The Fractionation of California Petroleum by Diffusion through Fuller's Earth

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

PHILIP SCHNEEBERGER

JUNE, 1913

EASTON, PA.
ESCHENBACH PRINTING CO.
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Fractionation of California Petroleum by Diffusion through Fuller's Earth.[1]

For several years investigations have been in progress in this laboratory upon the effect produced by diffusion of petroleum oils through fuller's earth. These investigations were pursued in order to obtain some idea of the changes produced in the process of diffusion to which the oils have been subjected in their passage from the place of formation to their present location; also, to gain some idea of the substances present in the natural oil by a separation of the constituents by a process not involving the use of heat, and thereby producing changes by cracking and otherwise. The results obtained when a light oil from Pennsylvania and a heavier oil from Illinois were thus fractionated have already been published.[2] In the present investigation, this method of fractionation was extended to a very heavy petroleum from California. As will be later described, the different fractions obtained by such diffusion were studied with regard to their content of

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[1] This research was aided by a grant received from the C. M. Warren Committee of the American Academy of Arts and Sciences.

[2] Gilpin and Cram: "The Fractionation of Crude Petroleum by Capillary Diffusion," *Am. Chem. J.*, **40**, No. 6, December, 1908. Gilpin and Bransky: "The Diffusion of Crude Petroleum through Fuller's Earth," *Ibid.*, **44**, No. 3, September, 1910.

paraffin, benzene, and olefin hydrocarbons, and to the amount of sulphur and nitrogen compounds found in them and in the earth through which they passed. For the sake of comparison, the behavior of mixtures of known amounts of benzene and pure paraffin oil, when allowed to diffuse through fuller's earth, were also studied.

DESCRIPTION OF OILS USED

California Oil I.—Viscous, brownish black in color; of a syrupy consistency, and failed to flow from a small vessel when cooled to —10°; possessed a disagreeable odor, suggestive of organic sulphur compounds; specific gravity at 20°, 0.912; when distilled, the first fraction came over at 90°, colorless and agreeable in odor; the last fraction came at 380°, brown, disagreeable in odor, resembling garlic, but supposed to be due to hydrides of the hydrocarbons, formed during the cracking of the oil; analysis showed appreciable amounts of sulphur compounds present. This oil came from Kern County, California.

California Oil II.—Less viscous than the first oil, and of less disagreeable odor; specific gravity, taken with a delicate Westphal balance at 20°, 0.8890; when distilled, fractions were obtained from 100° to 350°; contained a small proportion of benzene hydrocarbons and 0.760 per cent. of nitrogen compounds; no trace of sulphur compounds was found. The oil came from Well No. 1, Section 30–30–24, Elk Hills, Kern County.

California Oil III.—Fairly viscous, brownish black oil, of somewhat disagreeable, smoky odor; specific gravity, 0.9118 at 20°; when distilled, fractions were obtained from 105° to 340°, attempts to obtain fractions at higher temperatures resulting in the cracking of the oil, giving fractions ranging around 270°; rich in benzene and olefin hydrocarbons, but entirely free from nitrogen and sulphur compounds; its properties resembled closely those of the first California oil. The petroleum came from Well No. 1, Section 30, Elk Hills, Kern County.

Pennsylvania Oil.—A light, thin, dark brown oil from Venango County, Pennsylvania; possessed an agreeable odor; specific gravity at 20°, 0.8470. This was the same oil that had been investigated by Gilpin and Cram, and Gilpin and Bransky. Between the time when this oil was first studied and its investigation in 1912 and 1913, its specific gravity had increased from 0.810 to 0.8470 by evaporation through the barrel staves.

INVESTIGATION OF CALIFORNIA OIL I

The oil first studied was the heavy petroleum from Kern County, California. A description of this oil, named the California Oil I, is found on page 6.

The method of handling this oil was practically the same as that introduced by Gilpin and Cram and improved by Gilpin and Bransky. The apparatus in which the diffusion was carried out was similar to that employed by Gilpin and Bransky. Two minor additions were made to the apparatus. The first of these was a manometer which recorded pressures from 730 mm. to 0 mm. when attached to the exhaust system. The other was a device which it was found necessary to put in series with the exhaust system, owing to the fact that the exhaust was obtained by use of a large Chapman water pump. Fluctuations in the water pressure were accompanied by fluctuations in the amount of exhaust. The device by which the suction could be maintained uniform for any length of time consisted of a sliding tube with perforations at its lower end, that could be adjusted by raising or lowering in a reservoir of mercury according as lower or higher pressures were desired.

It was found at the start that an oil as heavy as this one could not be made to diffuse of itself by capillarity at room temperatures (19° to 23°). To produce the necessary diffusion, reduced pressures were brought to bear, pressures as low as 12 mm. of mercury being maintained for days at a time.

In the preliminary experiments, sixteen tubes were filled with fuller's earth.[1] The tubes were filled by dropping into them an amount of earth that would form a column about a

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[1] This earth, known as "XXF Clay," and the fuller's earth used in later work were obtained by courtesy of the Atlantic Refining Co., Philadelphia, Pa.

foot in height. Since all ranges of compactness of the earth were desired, the earth in some tubes was not compressed in any way. In others it was rammed slightly by a rod tipped with a rubber stopper. In a third set, it was rammed fairly hard, and in a fourth as hard as possible. The tubes were then allowed to stand undisturbed for a short while, so as to permit the cushions of air held between layers of the earth to escape. A second column of earth a foot in height was then added, the same degree of packing observed, and the process repeated until the tubes were filled. They were then placed with their lower ends in separate reservoirs of oil, and a reduced pressure of 600 mm. was then applied to the upper ends. This failed to produce any diffusion, as could be determined by the level of the oil in the reservoirs, so the pressure was gradually reduced until 20 millimeters of mercury were registered on the manometer. There was, however, no sign of actual fractionation of the oil in any of the tubes, but, instead, at the low pressure that was employed the oil was drawn up through the earth unchanged in any of its properties.

An explanation of the failure of the oil to fractionate was found in the high viscosity of the petroleum. The oil, instead of diffusing through each minute particle of earth, was sucked around the particles and emerged unaltered at the top of the tube.

The cause of the high viscosity of the oil was doubtless the very large quantity of bitumen and the complex hydrocarbons present, whose boiling points were as high as 380°. Accordingly, efforts were directed toward reducing the viscosity of the oil by coagulating the bitumen. It was shaken with a solid electrolyte and with a solution of the same, but repeated experiments failed to show any perceptible reduction in specific gravity or viscosity, nor was there any noticeable coagulation of the bituminous material held in suspension in the oil.

It was observed, however, that any rise in temperature of the oil was accompanied by a marked decrease in viscosity. Accordingly, the effect of this reduction in viscosity upon the fractionation of the crude petroleum was next studied. In order to secure uniform conditions, it was deemed advisable to have the reservoirs for the oil and also the lower part of the tubes immersed in a large water bath, the temperature of which could be regulated and maintained uniform by a gas thermostat. An appliance that could withstand the action of the heated water and oil was, therefore, devised. Glass bottles, fitted with water-tight stoppers and safety tubes, could not be employed, for these broke when temperatures above 60° were reached. For the fractionation at high temperatures, each tube was constructed of brass, and was made to fit snugly into a closed reservoir of a liter in volume. Contact between the tube and the neck of the reservoir was made perfect by having a lead washer which was held rigidly between the two by a nut that screwed down upon the neck of the reservoir.

To determine the most desirable temperature at which the experiments should be carried out, the viscosity of the oil was measured at different temperatures. The apparatus was the same as used by a previous experimenter.[1] With the viscosimeter it was found that a measured quantity of the oil used by Bransky diffused at the following rates:

4.5 cc. of Pennsylvania Oil (sp. gr. 0.8470):

	Minutes
At 20°	10.25
At 40°	6.00

When a similar quantity of the California Oil I was run through the viscosimeter, it was found that the time required was vastly greater. The following results were obtained at different temperatures:

Table I

4.5 cc. California Oil I (sp. gr. 0.912)

	Minutes
At 20°	84.0
At 40°	41.0
At 60°	17.5
At 75°	11.3
At 90°	8.1

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[1] *Am. Chem. J.*, **44**, No. 3.

From the above results, it is apparent that a temperature of at least 75° is necessary for diffusion, since the viscosity of the oil at lower temperatures was so great as to prevent its fractionation by diffusion. The temperature of 90° was ruled out because at that temperature there was a tendency for the lightest ingredients of the oil to distil off. This was determined by keeping a measured quantity of the oil at 90° for a week. A quantity amounting to about two per cent. was found to distil off. For this reason it was deemed advisable to carry on the diffusion of the oil at 75°.

