, between 2 and 3 feet of the tube was filled at one time.

The tubes were then placed individually in reservoirs containing 950 cubic centimeters of the crude oil, after which diminished pressure was applied at the top of the tubes. The oil rose rapidly at first, then diffused more and more slowly as it approached the tops of the tubes. When the oil in the reservoirs was completely exhausted the tubes were disconnected from the branced glass tube (see fig. 1, p. 13), and the oil-laden earth was shaken into two breakable cylinders. The following divisions of the earth were made: Fraction A, the first 10 centimeters measured downward from the level to which the oil had ascended; fraction B, the next 15 centimeters; C, 20 centimeters; D, 30 centimeters; E, 35 centimeters; and F, the remainder to the bottom of the tube. In the first fractionation up to lot 28, fraction F was discarded; from lot 28 to the end of the first fractionation, E and F were collected together.

After the earth was thus divided the several portions were placed in separate receptacles and treated with water. After each addition of water each portion was thoroughly mixed with it. The earth, when the oil first appeared, was granular; as more water was added, liberating more oil, the earth became muddy, and when as much oil as possible had been expelled by the water, the earth had the consistency of glue.

The portions of oil liberated by successive additions of water were collected separately. As Gilpin and Cram [1] pointed out, the oil that is first expelled, if not very small in volume as compared with the succeeding portions, possesses a lower specific gravity than the oil liberated by further additions of water; the latter in turn is lighter than the next succeeding oil. The oil that is liberated last, therefore, possesses a higher specific gravity than any of the portions preceding it. Sometimes, however, the specific gravity remains constant after the second or third extraction. This fractionation by means of water was combined with the fractionation effected by the fuller's earth. In the tables that follow A^1 represents the oil first liberated, A^2 the oil next liberated, etc. In the lower fractions (C, D, and E), three and sometimes four extractions were made before all the oil that could possibly be liberated by water was recovered.

The specific gravity of the oils was determined by means of the Mohr-Westphal balance. As mentioned before, the fourth decimal is not to be considered as rigidly accurate, but it gives a closer approximation to the truth than if it were entirely discarded. The temperature at which the specific gravity was measured was exactly 20° C.

Results of first fractionation.

	1		2		3			
Number of tubes	15		5		10			
Hours required [a]	18, 14 tubes; 23, 1 tube.		16		17, 8 tubes.		45, 2 tubes.	
Fraction.	Specific gravity.	Cubic centimeters [b]	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A^1	0.8250	312	0.8285	73	0.8223	138	0.8233	50
A^2	.8287	90	.8310	59	.8270	54		
B^1	.8367	485	.8370	218	.8372	258	.8405	130
B^2	.8392	250	.8408	78	.8400	200		
C^1	.8413	828	.8440	272	.8442	290	.8505	120
C^2	.8460	228	.8442	136	.8455	235	.8535	65
C^3	.8488	126			.8480	148		
D^1	.8470	1,014	.8430	313	.8488	538	.8546	235
D^2	.8495	375	.8464	150	.8500	295	.8619	30
D^3	.8514	200	.8500	112	.8540	115		
D^4	.8555	172						
E^1	.8527	720	.8475	285	.8537	380	.8615	172
E^1	.8540	430	.8509	135	.8550	245		
E^3	.8570	400	.8540	118	.8570	170		

[a] Chapman pump was run day and night. Manometer indicated pressures ranging from 30 to 80 millimeters.
[b] In lots 1 to 5, 1,000 cubic centimeters of crude oil was supplied to each tube.

[1] Am. Chem. Jour., vol. 40, 1908.

Results of first fractionation—Continued.

	4		5		6			
Number of tubes	10		8		10[a]			
Hours required	16		17, 7 tubes; 24, 1 tube.		17, 1 tube;[b] 40, 3 tubes; 96, 1 tube.		17, 3 tubes; 40, 1 tube; 150, 1 tube.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A^1	0.8295	170	0.8313	130	0.8320	[c]72	0.8287	[c]85
A^2	.8315	100	.8357	56	.8352	22	....	....
B^1	.8375	327	.8392	358	.8405	184	.8390	134
B^2	.8413	250	.8453	92	.8451	124	.8485	35
C^1	.8418	505	.8419	425	.8443	270	.8441	218
C^2	.8442	223	.8439	138	.8495	147	.8507	67
C^3	.8495	74	.8465	130	....	....	....	....
D^1	.8449	495	.8454	640	.8483	368	.8450	302
D^2	.8455	328	.8500	167	.8517	210	.8490	132
D^3	.8490	260	.8509	195	....	....	....	....
E^1	.8500	545	.8495	575	.8500	360	.8537	215
E^2	.8510	295	.8513	185	.8569	185	.8564	174
E^3	.8567	170	.8555	130	....	....	....	....

	7				8		9	
Number of tubes	9				10		10	
Hours required	20, 7 tubes.		20, 1 tube; 24, 1 tube.		19, 8 tubes; 22, 2 tubes.		24, 2 tubes; 40, 8 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A^1	0.8325	66	0.8175	45	0.8364	88	0.8215	145
A^2	.8356	30	....	....	.8365	64	.8234	90
B^1	.8395	164	.8333	110	.8400	215	.8330	397
B^2	.8418	140	....	....	.8420	240	.8350	155
B^3	....	....	....	....	....	....	.8400	87
C^1	.8408	475	.8417	132	.8445	368	.8415	350
C^2	.8468	123	.8500	22	.8467	225	.8436	255
C^3	....	....	....	....	.8495	82	.8480	[d]160
D^1	.8449	500	.8468	110	.8465	460	.8485	507
D^2	.8487	270	.8498	106	.8478	260	.8495	280
D^3	....	....	....	....	.8500	260	.8545	247
E^1	.8500	483	.8533	228	.8490	450	.8548	313
E^2	.8524	318	....	....	.8495	354	.8550	275
E^3	....	....	....	....	.8521	233	.8580	375

[a] Beginning with lot 6, 950 cubic centimeters of crude oil was supplied to each tube.
[b] The pressure in the tubes was diminished intermittently.
[c] See page 14.
[d] Several cubic centimeters of this fraction were mixed, accidentally, with fraction E^3.

