

metals, especially of the platinum group, and especially to the papers of Whitney and his coworkers, recorded in this Journal.

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COMPOSITION OF AMERICAN PETROLEUM.¹

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PETROLEUM may be regarded as one and the same substance with great variations in properties and proportions of constituents, selecting as extremes such light oils as the light colored oil found in Kansas and the extremely thick oils of Wyoming, which are nearly as heavy as water. The series of hydrocarbons that have been identified in petroleum from different fields, in this laboratory, include the following: C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , C_nH_{2n-6} ; doubtless the heavy asphaltic oils contain hydrocarbons even poorer in hydrogen.

The series of hydrocarbons which form the portions of American petroleum distilling below 350° *in vacuo*, corresponding to 475° at atmospheric pressure, are now well understood, and the members of the various series have been identified with respect to their molecular weights. But concerning the structure of these hydrocarbons, except those of the series C_nH_{2n+2} and the lower cyclic hydrocarbons, nothing whatever is known. It is reasonable to assume that the members of the series C_nH_{2n+2} , or the so-called paraffin hydrocarbons, have the open-chain structure which characterizes the lower members of this series. In the earlier literature on petroleum it was generally assumed that the ethylene hydrocarbons, series C_nH_{2n} , formed a considerable proportion of the constituents, and even after the discovery of the cyclic series C_nH_{2n} , the naphthenes, according to the earlier nomenclature of Markownikow, many writers, with no foundation on facts, still insist on the presence of ethylene hydrocarbons. It is now safe to assert that these bodies are present in any petroleum, at most in very small amounts. We have found them apparently in Canadian petroleum, but in very small quantities.

The series C_nH_{2n} , which has been identified in petroleum from many sources, is now well known as the cyclic series. In a paper published in 1902 on the composition of Pennsylvania petroleum, I purposely abstained from naming the hydrocarbons with high boiling-points of this series which we had separated and identified, for although it seemed probable that these bodies were cyclic compounds, I preferred not to suggest names for the several members until more was known concerning their structure. The names suggested

¹ Presented in abstract at the New Orleans Meeting of the American Chemical Society.

by Mr. Bogert in his summary of the results described in the paper for this Journal seem to refer those hydrocarbons to the ethylene series; but any nomenclature for these bodies must await sanction by proof of structure when some courageous investigator shall force his way into this difficult field.

An important feature of the petroleum problem is the character of the hydrocarbons which form the highest boiling portions—the so-called asphaltic hydrocarbons. The main body of these high-boiling oils is no doubt composed of series poorer in hydrogen than the methylenes, saturated cyclic compounds, consisting of the series C_nH_{2n-2} , C_nH_{2n-4} , etc. The hydrocarbons of these series also appear in the higher boiling portions of Pennsylvania, Ohio, Canada, etc., petroleum, as we have shown in papers recently published.

It does not seem clear how this problem shall be attacked. By exclusion of air and depression of boiling-points the petroleum hydrocarbons can be distilled indefinitely as high as 350° . Between 300° and 400° cracking begins, and it cannot be avoided by straight distillation even *in vacuo*. The heavy hydrocarbons seem to be so inert, by reason of their high molecular weights, they cannot retain their atomic composition at their boiling-points; they simply fall to pieces through the influence of mass. In distillation from the crude oil evidently another influence comes into operation—the effects of the oxygen, nitrogen and sulphur constituents. Since fractional distillation is the only means at present known for the separation of the homologous members of these series, the problem of their isolation becomes a difficult one.

In presenting a general summary of present knowledge concerning the composition of petroleum, it may be of interest to refer to what was known on this subject twenty years ago and when I began the work. At that time the only petroleum on the market in America was obtained from the Pennsylvania fields and the territory in Canada. The composition of Russian petroleum was then under investigation by Markownikow. As a result of their elaborate investigations on American petroleum Pelouze and Cahours had assigned the formula C_nH_{2n-2} as representing the principal series of hydrocarbons. But the high specific gravity of their distillates could not have been given by hydrocarbons separated from Pennsylvania petroleum, since these bodies give much lower values. Since the source of their products was not mentioned, it must be assumed that they came from the heavier Canadian oil, although the hydrocarbons in this oil have not the composition of the series C_nH_{2n-2} which Pelouze and Cahours deduced from their analyses, but, as we have found by results recently published, the composition of the series C_nH_{2n} . Pentane, hexane, heptane and octane had been identified by Schorlemmer, and the classic work of C. M. Warren had shown

the existence in Pennsylvania petroleum of the two series of isomeric hydrocarbons from pentane to octane. The large deposits of petroleum in northern Ohio and Indiana, Texas, Colorado, Wyoming and Kansas had not then been discovered.