Accordingly, eight tubes packed with varying degrees of hardness were maintained at 75°, and at the end of nine days these yielded the first fractions of the heavy California oil (specific gravity, 0.912). Nearly 90 liters of the oil had to be used to obtain the four fractions in the amounts shown below:

Table II—First Fractionation of California Oil I

Fraction	Sp. gr.	Quantity Liters
1–A	0.8695[1]	1.2
1–B	0.882	1.4
1–C	0.9025	1.8
1–D	0.904	1.75
	Total	6.15

There was thus secured a small proportion of available fractions. This was obtained, however, only after very great difficulties had been overcome and with a loss of nearly 93 per cent. of the original oil. The results demonstrate, nevertheless, the possibility of fractionating a heavy, viscous petroleum. Owing to the difficulties encountered in working with large quantities of the oil at elevated temperatures, it was decided to discontinue work on this heavy petroleum until more adequate means of handling it under the necessary conditions were at the disposal of the experimenter.

The four fractions from the California Oil I, designated as 1–A, 1–B, 1–C and 1–D, were then analyzed for their sulphur

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[1] All specific-gravity measurements were taken at exactly 20° with a delicate Westphal balance.

content. Similar determinations were made for the oil retained by the earth.

Determination of Sulphur Compounds in the California Oil I

The odor of the high-boiling fractions of this oil led to the suspicion that sulphur compounds were present. Accordingly, qualitative tests were made to detect the presence of this element. These tests were as follows:

About 10 cc. of the sample to be tested were heated to boiling in a flask provided with a reflux condenser. About half a gram of metallic sodium was introduced, and the liquid heated to the boiling point for about thirty minutes. After cooling to room temperature, water was gradually introduced through the condenser and the flask shaken until the sodium had gone into solution. The solution of the hydroxide containing the sodium sulphide was separated, and the addition of sodium nitroprusside produced a purplish blue or deep purple coloration. A quicker method for the qualitative determination of sulphur was one that is employed in the petroleum industry. A solution of litharge in concentrated potassium hydroxide solution was prepared. The undissolved litharge was allowed to settle, and the clear solution decanted. Several cc. of the oil to be tested were shaken with a small quantity of the potassium plumbite solution, and the oil allowed to rise. The plumbite solution was colored from pale brown to black, according to the amount of sulphur present.

Quantitative determination of sulphur by the usual Carius method failed, the bombs exploding in every one of the fifteen analyses that were attempted. Carius determinations made in hard glass tubes gave no better results. A modified Carius method was then employed. This was essentially as follows: A weighed sample of the oil was introduced into a Carius tube and 5 cc. of fuming nitric acid were poured upon it. The open tube was then heated for two hours in a water bath at 100°. Five more cc. of the acid were then added, and the heating re peated for two more hours. Then five cc. of the acid were again introduced, the tube was drawn out and sealed, and then heated for two hours in a bomb furnace at 280°. The charge of the tube, when cool, was emptied into several hundred cc. of water, and the sulphur determined as barium sulphate by the usual method. This modified Carius method gave results that were somewhat lower than the results obtained by the methods finally employed. This was probably due to the volatilization of the sulphur compounds when the open tube was heated.

The methods found to be most satisfactory, however, were the Sauer combustion method, described in detail in Morse's Exercises in Quantitative Chemistry (pp. 258–60), and a method by which the oil was oxidized in a flask by concentrated nitric acid and potassium chlorate. The two methods gave concordant results. In every instance duplicate analyses were made, and the mean result given in the table below. The fractions analyzed were those described on p. 10.

Table III—Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A	0.8695	0.11
1–B	0.882	0.144
1–C	0.9025	0.174
1–D	0.904	0.29
Crude oil	0.912	0.541

In order to see if the proportion of sulphur could be further reduced by filtration through fuller's earth, Fractions A and B were refractionated and the results of the second fractionation were analyzed with respect to their sulphur content. The fractions from A are designated as 1–A 1, 1–A 2 and 1–A 3; those from 1–B as 1–B 1, 1–B 2 and 1–B 3.

Table IV—Second Fractionation: Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A 1	0.857	0.06
1–A 2	0.8604	0.07
1–A 3	0.869	0.104
1–B 1	0.8625	0.072
1–B 2	0.8771	0.09
1–B 3	0.8803	0.141

The results tabulated above show that there is a gradual absorption of sulphur compounds by the fuller's earth. Those fractions that collect at the top of the tubes have the smallest proportion of the sulphur compounds in them, and the amount increases as fractions lower down are taken. The explanation of the comparatively small amount of sulphur in the uppermost fraction is probably as follows: the original petroleum penetrates a grain of the porous fuller's earth, emerges on the other side and has a portion of its sulphur removed and retained by the earth. The possible mechanism of this selective absorption by the earth is discussed later. The oil then enters another grain of earth, the absorptive action of the earth is repeated, and more of the sulphur is removed. The oil that thus penetrates by diffusion up to the top of the tube has passed through the greatest number of grains of earth and thus contains less sulphur than the oil that has not penetrated so far. Moreover, the oil that follows in the track of the first particle of oil which penetrates the earth finds particles of earth that have already taken up the greatest quantity of sulphur that is possible for them to absorb. Hence the second particle of oil passes through earth that is already saturated with respect to its power to absorb sulphur compounds, and it may pass through unchanged, or nearly so. This accounts for the fact that the fractions that are nearest to the original petroleum have chemical and physical properties that closely resemble those of the crude petroleum.

Judging from the results obtained from the second fractionation, it is probable that if enough of the lighter fractions were available for carrying on several more fractionations, the sulphur could be entirely removed.

In order to show to what extent the earth retained the sulphur compounds which were originally in the oil, the earth from which the oil had been displaced by the addition of water was extracted with ether. By this process, oils were obtained which were heavier than those oils expelled by the addition of water. These were analyzed for sulphur, with the following results:

Table V—Analysis of Oil Retained by Earth

Section of earth	Sp. gr.	Per cent. sulphur
Oil extracted from A	0.8955	0.11
Oil extracted from B	0.9038	0.237
Oil extracted from C	0.9105	0.42
Oil extracted from D	0.927	0.675

These results show that it is undoubtedly the earth through which the oils pass that retains the sulphur compounds. They show, moreover, that the earth in the lowest parts of the tube absorbs so much of the sulphur compounds from the oil that passes through them that the proportion of these compounds in the lower end of the tube indicates a concentration that is greater than that in the original petroleum.

INVESTIGATION OF CALIFORNIA OIL II

In working with the heavy California petroleum from which the fractions described above were obtained by diffusion at elevated temperatures, it was pointed out that such fractionation was exceedingly difficult to effect, and at an enormous loss of petroleum. Owing to these results a lighter oil from the same locality was secured. This lighter oil was the one described as the California Oil II (see p. 8). Its properties were somewhat different from the oil first studied. The principal physical differences noted were viscosity and specific gravity, the latter being 0.889 in contrast to 0.912, that of the California Oil I. The viscosity was taken at various temperatures with the following results:

Table VI—Viscosity Measurements of California Oil II (4.5 cc. Run Through)

Temperature of oil	Time Minutes
20°	24.0
30°	17.1
40°	12.2
50°	9.1

It was decided to work with this oil at room temperature, owing to the difficulties arising from the fractionation of large quantities of oil at elevated temperatures. Attention was then turned toward the problem of finding the length of tube most desirable for fractionating an oil of specific gravity 0.889 at 20°.

It was necessary, in addition, to ascertain the proper amount of pressure that should be brought to bear to bring about diffusion. For this purpose glass tubes of 3.2 cm. in diameter and varying in length from 30 to 150 cm. were employed. The object in using glass tubes was to enable the observer to see to what extent fractionation was taking place as the amount of pressure on the tubes was changed. It was soon found that a fractionation of the petroleum could be produced working at room temperatures. While the results obtained were not as satisfactory as those obtained with light Pennsylvania oil of specific gravity 0.8470, they demonstrated the possibility of fractionating an oil of specific gravity 0.889 by diffusion through fuller's earth at ordinary temperatures. The yield of available fractions, however, amounted to only twenty per cent. of the oil used, while in the case of the lighter Pennsylvania oil, it was 45 to 50 per cent. of the petroleum used.

The length of tube that gave the most satisfactory results was found to be about 90 cm. The degree of compactness of the earth that gave best results was obtained by tapping the sides of the tube, and refraining from ramming, as all previous packing had been done. A column of earth a foot long was introduced into the tube, and it was tapped lightly on its side until the top of the column presented a firm surface.

The method employed in extracting the oil from the earth into which it diffused consisted in taking measured sections from the earth[1] after it had been carefully emptied into a cylinder that was split longitudinally, and adding water to each section. The water formed a thick emulsion with the earth and expelled a part of the oil, retaining, however, an oil that was heavier than that expelled. It was noticed that the lighter oils were displaced in much greater proportion than were the heavier oils, for the earth showed a tendency to remain in mechanical combination with the oil, holding almost

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[1] The section of earth from the uppermost part of the tube was called A, and the oil extracted therefrom called 2–A. The next lower section was called B, and its oil 2–B, etc.

100 per cent. if the specific gravity approached 0.9. When an examination of the oil retained by the earth was desired, the oil was extracted from the dried earth by ether. By the ether extraction an oil of different physical and chemical properties was secured. This proved that the fractions obtained by displacement of the oil by water did not represent the actual fractions formed during diffusion through the earth, but only a small part of such fractions.

