CHEMICAL INVESTIGATION OF THE ASPHALT IN THE TAR SANDS OF NORTHERN ALBERTA

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A CHEMICAL INVESTIGATION OF THE ASPHALT IN THE TAR SANDS OF NORTHERN ALBERTA.

This is presented as a partial fulfillment of the requirements for the Ph.D. degree by W.F.Seyer.

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A CHEMICAL INVESTIGATION OF THE ASPHALT IN THE TAR SANDS OF NORTHERN ALBERTA.

INTRODUCTION.

Asphalt is a commodity of continually increasing importance. Although its chief use is still as a binder in the construction of asphalt pavements, it is not limited to this, but is now utilized in the manufacture of paints, varnishes, roofing material, insulating material etc. Much has been written about the physical and chemical properties of asphalt as a whole, such as change in structure upon heating, exposure to light and air, the action of solvents and acids, yet amongst this mass of literature one finds very little information on their ultimate chemical constitution. The reason for this is apparent when one considers the nature of the substance and the great difficulties involved in working with it, as there has been no simple and easy method for isolating any of the constituents.

Asphalts are bituminous substances of varying composition.

Their carbon content varies between 75% and 85%, the hydrogen between 7% and 14%, sulphur between 0.6% and 10%, while the nitrogen content is never greater than 2% and usually about 1%. Few have any oxygen. Their chemical composition bears a close relation to that of the petroleum, from which through polymerization by heat, oxygen or sulphur they are supposed to have arisen. As a class asphalts contain more carbon and less hydrogen than petroleums and are solid or semi-solid while the latter are liquids, although at times exceedingly viscous. In fact there is a gradual transition from petroleums to asphalts both from point of view of consistency and chemical composition. Many authorities regard them merely as the solid members of the petroleum series. There is however this difference, in that asphalts contain little, if any paraffins. The general opinion is that the structure of the constituents are largely of a cyclic nature, the lower members being monocyclic, and the higher polycyclic or bridge compounds.*

The investigation of the liquid hydrocarbons of the petroleums has been of a simple although tedious

* Richardson C. The Modern Asphalt Pavement. (1908)
Abraham H. Asphalts and Allied Substances (1919)

proceedure, owing to their more or less volatile nature. Attempts have been made to fractionally distil the asphalts, but this has been unsuccessful owing to the instability of many of the constituents and their low vapor pressure. The scarcity of information regarding the nature of asphalts has not been due to the lack of interest in them, but to their general inertness, non crystallizing tendency and non volatile nature.

HISTORICAL.

Boussingault* in 1837 appears to have been the first to make any attempt to ascertain the nature of the constituents of asphalts. He subjected some Pechelbronn asphalt to distillation and obtained a distillate which he termed "petrolene" whose chemical composition he found to be $C_5 H_8$ which he pointed out was isomeric with the oil of turpentine. The non volatile portion, he called "asphaltene". From this time until the end of the century little advance was made beyond the ultimate analysis and classification of different asphalts as they were discovered.**

* Boussingault. Sur la composition de l'asphalte.
An. Chem. & Phys. 64, (1837) 141.
73, (1840) 442.

** Malo Leon. Note sur l'asphalte, son origine sa preparation. etc. (1863)
Meyn L. Der Asphalt. (1872)

In 1897 Endemann published a paper in which he claimed to have isolated two acids from asphalts after heating the substance to 250° for some hours. These acids, he added, were obtained from the asphaltene or non volatile portion of the asphalt and had the empirical formula $C_{26} H_{26} O_4$, $C_{26} H_{20} O_{12}$ to which he gave the names asphaltic and asphaltulmic acid respectively.* A short time later C. Richardson brought out a paper on the nature and origin of Trinidad asphalt. ** In this paper he distorted the names asphaltenes and petrolenes to mean those parts of the bitumen or asphalt which are insoluble and soluble respectively in petrol ether.