In 1885, soon after the first well was drilled that yielded oil from the Trenton limestone, two oil inspectors brought me a five-gallon can of Trenton limestone oil and remained while I examined it for them. This was my first acquaintance with the sulphur petroleums. I recognized at once the large percentage of sulphur, and soon afterwards began a study of the sulphur compounds. Not long afterward I procured the Canadian sulphur oil, and carried along together the study of these products, the one from Trenton limestone and the other from the Canadian Corniferous limestone. The composition of Ohio oil has only recently been determined, with respect to the principal series of hydrocarbons, by a research completed seven years after it was begun.

At first I had no preconceived ideas as to the series of hydrocarbons which compose these crude oils, except what knowledge I had gathered from the work of my predecessors; but after the work had progressed far enough to see that the crude oils from the different fields were essentially different in certain constituents, especially in sulphur, I was inclined to look on the Trenton and Corniferous limestone crude oils as a separate species, the sulphur petroleums, and to agree with Peckham in his specific classification of the different petroleums as varieties of bitumens. But I soon became convinced that no such sharp distinctions based on composition could be drawn. Now, after these years of arduous labor, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of a simple definition—a mixture in variable proportions of a few series of hydrocarbons, the product of any particular field differing from that of any other field only in the proportion of these series and the members of the series. I arrived at this conclusion only recently, when it was found that the higher distillates from Pennsylvania petroleum contained the series C_nH_{2n-2} , which until then I had supposed was only to be found in the heavier California and Texas oils, or the so-called asphaltic oils. Results recently published show that Ohio petroleum has a similar composition.

In support of this definition I would suggest that, so far as known, all petroleums contain nitrogen and sulphur, although the proportion of nitrogen in Pennsylvania and Ohio crude oils is much smaller than that in California oil, and that the percentage of sulphur is much smaller in Pennsylvania sandstone oils—only a trace as compared with the larger amounts in the Trenton limestone, Corniferous limestone, in California and Texas oils. With this definition the distinction drawn, at least in commercial

circles, between paraffin and asphaltic oils disappears, for Pennsylvania crude oil contains the asphaltic hydrocarbons, although I cannot assert that California oil contains paraffin. I have crystalline hydrocarbons separated from California oil, but their identity is not yet fully established. The refiner is more definite in his classification; he knows from experience that the best yield of gasoline is from Pennsylvania oil, and none from California oil. He is fully aware that it is useless to expect to obtain a respectable yield of burning oil, at least without cracking, from California or Texas petroleum, and that he cannot hope to obtain paraffin from those heavy oils. But his very heavy lubricating oils and heavy pitches and asphalts he knows can only come from the heavier petroleums, unless indeed like Byerlyte they are made by cracking.

With reference to a nomenclature of the petroleum series and hydrocarbons, no system can be safely adopted until the structure of these bodies is better understood. The aromatic hydrocarbons, benzene and its homologues, are present in all petroleums so far as examined, but in widely variable proportions. Pennsylvania crude oil contains the lower members in small amounts, but not the higher homologues. It is true that anthracene and its congeners have been described as separated from petroleum residues, but it is probable that such bodies are not present in the original oil; they are doubtless formed by decomposition during distillation. California petroleum contains much larger proportions of the aromatic hydrocarbons, especially of the xylenes and others with higher boiling-points. In one of our distillates from California crude oil so much naphthalene was present that the distillate became solid on slight cooling. This distillate came over at about 215° . The only other instance in which naphthalene has been found in petroleum was its separation by Warren and Storer from Rangoon petroleum.

The terminology of the series C_nH_{2n+2} has been well defined, and the names adopted by Kraft for the members with high boiling-points, liquids and solids, which he separated from shale distillates are applicable to the corresponding bodies in Pennsylvania crude oil. It is interesting to note that Pennsylvania petroleum alone, unless we include the analogous Berea Grit and other similar sandstone oils of southern Ohio and Virginia, contains the unbroken series up to and including the solid paraffin constituents. Although the Ohio Trenton limestone oil and the Canadian Corniferous oil contain paraffin, the former in large proportions, the liquid members of the series C_nH_{2n+2} stops with $C_{11}H_{22}$ in both Canadian and Ohio oil. The liquid hydrocarbons from there on, so far as examined, are members of the series poorer in hydrogen.

