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CHEMICAL SECTION.

Stated Meeting of March 19, 1895.

DR. W. C. DAY, President in the Chair.

[The President announced the paper for the evening, and introduced the speaker.]

COMPOSITION OF THE AMERICAN SULPHUR PETROLEUMS.

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One of the most interesting exhibits in the Department of Mines in the Columbian Exposition was the extensive collection of crude petroleum, refined products and diagrams illustrating the petroleum industry, shown by the Standard Oil Company. Of the marvelous development of our natural resources during the last thirty years, perhaps a more striking illustration could not be presented than that afforded by the petroleum exhibit.

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Since the early discovery of petroleum in this country the manufacture of products obtained from it has been distinctively an American industry. In the history of its development we are struck with the great skill and originality in methods which were devised for sinking wells to great depths, and, when necessary, for removing obstacles to the free outflow of oil by exploding the wells with torpedoes, as well as in the application on a large scale of methods of fractional distillation for the separation, in a single operation, of commercial products from the crude oil. We are also impressed with the inventive genius displayed in the construction of peculiar forms of lamps, burners and heaters for household use; and in the discovery of manifold uses for the various distillates in cleansing, lubrication and medicine, and in the manufacture of soaps, candles, solvents, electric light carbons and numerous other products.

The specimens of crude oils in the Columbian Exposition showed all gradations in color between transparent or nearly colorless oils and those which were very dark and opaque, such as are used in the ordinary processes of refining. So far as it appears from the results of numerous investigations on the composition of crude petroleums from different localities, they are more nearly alike than is indicated by the inequalities in color. The main points of difference depend upon variations in the proportions of the hydrocarbons, which constitute the commercial products, such as the naphthas, gasolines, burning oils and lubricating oils.

The single method available for the examination of crude petroleums depends upon the wide variation in the boiling points of the constituent hydrocarbons, which renders possible a separation sufficiently complete for the preparation of commercial products. By this method the hydrocarbons of lower boiling points have been isolated and identified, and the composition of the more volatile portions of the crude oils has been determined with precision. Unfortunately the less volatile constituents, the hydrocarbons which distill above 250° or 300° , suffer decomposition during distillation, or, as it is termed by the refiners, they undergo "cracking." Even under diminished pressure, although a

larger quantity may be distilled, the temperature soon rises to a point at which there is considerable decomposition of the heavier distillates, and this increases with the temperature, until finally there is left in the still a mass of porous carbon representing a considerable portion of the original oil. On account of this decomposition by distillation, and the lack of any other method for the separation of the less volatile constituents of crude oils, our knowledge of this subject is still incomplete.

The discovery and subsequent development of the Ohio sulphur petroleum mark a notable epoch, even in the midst of the wonderful growth of the petroleum industry in other fields. Even with the advantage of former experience, the novel problems presented for solution in the new fields, at first, baffled the best skill of the driller and the refiner. Fortunately, from the beginning, ample opportunities were afforded for thorough scientific study of the geological formations encountered in sinking wells and the mode of occurrence of the oil, as well as of the technological features of its production. To appreciate the thorough manner in which such knowledge of the Ohio gas and oil fields has been collected and placed on record by Prof. Edward Orton, State Geologist of Ohio, it is only necessary to consult the Eighth Annual Report of the U. S. Geological Survey, and the Reports of the Ohio State Geological Survey for 1888 and 1890. These reports contain a vast amount of valuable information concerning the new gas and oil territory.

In attempting to present the merest outline of the mode of occurrence of the Ohio sulphur petroleum, I shall refer to some of the results obtained by Professor Orton in his exhaustive study of the Trenton limestone formations, with which the oil deposits are associated.

It is now well known that the distribution of petroleum within the United States is restricted to quite limited districts as compared with the total area, and that besides differences in the oils from different localities, of color, transparency and varied proportions of the individual constituents, the oils of certain fields have peculiar characteristics which

depend upon the presence of a considerable proportion of sulphur compounds. It is interesting to note that these sulphur petroleums are found only in districts quite distinct from those of the sulphur-free oils.

Public attention was first attracted to the Ohio sulphur petroleum by the discovery, in November, 1884, at Findlay, in that State, of oil and gas in considerable quantities. In that part of the Northwestern section of Ohio, known as the Black Swamp, the presence of gas and oil in creeks and pools has been known since this section of country was first inhabited; but the last decade has here witnessed a marvelous development of these natural products. The immense deposits of gas are now apparently nearly exhausted, but the copious flow of oil still continues. In the exploitation of oil in Ohio, the prospectors had all the advantage of twenty years' experience in the fields of Pennsylvania. The methods of sinking wells, as well as the manipulation of oil and the modes of treatment in refining, had been highly perfected. Markets were ready to receive the refined oils, and no time was lost in waiting for the discovery of uses for the various products. It is true that an over-stocked market has led to a large consumption of the crude oil for fuel at a quarter of its real value, but this destructive use cannot long continue.

The first oil was obtained from a well drilled at Lima, in May, 1885, and soon afterward, in the same year, oil flowed freely from a well bored at Findlay. The first production from the Hume well, in 1886, was at the rate of 250 barrels per day. In May, 1887, there were, in the Lima field alone, 445 wells producing daily 9,488 barrels; the greatest daily production of any single well was stated to be 5,000 barrels.