The method of securing fractions of oil by displacement by water was then dispensed with and another method introduced. This consisted in allowing the oil to diffuse to the top of the tube and then letting it overflow into small tubes of about 70 cc. capacity. The oil that first overflowed and collected in the upper reservoir constituted the first fraction. The first fraction was usually very light in color and specific gravity. As the diminished pressure continued to be applied, a heavier oil began to flow into the upper reservoir. When a change in color was noticeable, the reservoir was emptied or exchanged for another, and the pressure was temporarily cut off from the tube by means of pinchcocks while the change was being made. The second fraction was then collected until a change in color was noticed, and so on with a third, until an oil that was colored brown by the bitumen of the petroleum drained into the upper reservoir. The reduced pressure was then cut off, the tubes cleaned and refilled with fresh fuller's earth, and the process repeated.

By repeated experiment, the amount of pressure that gave the best results was determined and regulated as follows: the tubes were allowed to stand in the reservoirs of petroleum for abour 24 hours, without any reduced pressure being applied. Then, for a period of about three days, the pressure was gradually reduced until the manometer registered 650 mm. of mercury. After being maintained at this height for several days, the pressure was then lowered to 500 mm. and kept there until the first fractions overflowed into the upper reservoirs. When this pressure failed to draw up a slow, steady stream of oil into the reservoirs, it was still further reduced, usually being made as low as 200 mm., by the time that the last available fraction had been collected.

By this method of operating, the California Oil II was found to be capable of fractionation into five distinct fractions. The lightest, termed Fraction 2–A, was of specific gravity 0.8264; the heaviest, 2–E, 0.8737, showing a wide range in density (see p. 18).

The basis upon which the various fractions were differentiated was their color, as it was observed that the depth of color was an approximate measure of the specific gravity of the oil.

The fractions 2–A to 2–E were examined for nitrogen, and all of them showed signs of its presence. Careful analyses of these were then made, and similar analyses of the earth in various parts of the tube were made. Fractions 2–A and 2–B were then subjected to a second fractionation, and the results also studied with regard to their nitrogen content.

Determination of Nitrogen Compounds in California Oil II

Nitrogen compounds were found to exist in the California Petroleum II to the extent of nearly 0.8 per cent. Accordingly, this oil was subjected to fractionation by the improved method that was adopted by the investigator (see p. 16). This was necessary since the oil was too heavy to be worked by the method of Cram and Bransky unless elevated temperatures were resorted to in order to reduce the viscosity. Besides, it was feared that high temperatures would bring about the loss of the nitrogen compounds by volatilization.

The method for determining the nitrogen was that known as the Gunning-Arnold-Dyer modification of the Kjeldahl method. It is described in detail in Sherman's Organic Analysis (pp. 291–4). It was found necessary to digest the light oils as long as 3 or 4 hours and the heavy ones as long as 8 hours before the contents of the digestion flask became colorless. Another necessary precaution had to be observed in applying heat very gradually to the flask at the beginning of the digestion, otherwise the nitrogenous material distilled off, giving results that were far below those obtained when greater precaution was exercised.

Table VII— Nitrogen Determinations

Fraction	Sp. gr.	Per cent. nitrogen
2–A	0.8264	0.08
2–B	0.8421	0.116
2–C	0.852	0.289
2–D	0.8614	0.315
2–E	0.8737	0.332
Crude oil	0.889	0.761

These results show that the proportion of nitrogen compounds is reduced in the lightest fraction to nearly one per cent. of its total amount. This proportion of nitrogen was still further reduced by the second fractionation of the two lightest fractions. The fractions obtained from 2–A are designated by 2–A 1, 2–A 2, etc. Those from 2–B are designated by 2–B 1, 2–B 2, etc.

Table VIII—Second Fractionation of California Oil II

Fraction	Sp. gr.	Per cent. nitrogen
2–A 1	0.8117	Trace
2–A 2	0.8186	Trace
2–A 3	0.8193	0.03
2–A 4	0.8240	0.06
2–B 1	0.8205	Trace
2–B 2	0.8386	0.045
2–B 3	0.8414	0.09
2–B 4	0.8421	0.109

From the above results it is apparent that the fuller's earth is particularly potent in selectively absorbing nitrogen compounds from the oil. In view of the fact that but two filtrations through the earth succeeded in reducing the amount of nitrogen present to such a small proportion as compared to that in the petroleum, it is probable that a third filtration would have reduced it to zero. A third fractionation would have been made, but lack of workable material rendered this impossible.

The analysis of the oil retained by the earth taken from the upper, middle and lower ends of the tubes showed that the part in the lowest sections of the tube had absorbed the greatest amount of the nitrogen compounds from the petroleum. The oil was extracted from sections of earth, taken at different levels from the tubes, by ether. The ether was evaporated off in an electrical drying oven at 50°.

Table IX—Analysis of Oil Retained by Fuller's Earth

Section of tube	Sp. gr.	Per cent. nitrogen
Upper end	0.8413	0.205
Middle section	0.8655	0.43
Lower end	0.9172	0.94

The concentration of the nitrogen compounds in the lower end of the tubes is apparent. It is noticeable that the percentage of nitrogen here is slightly greater than it was in the original petroleum. This was to be expected, inasmuch as the earth in the lower end of the tube came into contact with the greatest amount of oil and could thus selectively absorb more of the nitrogen compounds than earth in the upper end. Moreover, earth in the upper end came into contact with oil that had already had a portion of its nitrogen compounds removed and could not, for that reason, extract as much nitrogenous material from it as it could from oil that was much richer in nitrogen compounds.

The study of the benzene and olefin hydrocarbons in California petroleum was next contemplated. Before taking this up, it was considered advisable to study with some degree of accuracy the behavior of known mixtures of benzene and pure paraffin oilwhere such mixtures were allowed to diffuse through fuller's earth. This problem had been investigated before by earlier workers in this field, and certain conclusions arrived at, but a further study of the same, working under somewhat different conditions, was now resumed.

FRACTIONATION OF MIXTURES OF BENZENE AND PARAFFIN OIL

In previous work by Gilpin, Cram and Bransky on the fractionation of crude petroleum, it was noted that there was a tendency for the pure paraffin hydrocarbons to collect in the upper section of the tube through which the petroleum was allowed to diffuse. To investigate this more closely, Gilpin and Bransky studied the behavior of mixtures of benzene and paraffin oil, such mixtures being of definitely known composition, and plotted their results in curves that showed the relative amounts of benzene and paraffin oil that collected in all parts of the tube. The curves show, moreover, that the proportion of benzene decreases gradually as one passes from Grade F (the oil from the lowest section of the tubes) to Grade C (the oil from the third section of the tubes), Grade A being considered that fraction from the uppermost part of the tubes. Above Grade C, there is a sharp decrease in the proportion of benzene, the same dropping far below the proportion in the original mixture that was put into the reservoir. It was also noted that the curves representing the specific gravities of the various sections were about parallel with those representing the percentages of benzene. This was to be expected, since the benzene was of considerably higher specific gravity than the paraffin oil. The tubes employed measured five feet six inches in length.

With the view to determine more accurately the exact location of the break in the curve, and to ascertain if it was a function of the length of the tube, investigation along this line was begun by the authors. In order to study the latter problem, it was decided to use shorter tubes, those of two feet nine inches in length being chosen. Correspondingly smaller sections of earth were taken, and the oil was displaced from them by the addition of water.

The benzene used was of specific gravity 0.879. The method of analysis used to determine the proportion of benzene and paraffin oil in each fraction consisted in shaking 10 cc. of the oil with three or four times its volume of concentrated sulphuric acid, until all of the benzene had been sulphonated. Then the shaken material was poured into a burette and allowed to stand until all the paraffin oil mechanically held in combination with the acid had separated out.

To determine the length of time necessary for shaking in order to remove all the benzene, 10 cc. of benzene were mixed with an equal quantity of pure paraffin oil and the mixture shaken with four times its volume of concentrated sulphuric acid in a machine that agitated the mixture about 450 times per minute. The amounts of benzene that were absorbed after definite periods of time were as follows:

Table X —Action of Sulphuric Acid on Benzene and Paraffin Oil

Time of shaking Minutes	Per cent. benzene absorbed
15	52.1
30	79.0
45	91.4
60	100.0

All samples for analysis were, therefore, shaken for more than an hour, until further shaking failed to reduce the volume of the oil.

The paraffin oil used was a light, pale yellow oil of very disagreeable odor. Its specific gravity was 0.7895 at 20°. After purification by the method described below, the specific gravity became 0.7775. The oil was purified as follows: A quantity was agitated with one-third its volume of concentrated sulphuric acid for 6 hours in two 2-liter bottles that revolved slowly about an axis placed between the two. The acid became dark brown, and the evolution of sulphur dioxide indicated chemical action. The acid was then drawn off in a large separatory funnel and a fresh supply added to the oil. This was again agitated for six hours and separated off as before. By this process the volume of oil decreased 9.3 per cent., and lost its disagreeable odor and became colorless. It was then shaken with a small quantity of dilute alkali until neutral, washed with water, and finally shaken for several hours with calcium chloride, and filtered. By repeated tests it was shown that the oil, after this treatment, did not decrease in volume when shaken with sulphuric acid.