Muntz & Le Bel, Farbstoff des Frdpech's von pechelbronn.Ber. Deu. Chem. Ges. V 222, 1872.
Delachanal B. Constitution de l'asphalte ou bitumen provenant de la Judee. compt. rend. 97, 491.
Day, Asphalts from Animal and Vegetable Material, Amer.Chem. Jour. 21, 478.
Ochrenius, Palena, Asphalt. Jour.Soc.Chem.Ind. XI 1892.
Cubian Deposits of Asphalts ibid. XIV 1895,
Asphalt Mined in Syria ibid. XII 1893, 150.
Asphalt of the East. ibid. VIV 1895, 121.

* Analysis Chemistry of Asphalt Jour. Soc. Chem. Ind. XVI 1897.

** Nature and origin of Trinidad Asphalt Jour. Soc. Chem. Ind. XVII 1898.

This is now the general accepted meaning of these words. He established the fact that many asphalts which had hithertoo been thought to contain oxygen contained none. In distilling the Trinidad asphalt he obtained a brown oil. He attempted to fractionate this at reduced pressures but failed owing to the decomposition of the constituents. However by leading in a current of carbon dioxide and reducing the pressure inside the flask to 60 m.m. he was able to separate a few fractions. They still possessed their brown color even after purification with sulphuric acid. A combustion analysis and a molecular weight determination of the two lowest fractions boiling at 214°-217° indicated the hydro-carbons $C_{13}H_{26}$ and $C_{14}H_{28}$ which belong to the C_nH_{2n} or naphthene series. Their density and refractive index also pointed to this series. He further pointed out there were indications of the presence of C_nH_{2n} and C_nH_{2n-2} and C_nH_{2n-4} series.

More recently, in 1917, C.B. Mabery published the results of the distillations of Gilsonite and Grahamite;two substances closely related to the natural asphalts and considered by Mabery to stand midway between petroleum and asphalts. By heating the Gilsonite and Grahamite slowly in an iron pipe to 400°C. he obtained a heavy oil. This on fractional distillation yielded a number of fractions which after purification and analysis indicated the presence of the series $C_n H_{2n}$ and C_{2n-2}.

Objects of this Investigation.

The greatest field of bituminous material found in the world is comprised in the Tar Sands of Northern Alberta. The field lies roughly in a circle having a radius of fifty miles with Fort Mc. Murray as centre. Out crops of varying thickness occur along all the river banks in that region. The asphaltic material is mixed with sand of varying degrees of fineness, and contains from 7 to 20% of bituminous matter, the sample investigated containing 17,85%.

The problem that presented itself to those interested in the resources of the Dominion of Canada was to discover some means whereby this field could be utilized. It was obvious that the "Tar" as such was quite valueless and that its value would depend upon the possibility of transforming it into substances which were valuable. In order to attack this problem successfully it was thought by Prof. A. Lehmann of the University of Alberta that a knowledge of the constituents of the asphalt should be obtained. It was toward this end that the following work has been directed.

The Sample.

The sample upon which the following work has been done was the remnant of a lot used by Mr.S.C. Ells formerly of the mines Branch, Ottawa, for paving experiments in the city of Edmonton. It was stated by Mr. Ells * to have been taken from an exposure on the Hangingstone river about 3 miles from Fort Mc. Murray and brought to Edmonton during the winter of 1914-15.

* Ells S.C. Preliminary Report on the Bituminous Sands of Northern Alberta. No. 281. Mines Branch, Department of Mines, Canada. 1914.

Physical and Chemical Properties of the Asphalt.

The asphalt when freed from the sand is of the semi-liquid variety which are classed by Richardson as malthas.

Spec. gravity	at 20°	1.022
Penetration	"	00

Solubility.

Solvent	% soluble	nature of residue
Carbon bisulphide	100	
" tetra chloride	100	
Chloroform	100	
Benzene	98	black solid.
Ether (hot)	86.9	brown "
Acetone "	70.	" "
Alcohol "	33.	" "
Sulphuric acid con.	100 after several days.	
Nitric acid "	100 " " "	

Application of Marcusson's Method of Analysis.