The discovery of a productive source of oil in the lower Silurian limestone seems to have been a great surprise to both geologists and oil-men, although the presence of oil in this limestone had previously been maintained by T. Sterry Hunt (*Am. Journ. of Science*, II, **35**, 168). As was expressed by Orton, the enormous flow of gas and oil from the dolomitic Trenton limestone constituted a new chapter in the history of petroleum production, and one of great interest, since the

Trenton beds form the most important single source of petroleum in the United States. Later developments have not only confirmed earlier observations, but have shown also that the sulphur petroleums are to be obtained in quantity, in the central part of the United States and Canada, only from the older limestones.

The Trenton limestone, one of the older formations of the continent, extends from New England to the Rocky Mountains. Occasionally outcropping, it forms excellent building stones; when burnt, valuable lime; and, by decay, fertile soils. Frequently it underlies the entire strata of large areas without appearing at the surface. In northwestern Ohio, where it forms the reservoir of the sulphur petroleums, it is usually from 1,000 to 2,000 feet below the surface, beneath a succession of shales (Utica, Hudson River and Medina) from 400 to 1,000 feet in thickness. Although the limestone seems to be permeated throughout with oil, the uppermost beds, to a depth of from 20 to 30 feet, contain the accumulated stocks, a bittern of peculiar composition occupying the space beneath.

With the history of the development of Trenton limestone oil and gas, as one of the centers of enormous production, the town of Findlay is intimately associated. The dolomitic composition of the limestone, which experience has shown to be an essential condition for gas or oil, is here present. Gas is derived from areas less than 400 feet below the sea-level, with Niagara limestone as the surface rock. The village is divided into two nearly equal portions; the east side, occupied by the Niagara limestone, is gas territory; and the west side, occupied by the Lower Heldeberg or water lime, is oil territory.

The essential features of petroleum production are source, reservoir and cover. In the Ohio fields the Trenton limestone, as the reservoir, is never wanting in oil; and the superimposed beds of impervious shales, in depths of from 500 to 1,000 feet, furnish the cover. The necessary porosity is due to the fact that the oil rock is a dolomite of highly crystalline structure. The intercrystalline spaces furnish adequate storage for large deposits of oil. The thickness of

the upper strata of the dolomitic limestone which constitutes the reservoir, is usually from five to ten feet, occasionally from fifty to 100 feet. In the Lima field, thirty feet below the surface of the Trenton limestone is recognized as the limit of the level of value for oil. The conditions, then, for the storage of oil in economic quantities depend upon a dolomitic composition of the limestone (which seems, also, to be the source as well as the reservoir), with an overlaying, impervious shale, as a cover.

Around each productive field there appears to be a sharply drawn "dead line," marking the boundaries between oil or gas and salt water, which is the propelling force of the confined oil or gas; and they occupy different levels, depending upon the height of the reservoirs. At Findlay and in the Lima fields, the highest level of the reservoirs is 300 feet below tide; the salt water level was originally 500 feet below tide at Findlay, and 400 feet below at Lima. In Indiana, the "dead line," or salt water line, in the porous reservoir, is less than 100 feet below tide. This area of 30,000 square miles is a plain over nearly its entire extent, with the Niagara limestone as the surface rock where gas is found, and the Lower Helderberg the surface rock, where oil is abundant. In the absence of outcropping oil rock, these surface indications are important guides for the location of new wells. The location and limits of the salt water line were soon learned, and, with minor exceptions, 500 feet was accepted as the limit below which it is not profitable to drill.

In 1863, Dr. T. Sterry Hunt (*Amer. Jour. of Science*, II, **35**, 170) explained that the petroleum supply of Western Ontario was derived from a broad, low anticlinal; and he maintained that the anticlinal structure is necessary in connection with hydrostatic pressure to the production of a large supply of oil. This theory has been fully confirmed in Ohio, where the flat, low-lying terraces, having a very slight elevation above the surrounding country, afford sufficient storage for immense quantities of oil. For the most part, the Ohio terraces are nearly level, with slopes of less than 1° ; in general, the range in elevation throughout 100 square miles does not exceed 100 feet.

In extent, the Lima field is from eight to ten miles in length, and from two to three miles in breadth. The elevation of the surface above the sea level is from 800 to 900 feet; the gas rock is nearly level and about 380 feet below tide.

The Findlay field is also a low, nearly horizontal terrace of Trenton limestone, about 1,250 feet deep and two miles wide in a north and south line, by less than five miles east and west. The plains of Northern Ohio form the cover of the most prolific oil field yet found on the American continent, and second only to the great Russian field in the Caucasus (Orton, *Geol. Report*), and yet the deposits of oil seem to be singularly restricted in area. Outside of the Ohio and Indiana horizon, drillings 1,000 miles distant have yielded neither gas nor oil, the Trenton limestone failing to be a source beyond this limited district.

The two conditions under which Trenton limestone has yielded oil or gas are porosity and relief. The highly crystalline dolomitic composition supplies porosity, and a slight warping of the strata furnishes a reservoir in which are stored the enormous quantities of oil and gas above the salt water. Dr. Hunt described this brine as derived from the saline deposits evaporated from the ancient seas. In an examination of the brine from Trenton limestone, Lord found that it consisted chiefly of the chlorides of sodium, calcium and magnesium. In numerous examinations made in this laboratory, of salt brine collected in wells drilled for gas, there have been found bromine, iodine and lithium.