Mixtures of benzene and pure paraffin oil were then allowed to diffuse through fuller's earth. The earth in the tubes had been as tightly packed as it was possible to secure by ramming the earth with a rod tipped with a rubber stopper. The proportions of benzene and paraffin oil in the mixtures were as follows:

Name applied to mixture	Per cent. benzene	Per cent. paraffin oil
Series No. 5	20	80
Series No. 6	33	67
Series No. 7	50	50
Series No. 8	75	25
Series No. 9	20	80
Series No. 10	33	67
Series No. 11	50	50
Series No. 12	20	80
Series No. 13	75	25
Series No. 14	20	80

Sections of varying lengths, as shown in the tables accompanying the curves (pp. 23 to 29), were taken, and the oil was displaced by addition of water (in Series No. 5 to No. 8, inclusive), by extraction with ether (Series No. 9), or by letting the oil overflow into upper reservoirs by the new method described on page 16 (Series No. 14).

The sections of earth from which the oil was extracted were made considerably smaller than similar sections taken by Bransky in his work. The uppermost section, called A, varied in length from 25 to 12 cm. The fraction of oil that it yielded was called 5–A, 6–A, according to the series to which it belonged. The next lower section of earth, usually a little shorter than A, was called B. Its oil was termed 5–B, 6–B, or 7–B, according to the series to which it belonged. The short tube and short sections of earth from which the oil was extracted were chosen so as to locate more accurately the point at which a sharp decrease in the amount of benzene occurred. This point of sudden change was found to be invariably located from 20 to 40 cm. from the top. The specific gravity of each fraction of the oil was taken for the first five tubes. Since this in every case was a function of the proportion of benzene and paraffin oil present, it was discontinued after the first five series were run.

Series No. 5 consisted of the following: A tube was filled with earth and the reservoir below filled with 500 cc. of a mixture of 20 per cent. of benzene of specific gravity 0.879 and 80 per cent. of paraffin oil of specific gravity 0.7775. When diffusion had taken place, the fractions were analyzed as before described, and it was found that the break in the curve occurred at about 35 cm. from the top. The specific gravity of that fraction that contained least benzene was the lowest. It was noticeable that the proportion of benzene to paraffin oil was nearly a constant, until the point B was reached (see Fig. I).

Table XI—Series No. 5

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 88 cm.

Fraction	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
5–A	20	46	0.787	10.4	89.6
5–B	15	44	0.790	19.1	80.9
5–C	15	43	0.791	21.3	78.7
5–D	15	36	0.792	21.0	79.0
5–E	12	30	0.792	21.3	78.7
5–F	11	39	0.795	23.3	76.7

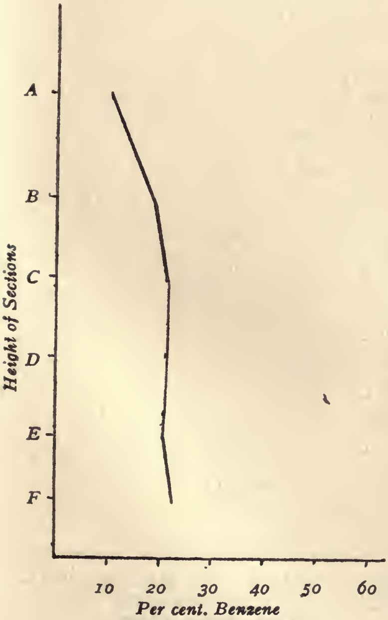

Fig. I.—Series No. 5

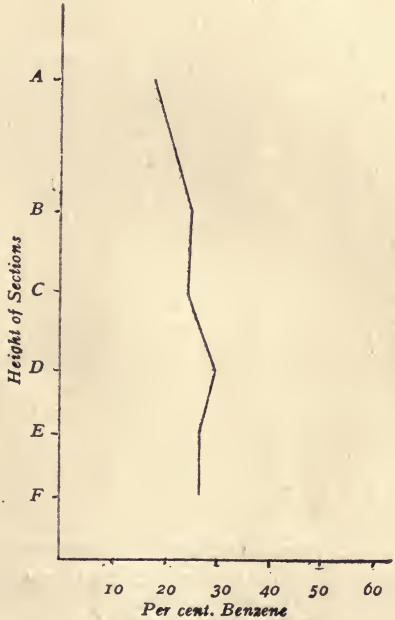

Fig. II.—Series No. 6

In Series No. 6 there was not noticed as marked uniformity in specific gravity or in the proportion of benzene to paraffin oil as in Series No. 5. The break in the curve occurred about 25 cm. from the top (see Fig. II).

Table XII—Series No. 6

Benzene, 33 per cent. Paraffin Oil, 67 per cent.
Rose to a height of 95 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
6–A	25	31	0.725	18.4	81.6
6–B	15	38	0.798	25.7	74.3
6–C	15	42	0.798	25.3	74.7
6–D	12	38	0.799	25.9	74.1
6–E	12	35	0.7995	27.3	72.7
6–F	12	45	0.799	27.0	73.0

Series No. 7, with equal quantities of benzene and paraffin oil, gave a curve that broke sharply at Section B, 16 cm. from the top. Up to this point the amounts of the two oils remained nearly constant (see Fig. III).

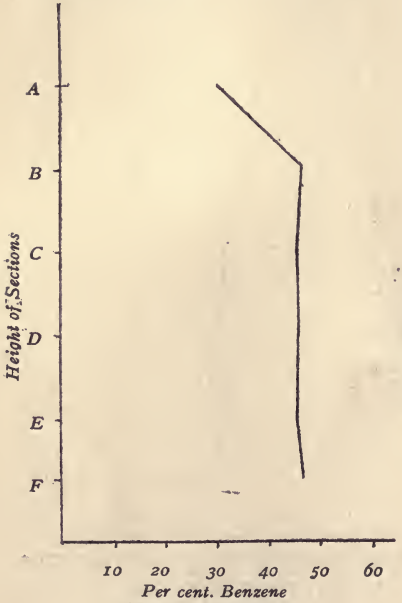

Fig. III.—Series No. 7

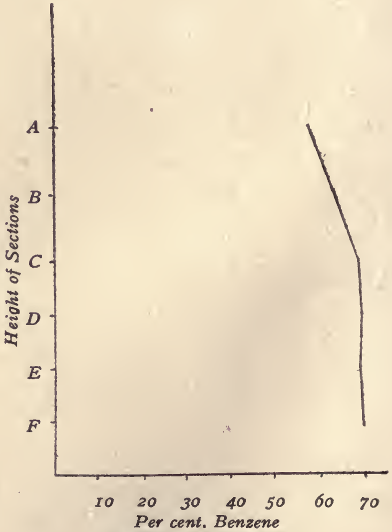

Fig. IV.—Series No. 8

Table XIII—Series No. 7

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 90 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
7–A	16	21	0.8023	30.5	69.5
7–B	16	34	0.8155	47.0	53.0
7–C	16	44	0.8160	45.8	54.2
7–D	16	50	0.8165	45.7	54.3
7–E	12	48	0.8165	45.7	54.3
7–F	12	53	0.817	47.2	52.8

In Series No. 8 the break was not such a sharp one, and occurred about 30 cm. from the top (see Fig. IV).

Table XIV—Series No. 8

Benzene, 75 per cent. Paraffin Oil, 25 per cent.
Rose to a height of 84 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
8–A	15	25	0.832	58.1	31.9
8–B	15	37	0.833	64.5	35.5
8–C	12	38	0.8385	69.0	31.0
8–D	12	44	0.839	69.8	30.2
8–E	12	43	0.839	69.7	30.3
8–F	12	51	0.842	70.1	29.9

In order to determine whether the proportion of benzene to paraffin oil in the fractions was affected by the displacement of the oil by water, the fractions secured from Series No. 9 were extracted with ether. The results plotted in the curve on page 26 show that the water plays no part whatever in the action. The break in the curve, showing a sudden sharp decrease in the proportion of benzene to paraffin oil, occurred in about the same locality.

Table XV—Series No. 9

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 70 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
9–A	12	44	8.9	91.1
9–B	12	34	18.4	81.6
9–C	12	38	20.0	80.0
9–D	10	37	21.7	79.3
9–E	10	39	21.3	79.3
9–F	10	44	22.1	78.9

In Series No. 10 and No. 11 (Figs. VI and VII) the individual fractions were analyzed immediately after the displacement of the oil in the earth by water. This was done so as to avoid any possible loss of either oil by evaporation. The same general characteristics are apparent in the curves that express the results of the fractionation.

