THE FRACTIONATION OF CALIFORNIA PETROLEUM BY DIFFUSION THROUGH FULLER'S EARTH: DISSERTATION

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The Fractionation of California Petroleum by Diffusion Through Fuller's Earth: dissertation by Philip Schneeberger

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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

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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

[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 Ve-

nango 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

[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