Results of first fractionation—Continued.

	10		11		12		13	
Number of tubes	8		10		9		10	
Hours required	17		17		42		24, 8 tubes; 40, 2 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A1	0.8273	130	0.8258	215	0.8325	125	0.8323	122
A2	.8288	75	.8318	70	.8345	87	.8352	96
B1	.8395	220	.8370	340	.8430	235	.8438	245
B2	.8418	160	.8480	180	.8467	120	.8470	180
C1	.8423	240	.8422	488	.8470	278	.8464	317
C2	.8440	195	.8450	205	.8487	288	.8505	235
C3	.8500	150	…	…	…	…	…	…
D1	.8460	410	.8465	565	.8495	452	.8500	312
D2	.8475	210	.8490	310	.8522	305	.8492	375
D3	.8500	348	.8530	187	…	…	.8518	150
E1	.8532	320	.8510	297	.8505	475	.8505	450
E2	.8535	282	.8520	405	.8533	490	.8489	395
E3	.8550	215	.8533	155	…	…	.8518	180

	14		15				16	
Number of tubes	5		6				15	
Hours required	24 [a]		26, 3 tubes.		26, 3 tubes.		40, 11 tubes; 64, 4 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A1	0.8355	132	0.8381	60	0.8305	73	0.8370	200
A2	…	…	…	…	…	…	.8357	108
B1	.8470	236	.8487	94	.8452	143	.8449	490
B2	…	…	…	…	…	…	.8445	226
C1	.8565	98	.8430	110	.8465	138	.8475	635
C2	.8560	150	.8480	57	.8509	88	.8509	235
C3	…	…	…	…	…	…	.8562	90
D1	.8523	170	.8475	212	.8505	158	.8540	825
D2	.8550	205	.8517	104	.8522	178	.8530	495
D3	…	…	…	…	…	…	.8575	150
E1	.8540	150	.8467	184	.8561	192	.8538	775
E2	.8532	325	.8502	152	.8585	140	.8562	620
E3	…	…	…	…	…	…	.8595	205

[a] When the pressure in the tubes was diminished the oil rose rapidly, and in a short time the reservoirs were nearly two-thirds exhausted. The pump was stopped and the remainder of the oil was allowed to diffuse during the night under normal pressure.

Results of first fractionation—Continued.

	17		18		19		20	
Number of tubes	9		8		10		10	
Hours required	40		24, 5 tubes; 48, 2 tubes; 64, 1 tube.		40, 8 tubes; 64, 2 tubes.		20, 6 tubes; 30, 4 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8258	225	0.8322	112	0.8320	146	0.8281	236
B	.8432	452	.8435	335	.8438	385	.8413	518
C[1]	.8480	450	.8495	250	.8480	300	.8450	350
C[2]	.8488	168	.8500	250	.8472	315	.8495	300
D[1]	.8530	520	.8530	320	.8509	422	.8508	325
D[2]	.8550	350	.8540	350	.8536	355	.8538	460
E[1]	.8585	385	.8547	[a] 90	.8492	580	.8513	445
E[2]	.8598	460	.8526	640	.8560	415	.8540	550

	21		22		23		24	
Number of tubes	10		10		10		10	
Hours required [b]	24, 6 tubes; 40, 2 tub s; 64, 2 tubes.		40, 6 tubes; 64, 4 tubes.		48, 5 tubes; 72, 5 tubes.		40, 4 tubes; 64, 6 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8275	245	0.8281	210	0.8241	330	0.8250	287
B	.8410	615	.8405	508	.8395	615	.8408	535
C[1]	.8452	520	.8459	265	.8448	420	.8463	475
C[2]	.8488	226	.8472	410	.8470	305	.8505	186
D[1]	.8512	533	.8505	435	.8533	400	.8540	525
D[2]	.8535	415	.8523	450	.8541	465	.8540	360
E[1]	.8557	375	.8615	385	.8650	305	.8623	393
E[2]	.8625	282	.8585	365	.8624	350	.8645	335

[a] This irregularity—that is, the liberation of oil with a specific gravity higher than those of the oils immediately following—is observed when an amount of water is added sufficient to replace a very small amount of oil for the first fraction.

[b] Pressure in the tubes was diminished intermittently.

Results of first fractionation—Continued.

	25		26		27		28	
Number of tubes	9		10		10		10	
Hours required [a]	48, 8 tubes; 72, 1 tube.		17, 2 tubes; 24, 4 tubes; 41, 4 tubes.		17, 4 tubes; 29, 6 tubes.		24, 7 tubes; 28, 3 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8270	225	0.8284	315	0.8312	230	0.8333	240
B	.8425	410	.8422	550	.8440	370	.8440	410
C¹	.8495	[b] 75	.8473	520	.8460	400	.8458	415
C²	.8492	250	.8508	178	.8478	232	.8500	177
D¹	.8509	320	.8515	600	.8482	435	.8470	387
D²	.8510	480	.8540	230	.8500	420	.8498	400
E¹	.8556	335	.8559	490	.8520	465	.8492	[c] 690
E²	.8570	395	.8586	135	.8565	335	.8505	600

	29		30		31		32	
Number of tubes	10		15		10		15	
Hours required [a]	18, 5 tubes; 40, 5 tubes.		20, 7 tubes; 41, 6 tubes; 63, 2 tubes.		44, 4 tubes; 89, 6 tubes.		40, 7 tubes; 89, 4 tubes; 103, 4 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8262	300	0.8348	335	0.8292	245	0.8270	445
B	.8395	505	.8468	630	.8439	576	.8423	726
C¹	.8463	390	.8490	560	.8495	465	.8500	730
C²	.8488	270	.8505	277	.8523	205	.8500	220
D¹	.8520	510	.8485	750	.8517	670	.8545	750
D²	.8543	290	.8502	540	.8552	210	.8543	540
EF¹	.8550	417	.8520	1,125	.8555	805	.8580	870
EF²	.8559	645	.8528	880	.8610	360	.8598	910
		3,327		5,097		3,536		5,191

[a] Pressure in the tubes was diminished intermittently.
[b] Some oil of this fraction was lost.
[c] Beginning with lot 28, fractions E and F were collected together.