The series C_nH_{2n} has been variously named. When first

discovered in petroleum, and the hydrocarbons found to be identical with the hydrogen addition products of benzene and its homologues, the hydrocarbons from petroleum were described as hexahydro-bodies. On the discovery of a long series of these hydrocarbons in Russian oil, Markownikow suggested the name naphthenes. But when later the origin and nature of the compounds were better understood and cyclic hydrocarbons found in petroleum were shown to be identical with the synthetic products, the name cyclic was adopted for the lower petroleum hydrocarbons. These closed-chain hydrocarbons differ in their deportment towards reagents from those with an open-chain, C_nH_{2n+2} . While it is to be assumed that the series C_nH_{2n} is represented in its higher members by the methylenes, some extension of the nomenclature is necessary to include those bodies. There can evidently be but one ring with these proportions of carbon and hydrogen. For instance, the hydrocarbon $C_{12}H_{24}$ must be regarded as a long chain with the ends connected, dodecamethylene, or a lower ring with a number of side chains.

When the series C_nH_{2n-2} is reached it becomes necessary to assume a union of two rings attached by one carbon atom in each ring, or two rings having two carbon atoms in common. In the series C_nH_{2n-4} the union would be between two carbon atoms in each ring and the members should include, for instance, octohydronaphthalene which would represent the hydrocarbon $C_{10}H_{16}$. In the line of this suggestion, following the analogy of naphthalene, one side chain should be capable of oxidation, giving a derivative of phthalic acid. But the cyclic hydrocarbons seem to possess a different order of stability toward the action of reagents, and we have observed this peculiarity in bodies separated from petroleum which appear to belong to this series. For instance, the nitrogen compounds separated from California crude oil cannot be oxidized into closely allied products, the oxidation always proceeding to the formation of ultimate products, nitrogen and carbon dioxide, and we have found it impossible to control it.

The same is true of the sulphur compounds, which also appear to be cyclic derivatives. These bodies oxidize with the greatest ease to sulphuric acid, and it is difficult to control the oxidation. In general terms, the addition of hydrogen to benzene and its homologues weakens the resistive action towards reagents. This difference in stability between the series C_nH_{2n+2} , and the series poorer in hydrogen appears in commercial use of the heavier products. We have recently compared the flashing point and fire test of heavy distillates from Pennsylvania crude oil and crude oils from California, Texas, etc., and it appears that the products from Pennsylvania oil have higher flashing points and fire tests than those from other fields. We have an excellent opportunity to ascertain the general application of this observa-

tion, for we have at hand samples in gallon lots of the principal lubricators made from Pennsylvania and Ohio oils on the market, and also samples of crude oils from the various fields; for example, two barrels of crude oil from Baku in the Russian field.

Products have been prepared from the crude oils to compare with Pennsylvania lubricating oils. The inferior stability of petroleum in which the series C_nH_{2n} or series poorer in hydrogen predominates has appeared in all our work on the various crude oils. For instance, the admission of air into hot Pennsylvania distillates never causes an explosion; but explosions are sure to follow the contact of air with hot distillates from other fields where the principal series is lower than the series C_nH_{2n-2} .

In combustion it is easy to see the difference in stability, in the readier separation of carbon. Then in analysis of a series, say from $C_{12}H_{24}$ to $C_{22}H_{44}$, in the lower members no carbon separates in the boat, but it gradually appears with increasing molecular weight, in larger and larger amounts.

The greater stability of the hydrocarbons C_nH_{2n-2} doubtless explains the superior quality of burning oils prepared from Pennsylvania petroleum, together with the fact of a larger proportion of hydrogen. The series poorer in hydrogen more readily separates carbon as soot and is more difficult to burn. A mixture of the two series C_nH_{2n-2} and C_nH_{2n} forms a good burning oil, and probably accounts for the excellent quality of Russian burning oil.

In the study of the physical constants of the petroleum hydrocarbons with boiling-points above 125° much remains to be done. For instance, the heat of vaporization and the specific heats have not been determined. We have done some work on the specific heats and heat of vaporization of the hydrocarbons with lower boiling-points. The heat of combustion and consequent heat of formation of these bodies is an important constant. We now have considerable data on the series C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} . Determinations have been made of the complete series C_nH_{2n+2} from Pennsylvania oil and from Ohio oil and of some other series poorer in hydrogen.

The decrease in the heat of combustion in each series with increase in molecular weights is in accordance with other observations which have shown a decrease in stability with increase in boiling-points. The series C_nH_{2n-2} decomposed with ignition in presence of air at about 350° *in vacuo*, if air is let in. The series C_nH_{2n} is much less stable. In contact with air the vapors of these hydrocarbons produced *in vacuo* readily explode even in the absence of an initial flame.

We are now occupied with the study of the decomposition products of these hydrocarbons, especially with the constituents of kerosene, gasoline, paraffin and lubricating oils. The nitrogen compounds are also under examination.