Oil is very widely distributed in the Ohio limestone. Hunt estimated the Chicago oil dolomite to be one foot thick and to contain one-tenth of one per cent. of oil. The same quantity in the Ohio rock would furnish, in every square mile of strata 500 feet thick, more than 2,500,000 barrels of oil; in a depth of 1,500 feet, 75,000,000 barrels. As determined by Lord, the amount of oil in the shales is equivalent to one-fifth of one per cent. Calculating this proportion for each square mile, to a depth of 1,000 feet, the total amount would exceed 10,000,000 barrels (Orton). The amount of oil in the Ohio rocks, therefore, is large even beyond computation,

but it has no economic value except when accumulated under pressure in reservoirs.

Throughout the oil and gas regions in Ohio and Indiana, the salt water in the Trenton limestone rises under free flow to about 600 feet above tide. The pressure is attributed to salt water collected in artesian reservoirs in the porous limestone which rises to the surface in Michigan and Illinois. It is there open to the admission of surface waters, which exert a pressure proportionate to the head, and the oil and gas collecting by gravitation in the limestone reservoirs are subjected to a corresponding pressure.

Professor Orton suggests as a probable explanation of the formation of the oil rock, that the original pure limestone, formed from crinoids, was replaced in part by magnesian carbonate derived from sea water, and as the new crystals did not completely occupy the spaces left vacant by the removal of the crystals of calcic carbonate, the infiltration of liquids became possible. The limited series of collected facts and observations is not sufficient to explain the precise character of the metamorphic changes.

In Canada, petroleum seems to be distributed in limited quantities over an extensive area, but not in sufficient accumulations to have economic value. The presence of oil on the waters of creeks and pools first attracted attention at Oil Springs in 1860-61. Dr. Winchell estimated that not less than 5,000,000 barrels of oil flowed off on the waters of Black Creek during the spring and summer of 1861. The sole supply of oil is derived from the territory at Petrolia and at Oil Springs, the former with an area of eight square miles, and the second two square miles in extent. The geological formations are here even less complicated than in the Ohio oil fields, since the oil deposits are much nearer the surface. The same conditions of structure are found, viz.: source, reservoir and cover, that have been established in Ohio. Instead of the Trenton limestone, the prolific source in the neighboring territory, the Corniferous limestone contains the oil deposits, with a corresponding shale above, which serves as an impervious cover. The following section of a well at Oil Springs (H. P. Brummel, *Can. Geol. Rep.*, 1888-

1889) explains the composition of the rock strata at this point.

	<i>Feet.</i>
Surface	60
Upper limestone	35
Shale (upper soapstone)	101
Middle limestone	27
Shale (lower soapstone)	17
Lower limestone	130
	<hr/>
	370

The wells are supposed to be sunk sixty feet into the Corniferous limestone.

Section near the Imperial refinery, Petrolia—

	<i>Feet.</i>	
Surface	104	Hamilton
Upper limestone	40	
Shale (upper soapstone)	130	
Middle limestone	15	
Shale (lower soapstone)	43	
Hard white limestone	68	Corniferous
Soft limestone	40	
Gray limestone	25	

The geology of the Canadian oil deposits was first investigated by the late Dr. T. Sterry Hunt, and on his conclusions was based the first and most probable explanation of the origin and storage of limestone oils (*Am. Journ. of Science*, II, 35, 168). He asserted that these oils owe their formation to the decomposition of animal remains in the midst of a marine calcareous deposit. The cavities of the shells and corals afforded sufficient space for the storage of the oil as it was formed. It is here clearly stated that the limestone is both source and reservoir. Whatever may have been the conditions of formation of petroleum and its deposition in other regions, subsequent developments in the Ohio fields have fully confirmed that portion, at least, of Hunt's hypothesis, which makes the older limestone formations the reservoir of the petroleum in question.

The Canadian oil deposits are much nearer the surface than those in Ohio. As shown above, the depth of wells at Petrolia was formerly less than 400 feet, and at Oil Springs

less than 200 feet. In the township of Enniskillen the depth and flow of several early wells were as follows :

			<i>Barrels Daily.</i>
At a depth of	155 feet		2,000
"	" 158 "		3,000
"	" 167 "		6,000
"	" 188 "		6,000
"	" 237 "		7,500

It is therefore evident that the flow of oil from some of the Canadian wells has been very large. In 1889 there were thirteen refineries, nine at Petrolia and four at Oil Springs.

The supply of oil came from 3,500 wells, of which 2,500 were at Petrolia. The monthly production at Oil Springs amounted to 20,000 barrels, and the annual consumption, as nearly as could be estimated, was 704,690 barrels. At present the total number of wells is 8,000, of which about 6,000 are in operation at Petrolia. The annual production, as estimated by one of the best-informed oil men at Petrolia, is 800,000 barrels annually, including the monthly output at Oil Springs, which is 17,000 barrels. The average depth of wells at Petrolia is now 465 feet, and at Oil Springs, 380 feet. From the large number of wells, it is evident that the average daily production of individual wells is small. When first drilled, a well may yield a barrel or more daily, but the flow finally falls to one-half or one-third of a barrel. The small daily yield, however, is offset by the long life of the wells. Most of the wells flow steadily during long periods, some as long as thirty years.