Results of first fractionation—Continued.

	33		34		35	
Number of tubes	10		10		9	
Hours required[a]	41, 4 tubes; 65, 4 tubes; 89, 2 tubes.		44, 6 tubes; 68, 4 tubes.		48, 6 tubes; 72, 3 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8330	290	0.8355	320	0.8380	235
B^1	.8440	365	.8475	525	.8460	452
B^2	.8462	165	....	....	....	....
C^1	.8502	500	.8508	470	.8508	345
C^2	.8540	160	.8543	190	.8525	245
D^1	.8555	655	.8575	530	.8549	580
D^2	.8562	250	.8585	325	.8573	335
EF^1	.8575	735	.8535	895	.8557	645
EF^2	.8585	480	.8555	405	.8570	492
		3,600		3,660		3,329

[a] Pressure in the tubes was diminished intermittently.

Specific gravity.—The range of the specific gravity extended from 0.8175, the value of fraction A^1 of lot 7, to 0.8650, the value of fraction E^1 of lot 13. The specific gravity of the crude oil itself was 0.8375. The range of the specific gravities of the individual lots averaged from 0.820 to 0.860. The specific gravity decreases gradually from E to B, but in most of the lots the decrease between B and A is much greater than between any two consecutive lower fractions. This marked change was also observed in the study of the diffusion of benzene in solution. A detailed investigation of the cause will be undertaken in the near future.

Color.—The color of the fractions obtained ranged from green to black. The lighter oils possessed a beautiful green fluorescent color, which shaded gradually to brown, and then to the deep black of the heavier oils.

Odor.—The unpleasant odor of the crude petroleum disappeared almost entirely in the oils of fractions A and B; but the other fractions still possessed to a greater or less extent the odor of the natural oil.

Volume of oil retained by the fuller's earth.—The amount of oil retained by the earth averaged about 55 per cent of the amount supplied. In the first fractionation of the crude Pennsylvania oil, specific gravity 0.810, Gilpin and Cram found that approximately 40 per cent of the oil was retained by the earth. It is evident, therefore, that the amount of oil remaining in the earth depends chiefly on the character of the oil. The Pennsylvania petroleum contains a much smaller percentage of unsaturated hydrocarbons, sulphur, and asphaltic substances than the Illinois oil employed in this investigation. Inasmuch as the fuller's earth readily removes these substances in the process of fractionation, as will be shown later, the large percentage of Illinois oil retained by the earth is thus clearly explained. It is safe to conclude that if the heavy Texas or California oil was allowed to diffuse through fuller's earth, the amount of oil retained would exceed the amounts of either of the above-mentioned oils lost in the earth.

SECOND FRACTIONATION.

The products obtained from the first fractionation were united according to the following arrangement:

Specific gravity of oils united for second fractionation.

Lot.	Specific gravity.	Specific gravity of the oils united.
36	0.8293	0.8250-0.8350
37	.8390	.8350- .8400
38	.8433	.8400- .8450
39	.8433	.8400- .8450
40-43	.8490	.8450- .8500
44-50	.8543	.8500- .8600

The oils thus combined were subjected to chilling and filtration for the purpose of removing as much dissolved paraffin as possible. The procedure was as follows: The oils were first chilled at temperatures ranging from 0° to 10° C., and then filtered through plaited filter papers. When the oil ceased to drip from the funnel, the residue upon the filter paper was placed in a larger filter press, and the remaining oil was separated by pressure from the paraffin. The filter press was simple in construction. A piston, fitted closely in an iron cylinder, was gradually forced down upon the oil-laden paraffin, which rested upon a membrane of cotton duck, fastened between perforated tin supports. The retained oil was forced through the membrane and was collected from the outlet below. The lighter oils deposited very little paraffin; somewhat more paraffin was separated from the heavier ones. Owing to the high viscosity of the heavier oils, the filtration proceeded very slowly, and as too much time was consumed in this process, the paraffin of some of the oils of fraction E was not removed. A slight change in specific gravity occurred in the oils from which the paraffin was removed.

The final specific gravities of the united oils were as follows:

Final specific gravity of oils for second fractionation.

Lot.	Specific gravity.	Paraffin removed.
36	0.8305	Yes.
37	.8415	Yes.
38	.8433	No.
39	.8455	Yes.
40-42	.8515	Yes.
43	.8540	Yes.
44-48	.8543	No.
49-50	.8557	Yes.

When these oils were again allowed to diffuse upward through fuller's earth, the following fractionation was obtained:

Results of second fractionation.