Pennsylvania Petroleum.—As mentioned above Pennsylvania crude oil contains minute amounts of sulphur and nitrogen compounds, and a small proportion of benzene derivatives, but the great bulk of the oil is composed of the series C_nH_{2n+2} , beginning with the butanes and ending with solid hydrocarbons of such high molecular weights that they cannot be determined by any method now known. We have reached the hydrocarbon, $C_{28}H_{58}$, and it is the last one of the series whose molecular weight could be determined. It is quite probable that there are as many as eight or even more of the hydrocarbons with greater molecular weight.

It has been an open question with practical oil men, and perhaps is still with some, as to whether solid paraffin is contained in crude petroleum or whether it is formed in the process of distillation. In the ordinary processes of refining crude oil, a very considerable proportion of the hydrocarbons is lost in the last stages of the destructive distillation which ends with a large mass of coke. On comparing the thin liquid crude oil with products obtained from it in refining, it would be natural for the superficial observer to reason, from the appearance of coke at the end of distillation and other heavy products, that solid paraffin should be formed in a similar way by decomposition of the liquid crude oil. But careful consideration of the nature and origin of petroleum precludes the possibility of its formation by distillation. It is true that paraffin was first obtained by Reichenbach by the distillation of vegetable and animal organic matter, and there is no question that it has been formed in a similar manner by natural processes. But petroleum must be regarded as a final product of decomposition, and while the series may be changed from one to another to a limited extent, decomposition of the constituents leads to the formation of simpler products until finally carbon is reached. Therefore, instead of paraffin as a result of decomposition of other hydrocarbons, paraffin itself is decomposed into hydrocarbons of lower molecular weight. But while this view is well supported by the facts observed relating to the nature of paraffin, we have not been satisfied with less than actual proof by experiment of its presence in crude oil. We placed several liters of crude petroleum in a large flue of the laboratory, with strong draft, and allowed it to evaporate during several weeks. Much the larger portion of the original oil evaporated, and the residue was so very thick it would scarcely flow. By careful extraction of the oil with ether and alcohol we obtained a small amount of solid paraffin, as shown by its melting-point and resemblance to ordinary solid paraffin hydrocarbons.

In another line of work we procured ten gallons of a semi-solid mass of hydrocarbons from a refining company at Coreopolis, Pa., that had been collected from the sucker rods in pumping oil and had never been distilled; this oil is very heavy, light yellow

in color and is used for the preparation of commercial cosmoline and vaselines. By cooling some of this product and crystallization we were able to separate from it a mixture of hydrocarbons closely resembling paraffin. A considerable portion of this pasty mass was subjected to fractional distillation, and a series of hydrocarbons separated with the composition of the series C_nH_{2n+2} . The oils separated by cooling and pressure gave results on analysis corresponding to series poorer in hydrogen.

We next took up the composition of the mixtures that form the vaselines and cosmoline. The refiner makes a distinction between crystallizable and uncrystallizable paraffin. But there seems to be but one form of solid paraffin hydrocarbons. Vaseline is simply a very heavy oil saturated with paraffin, and containing an excess of solid paraffin in the form of an emulsion. The oil is composed of the heavy oils of the series C_nH_{2n} and C_nH_{2n+2} , and the solid body of members of the series C_nH_{2n-2} . The so-called scale paraffin of the refiner is solid paraffin containing sufficient of the heavy oils to prevent it from a well-defined, crystalline condition.

The appearance of the series C_nH_{2n} and the series C_nH_{2n-2} in Pennsylvania petroleum distillates, as shown in a paper published recently, indicates that the so-called asphaltic hydrocarbons form a part of this petroleum with very high boiling-points. This places Pennsylvania petroleum in the same category with the heavier petroleum from such fields as California and Texas, the chief difference being the predominating series C_nH_{2n+2} in Pennsylvania oil and the series poorer in hydrogen in the heavier products. As explained above, the large proportion of the paraffin hydrocarbons in the heavier portions of Pennsylvania oil apparently renders the lubricating distillates more stable. Just what effect it has on the lubricating qualities, so far as I know, has not been completely determined. Some experiments on the very heavy lubricants from Beaumont oil have demonstrated very superior lubricating qualities.

Ohio Trenton Limestone Petroleum.—Since the first discovery of this petroleum, there has been uncertainty concerning its composition. In the preparation of commercial products, the refiner discovered essential differences between it and Pennsylvania oil, which were fully understood with reference to its refining qualities. The first serious obstacle was the large amounts of sulphur compounds that must be removed for the production of an acceptable burning oil. Innumerable patents were issued for processes which included distillation over quartz, precipitation with mercuric chloride, oxidation with potassium permanganate, and numerous other impracticable ideas that had been tried only on paper. The ordinary refiner distills over scrap iron and refines with alkaline lead oxide. From much the greater part of refining oil sulphur is removed by distilling over heated copper

oxide and the recovery of the oxide, a process that is said to have originated in Canada, but is known as the Frasch process. Probably fifty tons of sulphur daily is a conservative estimate of the amount extracted from Ohio oil and burned off into the atmosphere. It is claimed for this process that it is capable of removing the sulphur to 0.02 per cent., which is probably correct. Excellent burning oils are made from Ohio petroleum.