A peculiar method of storage has here been adopted, depending upon the impervious quality of the Erie clay. It consists of a tank, in the earth, 30 feet in diameter and from 50 to 60 feet deep, having a wooden lining to a depth of 30 feet. The surface of the tank below the wooden casing is of clay, and the capacity of the tank is from 5,000 to 10,000 barrels. The total capacity of the tanks in both fields is 1,000,000 barrels. Oil is collected from the individual wells in wagon tanks and brought to receiving tanks, from which it is pumped to the central stations near the refineries.

Canadian oil is refined in the ordinary manner. Much gas is evolved, which, as usual, is serviceable in heating the retorts. In the crude still, gasoline and burning oil are run off to 37° Beaumé, and the residue is then transferred to the tar still, from which heavy oils are distilled to 30°·5 Beaumé, and the residue coked. The last distillate is again distilled and the residue coked as before. In refining, much depends upon the skill of the operator. With careful treatment and the use of an alkaline solution of plumbic oxide, a burning oil of excellent quality is prepared. From Petrolia crude two per cent. of naphtha is obtained, and from Oil Springs, seven per cent. The yield of burning oil from both sources is forty-three per cent. The quantity of tar is thirty per cent. of the crude oil, from which the yield of heavy oils is twenty per cent., with a residue of coke equivalent to ten per cent.

The anticlinal system is well marked in the Canadian fields, and is similar to that of the oil-bearing limestone formation in Ohio. The anticlinals are low terraces, and the oil collects on the slopes toward the summit, where it is held under pressure by the salt water. The variations in the oil-bearing strata have been carefully studied by Messrs. M. G. Woodward and F. J. Carman, from whom I obtained valuable information concerning this and other features of oil production in the Canadian fields.

At present the main producing field at Petrolia is five miles in length and two miles in maximum width, on an anticlinal, which takes the direction of W.N.W. by E.S.E. Much prospecting has been carried on outside of the producing fields, and has shown that the Corniferous limestone is reached at Petrolia, at 335 feet. Sixteen miles distant from Petrolia, at Sarnia, in a west-northwesterly direction, it descends to a depth of 503 feet. East of Petrolia the stratum again dips to 390 feet, and again rises, and at this point many attempts, some partially successful, have been made to discover another deposit similar to that at Petrolia. Still farther distant, in a southeasterly direction from Georgian Bay, the Corniferous limestone outcrops; and still farther away, the Trenton limestone appears at the surface.

The latter formation may be reached beneath the Petrolia anticlinal at a depth of 2,000 feet or more, but it is not, as in Ohio, an important reservoir of oil. Independently of the main producing fields in this section, much oil has been taken from "pockets;" indeed, the great producing wells seem to have derived their supply from these sources. Two years ago, while surveying a section just outside the line of productive territory, and partly surrounded in a semicircle by flowing wells, an oil man suggested the possibility that a pocket might be found in this space. Upon sinking a well, oil was found in quantity, and it proved to flow, as predicted, from a pocket which has since yielded a large supply.

The oil territory at Oil Springs is situated on an anticlinal parallel to that which supplies oil at Petrolia, and ten miles distant. As already explained, the oil rock is nearer the surface, and in addition to the great wells which undoubtedly came from pockets, until recent years the daily flow was ten or fifteen barrels. At present it does not much exceed the flow at Petrolia previously mentioned. It has been thought very probable that the anticlinal which contains the Oil Springs deposit encloses other deposits, and, consequently, much prospecting has been done along the direction of this anticlinal, especially in the township of Euphemia, where oil has been found in limited amounts, at a distance of twenty miles from Oil Springs.

In studying the geology of the sulphur petroleums, striking differences are observed in comparing the geological formations in different localities. While it seems very probable that the deposits of oil in the Ohio and Canadian territory have been formed in the limestones by the decomposition of animal remains, in other localities sulphur petroleums are found in rock formations essentially different from the limestone deposits. In the volume of the Geological Survey of Kentucky, published in 1891, Orton gives an account of the geological formations connected with the oil deposits in that region. While similar conditions of source, reservoir and cover are there found with porosity and the anticlinal structure, a black shale constitutes the rock in which the oil is stored, placing the oil in the Devo-

nian formation instead of in the lower Silurian, which is the horizon of the Ohio sulphur oil. It is explained that the essential difference in the rock formations in which oil is stored is only in degree, as is shown by the wide distribution in Ohio, where there is scarcely a geological formation that does not contain oil. The different shales contain it in variable quantities, but the necessary conditions of accumulation (impenetrable cover, etc.) for economic production are wanting.

In reviewing the distinctive properties of the limestone oils, as compared with Pennsylvania oil, Orton states in this report that they are dark in color, heavy, with a high specific gravity, and a rank odor from the sulphur compounds they contain. In these respects it is found that the oils of Canada, Kentucky and Tennessee, the new field in Northwestern Ohio, and the oil of the Utica shale and Hudson River group, in the latter State, are similar. In accounting for the storage in the shales, their natural agency is based upon their impervious quality, which prevented rapid decomposition of vegetable matter, with the aid also of the affinity of the clay for oil.