	36		37		38		39	
Specific gravity	0.8305		0.8415		0.8433[a]		0.8455[b]	
Number of tubes	5		4		8		8	
Hours required[c]	44, 3 tubes; 48, 2 tubes.		51		48, 7 tubes; 64, 1 tube.		29, 4 tubes; 45, 3 tubes; 64, 1 tube.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8272	160	0.8292	135	0.8331	180	0.8290	255
B 1	.8315	216	.8421	215	.8447	175	.8432	355
B 2	.8331	58	....	....	.8455	210	.8458	110
C 1	.8334	350	.8467	295	.8490	305	.8492	455
C 2	.8355	85	....	....	.8505	175	.8513	180
D 1	.8330	360	.8468	340	.8492	400	.8505	740
D 2	.8339	320	.8485	152	.8509	295	.8527	275
EF 1	.8347	720	.8480	535	.8508	710	.8546	1,166
EF 2	.8356	320	.8489	215	.8518	355	.8560	350
		2,589		1,887		3,886		2,805

	40		41		42		43	
Specific gravity	0.8515		0.8515		0.8515		0.8540	
Number of tubes	9		5		5		4	
Hours required	48, 5 tubes; 72, 4 tubes.		40		69		10 days, 2 tubes; 17 days, 2 tubes.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8305	380	0.8316	235	0.8325	210	0.8435	65
B 1	.8438	515	.8460	290	.8487	265	.8546	115
B 2	.8453	155	.8480	65	.8515	54	....	....
C 1	.8518	600	.8523	375	.8540	335	.8575	200
C 2	.8539	170	.8540	100	.8567	56	....	....
D 1	.8550	685	.8558	470	.8572	420	.8605	220
D 2	.8560	330	.8571	110	.8582	175	.8640	50
EF 1	.8605	780	.8620	580	.8640	675	.8650	225
EF 2	.8620	600	.8622	320	.8650	200	.8615	78
		4,215		2,545		2,420		953

[a] Paraffin was removed from the oil.
[b] Paraffin was not removed from the oil.
[c] In this series, as well as those following, the pressure in the tubes was diminished intermittently.

Results of second fractionation—Continued.

	44		45		46		47	
Specific gravity [a]	0.8543		0.8543		0.8543		0.8543	
Number of tubes	3		5		5		5	
Hours required	48, 2 tubes; 96, 1 tube.		66		93		13 days.[b]	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8330	85	0.8362	170	0.8332	210	0.8340	145
B [1]	.8505	175	.8510	210	.8480	260	.8500	275
B [2]	....	....	.8522	80	.8505	50	....	....
C [1]	.8582	155	.8562	265	.8554	300	.8553	320
C [2]	.8605	65	.8585	50	.8567	95	.8576	50
D [1]	.8605	195	.8567	425	.8600	370	.8595	430
D [2]	.8620	120	.8580	100	.8613	120	.8618	70
EF [1]	.8672	240	.8659	615	.8666	610	.8665	330
EF [2]	.8680	175	.8670	150	.8680	130	.8670	215
		1,210		2,065		2,145		1,835

	48		49		50	
Specific gravity	0.8543 [a]		0.8557 [c]		0.8557 [c]	
Number of tubes	5		7		5	
Hours required	14 days.[d]		48		72, 4 tubes; 89, 1 tube.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8385	125	0.8341	255	0.8320	170
B [1]	.8530	275	.8505	395	.8485	230
B [2]	....	....	.8520	95	.8500	70
C [1]	.8568	320	.8560	380	.8565	300
C [2]	.8586	90	.8572	230	.8577	100
D [1]	.8610	325	.8620	500	.8609	480
D [2]	.8623	115	.8625	290	.8626	125
EF [1]	.8695	330	.8705	500	.8685	640
EF [2]	.8700	80	.8705	580	.8700	235
		1,660		3,225		2,350

[a] Paraffin was not removed from the oil.
[b] Owing to the weakness of the water pressure, the pressure in the tubes was only slightly diminished. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 35, 25, 30, 20, and 10 centimeters from the tops of the tubes.
[c] Paraffin was removed from the oil.
[d] Owing to the weakness of the water pressure, the pressure in the tubes was diminished but slightly during this time. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 50, 35, 30, 60, and 55 centimeters from the tops of the tubes.

Specific gravity.—The range of the specific gravities grows smaller as the oils to be fractionated become lighter and less complex. Thus, in lot 36, the range of specific gravity extends from 0.8272, the value of fraction A, to 0.8356, the value of EF^2, the difference between them being 0.0084. In lot 38, the mother oil, specific gravity 0.8433, yielded fractions whose specific gravities ranged from 0.8331 to 0.8518, amounting to a difference of 0.0187. This fact appears to be general throughout the various lots, and points to the gradual formations of mixtures which will pass through the earth unaltered, just as the fractionation by distillation tends to produce compounds with definite boiling points.

Color.—The color of the oils in this fractionation shaded from a very light yellow to greenish black.

Odor.—The odor of the crude petroleum vanished completely from the oils of this fractionation.

Volume of oil retained by the fuller's earth.—The oil retained by the earth in this fractionation amounted to approximately 50 per cent, a smaller percentage, as is naturally to be expected, than in the fractionation of the crude petroleum.

THIRD FRACTIONATION.

The following oils obtained from the second fractionation were united for the third fractionation.

Oils used for third fractionation.

Lot 51.

[Specific gravity, 0.8316.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
36	A	0.8272	160
39	A	.8290	255
37	A	.8292	135
40	A	.8305	380
36	B^1	.8315	216
41	A	.8316	235
50	A	.8320	170
42	A	.8325	210
44	A	.8330	85
36	B^2	.8331	58
38	A	.8331	180
46	A	.8332	210
36	C^1	.8334	350
49	A	.8341	255
			2,899

Lot 52.

[Specific gravity, 0.8343.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
36	D^1	0.8330	360
36	D^2	.8339	320
47	A	.8340	145
36	EF^1	.8347	720
36	EF^2	.8356	320
36	C^2	.8355	85
			1,950

Lot 53.

[Specific gravity, 0.8433.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
45	A	0.8362	170
48	A	.8385	125
37	B^1	.8421	215
39	B^1	.8432	355
40	B^1	.8438	515
38	B^1	.8447	175
40	B^2	.8453	155
38	B^2	.8455	210
39	B^2	.8458	50
			1,970

Lot 54.

[Specific gravity, 0.8473.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
39	B^2	0.8458	60
41	B^1	.8460	290
37	C^1	.8467	295
41	B^2	.8480	65
50	B^1	.8485	230
42	B^1	.8487	265
39	C^1	.8492	455
38	C^1	.8490	305
			1,965

Oils used for third fractionation—Continued.