The composition of Ohio petroleum, so far as the portions readily distilled are concerned, has only recently been ascertained. Several years ago an examination of the sulphur petroleums, as Ohio and Canadian petroleum were then designated, showed that the series C_nH_{2n+2} formed the portions of Ohio crude oil which distilled below 212° , and the same members were discovered that had been previously identified in Pennsylvania oil, although the proportion of these hydrocarbons was smaller than in Pennsylvania oil. The proportion of aromatic hydrocarbons is higher in Ohio than in Pennsylvania oil. The lower cyclic compounds are also probably contained in larger proportion in the Ohio oil. An investigation finished not long ago on the hydrocarbons contained in the limits between 112° and 280° , at 30 mm. pressure, has identified thirteen hydrocarbons, with very satisfactory data on the proportions of carbon and hydrogen, which establish the series, and the molecular weights and indices of refraction identifying the members of the series. The following hydrocarbons of the series C_nH_{2n} were found: $C_{12}H_{24}$, $C_{13}H_{26}$, $C_{14}H_{28}$, $C_{15}H_{30}$, $C_{16}H_{32}$, $C_{17}H_{34}$. Unfortunately the distillate that should yield the hydrocarbon $C_{18}H_{36}$ was lost, although its specific gravity was ascertained before filtration.

Of the series C_nH_{2n-2} , the following hydrocarbons were identified: $C_{10}H_{18}$, $C_{20}H_{38}$, $C_{21}H_{40}$, $C_{22}H_{42}$, and of the series C_nH_{2n-4} , the hydrocarbons $C_{23}H_{42}$, $C_{24}H_{44}$, $C_{25}H_{46}$.

The change in series is attended with a greater difference in specific gravity between adjacent hydrocarbons; for instance, the last change in series is very marked, as the following table shows:

Distillate.	Sp. gr.	Hydrocarbon.	Difference in sp. gr.
224-227°	0.8614	$C_{21}H_{40}$
237-240°	0.8639	$C_{22}H_{42}$	0.0025
253-255°	0.8842	$C_{23}H_{42}$	0.0225
263-265°	0.8864	$C_{25}H_{48}$	0.0022

The distillates from which these hydrocarbons were separated above 150° , 30 mm., contained a large proportion of solid paraffin. The higher fractions were solid at ordinary temperatures, but no attention was given to the solid constituents, for without doubt they are identical with the solid hydrocarbons identified in Pennsylvania oil. Much difficulty was met with in separating the liquid constituents. The distillate was first cooled to 0° and filtered, and the filtrate then cooled to -10° and again filtered.

In purifying these heavy oils they were first dissolved in gasoline, and after purification the gasoline was removed by distillation. The greater preponderance of the series poor in hydrogen in Ohio oil over Pennsylvania oil explains the higher specific gravity of Ohio crude oil. The series C_nH_{2n-4} does not appear in Pennsylvania oil within the range of distillates below 300° , but it does appear in Ohio oil. The proportions of the series still poorer in hydrogen in the residues of distillation from Ohio oil are doubtless still greater.

Canadian Corniferous Limestone Petroleum.—In the paper referred to above, the composition of the distillates from Canadian oil was explained, including the hydrocarbons $C_{11}H_{22}$ and $C_{12}H_{24}$, which were identified in the fractions 196° and 214° . This limits the series C_nH_{2n-2} in Canadian oil to the lower members. Some years ago the higher fractions were examined for the individual hydrocarbons and results obtained, not yet published, that show a continuation of the series C_nH_{2n-2} ; and the hydrocarbons separated included the following: $C_{12}H_{24}$, $C_{13}H_{26}$, $C_{14}H_{28}$, $C_{15}H_{30}$, $C_{16}H_{32}$.

These bodies were identified by combustion for the series, and their molecular weights ascertained for the individual members of the series; the specific gravity of each hydrocarbon agrees closely with that of the corresponding hydrocarbon of Ohio petroleum. These values are still further confirmed by the formation and analysis of the chlorides.