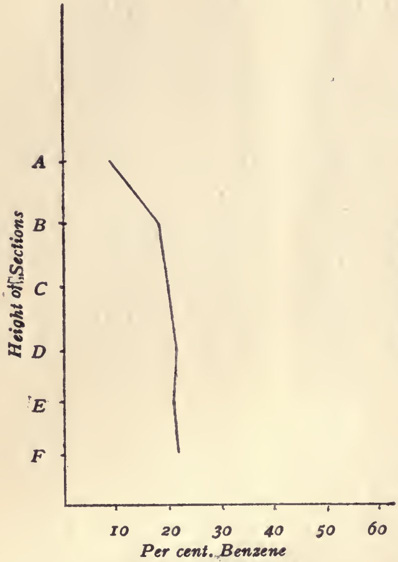

Fig. V.—Series No. 9

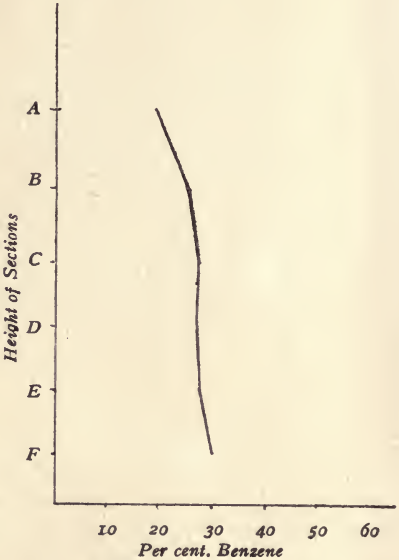

Fig. VI.—Series No. 10

Table XVI—Series No. 10

Benzene, 33 per cent. Paraffin Oil, 67 per cent.

Rose to a height of 81 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
10–A	15	36	20.1	79.9
10–B	15	53	26.2	73.68
10–C	12	45	28.0	72.0
10–D	12	52	27.7	72.3
10–E	12	42	28.1	71.9
10–F	10	37	30.4	69.6

Table XVII—Series No. 11

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 74 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
11–A	15	35	32.1	67.9
11–B	12	42	47.1	52.9
11–C	12	37	47.1	52.9
11–D	10	41	46.9	55.1
11–E	10	36	50.4	49.6
11–F	10	35	50.9	49.1

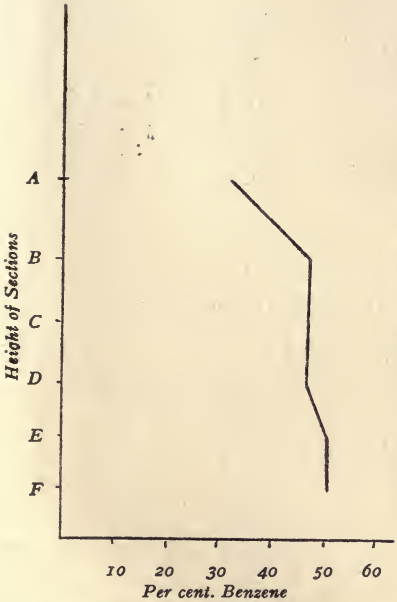

Fig. VII.—Series No. 11

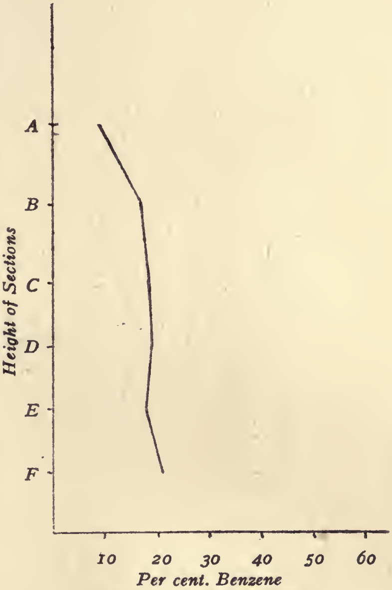

Fig. VIII.—Series No. 12

In all tubes up to Series No. 12 the oil was drawn up to a height under two feet nine inches. Although tubes five feet nine inches long were used, the quantity of oil placed in the reservoir was such as allowed only the lower half of the earth in the tube to become impregnated. In order to avoid the possibility of the more volatile oil evaporating into the dry earth above it, tubes of 2 feet 9 inches in length were used for Series No. 12 and No. 13. The curves representing the results from these series (pp. 27 and 29) show that this precaution failed to produce any noticeable difference in the proportion of benzene and paraffin oil or in the characteristic behavior of the fractions that were obtained by diffusion through fuller's earth.

Table XVIII—Series No. 12

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Rose to a height of 80 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
12–A	15	31	9.5	90.5
12–B	15	40	16.8	83.3
12–C	12	54	18.6	81.4
12–D	12	52	18.8	81.2
12–E	12	56	18.0	82.0
12–F	12	53	21.1	79.9

Table XIX—Series No. 13

Benzene, 75 per cent. Paraffin Oil, 25 per cent.

Rose to a height of 80.5 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
13–A	15	30	60.0	40.0
13–B	15	41	69.1	31.9
13–C	12	37	72.8	27.2
13–D	12	41	71.3	28.7
13–E	12	47	74.0	26.0
13–F	12	48	74.9	25.1

Series No. 14 was set up to test out the improved method of fractionating by means of the earth. Eight hundred cc. of a mixture of 20 per cent. benzene and 80 per cent. paraffin oil were drawn up through tightly packed fuller's earth, and six fractions of 50 cc. each were collected in the upper reservoir. The first of these was designated 14–A, and the last 14–F. The six fractions were separately analyzed and the results plotted in a curve (see p. 29).

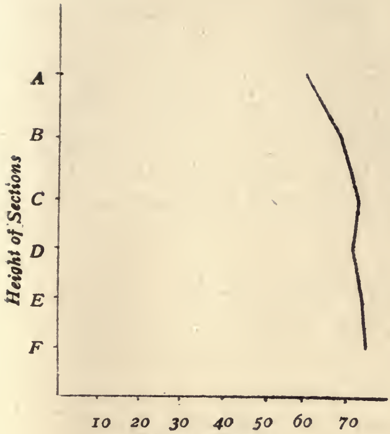

Fig. IX.—Series No. 13

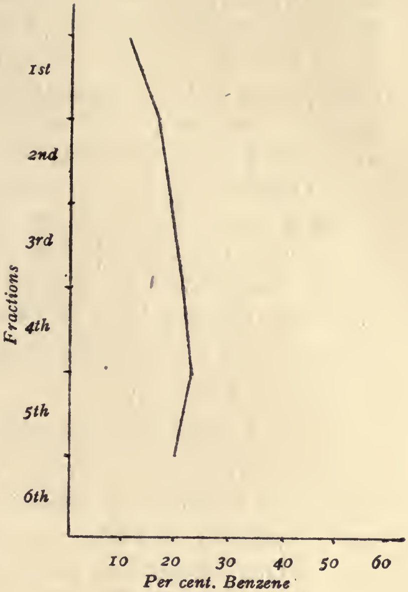

Fig. X.—Series No. 14

Table XX—Series No. 14

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Fractions	Cc.	Per cent. benzene	Per cent. paraffin
14–A	50	10.9	89.1
14–B	50	17.1	82.9
14–C	50	19.4	80.6
14–D	50	21.6	78.4
14–E	50	23.0	77.0
14–F	50	20.0	80.0

Extract of Earth Left in Tube

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
Upper half	70	215	15.9	84.1
Lower half	70	225	13.8	86.2

It was found that the proportion of benzene in the first fraction was the lowest, and that it gradually increased in the subsequent fractions. The curve above shows that the increase in benzene in the successive fractions is more gradual than when the oil was obtained by being expelled by water. There was, however, a marked increase in the amount of the benzene after the first 50 cc. had been drawn off. This corresponds to the increase indicated by the curves in every series that was run, and thus it appears that the new method of working gives the same results as the other methods of manipulation.

These results show that the degree of fractionation is not a question of the absolute height of the earth through which the oil passes, but of the relative height. The advantage, however, of using long tubes is that more material can be obtained and a greater number of fractions between the two extremes are possible.

FRACTIONATION OF CALIFORNIA OIL III

With a view to studying in some detail the fractionation of a heavy California petroleum, a tank of this material was secured from Kern County. It had a specific gravity of 0.9118 at 20°, and resembled in physical properties the California Oil I. A description of this oil, termed California Oil III, is found on page 6. In order to find the best conditions for securing large workable fractions of this oil, preliminary work was carried on by means of glass tubes so as to enable the investigator to observe the progress of the fractionation. The glass tubes measured 1.25 inches in internal diameter, and varied in length from two to five feet. The object of this was to find the length of tube which would give a maximum yield of workable fractions.

The tubes were filled with a fine-grained fuller's earth known as XXF clay. The method of packing these by ramming with a rod tipped with a rubber stopper was abandoned since this gave varying degrees of hardness, while strict uniformity was desired. It also failed to remove the cushions of air that persisted in remaining between layers of the earth, and these, it had been found in earlier work, were a grave source of trouble. Instead, the earth was run into the tubes until they were full. Then the tubes were tapped on their sides throughout their length until the earth failed to subside. More earth was added to fill in the space left vacant by the earth that had settled, and they were tapped again until further subsidence ceased.