Lot 55.

[Specific gravity, 0.8485.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
37	D^1	0.8468	340
37	D^2	.8485	152
37	EF^1	.8480	535
37	EF^2	.8489	215
38	D^1	.8492	400
47	B^1	.8500	275
			1,917

Lot 56.

[Specific gravity, 0.8508.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
50	B^2	0.8500	70
49	B^1	.8505	395
44	B^1	.8505	175
46	B^2	.8505	50
38	C^2	.8505	175
45	B^1	.8510	210
39	C^2	.8513	180
42	B^2	.8515	54
40	C^1	.8518	600
			1,909

Lot 57.

[Specific gravity, 0.8509.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
39	D^1	0.8505	740
38	EF^1	.8508	710
38	D^2	.8509	295
38	EF^2	.8518	355
			2,100

Lot 58.

[Specific gravity, 0.8558.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
49	B^2	0.8520	95
45	B^2	.8522	80
41	C^1	.8523	375
48	B^1	.8530	275
40	C^2	.8539	170
42	C^1	.8540	335
41	C^2	.8540	100
47	C^1	.8553	320
46	C^1	.8554	300
49	C	.8560	380
45	$C^{1\prime}$	.8562	265
50	C^1	.8565	300
42	C^2	.8567	56
46	C^2	.8567	95
48	C^1	.8568	320
49	C^2	.8572	230
43	C^1	.8575	200
			3,896

Lot 59.

[Specific gravity, 0.8563.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
39	EF^1	0.8546	1,166
40	D^1	.8550	685
41	D^1	.8558	470
39	EF^2	.8560	350
40	D^2	.8560	330
45	D^1	.8567	425
41	D^2	.8571	110
42	D^1	.8572	420
45	D^2	.8580	100
42	D^2	.8582	175
48	C^2	.8586	90
47	D^1	.8595	430
			4,750

Lot 60.

[Specific gravity, 0.8615.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
46	D^1	0.8600	370
49	EF^1	.8605	780
43	D^1	.8605	220
44	D^1	.8605	195
50	D^1	.8609	480
48	D^1	.8610	325
46	D^2	.8613	120
47	D^2	.8618	70
40	EF^2	.8620	600
41	EF^1	.8620	580
44	D^2	.8620	120
49	D^1	.8620	500
41	EF^2	.8622	320
48	D^2	.8623	115
49	D^2	.8625	290
50	D^2	.8626	125
42	E^1	.8640	675
			5,880

Lot 61.

[Specific gravity, 0.8680.]

Lot.	Fraction.	Specific gravity.	Cubic centimeter.
42	EF^2	0.8650	200
43	EF^1	.8650	225
45	EF^1	.8659	615
47	EF^1	.8665	330
46	EF^1	.8666	610
47	EF^2	.8670	215
45	EF^2	.8670	150
44	EF^1	.8672	240
46	EF^2	.8680	130
44	EF^2	.8680	175
50	EF^1	.8685	640
48	EF^1	.8695	330
50	EF^2	.8700	235
49	EF^1	.8705	500
49	EF^2	.8705	580
			4,975

The oils thus united were fractionated by fuller's earth again, with the results given below.

Results of third fractionation.

	51		52		53		54	
Specific gravity......	0.8316		0.8343		0.8433		0.8473	
Number of tubes.....	3[a]		2[a]		2		2	
Hours required......	60		60		48		48	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A..................	0.8213	92	0.8219	65	0.8266	73	0.8303	66
B..................	.8303	185	.8333	143	.8431	115	.8488	115
C^1..................	.8337	165	.8375	190	.8464	175	.8518	175
C^2..................	.8345	90	....	....	....	....	....	....
D^1..................	.8353	210	.8388	188	.8468	145	.8523	180
D^2..................	.8356	170	.8393	90	.8474	115	.8528	105
E^1..................	.8366	385	.8403	175	.8473	202	.8530	245
E^2..................	....	....	.8411	92	.8488	73	.8548	60
F..................	.8373	190	.8431	88	.8496	170	.8548	145
		1,487		1,031		1,068		1,091

	55		56		57		58	
Specific gravity......	0.8485		0.8508		0.8509		0.8558	
Number of tubes.....	2		2		2		4	
Hours required[b].....	48, 1 tube; 72, 1 tube.		96		96		72, 3 tubes; 90, 1 tube.	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A..................	0.8283	58	0.8313	75	0.8336	55	0.8318	170
B..................	.8457	100	.8488	135	.8491	130	.8531	260
C^1..................	.8515	155	.8546	170	.8528	180	.8578	205
C^2..................	....	....	....	....	....	....	.8592	105
D^1..................	.8521	220	.8553	150	.8551	185	.8588	205
D^2..................	.8543	50	.8560	92	.8573	45	.8593	340
E^1..................	.8540	270	.8553	145	.8568	170	.8603	325
E^2..................	....	....	.8563	90	.8588	70	.8613	170
F..................	.8566	180	.8575	130	.8611	170	.8628	275
		1,033		987		1,005		2,055

[a] The tin tubes used in these lots were 1½ inches in diameter.
[b] The pressure in the tubes was diminished intermittently.

Results of third fractionation—Continued.

	59		60		61	
Specific gravity	0.8563		0.8615		0.8680	
Number of tubes	5		6		5	
Hours required	72		72		5 days.[a]	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.[b]
A	0.8328	195	0.8343	195	0.8413	....
B	.8508	340	.8540	330	.8601	....
C^1	.8578	325	.8601	290	.8683	....
C^2	.8588	112	.8618	130	....	....
D^1	.8608	490	.8628	440	.8709	....
D^2	.8623	135	.8638	85	....	....
E^1	.8628	475	.8664	425	.8688	....
E^2	.8633	155	.8683	140	....	....
F	.8673	330	.8703	310	.8691	....
		2,557		2,345		....