The proportions of the lower members of the series C_nH_{2n-2} , which form the naphtha and gasoline in Canadian petroleum, is considerably smaller than in Ohio petroleum. The proportion of burning oil distillates is also less, and it is not possible to make from Canadian oil so good burning oil. The series C_nH_{2n} shows less stability on standing than the higher series C_nH_{2n-2} . I have samples of burning oil from Canadian petroleum that have stood ten years; they have changed from "water white," the original quality of the oil, to very dark yellow. Much larger quantities of gas are evolved in refining the Canadian oil, which is run back for heating the stills. Some paraffin is made, but the yield is small. The sulphur in the crude oil gives much trouble in refining, and it is not all removed in the burning oil. The percentage of sulphur is higher than in Ohio petroleum as a rule, usually 1 per cent. Canadian petroleum should give good grades of lubricators, but I have never examined these products.

California Petroleum.—In a paper published several years ago the composition of California petroleum oil from different sections of those fields was explained, and the principal series in the range of distillates examined, which included those below 214° in all specimens of crude oils, showed the series C_nH_{2n} .

Allusion was made in the former publication to a specimen of exceptionally heavy oil from Summerland, Santa Barbara County,

of special interest, since it came from wells sunk below the level of the Pacific Ocean at high tide. No distillates were collected from this oil below 200° atmospheric pressure. Under a tension of 60 mm. continued fractional distillation separated very heavy oils that were colorless or slightly yellow. They were purified by dissolving in gasoline and agitating with sulphuric acid, common and fuming, and the gasoline distilled off with the aid of a current of carbon dioxide. The composition of these products proved to be very different from that of the other California oils, or from any others we have examined. For instance, the fraction $210-215^{\circ}$, 60 mm., gave as its specific gravity at 20° , 0.9085, and the proportions of carbon and hydrogen corresponded to the hydrocarbon $C_{16}H_{34}$, or the series C_nH_{2n-4} . The higher members were the most viscous distillates that we have separated in what appears to be a pure form from any petroleum.

So far as we have carried the examination of California petroleum, no solid paraffin hydrocarbons have been found. From several fields oil has been obtained whose higher distillates on standing deposited large well-defined crystals, but unlike paraffin. From the fractions between 275° and 295° , 60 mm., separated from Torrey Cañon oil, a considerable quantity of crystals separated on standing several months that melted at 57° to 62° . These crystals were readily soluble in benzene and alcohol, and crystallized from hot alcohol on cooling, apparently in a pure form, unlike the solid paraffin hydrocarbons that are very sparingly soluble in alcohol; sufficient of this product for complete identification has not yet been obtained. The higher portions of heavy California petroleum offer an attractive field for study of the series poorer in hydrogen.

Texas Petroleum.—Much attention has been attracted by the discoveries of oil in Texas, and in some respects these deposits of oil possess a peculiar interest. The older Corsicana field yields an oil that is adapted for the preparation of a fairly good grade of burning oil, but it is inferior to Pennsylvania oil, since, as Richardson has shown, it is composed chiefly of the cyclic hydrocarbons. The heavier oil at Beaumont does not yield a sufficient proportion of burning oil distillate to make its preparation economical, but it is stated that a distillate can be separated in small quantities without cracking that can be refined into an inferior grade of burning oil. So far as examined the Beaumont oil does not contain members of the series C_nH_{2n+2} , which is essential in oils that yield the best grades of kerosene. The unique occurrence of this crude oil, underlying beds of sulphur under rather loose beds of shale, should exclude any of the most volatile constituents, such as are found in Pennsylvania oil. As we have demonstrated, the predominating series of hydrocarbons include the cyclic and condensed series. The crude oil is very heavy; it easily decomposes under distillation, but by

exclusion of air very heavy distillates may be separated without decomposition, from which superior lubricating oils may be prepared, especially of the heaviest type. The heaviest residue from Beaumont oil, if decomposition has been prevented, forms the best sort of petroleum asphalt, much heavier than similar products to be obtained from any other than California crude oil; in fact all the products to be obtained from Texas oil resemble those prepared from California oil.

The sulphur compounds in Texas oil seem to be much less stable than those in Ohio and Canadian oils, perhaps on account of their higher molecular weight. It is worthy of note that heavy petroleums, such as those from Texas and California fields, contain more sulphur than more volatile crude oils, like the Pennsylvania.

Petroleum from other fields, such as Colorado, Wyoming, Japan and South America, all partake of the properties of the heavier products from the fields in this country. The Japanese crude oils were very carefully sampled for our examination five years ago. There is promise of a great development of oil territory in South America. I scarcely believe that the sample of crude oil we examined some years ago represents the true condition of the oil fields there. The heavy petroleums are rapidly increasing in value as fuel.

California petroleum contains a larger proportion of nitrogen bases than any other, so far as known. Two per cent. of nitrogen, the amount contained in several specimens of crude oil examined, corresponds to 20 or 25 per cent. of the basic oils, or about one-quarter of the crude oil consists of the nitrogen compounds. In structure these bodies are tetra- or octahydro ring compounds in homologous series. The tetrahydro condition is shown by their instability.