Marcusson* has pointed out that in the usual analysis of asphalts many important constituents of asphalts had been overlooked such as the petroleum resins and asphaltous acids. The customary analysis consisted in finding the amount of the asphalt soluble in petrol ether of a specified density, and again finding the amount of this dissolved asphalt, soluble in sulphuric acid. Heating and penetration tests were also performed in this connection and considered part of the tests. The analysis of asphalts suggested by him is as follows:

1. Determination of free asphaltous acids.
2. " " " anhydrides.
3. 3. " asphaltenes.
4. " resins.
5. " petroleum oil.

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* Angew. Chem. 29, 346, 1916.

The amount of free acids could not be obtained by the method outlined by Marcusson. Emulsions were formed in every case which could not be broken up even after standing for several months. The acids are therefore included in the saponifiable matter which was determined by the method of Spitz and Honig.*

The amount of asphaltenes was determined by first dissolving a weighed quantity of the asphalt in 10c.c. of benzene and adding to this 250 c.c. of petrol ether (B.P. below 55), which caused these bodies to separate out as black solid substances. The petrol ether solution was then run through "Fuller's Earth" which removed the resinous bodies. The petrol ether solution upon evaporation left behind a petroleum like oil. The resins were removed by simply extracting the "Fuller's Earth" with benzene or chloroform.

The table below shows the relation the Alberta asphalt bears to two typical ones, the Trinidad and Bermudez.**

	Alberta.	Trinidad.	Bermudez.
Saponifiable	2%	10.3%	5.5%
Asphaltenes	22.5%	37.0%	35.3%
Resins	24.0%	23.0%	14.4%
Oily constituents	51.5%	31.0%	39.6%

* Examination of Hydro-carbon Oils and Saponif. Fats.Holde.Mu Mueller p. 161.

** Z. Angew Chem. 29, 346, 1916.

It will be seen that the resins and oily constituents are greater in the Alberta than in the Trinidad or Bermudez asphalts.

Ultimate Composition.

A combustion analysis of asphalt can be carried out only with great difficulty, owing to the formation of substances during the heating which are volatile and very hard to burn. The analysis of the Alberta asphalt was repeated several times but the results including the sulphur and nitrogen would never total 100. This would indicate the presence of some oxygen, although Richardson claims that asphalts do not contain oxygen at all.*

Ultimate Composition of the Alberta Asphalt in comparison with Certain Standards.**

	Sulphur.	Carbon.	Hydrogen.	Nitrogen.	Oxyg.
Trinidad (Lake)	6.23	82.33	10.69	0.81	0.0
Bermudez	5.87	82.88	10.79	.75	0.0
Nevada	9.76	79.58	9.31	1.30	0.0
Alberta	2.73	84.49	11.23	.04	1.51
Mexico	1.48	85.65	12.37	0.00	0.00
Texas	1.13	87.27	11.79	.23	0.00

*J.Soc. Chem. Ind. XVII 1898.

** J. Soc. Chem. Ind. XVII p.29.

The Alberta stands midway between the hard and the soft asphalts.

The first step in the isolation of constituents from the asphalt was an attempt at fractional distillation under atmospheric pressure. The fractions were collected over the temperatures as follows:

Fractional Distillation of Asphalt. (Free of Sand)

Temperature	%	Nature of oil.
83-100	4	Pale yellow oil.
105-155	5	"
155-160	5	"
160-265	3	Red oil.
265-400	40	Black oil.

The residue hardened to a solid mass. Decomposition or cracking of the oil began even before the thermometer showed a hundred degrees. In fact by mere changing of the rate of heating one could change the amounts of oil that came over within certain temperatures. Thus by heating the oil so the temperature rose slowly it was possible to double the yield of the lower fractions, owing to the decomposition of the oil as it fell back into the flask. The cracking was so great even at 150° C. that it soon appeared futile to continue this line of attack.

Separation of the Bitumen from the Sand by Distillation.

The object of subjecting the bituminous sands to distillation was two fold. In the first place it was hoped that distillation might serve as a method of separating the bitumen and the sand. Secondly, since the distillation would necessarily have to be carried on at red heat, and consequently much cracking taking place, it appeared possible that benzene or other commercially valuable products might be formed and separated in this way.