[a] See below. [b] The volumes of these oils were not recorded.

Specific gravity.—The decrease in the range of specific gravity as the oils supplied become lighter was observed in this fractionation as in the preceding ones.

Color.—The lightest oils were almost colorless; the heavier oils were dark brown to green.

Odor.—Most of the oils possessed an agreeable odor.

Prolonged diffusion.—In lot 61 the time required for the oils to reach the tops of the tubes was five days. No fractionation, as is evident from an examination of the specific gravities, occurred in the lower parts of the tubes. The heavier oils of fractions D, E, and F were exceedingly viscous.

Volume of oil retained by the fuller's earth.—The volume of oil retained by the earth in this fractionation amounted to approximately 45 per cent. The increase in the yield of oil indicates, therefore, a process of purification, in which, as will be shown later, such compounds as the unsaturated hydrocarbons are removed.

FOURTH FRACTIONATION.

The following fractions obtained from the third fractionation were united for the fourth fractionation:

Oils used for fourth fractionation.

Lot 62.

[Specific gravity, 0.8298.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
51	A	0.8213	92
52	A	.8219	65
53	A	.8266	73
55	A	.8283	66
54	A	.8303	58
51	B	.8303	185
56	A	.8313	75
58	A	.8318	170
59	A	.8328	195
			979

Lot 63.

[Specific gravity, 0.8343.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
52	B	0.8333	143
57	A	.8336	55
51	C¹	.8337	185
60	A	.8343	195
51	C²	.8345	90
51	D¹	.8353	210
51	D²	.8356	170
			1,040

Lot 64.

[Specific gravity, 0.8368.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
51	E¹	0.8366	388
51	F	.8372	190
52	C¹	.8375	190
52	D¹	.8388	188
			956

Lot 65.

[Specific gravity, 0.8430.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
52	D²	0.8393	90
52	E¹	.8403	175
52	E²	.8411	92
53	B¹	.8431	115
52	F	.8431	88
55	B¹	.8457	100
53	C¹	.8464	175
53	D¹	.8468	145
			980

Lot 66.

[Specific gravity, 0.8483.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
53	E¹	0.8473	202
53	D²	.8474	115
54	B¹	.8488	115
56	B¹	.8488	135
53	E²	.8488	73
59	B¹	.8508	330
			970

Lot 67.

[Specific gravity, 0.8513.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
57	B¹	0.8491	130
59	B¹	.8508	10
55	C¹	.8515	155
54	C¹	.8518	175
55	D¹	.8521	220
58	B¹	.8531	260
			950

Lot 68.

[Specific gravity, 0.8533.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
54	D¹	0.8523	180
54	D²	.8528	105
57	C¹	.8528	180
54	E¹	.8530	245
60	B	.8540	330
			1,040

Lot 69.

[Specific gravity, 0.8556.]

Lot.	Fraction.	Specific gravity.	Cubic centimeters.
55	E¹	0.8540	270
55	D²	.8543	50
56	C¹	.8546	170
54	E²	.8548	60
54	F	.8548	145
57	D¹	.8551	185
56	D¹	.8553	150
56	E¹	.8553	145
56	D²	.8560	92
56	E²	.8563	90
55	F	.8566	180
57	E¹	.8568	170
57	D²	.8573	45
56	F	.8575	130
			1,882

Oils used for fourth fractionation—Continued.

Lot 70. [Specific gravity, 0.8596.]				Lot 71. [Specific gravity, 0.8638.]			
Lot.	Fraction.	Specific gravity.	Cubic centimeters.	Lot.	Fraction.	Specific gravity.	Cubic centimeters.
58	C^1	0.8578	205	59	D^2	0.8623	135
59	C^1	.8578	325	60	D^1	.8628	440
58	D^1	.8588	205	59	E^1	.8628	475
59	C^2	.8588	112	58	F	.8628	375
57	E^2	.8588	70	60	D^2	.8638	85
58	C^2	.8592	105	59	E^2	.8633	155
58	D^2	.8593	340	60	E^1	.8664	425
60	C^1	.8601	290				1,990
58	E^1	.8603	325				
59	D^1	.8608	490				
57	F	.8611	170				
58	E^2	.8613	170				
60	C^2	.8618	130				
			2,937				

Results of fourth fractionation.

	62		63		64		65	
Specific gravity	0.8298		0.8343		0.8368		0.8430	
Number of tubes	1		1		1		1	
Hours required	72		72		90		48	
Fraction.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A	0.8243	32	0.8273	45	0.8297	41	0.8308	42
B	.8298	71	.8357	75	.8378	57	.8428	70
C	.8323	90	.8378	95	.8401	81	.8463	92
D	.8330	115	.8383	130	.8408	115	.8473	130
E	.8333	130	.8388	98	.8413	135	.8471	130
F	.8341	75	.8393	95	.8418	70	.8483	80
		513		538		499		544

Specific gravity.—As in the preceding fractionations, the decrease in the range of specific gravity as the mother oils became lighter was again observed in this fractionation. It was evident, moreover, that there was a constant forward accumulation toward definite and constant mixtures. The lighter oils of one lot were found to possess specific gravities closely approaching those of the heavier oils of the preceding lot.

Color.—The oils of fraction A were almost colorless; the color of the heavier oils ranged from green to light brown.

Odor.—All the oils of this fractionation possessed agreeable odors.

Volume of oil retained.—The volume of oil retained by the earth amounted to approximately 40 per cent.

Deposition of paraffin.—In fractions A and B of several of the lots a fine crystalline deposit separated out and collected upon the bottom of the bottles containing the oils. When the oils were warmed, this deposit dissolved completely, showing it to be paraffin.

CHEMICAL EXAMINATION OF FRACTIONATED OILS.

UNSATURATED HYDROCARBONS.