With tubes packed as indicated above, the fractionation of the oil by suction was commenced. It was soon apparent that the amount of fractionation by using the fine-grained earth would be exceedingly small, and that it would possibly require four or five weeks' suction to bring the oil to the top of the longer tubes, so the effect of using a coarse-grained earth was suggested. Accordingly, fuller's earth of the size 30 to 60 mesh was secured. The tubes were packed uniformly by the method above described, and placed in the reservoirs. The pressure was reduced to 650 mm. of mercury. Even at this slight reduction in pressure, the oil was drawn up through the tubes, the products showing, however, no signs of fractionation. Accordingly, after repeated experiments, the tubes were allowed to stand 48 hours with no suction applied, and then the pressure on the top of the tubes was reduced to 730 mm. --With this, the oil started to rise slowly and steadily through the earth, the uppermost part showing signs of marked fractionation. When the oil had risen to the height of about 18 inches, the pressure was reduced to 700 mm.; at a height of 3 feet, it was reduced to 650 mm.; and above 4.5 feet it was maintained at 600 mm. until all of the available oil was drawn over into the upper reservoirs. By use of the coarse-grained fuller's earth the time required for fractionation of a series of tubes was found to be from ten to twelve days. The fractions of oil that were drawn up and collected were classified on the basis of color. With this as a criterion, six distinctly different fractions were obtained, and these showed a wide range in color and specific gravity.

The total amount of these six fractions was, however, only 15 per cent. of the oil put into the lower reservoir, there being a loss of 85 per cent. due to the speedy darkening of the earth by the bitumen present in the petroleum. Results, with a brief description of the fractions obtained, are tabulated below:

Table XXI—Preliminary Fractionation of California Oil III

Fraction	Sp. gr.	Description
1	0.8364	Nearly colorless; pale green fluorescence
2	0.8449	Pale yellow; pale green fluorescence
3	0.8609	Yellow; quite fluorescent
4	0.8701	Light brown; strong fluorescence
5	0.8770	Brown; strongly fluorescent
6	0.8866	Dark brown; deep green fluorescence

These were the first results that were ever obtained with an oil of as high specific gravity and viscosity as this one, for all investigations carried on at room temperature with an oil of this high density had failed thus far to produce any results. When these six fractions were next examined as to their chemical properties, it was found that the diffusion through the earth had not only lowered the viscosity of the oil, removed the bitumen, and thereby greatly decreased the specific gravity of the oil, but it had also absorbed from the petroleum a large proportion of benzene and olefin hydrocarbons.

The amounts of the two last-named ingredients were ascertained by treatment of the oil with concentrated sulphuric acid. This did not determine the benzene and olefin hydrocarbons separately. It is fair to assume that the concentrated acid acted upon the other materials in the oil, but that it removed all the benzene and olefin hydrocarbons was conclusively proved by a method described later on.

The method by which the benzenes plus the olefins were determined was as follows: Ten cc. of each fraction were carefully measured from a burette. The light oils were shaken with three times their volume of concentrated sulphuric acid until no further diminution in the volume of the oil occurred. The shaking was accomplished in a machine that vibrated 400 times per minute. The bottles containing the oil thus treated were emptied into burettes, rinsed with a few cc. of acid and allowed to drain overnight. The oil not acted upon rose in this time above the acid, and could be read off and directly translated into percentages of paraffin hydrocarbons present.

This last statement is based upon the fact that paraffin hydrocarbons are not acted upon by cold, concentrated sulphuric acid, while the benzene and olefin hydrocarbons react with the acid to form sulphonic and alkylsulphuric acids, respectively. That the benzene and olefin hydrocarbons were entirely removed by two hours' agitation with a large excess of sulphuric acid was proved by the absence of these compounds in the oil after it had been acted upon. The test for benzene was the action of nitric acid to give nitro derivatives and the subsequent reduction to give amino compounds. The tests for olefin were the direct addition of bromine and the action of alkaline permanganate solution.

The treatment of the heavier oils with sulphuric acid was somewhat different from that of the light oils, in that in the case of the former the action of the acid produced a mixture so dark and viscous that the line of demarcation between the acid and the unabsorbed oil was invisible. Therefore, the sample of heavy oil was treated in one of the following ways:

I. It was mixed with twice its volume of pure paraffin oil that had been treated previously with concentrated acid until none of it was absorbed by further action of the acid upon it (see p. 21). The diluted oil was then shaken for five hours or more with three times its volume of acid until further diminution in volume of the oil ceased;[1] or

II. The sample was shaken with thirty cc. of sulphuric acid for two hours, and the mixture was thinned out by diluting with twenty cc. of the paraffin oil, shaken for a few minutes, drained into the burette, and the amount of benzenes and olefins present determined by difference between thirty cc. and the amount of oil unabsorbed by the acid. The methods of determining the sulphuric acid absorption gave results that were concordant to within 0.5 per cent. The accuracy of the analysis by this method was within one per cent., as was proved by analysis of known mixtures.

The percentages of benzene and olefin hydrocarbons that

[1] For diluting the 10 cc. sample for analysis and shaking with 90 cc. of sulphuric acid, it was necessary to have a burette of over 120 cc. capacity. This was secured by blowing a bulb of 80 cc. at the lower end of a 50 cc. burette, leaving a volume of about 40 cc. above by which to read the amount of oil that was not acted upon.

were found in the various fractions of the oil (see p. 32) were found to vary from 5.15 per cent. to 27.7 per cent., as shown in the following table:

Table XXII—Preliminary Determination of Benzenes and Olefins in California Oil III

Fractions	Per cent. benzenes and olefins
1	5.15
2	10.4
3	15.2
4	16.8
5	20.6
6	27.7

It is thus seen that the earth through which the oil passed exerted an absorptive effect upon the benzene and olefin hydrocarbons. This effect has been termed selective absorption or adsorption, by which is meant that the earth exerts an action upon the complex oil by which it retains an appreciable quantity of certain of its ingredients. It is not a filtration effect, for when the petroleum is drawn quickly through coarse or fine fuller's earth by means of low pressure, it filters through, depositing any solid matter that may be suspended, but being otherwise unaltered.

If the action of the earth is explained as a phenomenon of adsorption, the statement might be made that the separation of the bituminous material from the petroleum was by the coagulation and adhesion of the bitumen to the very extensive internal surface that the grains of fuller's earth possess. For it is a well-known fact that porous media like charcoal, dried clays, colloidal and finely divided metals, platinum sponge, etc., possess an enormous amount of surface energy, due to the forces that are active at their extensive surface, and that such substances show the phenomenon of adsorption to a marked degree. The separation of the bitumen, carrying with it the benzene hydrocarbons, the olefins, the sulphur and nitrogen compounds, may thus be regarded as a special case of adsorption.

If the bitumen is considered as existing in the colloidal condition, the effect of the internal surface of the fuller's earth could be explained as bringing about the coagulation of the colloidal bitumen into discrete particles which would carry with them all materials in the oil, save the paraffin hydrocarbons. That all the above-mentioned materials are held behind by the fuller's earth has been conclusively established by direct and indirect proof. In retaining the bitumen with benzenes, olefins, nitrogen and sulphur compounds and permitting the paraffin oils to diffuse through, the fuller's earth acts as a dialyzer, proving more or less impervious to the substances held in solution in the paraffin oils, but not so to the solvent itself.

Fractionation of California Oil III

For the more accurate study of the physical and chemical properties of the fractions obtained from this oil, large quantities of these fractions were necessary. Accordingly, a slight alteration was made in the apparatus employed, so as to be able to handle larger quantities. The tubes originally used measured 1.25 inches by 5.5 feet. It was now decided to test out tubes of greater diameter and length, and the size finally adopted was 2.75 inches in diameter by six feet in length. In order to be able to observe the behavior of the oil, a glass tube of the same size was joined in parallel with the tin tubes. With tubes of this diameter it was found that the best results were obtained by using very little suction, and by extending the suction over a period of about two weeks, as the yield of available fractions was found to increase through this method of working. This was ascertained by measuring the amounts of each of the fractions that were obtained from a single tube placed in a measured amount of petroleum. From this tube 14 distinct fractions were secured, the basis of distinction being the color of each. The amounts of each fraction and a brief description of the same are as follows:

Table XXIII—Preliminary Fractionation of California Oil III

Fraction	Amount Cc.	Description
1	35	Colorless, pale blue fluorescence
2	38	Colorless, pale green fluorescence
3	40	Pale yellow, pale green fluorescence
4	40	Yellow, pale green fluorescence
5	48	Yellow to deep orange-brown, increasing green fluorescence as fractions increased in sp. gr. and viscosity
6	45	
7	47	
8	60	
9	65	
10	63	Light to dark brown in transmitted light; fluorescence less pronounced, but still very noticeable
11	75	
12	85	
13	88	
14	110	

The total amount of available fractions was 839 cc. The amount of petroleum used was 3500 cc. The yield was 23.7 per cent.

It is seen from the above figures that the yield of heavier fractions is increasingly greater than that of the lighter oils. It is also to be noted that this slower method of working increased the total yield of available fractions from 15 per cent. to nearly 24 per cent. Fractions that were colored darker than the fourteenth were discarded as being contaminated with too much bitumen.