The distillation was accomplished by placing the bituminous sands in an iron pipe 1½ inches in diameter and 2 feet in length. One end of this pipe was closed and to the other end was fitted a ½ inch iron pipe 3½ feet long which served as a condenser. By heating the loaded pipe in a combustion furnace for one-half hour at red heat, 12 to 13% of bitumen distilled over as a thick, greenish black oil, and much gas mixed with a persistent yellow fog was also formed. 150 gms. of the bituminous sands yielded approximately 4 litres of gas at room temperatures. An exact measurement could not readily be made on account of the gases containing hydrogen sulphide, which would dissolve in the water, displaced in the gas holder, by the gases collected. In addition to hydrogen sulphide the gas contained carbon dioxide. It burned with a bluish flame.

The distillate upon standing became less mobile and after a thin layer had been exposed to the air for several weeks it closely resembled the original asphalt extracted with carbon bisulphide. A fractional distillation of this gave the same results as the distillation of the sand free asphalt. (See page 12).

The distillate in each case had a rank odor and appeared to be chiefly olefines, as no benzene or its derivatives were found by testing with nitric or sulphuric acids. They decolorized a potassium permangate solution, absorbed bromine and iodine, and reacted emergetically with nitric acid. Concentrated sulphuric acid produced polymerization, all the distillates forming black, viscous substances similar to the original bitumen.

Distillations at reduced pressures varying between 10 and 20 C.M. gave no better results.

Action of Sulphuric Acid.

It appeared evident that the constituents could not be isolated as such. Consequently the next step was to transform these constituents into ~~some of~~ their derivatives and attempt to isolate these. With this end in view the asphalt was treated with various concentrations of sulphuric acid at different temperatures. As has been stated, the asphalt dissolved in concentrated sulphuric acid with the evolution of sulphur dioxide. When this solution was poured into ice water, a part sank as a black solid, a part floated on the water and another part went into solution. After removing the oil and solid matter, the aqueous solution was yellow but it contained only a trace of sulphonates. After heating the asphalt with concentrated acid to 200° C. for some hours a white solid collected in the neck of the flask. Only a small amount of the solid was collected and recrystallized from water. It was soluble in alcohol, acetone and sulphuric acid but only slightly in water. The purified product melted at 280°. This and its other properties suggested mellitic acid, but owing to the fact that this acid can be formed from so many diverse substances. little information could be deduced from its presence.*

The Action of Nitric Acid.

It is a well known fact that concentrated nitric acid acts as a nitrating agent upon aromatic compounds and

* 1. Wohler, Ann. 37, Page 263. 1841.
Schwarz, Ann. 66, Page 77, 1878
Lippmann, V. Ber. 27, Page 3408, 1894.

as an oxidizing agent when in contact with unsaturated hydro-carbons, breaking the chain at the point of double linkage. It was therefore thought that treating the bitumen with concentrated nitric acid might result in the nitration of the aromatic compounds present or at least in the oxidation of certain unsaturated ones with the formation of simpler substances that could be easily removed. With this end in view 30 gms. of bitumen were treated with 25 c.c. of nitric acid and allowed to stand at room temperature. The reaction was very slight at first but gradually increased until after 2 hrs., it suddenly reacted with almost explosive violence, brown fumes of nitric oxides being evolved. The acid solution became red in color and when allowed to evaporate left an amorphous, red resin like mass which was soluble in ether, acetone, alcohol and alkaline solutions. This last property showed that part of the bitumen had been transformed into acids. The alkali salts of these acids appeared to possess soap like properties, resembling the so called naphthenic soaps.* The residual bitumen upon further treatment with nitric acid and heating on the water bath, formed resin like substances like those above. An analysis of this resinous material

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* Seifensiederzeitung, 1909 Nr. 51/52.

showed that nitration as well as oxidation had taken place. Prolonged treatment in every case yielded nothing but carbon dioxide, acetic acid which could be detected by the odor, and oxalic acid which crystallized out of the final nitric acid solution upon evaporation.