A marked peculiarity in the geological formation containing deposits of sulphur petroleum is found in California. These deposits have been carefully studied by Professor S. F. Peckham (*Geol. Surv. of Cal.*, Vol. 2, Appendix). The source of the California bitumen is invariably a bluish slate or shale, more or less compact, with a variable mixture of fine quartz sand. There are occasionally outcroppings of bitumen, but the conditions of reservoir and cover, which have been found essential in oil deposits where oil is stored under pressure, here seem to be largely or entirely wanting, with the result that the oil deposits exert a low pressure if any. The oils obtained from these deposits are quite different in their properties from the Pennsylvania oils, and, in fact, from any other American oils that are the source of commercial products. Their specific gravity is very high (0.875-1.653), and very small quantities distill within the limits of burning oil distillates; in fact, without resorting to cracking, probably very small quantities of illuminating

oils can be prepared from this petroleum. The percentage of sulphur is higher than that of the other sulphur petroleums, as well as the percentage of nitrogen, which varies between 0.56 and 1.12. As is pointed out in the description of this petroleum, there is strong evidence in favor of its formation from animal remains. Certain constituents of the crude oil are so unstable that when exposed to the air for some time the oil becomes impregnated with maggots.

A description of the occurrence of petroleum in any particular district can hardly be considered complete without some reference to the enormous deposits of oil at Baku, on the shore of the Caspian Sea. Although the oils from this region contain no considerable quantity of sulphur, in some respects and with reference to certain other constituents, the sulphur oils may be found to resemble the Russian product. As in other oil regions the sections furnishing oil at Baku are quite limited in extent. The great district of Balakhani, with an area of from four to five square miles, is about eight miles north of Baku on the coast; and two or three miles south of Baku on the seashore is another very small district, Bibi-Eibat. Statistical or other reliable information concerning the Russian oil fields is meagre, and the points here presented are taken from the report for 1886 of the United States Consul, J. C. Chambers, at Batoum. According to this report the depth of the wells varies between 175 and 1,030 feet.

The deepest well at Bibi-Eibat, 700 feet deep, produced from 30,000 to 40,000 barrels daily during fifteen days, after which it ceased to flow. Very little information is accessible concerning the geology of the Baku district beyond the fact that the oil is derived from the Tertiary formation.

FORMATION OF PETROLEUM.

The formation of petroleum has received much attention from both the chemical and the geological point of view, and the prevailing theories have been ably presented and discussed by Professor Orton in the reports mentioned above. Until the discovery of great quantities of oil in the Trenton limestone, the geologists, in this country at least,

attributed the formation of petroleum exclusively to the decomposition of vegetation. The early suggestions of Hunt that the formation should be referred to animal remains in the limestones of the primitive rocks, attracted little attention until they received support from recent discoveries. Abroad, the prevailing belief seems to have been that the formation of all petroleums should be referred to the decomposition of animal remains. Credence is still given by some writers to the theory of Mendelejeff that all petroleums have been, and are still, formed by the action of water on iron or iron carbides, highly heated within the earth; but for lack of proof and the serious objections based upon observed facts, urged by geologists, this explanation is not generally accepted. At present the data collected seem to be insufficient to establish any particular method of formation. Even if the theory of animal origin be accepted for the limestone oils, it cannot be asserted that vegetable remains may not have been in part instrumental.

In 1865 Warren and Storer (*Mem. Amer. Acad., N. S.*, **9**, 177) subjected a lime soap prepared from menhaden oil to destructive distillation, and obtained a hydrocarbon, naphtha, from which they separated several series of hydrocarbons identical with those which Warren (*Mem. Amer. Acad., N. S.*, **9**, 156) had previously identified in Pennsylvania petroleum. More recently, Engler (*Ber. der deutsch. chem. Gesellsch.*, **21**, 1816) submitted the American menhaden oil to destructive distillation under high pressure, and, in the product distilled, was able to identify the constituents ordinarily separated from natural petroleum, including naphtha, the burning oil hydrocarbons, and paraffine. Engler therefore concludes that all petroleum has been derived from the decomposition of similar organic remains under the same conditions. Probably no better summary of the present state of the theories concerning the origin of petroleum can be given than that suggested by Orton (*Geological Survey of Ohio*, Vol. VI., p. 82).

(1) "Petroleum is derived from organic matter.

(2) "Petroleum of the Pennsylvania type is derived from

the organic matter of bituminous shales, and is probably of vegetable origin.

(3) "Petroleum of the Canada type is derived from limestone and is probably of animal origin.

(4) "Petroleum has been produced at normal rock temperatures (in American fields), and is not a product of destructive distillation of bituminous shales.

(5) "The stock of petroleum in the rock is already practically complete."

CHEMICAL COMPOSITION OF PETROLEUM.