It is, therefore, apparent that a similar condition of instability prevails in the cyclic hydrocarbons, and in the sulphur and nitrogen compounds from heavy petroleum. The sulphur and nitrogen bodies are found in considerable quantities only in such petroleum as is mainly composed of the cyclic compounds or the series poorer in hydrogen.

Another interesting series of bodies found in California, but not in Eastern oils, at least to the same extent, are the phenols, which are present in considerable quantities in some California oil.

Kansas Petroleum.—I have made no examinations of Kansas petroleums with reference to ascertaining the predominating series of hydrocarbons. But I have examined sufficiently numerous specimens of crude oil from the different Kansas fields to show that oils from these fields differ more widely in composition than oils from any other sections that have come under my observation. The very light, nearly colorless oil contains much gasoline and is evidently composed to a very considerable

extent of the series C_nH_{2n+2} . But in the other extreme, the heavy oils with specific gravity above 0.99 contain only a small percentage distilling below 150° , the limit for gasoline, a small percentage of burning oil, and this with low specific gravity $40-42^\circ$ Bé., indicating more of the series C_nH_{2n-4} . These heavy oils are largely composed of series poorer in hydrogen, of the very heavy lubricating oils and of asphalt. So far as I am aware no other oil territory presents such a wide variation in composition as the Kansas field.

NATURAL FORMATION OF PETROLEUM.

Much as has been said on this attractive subject, a broader knowledge of facts is necessary before definite conclusions can be reached. What is known forms the basis for only one explanation concerning the formation of petroleum, and that is that it was formed from vegetable or animal matter by slow decay or breaking down from complex forms of vegetable or animal life under the influence of natural forces, with no great elevation of temperature such as is necessary for distillation.

Mendeléeff's theory of the formation from carbides at high temperatures, recently asserted with greater force on the basis of Moissan's work with the electric furnace, demands too many hypothetical assumptions, and has too little support on the basis of fact. To reason from the artificial formation of alloys and carbides in an electric furnace to the natural formation of petroleum containing nitrogen, sulphur and oxygen, in the form of hydrothiophenes, hydroquinolines and phenols, demands a too broad reach of imagination to make the connections.

Bearing in mind the fact that petroleum may now be regarded as one and the same substance whatever its source, and that the deposits in different fields are composed of the same series, differing only in the proportions of these constituents, it must be admitted that it had one origin and one only. With reference to the series of hydrocarbons, it is immaterial whether its source was animal or vegetable, for under the influence of natural agencies it could have been formed as well from one as from the other.

This question has been attacked on chemical grounds from the wrong direction. Because hydrocarbons of the marsh gas series, ethylene series or acetylene series at temperatures of decomposition form minute quantities of compounds of the aromatic series, or because hexahydroaromatic bodies are formed from the aromatic hydrocarbons by heating with hydriodic acid, to assume that these same changes were produced by natural agencies and resulted in the formation of the hydrocarbons which now constitute petroleum, together with the other constituents of petroleum, ascribes to these natural agencies a direction of action and power that we do not know they possess.

In considering our present knowledge with reference to the

natural formation of petroleum, it seems to me that the following questions must be answered:

(1) What is the chronology of petroleum, in what order were the deposits formed in different fields?

(2) Were the least volatile constituents formed from the most volatile or the reverse?

(3) What is a reasonable explanation of the formation of the other constituents of petroleum?

The first question must be answered by the geologist.

It is natural to assume that the limestones formed by the accumulation of the shell remains of animal life were deposited first from the ancient sea. The sandstones, as products of erosion from the older rocks, were deposited last. The question as to whether the different deposits of petroleum were formed in situ, or formed in other strata and by some natural agency transferred to their present location, has not, I believe, been satisfactorily answered by the geologists. In case of the limestone petroleum, it would seem that it must have been formed where it is now to be found, as Hunt and Orton have ably maintained.

The theory of distillation from some other strata is not tenable in the light of the present knowledge of the constituents of petroleum. Neither could any known constituents of plants that could form petroleum be distilled, nor could the heavier portions of petroleum be distilled; the result would be only very volatile distillates and deposits of coal or graphite. In this condition deposits of petroleum should always be accompanied by coal, or with coal in the near vicinity.