Similar results were obtained by Markownikoff * and Beilstein** when they treated Caucasian petroleum with nitric and sulphuric acids, from which these investigators first concluded that the constituents of this petroleum were cyclic bodies and that these upon oxidation first formed resinous products and then broke down completely into oxalic, acetic, and carbonic acids. These cyclic bodies, they afterwards proved, belonged to the series of hydrocarbons known as naphthenes.

It would thus appear that the constituents of asphalt are cyclic compounds. From the results of the foregoing experiments it became evident that no pure products could be separated from the asphalt as a whole.
It was therefore decided to separate the asphalt into as many different fractions as possible by the use of various solvents. As has been stated the bituminous material was only partially soluble in alcohol, petrol ether, acetone and ether.

* Markownikoff. An. Chem. Phys. 6, 372, 1884.
** Beilstein & Kurbatov. Ber.Deut.Chem.Ges.XIII 1830 p.181.

It was also found that the fraction soluble in alcohol was also soluble in acetoneand ether, and that the one soluble in acetone was likewise soluble in ether. By applying these facts it was possible to separate the asphalt into four fractions. These fractions were obtained by first extracting a definite quantity of the "Sands" in a soxhlet with alcohol for several days, then driving off the alcohol by heating gently, and extracting with acetone until no more was removed, then extracting with ether and finally removing the insoluble matter from the sands by carbon bisulphide. The quantities removed by the various solvents are given below.

<u>Solubility of the Asphalt in Various Solvents</u>.

Total percent soluble		Percent soluble by fractional solution.
A. Alcohol	33	33
B. Acetone	70	37
C. Ether	86.9	16.9
D. Carbon bisulphide	100	13.1

The alcohol and acetone fractions were red viscous substances, resinous in appearance. The ether fraction was brown, the carbon bisulphide a jet black and both were solid substances which broke with concoidal fractures. An analysis gave the approximate figures as follows:

	A. Alcohol.	B. Acetone.	C. Ether.	D. Carbon bisulphide.
Carbon	80.0	78.0	71.7	72.5
Hydrogen	10.5	9.7	8.6	7.0
Nitrogen	0.2	0.6	0.6	1.07
Sulphur	1.7	1.8	2.75	3%
Molecular weight. (Freezing pt. method.)	405	513	520	
Iodine No.	6.4	5.5	4.9	5.15

From the analytical results the substance (A), the alcohol soluble, appears to have the simplest molecular structure and was therefore the first to be further investigated. This fraction was almost completely soluble in petrol ether. This residue, about 1%, rapidly blackened when exposed to light and on analysis was found to contain inorganic substances. These proved to be chiefly iron, with a little aluminium and calcium which are no doubt present as salts of complex organic acids.

The presence of these is not surprizing as the Marcusson' test indicated that a certain amount of acids and acid anhydrides were present. Salts of this nature have been found in petroleum by Markownikoff.* He further found that petroleum, free of these acids would dissolve mineral substances when these were in the form of oxides or sulphides . Engler** also states that petroleum dissolves metals in the presence of air.

That portion soluble in petrol ether could again be separated into two fractions by the action of sulphuric acid. This was done by dissolving it in petrol ether and shaking the solution with concentrated sulphuric acid at 0° C. A heavy black oil was obtained which upon standing settled and could be removed. It contained all the sulphuric acid. The petrol ether solution was then concentrated and dissolved in alcohol. This solution upon the addition of nitric acid reacted vigorously and on concentration yielded colorless crystal which melted sharply at 123° C. Attempts to obtain this substance on a large scale were unsuccessful, as in this case oxalic acid was always formed.

Further reactions with nitric acid were carried out,

* An. Chem. Phys. 6. 11. 372. 1882.

** Ber. Deut. Chem. Ges. XII p. 2186.
Endemann H. J. Soc. Chem. Ind. XVII p. 1015. 1898.

such as treating the alcohol soluble portion with nitric acid directly at various temperatures and concentrations. From all this however only the following facts were established. There appear to be two definite stages in the reaction, during the first the nitric acid reacted energetically with the material (A) causing it to dissolve in the acid. The resulting material was of an acidic nature as it dissolved in alkalis and was very inert to chemical reagents. During the second stage these resinous acids were slowly oxidized to oxalic acid requiring from 4 to 5 days digestion on the water bath.