Although various attempts had previously been made to separate the constituents of petroleum, the first systematic examination was undertaken in 1862 by Pelouze and Cahours (*Compt. Rend.* **54**, 1241; **56**, 505; **57**, 62), who identified the presence of the series of hydrocarbons C_nH_{2n+2} , beginning with butane, boiling at 0° . From their results, Pelouze and Cahours assumed that the heavier oils and paraffine have the same composition as the hydrocarbons of lower boiling points, and, as a generic term for the series, Watt suggested the name paraffine hydrocarbons, by which these constituents of petroleum have since been known in chemical literature. Members of the same series were observed by Schorlemmer (*Journ. Chem. Soc.*, 1862, 419), in a product distilled from cannel coal; and in a distillation of American petroleum, Schorlemmer obtained other members of the series that had been overlooked by Pelouze and Cahours. C. M. Warren (*Mem. Amer. Acad., N. S.*, **9**, 156; *Proc. Amer. Acad.* **27**, 56) undertook a more thorough investigation of Pennsylvania petroleum, conducting the separations in a fractional condenser which he had devised especially for such distillations. In a long course of distillations, Warren separated two series of hydrocarbons, beginning with butane, with an homologous difference in boiling points for CH_2 of 30° , and with a difference in boiling points between the members of one series and the isomeric members of the other, of a little less than 8° . One of the series, C_nH_{2n+2} , identified by Warren, terminates at $127^\circ.8$, the other at 150° . The fractions of higher boiling

points were found to contain members of the series C_nH_{2n} . The results of Warren indicated, in the distillates above 150° , the absence of members of the series C_nH_{2n+2} , notwithstanding the assertions of Pelouze and Cahours, that distillates from these portions of petroleum have the composition homologous with marsh gas. In the earlier examinations of American petroleum by Pelouze and Cahours and by Schorlemmer, it is somewhat uncertain to what extent Pennsylvania crude oil was employed, and to what extent Canadian oil, since in allusions to the crude product American petroleum is mentioned, with occasional reference to Pennsylvania or to Canada as the particular source.

The presence of aromatic hydrocarbons in American petroleum was first established in 1856, by Schorlemmer, who identified benzol and toluol in a distillate collected below 150° from Canadian petroleum, by treating this portion of the oil with nitric acid, reducing with tin and hydrochloric acid and distilling with sodic hydrate. The oil distilled had the odor of aniline and gave the rosaniline reaction with bleaching powder. The distillate between 150° and 170° gave a mixture of liquid and solid nitro-products, and the solid portion was recognized as trinitrocumol. Benzol and its homologues have since been found in Pennsylvania petroleum by several chemists. Petrocene was investigated by Sadtler (*Amer. Chem. Journ.*, **1**, 30). From American kerosene, in a portion distilling at 170° – 190° , Engler (*Ber. der deutsch. chem. Gesellsch.*, **18**, 2234) separated pseudocumol and mesitylene, by the formation of nitro-compounds, and he estimated that the quantity present in crude Pennsylvania oil is equivalent to 0.2 per cent. Engler also identified these hydrocarbons in German, Galician, Italian and Russian petroleum; in the latter, to the extent of 0.1 per cent. After ascertaining in the petroleum of the Central Caucasus the presence of hexahydro-derivatives of the aromatic series, Beilstein and Kurbatoff (*Ber. der deutsch. chem. Gesellsch.*, **13**, 2028) examined American ligroin for the same hydrocarbons, but succeeded in identifying only hexahydroisoxylol. No at-

tempts were made to ascertain the presence of the higher homologues.

The petroleum from various localities in the Caucasus has been quite thoroughly investigated by Russian chemists, and it has been found to differ in its composition very essentially from Pennsylvania oil. It is held by Mendelejeff, Engler and others, that none of the petroleums, so far as they have been examined, differ essentially with respect to their components; but that the observed variation in the qualities of different oils depends rather upon a variation in proportions. This difference in proportions, however, is so marked, that in certain oils some of the constituents constitute nearly the whole body of the oil, with others present only in minute quantities, in comparison with other oils, in which the former constituents are almost entirely absent, the great body of the oil consisting of substances nearly wanting in the first. The thorough investigations on the composition of the Caucasus petroleum by Markownikoff and Ogloblin (*Ann. Chim. Phys.*, VI, **2**, 372) proved the presence, in oil from Baku, of benzol, toluol, iso-xylol, pseudocumol, mesitylene, iso-durol, durol and higher hydrocarbons with their structure not yet determined, $C_{11}H_{14}$, $C_{11}H_{12}$, $C_{12}H_{14}$, and $C_{13}H_{16}$, with indications of the homologues of styrol and phenylacetylene. The results of Beilstein and Kurbatoff indicate the presence in the petroleum from the Central Caucasus, of members of the series, C_nH_{2n+2} , with benzol and toluol, and that the oil from the coast of the Caspian Sea consists mainly of the homologues of hexahydrobenzol. In the oil from the Balechene plain on the Apscheron peninsula, Markownikoff and Ogloblin found large quantities of the aromatic hydrocarbons; but in oil from the Central Caucasus they found naphtenes to the extent of eighty per cent. of the crude oil, and the aromatic hydrocarbons to the extent of ten per cent. At first, Markownikoff looked upon the naphtenes as isomeric with the hexahydro-compounds; but later Markownikoff and Spady (*Ber.*, **20**, 1850) appeared to accept the identity of octonaphtene and hexahydroisoxylol. Markownikoff and Ogloblin proved also the presence of hexahydromesitylene,

besides other oils with the composition C_9H_{18} and the members intermediate to $C_{15}H_{30}$.