ACTION OF CONCENTRATED SULPHURIC ACID.

The percentage by volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure. Ten cubic centimeters of the oil to be examined was measured into a glass-stoppered bottle, and 30 cubic centimeters of concentrated sulphuric acid was added. The mixture was thoroughly shaken by a machine for 30 minutes and then poured into a burette. After sufficient time had been allowed for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbed oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil. The results of the analyses are given in the following table:

Oil absorbed by concentrated sulphuric acid, lot 51.

	Per cent by volume.
Fraction A	2.3
B	6.1
C^1	9.1
C^2	10.2
D^1	11.5
D^2	12.0
E	12.5
F	14.5

ACTION OF BROMINE.

The following method was employed for determining the amount of bromine absorbed by the oils. Between 0.5 and 0.9 gram of the oil to be examined was dissolved in 10 to 15 cubic centimeters of carbon tetrachloride. Five cubic centimeters of a standard solution of bromine in carbon tetrachloride was then introduced, and the solution allowed to remain, with occasional shaking, in a dark place for 30 minutes. Ten cubic centimeters of a 10 per cent solution of potassium iodide was then added, and the amount of iodine liberated was determined immediately by titrating with a standard solution of sodium thiosulphate. A few drops of a starch solution were introduced to mark accurately the end of the titration. The separate amounts of bromine absorbed by addition and substitution were not estimated. The amounts of bromine absorbed, expressed in the table below, are calculated on the basis of 100 grams of oil.

Bromine absorbed by oil.

First fractionation.

		Per cent.
Lot 32, fraction	A	5.02
	B	6.96
	C	7.40
	D	7.87
	E	8.00
Crude oil		7.64

Second fractionation.

		Per cent.
Lot 36, fraction	A	4.74
	B^1	5.40
	B^2	5.66
	C^1	5.56
	C^2	6.18
	D^1	6.81
	D^2	6.28
	EF^1	6.49
	EF^2	7.18

Third fractionation.

		Per cent.
Lot 51, fraction	A	3.27
	B	4.36
	C	4.47
	D	4.92
	E	4.71
	F	5.36

Fourth fractionation.

		Per cent.
Lot 62, fraction	A	2.86
	E	3.73

These results demonstrate conclusively that the unsaturated hydrocarbons tend to collect in the lower sections of a layer of fuller's earth through which the oil is allowed to diffuse. The figures confirm the results obtained by Gilpin and Cram in their work on Pennsylvania petroleum. In their investigation distillation by heat was employed in order to obtain fractions that could be readily studied. In the work here reported the relative amounts of the unsaturated hydrocarbons in the oils were determined directly as they came from the earth.

The percentages by volume of oil absorbed by concentrated sulphuric acid represent only approximately the percentages of unsaturated hydrocarbons, for, as was shown previously, any benzene which may have been present in the oils was also removed by the concentrated acid. This fact rendered impossible a quantitative separation of the aromatic from the unsaturated hydrocarbons. As no other methods besides nitration and sulphonation, neither of which could be here employed, were available, no results as to the relative amounts of the aromatic hydrocarbons in the various fractions could be obtained.

It is evident from the results of the bromine determinations that as the fractionation proceeds the amounts of unsaturated hydrocarbons become smaller and smaller. A comparison of the amounts of bromine absorbed by fraction A of the first, second, third, and fourth fractionations is given below for the purpose of bringing out this point more clearly.

Bromine absorbed by fraction A.

	Per cent.
First fractionation	5.02
Second fractionation	4.74
Third fractionation	3.27
Fourth fractionation	2.86

SULPHUR COMPOUNDS.

The amount of sulphur in the oils was determined by the usual method of combustion. For these determinations the oils obtained from one tube of lot 6 were employed. The results are given in the following table:

Sulphur in oils of lot 6.

	Specific gravity.	Per cent of sulphur.
Fraction A	0.8195	0.04
B	.8362	.05
C	.8440	Lost.
D	.8510	.09
E	.8600	.16

The percentage of sulphur in fractions A, C, and E of lot 51 was also determined. The results were as follows:

Sulphur in oils of lot 51.

	Per cent.
Fraction A	0.003
C	.040
E	.006

These results show that the sulphur tends to collect in the oils in lower sections of the tube. As the fractionation proceeds the proportion of sulphur becomes smaller. The figures below indicate that as the oil is subjected to repeated filtrations the sulphur is gradually removed.

Sulphur remaining after first, second, and third fractionations.

	First.	Second.	Third.
Fraction A	0.04	....	0.003
C	....	0.08	.040
E	.16	....	.006

SELECTIVE ACTION OF FULLER'S EARTH.

When the earth from which as much oil as possible has been extracted by prolonged treatment with water is dried and digested with ether, oils of surprisingly high specific gravity and viscosity are obtained.

In the experiments undertaken to study the selective action of fuller's earth, the following method of procedure was adopted. The earth under examination was treated with water until no more oil appeared. This muddy earth, of the consistency of thin liquid paste, was spread upon porous plates and allowed to dry at room temperature. Several weeks usually elapsed before the earth became completely dry. It was then pulverized, and after being thoroughly soaked and shaken with ether, the mixture was allowed to remain undisturbed for 24 hours or more. The mixture was then filtered and the dissolved oil recovered by distilling off the ether from the filtrate. The residual earth was then digested with ether for some time by means of an electric stove that completely surrounded the flask. The oil thus extracted was added to the oil first obtained. In several cases the residual earth was treated further with ether in the Soxhlet extractor. The results of these extractions are given in the following table:

Oils extracted by ether.