Numerous attempts were made to crystallize these resinous acids by transforming them into lead, copper, sodium and potassium salts, but in vain. As the presence of the phenyl group in a compound exerts a strong crystallizing tendency, attempts were made to introduce this group by treating the sodium salts of the acids with benzoyl chloride and although the group could be introduced, no crystallization resulted. As it was possible that hydroxy acids might be formed, the resinous substances were heated with phenylhydrazine to transform them into the hydrazids, which crystallize readily according to Emil Fischer* and Bulow,* but the resulting substance showed no signs of crystallization. A steam distillation of 10 grs. of the resinous material gave a few drops of a yellow oil with a strong odor of turpentine. The alcohol soluble portion was slightly unsaturated. Harries has shown that ozone is a valuable reagent for oxidizing unsaturated compounds, splitting them at the unsaturated bond and forming acids in the presence of water.** It sometimes happens that even cyclic bodies are broken up. These facts suggested the use of this reagent. A stream of ozonized oxygen (containing 2 to 3% of ozone) was led into a chloroform solution of (A) the alcohol soluble fraction for 12 hrs.,after which the solvent was removed and the residue which appeared to have undergone no change was digested with water and subjested to steam distillation. When the aqueous solution was evaporated, there were left traces of volatile organic matter and of some crystalline substance.

It was apparent that oxidation with nitric acid produced no compounds which could be easily isolated and

* Fischer Emil. Annal. Der. Chemie No. 190 p.71.
Bulow -- " " " 236." 196.

** Ber. Deut.Chem.Ges.41,3704.
Annal. Der. Chemie 343. 1906.

and examined. Other oxidizing agents were sought,viz. potassium permanganate and potassium bichromate. Neither of these reacted in alkaline solution. The latter was without effect even in acid solution. Markownikoff found the same thing in regard to the Caucasian petroleum. The permanganate, however, reacted quite energetically at first with the alcohol soluble portion, (A),dissolved in acetic acid which was used as a solvent on account of its non polymerizing action. The substance (A) had undergone some change for it was black and much less was soluble in acetic acid. No pure compounds were isolated from it, although when distilled with steam a few c.c.s. of a liquid were obtained which had an odor resembling turpentine.

The acetic acid solution,upon concentration, yielded a mass of crystalline products. This consisted chiefly of the acetates of potassium and manganese with a small amount of other organic acids which had been formed in the oxidation process. By fractional recrystallization most of the acetates were removed, but as the amount of recrystallized substance was small nothing further was done with it except heating it in a hard glass tube with the result that a few drops of a dark brown oil collected on the sides. It smelled strongly of pyridine.

The analysis of the alcohol substance (A) indicated the presence of some oxygen, which it was thought might be present in the saponifiable matter or in alcohols. Accordingly 10 grs. of the substance (A) were digested with a 5% alcoholic sodium hydroxide solution for several days to remove the saponifiable portion. The alcoholic solution was then diluted to preciptate the unsaponifiable material, then filtered and the filtrate evaporated, leaving a resinous residue. This was acidified with hydrochloric acid, taken up with ether, dried and weighed. It was found that 1.5% had been dissolved by the alkaline solution. The unsaponifiable portion was next digested with sodium in boiling ether. A brown preciptate soon formed which coated the sodium. Fresh metal was added until no more preciptate, was formed. The ethereal solution was poured off and alcohol was added to the preciptate to remove the sodium. Upon the disappearance of the sodium, water was added and the solution evaporated to dryness. The resinous residue was then treated with hydrochloric acid and the whole taken up with ether. By adding water and acidifying, the sodium compounds were again transformed into alcohols which dissolved in the ether. In this way it was found that the alcohol soluble fraction contained approximatly 1% of alcohols.

Separation of the Oily Constituents from the Asphalt.