Benzol and its homologues were identified in Hanover petroleum by Bussenius and Einstuck (*Ann. Chem. und Pharm.*, **113**, 167), and by Ulsmann (*Ann. Chem. und Pharm.*, **114**, 279). In petroleum, from Boryslaw, in Galicia, Lachowicz (*Ann. Chem. Pharm.*, **220**, 187) found benzol, toluol, isoxylol and mesitylene; but of the hexahydro series, only hexahydroisoxylol. Pawlewski (*Ber. der deutsch. chem. Gesellschaft*, **18**, 1915) found in Galician petroleum two per cent. of aromatic hydrocarbons, chiefly benzol and *p*-xylol, the latter recognized for the first time in any petroleum. Naphthalene, anthracene, their homologues and other allied hydrocarbons, have been reported from various sources.

Concerning the presence of unsaturated hydrocarbons in crude petroleum, there seems to be a wide difference of opinion. Some investigators have doubted the existence in crude oil of these bodies, and where they have been found in distillates it has been assumed that they have resulted from decomposition by distillation. In the lower fractions of Galician oil, Lachowicz obtained no reaction with bromine, even after long standing. Above 200° , the presence of unsaturated hydrocarbons, indicated by the ready absorption of bromine, was attributed to decomposition. On the other hand, Engler states that petroleum from Elsass (Pechelbronn), Oelheim (Hanover), Tegernsee, Pennsylvania, Galicia and Baku, contains members of the series, C_nH_{2n+2} , and the series C_nH_{2n} , both unsaturated hydrocarbons and naphtenes. Markownikoff and Ogloblin (*Ber.*, **16**, 1873) allude to the presence of unsaturated aromatic hydrocarbons in the oil from Baku.

Before the discovery, by Wreden, of the hexahydro-aromatic compounds, Warren separated from Pennsylvania petroleum a series of hydrocarbons C_nH_{2n} , which were probably of the same series. It now seems probable that the constituents of Pennsylvania petroleum above 150° , assigned by Pelouze and Cahours to the series C_nH_{2n+2} , really belong to another series.

It has long been known that analyses of crude petroleum

have shown less than 100 per cent. of carbon and hydrogen, and the deficiency has been attributed to the presence of oxygen. The first attempt to separate oxygen compounds from crude petroleum was made in 1874, by Hell and Medinger (*Ber.*, **7**, 1216), who agitated crude petroleum with a solution of sodic hydrate and then added sulphuric acid in excess to the alkaline solution. The oil which separated was distilled and converted into a methyl ether; by saponification of this ether an acid was obtained, to which was assigned the provisional formula $C_{11}H_{20}$. Aschan (*Ber.*, **23**, 867; **24**, 1864; **25**, 3661) obtained a mixture of acids by the addition of sulphuric acid to the sodic hydrate solution used in the refining of Baku oil; one acid, $C_8H_{14}O_2$, was obtained, that distilled at $237-239^\circ$; and another, $C_9H_{16}O_2$, that distilled at $251-253^\circ$. Aschan called the first acid octonaphtenecarboxylic acid; by distillation with hydriodic acid it was converted into hexahydroxylol. By similar methods Zaloziecki (*Ber.*, **24**, 796, 1808) separated oxygen compounds from petroleum, which were readily oxidized to acids when exposed to the air. For one of these bodies, assuming it to be a lacto-alcohol, Zaloziecki suggested the formula

and to the hydrocarbon obtained by distillation, he gave the formula

Engler asserts that the acids separated by this method are oxidation products of other constituents of the crude oil. Markownikoff and Ogloblin stated that the distillate $75^\circ-85^\circ$, from Caucasus oil, contained 0.76 per cent. of oxygen compounds, and the fraction $220^\circ-230^\circ$, 5.21 per cent. The oxygen compounds are in part acid, in part neutral, and in part phenol. The acids $C_{10}H_9COOH$ and $C_{11}H_{11}COOH$ were

obtained as colorless oils (*Ber.*, **16**, 1878). Markownikoff and Ogloblin regarded these substances as naphthenecarboxylic acids. Sainte-Claire Deville (*Comptes Rendus*, **66**, 442; **68**, 485; **69**, 1007), showed that the percentage of oxygen in oils from different localities varies between 2.1 per cent. in the Canadian petroleums, and 5.6 per cent. in the oil from Zante.

Most of the petroleums contain nitrogen, usually in minute quantities. Beilby (*Jour. Soc. Chem. Ind.*, **10**, 120) found 0.08 per cent. of nitrogen in the residuum from Pennsylvania oil, and 0.37 per cent. in the coke, which corresponds to 0.008 per cent. of the crude oil; crude Russian oil gave .05 per cent. of nitrogen. In examining oils from different localities for nitrogen, Peckham (Geol. Survey of Cal., vol. ii, Appendix) found in petroleum from West Virginia, 0.54 per cent.; in Mecca oil, 0.23 per cent.; and in California oil, from 0.56 to 1.1 per cent. In Egyptian oil, Kast and Kunkler (*Chem. Centralbl.*, 1890, 932) found 0.3 per cent. of nitrogen, 1.21 per cent. of sulphur and 0.2 per cent. of oxygen. Certain alkaloid bases were detected in paraffine oils by Weller (*Ber.*, **20**, 2097), and Bandrowski (*Monatshefte für Chem.*, **8**, 224), by agitating Galician oil during several weeks with sulphuric acid, obtained a substance containing nitrogen. This substance solidified at 20°, and it formed a platinum salt containing 19.7 per cent. of platinum. Zaloziecki (*Monatshefte für Chem.*, **13**, 498) neutralized a sulphuric acid extract from the refining of a petroleum distillate with calcic hydrate, and distilled with steam. The oily distillate contained nitrogen, and it formed a platoso-chloride whose percentage composition corresponded to that of tetrahydrocorridine

or to the formula

another insoluble platoso-compound was obtained, to which was assigned either the formula