Lot.	Fraction.	Specific gravity at 50° C.	Lot.	Fraction.	Specific gravity at 20° C.
7	A	0.8470	25	A^3	0.8391
8	A	.8502	25	B	.8489
18	A^1	.8419	51	A	.8368
18	A^2	.8400	51	B	.8473
19	A^1	.8495	51	C	.8491
19	A^2	.8495	51	D	.8568
19	A^3	.8600	51	E	.8518
25	A^1	.8363	51	F	.8553
25	A^2	.8381			

The specific gravity of none of the ether-extracted oils of the first and second fractionation, except those of lot 19, could be determined at 20° C. All were extremely viscous; those of lot 25 were so viscous at this temperature that they would not flow when the bottles containing them were inclined. The color of the oils ranged from brown to black. The ethereal solutions, however, of many of the oils were very light in color.

It is interesting to compare the specific gravities of the ether-extracted oils with those of the corresponding water-extracted oils. For this purpose, the oils extracted by water and by ether from the earth of lot 51 are chosen. In the following table the specific gravities of these oils at the same temperature (20° C.) are given.

Comparison of specific gravities.

	Ether-extracted oils.	Water-extracted oils.
Lot 51, fraction A	0.8363	0.8213
B	.8473	.8303
C	.8491	.8337
D	.8568	.8353
E	.8518	.8366
F	.8553	.8373

As the figures indicate, the specific gravities of ether-extracted oils are much higher than those of the corresponding water-extracted oils. The presence of such heavy and viscous oils in the upper sections of the tube can be explained only by assuming that they were carried to these heights in solution with the lighter oils and were then removed by the earth. As such viscous oils are totally unable to diffuse by capillarity to any appreciable extent, it is not probable that their transportation to the upper parts of the tube was effected by capillary diffusion.

CHEMICAL EXAMINATION OF THE OILS EXTRACTED BY ETHER.

UNSATURATED HYDROCARBONS.

ACTION OF CONCENTRATED SULPHURIC ACID.

The percentage by volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure: Ten cubic centimeters of the oil to be examined was measured into a glass-stoppered bottle, and 30 cubic centimeters of concentrated sulphuric acid was added. The mixture was thoroughly shaken by a machine for 30 minutes and then poured into a burette. After sufficient time had been allowed for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbed oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil. The oils selected for examination were those extracted by ether from the earth of lots 36 and 51. The results of the analyses are expressed in the following table:

Action of sulphuric acid on oils extracted by ether and by water.

[Per cent by volume absorbed.]

	Ether-extracted oils.	Water-extracted oils.
Lot 36, fraction A	24	3
B	37	10.4
Lot 51, fraction A	7	2.3
B	11.5	6.1
C	17	9.1
D	16.4	11.5
E	16.5	12.5
F	18	14.5

ACTION OF BROMINE.

The method employed for determining the amount of bromine absorbed by the oils was as follows: Between 0.5 and 0.9 gram of the oil to be examined was dissolved in 10 to 15 cubic centimeters of carbon tetrachloride. Five cubic centimeters of a standard solution of bromine in carbon tetrachloride was then introduced, and the solution allowed to remain, with occasional shaking, in a dark place for 30 minutes. Ten cubic centimeters of a 10 per cent solution of potassium iodide was then added, and the amount of iodine liberated was determined immediately by titrating with a standard solution of sodium thiosulphate. A few drops of a starch solution was introduced to mark accurately the end of the titration. The separate amounts of bromine absorbed by addition and substitution were not estimated.

The amounts of bromine absorbed, expressed in the following table, are calculated on the basis of 100 grams of oil. The values for the corresponding water-extracted oils are also given for comparison.

Bromine absorbed by oil extracted by ether and water.

	Ether-extracted oils.	Water-extracted oils.
	Per cent.	*Per cent.*
Lot 32, fraction A	5.30	5.02
B	7.39	6.96
Lot 36, fraction A	5.72	4.74
B	6.10	5.40
C	6.72	5.56
Lot 51, fraction A	3.27	3.27
B	4.45	4.36
C	6.27	5.03
D	6.09	4.92
E	5.98	4.71
F	5.20	5.36

As these results clearly demonstrate, one of the properties of fuller's earth is to retain the unsaturated hydrocarbons, thus exercising a selective action.

SULPHUR COMPOUNDS.

The sulphur in the oils obtained by extraction with ether was determined by the usual method of combustion. The results are given in the table below.

Sulphur in oils extracted by ether and water.

	Ether-extracted oils.	Water-extracted oils.
	Per cent.	*Per cent.*
Lot 51, fraction A	0.004	0.003
B	.011	....
C	.050	.040
D	.060	....
E	.080	....
F	.080	.006

The selective action of the earth, in regard to the sulphur compounds, is indicated by these results. This fact was also pointed out by Richardson and Wallace. It is very probable that the earth also retains largely the nitrogen compounds in the oil, and it may also remove to a greater or less extent the benzene hydrocarbons.

These results seem to furnish evidence in favor of the view that the Illinois oil at some time in its history diffused through porous media, which exercised a selective action upon it, removing a large part of the unsaturated and sulphur compounds and probably the benzene and nitrogen compounds.

SUMMARY.

When a solution of benzene and a paraffin oil is allowed to diffuse upward through a tube packed with fuller's earth, the benzene tends to collect in the lower sections and the paraffin oil in the upper sections of the tube.

When crude petroleum diffuses upward through a tube packed with fuller's earth a fractionation of the oil occurs. The oil that is displaced by water from the earth from the top of the tube possesses a lower specific gravity than the oil obtained from the earth at the bottom of the tube.

As the fractionation proceeds the range of specific gravity covered in succeeding fractionations becomes smaller, indicating a movement toward the production of mixtures which will finally pass through the earth unaltered.

In the fractionation of petroleum by capillary diffusion through fuller's earth the amounts of unsaturated hydrocarbons and sulphur compounds in the resulting fractions increase gradually from the lightest oils at the top to the heavier oils at the bottom of the tube.

Fuller's earth tends to retain the unsaturated hydrocarbons and sulphur compounds in petroleum, thus exercising a selective action upon the oil.

O