The fractionation of considerable quantities of California Oil III was then undertaken, and differentiation was made between the various fractions on the basis of specific gravity, a hydrometer small enough to fit into the upper reservoirs being used[1] to indicate the specific gravity approximately. The boiling points of the various fractions were taken at atmospheric pressure. Every fraction was found to be a mixture of oils, for not any of the boiling points remained constant, but, instead, rose through a range of 11 to 35 degrees. In determining the boiling points, 5 cc. of each fraction were taken. In order to get the boiling point of the greatest part

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[1] The upper reservoirs were glass tubes 2.5 cm. × 16.5 cm. closed at one end. Two-hole rubber stoppers fitted in the tops which were flanged slightly to give air-tight connections.

of each, i. e., of that part which represented the average of the constituents, one cc. was distilled off, and the boiling point noted during the distillation of the next three cc. The boiling point of the last cc. was not taken. The distillates ranged from a colorless, thin oil with a smoky smell to a thick, dark brown oil of a very disagreeable odor resembling garlic.

The fractions from the California Oil III were termed 3–A, 3–B, etc. Those of a second fractionation were termed 3–A 1, 3–A 2, etc. The range of the fractions obtained was as follows:

Table XXIV—Fractionation of California Oil III

Fraction		Sp. gr.	Boiling point
1	3–A	0.8325	160°–195°
2	3–B	0.8347	172°–201°
3	3–C	0.8372	186°–219°
4	3–D	0.8462	210°–231°
5	3–E	0.8524	235°–260°
6	3–F	0.8551	247°–269°
7	3–G	0.8680	256°–280°
8	3–H	0.8781	268°–289°
9	3–I	0.8840	275°–310°
10	3–J	0.8885	284°–317°
11	3–K	0.8903	299°–326°
12	3–L	0.895	311°–328°
13	3–M	0.8972	317°–334°
14	3–N	0.8984	329°–340°
Crude petroleum		0.9118	105°–340°

These results show the very wide range in specific gravity between the first and last fractions of the petroleum under investigation. For comparison, the range of fractions obtained from a lighter Pennsylvania petroleum by Gilpin and Bransky are given in the following table:

Fractionation of Pennsylvania Petroleum

Fraction	Sp. gr.	Fraction	Sp. gr.
A–1	0.8250	D–2	0.8495
A–2	0.8287	D–3	0.8515
B–1	0.8367	D–4	0.8555
B–2	0.8392	E–1	0.8527
C–1	0.8413	E–2	0.8540
C–2	0.8460	E–3	0.8570
C–3	0.8488		
D–1	0.8470		

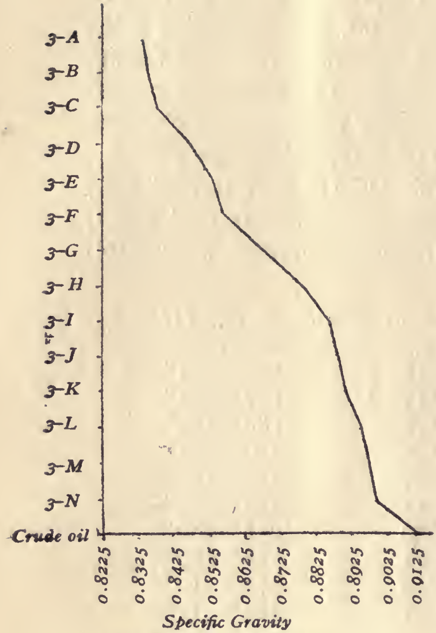

Fig. XI.—California Oil III

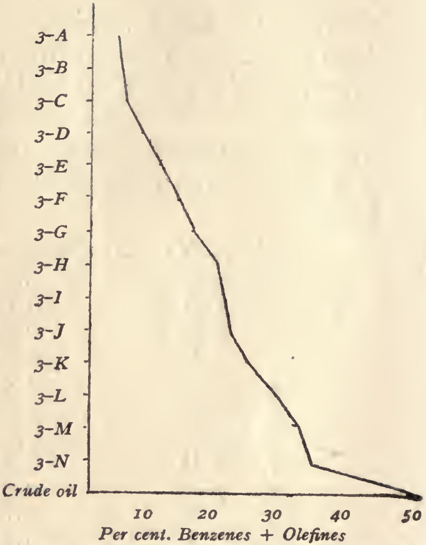

Fig. XII.—Sulphuric Acid Absorption of California Oil III

The range obtained by Bransky's method of working shows specific gravities varying from 0.8250 to 0.8570, as contrasted with the range of 0.8325 to 0.8984 obtained by the present investigator upon the heavy California oil.

Sulphuric Acid Absorption of the California Oil III

The sulphuric acid absorption was determined for the fourteen fractions. The method used was that described on pages 32 to 33. The results are tabulated with respect to the percentage of paraffin hydrocarbons in contrast to that of the benzene and olefin hydrocarbons taken together.

These figures show the great extent to which the diffusion through fuller's earth removes the benzene and olefin hydrocarbons. The first fraction consisted of nearly pure paraffin oils, reaching a degree of purity of 96 per cent., while, by contrast, the crude petroleum contained about 50 per cent. of paraffins.

Table XXV—Sulphuric Acid Absorption

Fraction	Per cent. benzenes and olefins	Per cent. paraffins
3–A	3.7	96.3
3–B	4.14	95.86
3–C	5.1	94.9
3–D	7.44	92.56
3–E	10.13	89.87
3–F	13.06	86.94
3–G	15.2	84.8
3–H	15.8	84.2
3–I	19.89	80.11
3–J	20.6	79.4
3–K	23.47	76.53
3–L	27.9	72.1
3–M	31.45	68.55
3–N	32.72	67.28
Crude petroleum	49.7	50.3

Bromine Absorption of California Oil III

In order to determine the amount of unsaturated or olefin hydrocarbons in the fourteen fractions of this oil, the quantity of bromine absorbed at room temperature (19°–23°) in the dark by a weighed amount of the oil was determined.

The method employed for the determination of the olefin content of the fractions was as follows: A weighed sample of the oil to be analyzed, about 0.6 gram for each determination, was dissolved in fifteen cc. of redistilled carbon tetrachloride. The vessel into which the solution was introduced was a 250 cc. Erlenmeyer flask with a ground glass stopper that fitted accurately and was sunk some distance into the neck of the flask so as to leave a gutter between the neck and the stopper. When the absorption of bromine was taking place, the gutter was filled with a couple of cc. of potassium iodide. It effectually prevented the escape of bromine vapor. The bromine was introduced in the form of a solution in pure carbon tetrachloride. The solution was made practically decinormal by dissolving 3.3 cc. of redistilled bromine in a liter of solvent. Its exact strength was determined by titrating against a known volume of a standard sodium thiosulphate solution. The bromine solution kept best in the dark, but frequent tests of its strength were necessary.

In determining the bromine absorption, a known quantity of the bromine solution was added to the solution of the oil in carbon tetrachloride. The amount added was more than twice that necessary to combine with the total amount of olefins present (as determined by a previous analysis). The flask was closed and shaken, the gutter filled with 2 cc. of a ten per cent. solution of potassium iodide, and the flask allowed to stand in the dark with occasional agitating for thirty minutes. Longer contact of the oil with the bromine gave substitution products as well as addition products, the former being indicated by the presence of hydrobromic acid. After thirty minutes, the flask was brought out of the dark, ten cc. of the potassium iodide solution were added, the flask closed and violently shaken, and the amount of iodine liberated by the excess of bromine present determined by titrating against the thiosulphate solution. Toward the end of the titration, a few cc. of a very dilute starch solution were added to indicate sharply the end point. Repeated shaking of the contents of the flask was necessary during the last part of the titration in order to free the iodine from its solution in the carbon tetrachloride. A blank determination was made parallel with each analysis in order to ascertain how much of the thiosulphate solution was exactly equivalent to the amount of bromine solution that was added. The results were translated directly into the percentage of olefins present in the various fractions and in the crude petroleum.

By the action of concentrated sulphuric acid on the oils, the percentage of benzenes and olefins together was ascertained. The action of bromine gave the percentage of olefins. In order to determine whether the difference between these results gave a value that represented the percentages of benzene alone, an investigation was carried out on the 1st, 5th, 9th and 14th fractions of the California Oil III. After being shaken for several hours with sulphuric acid, they were tested for the presence of benzenes and olefins, and blank results were obtained. Then fresh samples of these fractions were treated with an excess of bromine so as to brominate the olefins present, washed with water, dried and shaken with concentrated sulphuric acid for several hours. By this, an amount of the oil was absorbed which corresponded to the benzenes present. This amount, added to that secured by the action of bromine, gave the true percentages of benzenes and olefins together. The results, however, were in each case a little high, showing that the sulphuric acid must have acted upon the brominated oils, but the difference was not greater than 1.3 per cent. Since the sulphuric acid absorption method was accurate to within one per cent., it was concluded that the difference between the percentages of the oil absorbed by sulphuric acid and that acted upon by bromine could be taken to represent the amount of benzene hydrocarbons present.

The results that justified this conclusion are here given:

Table XXVI

Fraction	Per cent. benzenes	Per cent. olefins	Sum of columns 2 and 3	Per cent. benzenes and olefins by sulphuric acid absorption
3–A	1.09	2.79	3.88	3.7
3–E	5.35	5.05	10.4	10.13
3–I	8.72	12.46	21.18	19.89
3–N	14.03	19.35	33.38	32.72

In the table below, the percentages of the various hydrocarbons present in the oils investigated are given. In the first column are given the designations of the various fractions; in the second are given the mean values of the percentages of the olefins found by determining the bromine absorption (duplicate determinations made in every analysis); in the third are given the percentages of benzenes and olefins taken together, and determined by the sulphuric acid absorption method; in the fourth are given the percentages of benzenes determined by difference between the second and third columns.