Soon after the discovery of the Ohio sulphur petroleum, in a technical examination of crude oil which I was called upon to make, I observed that it contained an unusually large amount of sulphur. An examination of the crude oil was soon undertaken, with particular reference to the sulphur compounds, and there was finally separated an homologous series of sulphides $(C_nH_{2n+1})_2S$, including methyl-, ethyl-, propyl-, butyl-, isobutyl-, pentyl-, ethyl-pentyl-, hexyl-, with higher distillates containing sulphur compounds not yet identified (Mabery and Smith, *Proc. Amer. Acad.*, **24**, 218; *Amer. Chem. Journ.*, **16**, 83). Large quantities of distillates have been collected after long distillation *in vacuo*, which have proved to be mixtures of sulphur compounds, unsaturated hydrocarbons C_nH_{2n} , and apparently saturated hydrocarbons, either of the series C_nH_{2n+2} , or of the series of hexahydro-aromatic compounds C_nH_{2n} .

The sulphur compounds in Canadian oil have received some attention (preliminary examination, Mabery, *Amer. Chem. Journ.*, **16**, 89). Several members of the series $(C_nH_{2n+1})_2S$ have been recognized since that publication, with evidence of sulphides of another series. The separation of the sulphur compounds from the distillates is extremely tedious, even after a long-continued fractional separation of the sulphur oil. The sole method available, so far as we have proceeded, includes precipitation with alcoholic mercuric chloride and decomposition with hydric sulphide in the presence of alcohol. The product is a mixture, the constituents of which must be separated by prolonged fractional distillation.

The peculiar character of the distillates was observed while studying the sulphur compounds, and, as the Ohio petroleum had never been submitted to chemical examination, and the Canadian oil to only partial study, both products invited further attention. On account of the tendency to decomposition manifested by other constituents of the crude oils than the sulphur compounds, it was evident that these bodies could not be separated by the ordinary process of distillation without such serious decomposition as to render the results of little value. When dis-

tilled in contact with the air all distillates, except the most volatile, were highly colored. Attempts were therefore made to avoid decomposition so far as possible by the exclusion of air, and by conducting the distillations under reduced temperatures. In order, furthermore, to be sure that the distillates should represent as nearly as possible the original constituents, we started with crude oils instead of refinery distillates. In certain portions of our work connected with the separation of constituents that are present in minute quantities, requiring large quantities of material, we have used crude distillates as the starting point; but these distillates were not treated with reagents before we received them.

The distillation of considerable quantities of crude oil *in vacuo* involved certain difficulties which we were long in overcoming. Metallic stills could not be used, and glass was unsafe with large quantities of oil. Only earthenware and porcelain remained, and we have found it difficult to procure earthenware that would support a vacuum. Certain English and German stills of limited capacity have been found serviceable, but the stills which are perfectly satisfactory for such work are those manufactured in the Royal Berlin porcelain factory. One of these stills, with a capacity of fifteen liters, has been in use almost continuously during several months, and it has apparently suffered no deterioration.

In maintaining a vacuum for the continuous distillation of petroleum, especially those containing considerable quantities of sulphur compounds, rubber corks cannot be used in making connections, on account of softening action of the oil on the rubber. It is nearly impossible to select common corks sufficiently free from imperfections; but it was found that common corks could be treated with a rubber lute in such a manner as to make them air-tight. This lute is best made by dissolving pure caoutchouc in very light gasoline, which readily evaporates, leaving a thin, strong film of rubber. When this lute is applied to joints of the apparatus, during the formation of a vacuum, the film of rubber is drawn into the joints and pores of the corks,

thus sealing them permanently, and with an occasional application of the lute there is no difficulty in maintaining any desired vacuum.

In prolonged distillation it is important to regulate the tension, so that it shall be constant during the collection of all distillates. For this purpose a special form of regulator was devised, depending upon the introduction of air away from the still, through a glass stopcock, by means of a long lever. By this means it has been found possible to control the vacuum at any desired point with very little attention. The difference in boiling points in vacuum distillation varies between 60° - 65° for the lower constituents, and 100° - 125° for portions distilling at 300° - 350° . Vacuum distillation prevents serious decomposition even of the highest distillates. We have carried the temperature to 375° , and this is as far as distillation is possible with ordinary connections. The residue above this point is a thick oil, apparently undecomposed; cracking is easily observed, since it immediately destroys the vacuum. For further distillation of this residual oil an apparatus must be devised to avoid the use of any connections other than glass or porcelain.

We have undertaken an examination of Ohio and Canadian petroleum with reference to the various series of hydrocarbons, the nitrogen compounds, the oxygen compounds and the sulphur compounds. This paper gives an account of results obtained in an examination of distillates collected below 150 atmospheric pressure.

[To be concluded.]