In the case of Pennsylvania and the allied southern Ohio and West Virginia petroleum, it would be a great discovery to connect these deposits with coal formations, for then the source would unquestionably be vegetable growth and would support the prevailing opinion that this was the source of petroleum of this class. It is reasonable to assume, as is now believed, that Pennsylvania oil was not formed in the sandstones, but found its way there by natural agencies from lower strata, probably the Devonian shales. The infiltration of the crude oil through sandstones would have a purifying effect. It is quite probable that the very light yellow crude oils from the Berea grit and other sandstones were filtered a second time or more into their present positions.

With reference to the source of the limestone oils, the evidence is all in favor of animal origin, and the same is true of California oil, although its formation is far more recent than that of the others. Texas petroleum has not been sufficiently studied in relation to its occurrence and composition, but it is evidently of more recent origin, like California oil.

With reference to the second question, is it more reasonable

to assume, for instance, that the solid paraffin hydrocarbons were formed from the lower members of this series, or that the lower members were formed from paraffin? On this point some experimental evidence may be brought to bear. Reichenbach obtained paraffin from both vegetable and animal organic matter. Engler obtained paraffin by the distillation of fish oil, as Warren and Storer had done many years previously.

It is very well known that paraffin breaks down very readily into hydrocarbons with lower molecular weights, but it is not possible to polymerize the lower hydrocarbons into the solid paraffin hydrocarbons. The tendency in cracking of any constituents of petroleum is toward the formation of the lower series and finally carbon in the form of coke. So far as experimental evidence and observation have shown the nature and relations of the hydrocarbons which compose the different series of petroleum, the conclusion is convincing that the lower members of the series were formed from the higher. A single break in the ring of a methylene is sufficient to form by addition of hydrogen a paraffin hydrocarbon.

In answer to the third question, as to the formation of the sulphur, nitrogen and oxygen compounds in petroleum, these bodies have evidently not been built up synthetically, but are the products of decomposition of more highly organized constituents of organic bodies. It would seem that the small proportions of these bodies in Pennsylvania oil, as compared with the larger proportions in the limestone oils and California oil, should be strong evidence in favor of a different origin; that Pennsylvania oil came from organic vegetable remains, thereby explaining the small amounts of sulphur and nitrogen compounds in this class of oils.

But I think it can be asserted as a fact that the very large proportion of nitrogen compounds in California petroleum, amounting to one-fifth or more of the total weight of the oil, can only be accounted for by accepting animal remains as the source of their formation. As a summation of what is at present known of the origin of petroleum, the following answers may be given to the questions propounded above:

(1) Petroleum containing large proportions of the volatile hydrocarbons, especially of the series C_nH_{2n+2} , such as Pennsylvania petroleum, was formed from vegetable organic matter. The limestone petroleum was formed from organic matter of animal origin.

(2) Cellulose, starch and other similar bodies in plants, and the fats and nitrogen compounds in animal bodies, by gradual decomposition with exclusion of air, gave first the heavier bodies found in petroleum and by natural agencies during long periods of time, with no considerable rise in temperature, further de-

composition included as products the hydrocarbons with smaller molecular weights.

(3) The nitrogen and sulphur constituents of petroleum could only have been formed directly from or through the agency of animal organic matter.

There is an attractive field for the chemical geologist to study, more intimately than has ever been done, the occurrence of petroleum in connection with its composition.

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COTTON SEED OIL INDUSTRY OF THE SOUTH.¹

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COTTON seed oil is an oil obtained from the prolific cotton plant, which is the chief agricultural product of the South. It is obtained in the following manner:

The seed, after being freed from dirt and grit, is passed through gins to remove the greater part of adhering lint. From the gins it is passed through hullers, which cut and crack the hull of the seed. The hull is then removed from the contained meats as far as possible, by suitable machinery. The meats are then passed through rolls, and then to heaters provided with steam jackets and suitable stirring gear, where the meats are cooked, in order to allow a freer flow of oil. Finally the meats are transferred to hydraulic presses where the oil is expressed.

The products thus obtained are crude cotton seed oil and cotton seed cake, with which latter we are not here concerned.

Crude cotton seed oil is a vegetable oil, liquid at the ordinary temperature and varying in color from light red to black. It contains some moisture, often a little cotton seed meal, coloring-matter, and mucilaginous matter. It consists, aside from these impurities, of a mixture of the glycerides of chiefly oleic, palmitic and linolic acids, and small quantities of hydroxy acids, varying quantities of free fatty acids, and products entailed by hydrolytic decomposition, possibly some phosphorized fats, and the usual unsaponifiable matter.

It is seldom employed in the arts in its crude state, and its value deteriorates in this condition. For this reason it is usually refined soon after production.

Refining consists of treating crude oil with the proper quantity of caustic soda solution of suitable concentration. The caustic soda combines with the free fatty acid and other impurities above enumerated forming a crude soap stock, which on account of its

¹ Read at the New Orleans Meeting of the American Chemical Society.