These results demonstrate the selective absorption of the fuller's earth in its action upon the olefin hydrocarbons. As is indicated above, the proportion of olefins in the crude oil is

Table XXVII—Proportion of Various Hydrocarbons in Fractions of California Oil III

Fraction	Per cent. olefins	Per cent. benzenes and olefins	Per cent. benzenes
3–A	2.79	3.7	0.81
3–B	3.25	4.14	0.76
3–C	3.62	5.1	1.48
3–D	4.06	7.44	3.38
3–E	5.05	10.13	5.08
3–F	5.84	13.06	7.22
3–G	7.44	15.2	7.76
3–H	8.43	18.8	7.37
3–I	12.46	19.89	7.43
3–J	13.44	20.6	7.16
3–K	14.66	23.47	8.81
3–L	14.81	27.9	13.19
3–M	18.34	31.45	13.11
3–N	19.35	32.72	13.37
Crude petroleum	28.24	49.7	21.47

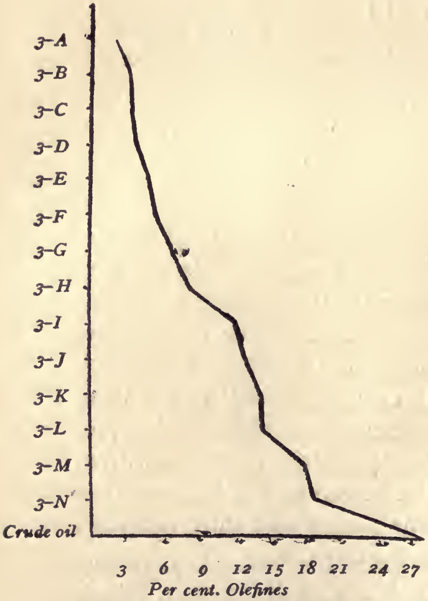

Fig. XIII.—California Oil III

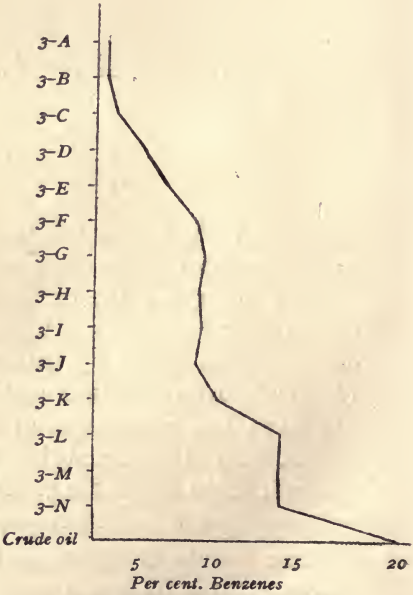

Fig. XIV.—California Oil III

28.24 per cent. In a single fractionation this is reduced to 2.79 per cent. in the first fraction obtained. The gradual increase in the proportion of olefins as the specific gravity of the fractions increases is parallel to the gradual increase, in successive fractions, of all the compounds in the petroleum thus far studied, i. e., of the sulphur compounds, nitrogen compounds, benzene hydrocarbons and olefin hydrocarbons. The results, when plotted in the form of curves, show that there is a noticeable parallelism in selective action of the fuller's earth upon the compounds above mentioned. The curves are found on pages 38 and 42.

In order to determine to what extent the olefins could be removed by further filtration through fuller's earth, a liter of Fraction 3–I was refractionated by means of a tube of smaller diameter. The nine fractions that were obtained were analyzed for their olefin content. The results were as follows:

Table XXVIII—Second Fractionation of California Oil III
(Refractionation of 3–I)

Fraction	Sp. gr.	Per cent. olefins
3–I 1	0.8661	8.55
3–I 2	0.8685	8.93
3–I 3	0.8740	10.06
3–I 4	0.8751	10.82
3–I 5	0.8759	10.77
3–I 6	0.8773	11.40
3–I 7	0.8782	11.67
3–I 8	0.8801	11.79
3–I 9	0.8807	11.89
3–I 10	0.884	12.06

These results demonstrate that a further removal of bituminous material is possible by refractionating a heavy fraction, for there was a slight loss of color occasioned by the diffusion through the earth. Only a part of the olefins was removed, however, by this second fractionation, and the reduction in viscosity was also very slight.

Efforts were made to determine the effect of shaking fractions of oil with large amounts of fuller's earth. Accordingly several portions of Fraction 3–E were shaken with varied quantities of fuller's earth for different periods of time. First, a quantity was shaken with three times its weight of earth for 30 hours and separated from the earth by suction. It was analyzed, with the following results:

Table XXIX—Fraction 3–E Shaken with Three Times Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
20	0.8305	4.01	Yellow
0	0.8524	5.05	Pale orange

When shaken with one-half its weight of earth for periods ranging from 10 to 50 hours, the following results were obtained:

Table XXX—Fraction 3–E Shaken with One-half Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
0	0.8524	5.05	Pale orange
10	0.8524	5.08	Pale orange
20	0.8521	5.00	Pale orange
30	0.852	5.00	Pale orange
50	0.8513	4.90	Same color, but slightly less fluorescence

These results show that the time that an oil is in contact with fuller's earth is of little or no importance as a factor in determining to what extent the earth absorbs certain ingredients from it. The important factor is the amount of earth with which it comes in contact. These experiments substantiate, then, the deductions that are given on page 88 *et seq.*, i. e., that it is the amount of surface of the earth to which the oil is exposed that determines the extent of its absorptive action.

This is in line with the action of those substances whose surface energy is capable of affecting a colloid. That the bitumen in the petroleum investigated exists in this form was proved by the following:

1. There was effected an actual separation of the petroleum into two distinct layers when an electromotive force of 110

volts was impressed upon parts of the oil separated by an unglazed porcelain septum. In order to make the oil conduct the current, one portion was shaken for several hours with one-fourth its volume of a 20 per cent. solution of hydrochloric acid, and another with an equal amount of a 20 per cent. solution of potassium hydroxide. The emulsions formed in this way proved poor conductors, but were sufficiently good to enable the bitumen partially to precipitate out as a brown layer of a very viscous liquid, containing no mineral residue. Its form indicated that the bitumen was held in the original petroleum as a colloid—that type that has been named by Oswald an emulsoid.

2. The high temperature coefficient of viscosity of California petroleum, as shown by earlier experiments (p. 9, Table I), is one of the most marked characteristics of emulsoids, i. e., that type of colloid solution in which the colloid is a liquid in a state of minute subdivision in a liquid medium.

3. The oil and bituminous material that were held back by the fuller's earth could not be removed by mechanical means. For, after the earth had been extracted with ether and carbon tetrachloride until no more could be extracted, it yielded a small quantity of oil upon distillation. This showed that the bituminous material that was in the oil had undergone a change of condition when it was adsorbed by the earth.

SUMMARY

1. The diffusion of petroleum through fine-grained fuller's earth failed to effect the fractionation of the petroleum when the latter was of specific gravity as high as 0.912 at 20°. Raising the temperature of such an oil to 75° made fractionation possible.

2. The effect of such a diffusion of a petroleum containing compounds of sulphur is to separate out the light fractions of the oil containing smaller proportions of sulphur than are found in the original petroleum.

3. The effect of fractionating by means of diffusion through fuller's earth of a petroleum containing nitrogen compounds is to remove the nitrogen compounds from the oil that diffuses

upward through the earth, and to cause them to concentrate in the earth through which the oil has passed.

4. Mixtures of benzene and paraffin oil, when fractionated by capillary diffusion through fuller's earth, give fractions that have marked general characteristics, both chemical and physical, based on the proportions of benzene and paraffin oil in each.

5. The fractionation of a petroleum rich in benzene and olefin hydrocarbons by the diffusion through fuller's earth gives fractions in which the proportions of benzene and olefin hydrocarbons increase regularly with the increase in specific gravity of the successive fractions.

6. An explanation of the above phenomena was found in the conception of the petroleum as an emulsoid, and in the action of the fuller's earth as a dialyzing septum, permitting the free passage of the paraffin oils, and causing by its extensive surface the adsorption and coagulation of the bituminous material, carrying with it the sulphur and nitrogen compounds and the benzene and olefin hydrocarbons.

BIOGRAPHY

Philip Schneeberger was born in Baltimore, Maryland, on November 22, 1887. His primary education was obtained in the public schools of that city and at the Baltimore City College, from which he graduated in 1906. His Collegiate education was obtained at the Johns Hopkins University, which he entered in 1906, and from which he received his A.B. in 1909. Thereafter he pursued graduate courses in chemistry at the Johns Hopkins University, and was laboratory assistant there in general inorganic and organic chemistry for the years 1910–11 and 1912–13. During his graduate work in chemistry, since October, 1909, his subordinate subjects have been physical chemistry and geology.

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