It will have become evident from the facts presented that the asphalt is a very complex mixture of substances whose chemical properties do not differ very markedly. The mixtures of even the fractions separated by the various solvents were still too complex for ascertaining any definite information regarding the constituents. The problem was then to devise some means of further reducing the complexity of the mixture. Marcusson's method of analysis for asphalts suggested the solution. This investigator had pointed out (see page 9) that asphalts could be separated into asphaltous acids, asphaltenes, oils and resins. As has been stated,his method was to first dissolve the asphalt in benzene, then to remove the acids, after that to preciptate the asphaltenes by adding petrol ether, and finally to filter the petrol ether solution through "Fuller's Earth". The intention was to carry this out on a large scale, thereby obtaining a large quantity of oil and then subjecting this to fractional distillation. In this way it was thought at least the series of hydrocarbons, present in the asphalt, might be determined.

That this could be done was amply demonstrated by the success of Mabery's work on the petroleums of this continent.*

To obtain large quantities of oil by Marcusson's method was impracticable. Consequently the "Tar Sands" were extracted directly with petrol ether, the solution was concentrated and then filtered through "Fuller's Earth" the filtrate ~~was~~ heated on a water bath to remove the petrol ether which left a red oil as a residue.

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* Proc. Amer. Acd. XXXII 121. 1897.
XXXVII 565. 1902.
XI 361. 349.

Method of Separating Oil on a Large Scale.

The petrol ether ordinarily purchased, contained certain constituents which boiled over 100° O. and it was essential to remove these, as they not only would dissolve more of the asphaltenes but would interfere in the fractional distillation by possibly contaminating the lower fractions. For these reasons a special gasoline was secured which had a larger amount of low boiling constituents than ordinary petrol ether. This was redistilled through a fractionating column 7ft.,in lenght and 1 in., in diameter, filled with glass beads. Only that distilling below 55°C. was used. The "Fuller's Earth" was crushed until it passed completely through a 40 # sieve but very little through a 20 #. The size of the particles was important, for if they were too large, filtration was too rapid and therefore inefficient, and if too small the particles tended to form a dense cake through which the solution passed very slowly. After crushing the earth was heated in an iron pipe to red heat, thereby removing not only the adhering but much of the combined water, and materially increasing the absorbtive power of the earth. It was then placed in iron pipes 3 to 4 ft.,in length and 2 in. in diameter which had a reducer at the lower end that connected with an outlet pipe of ½ in.

"Tar Sands" to the amount of 2-3 kilo. were placed in stone jars of about $1\frac{1}{2}$ litres capacity, fitted tightly with wooden lids. The "Sands" were covered with petrol ether and allowed to stand for several hours with intermittent stirring, after which, the solution was removed by decantation. This extraction was continued until the petrol ether became only slightly discolored, the decanted portions being put into large bottles to allow the fine particles of sand to settle out as they would otherwise clog the pores in the "Fuller's Earth" and hinder filtration.

The filtration was done in such a manner that the concentrated petrol ether solution first came into contact with earth that was already partially saturated with resins, while solutions partially decolorized always came in contact with fresh "earth", which removed all the red color and left the solution yellow.

It was also observed that temperature had a marked effect on the absorbing power of the "earth", the higher the temperature the greater efficiency. Further, the efficiency could be increased by using a concentrated petrol ether solution.

The material retained by the "Füller's Earth" which Marcusson termed "petroleum resins",can be removed by merely extracting the "earth" with benzene, chloroform, carbontetrachloride or carbon bisulphide. These resins have not been further investigated. It was however noticed that crystals separated from a benzene solution upon slow evaporation.

The material insoluble in the petrol ether, the asphaltenes, were black solid bodies, insoluble in acetone, ether and alcohol. They decomposed even before they reached the melting point. They have not been investigated as yet.

The oil after the solvent had been removed as much as possible by the aid of suction and by heating on a water bath was transparent and had a light red color. It appeared to possess good lubricating properties, for after a week's exposure to the air in thin layers it showed no signs of resinification.

Physical and Chemical Properties of the Oil.

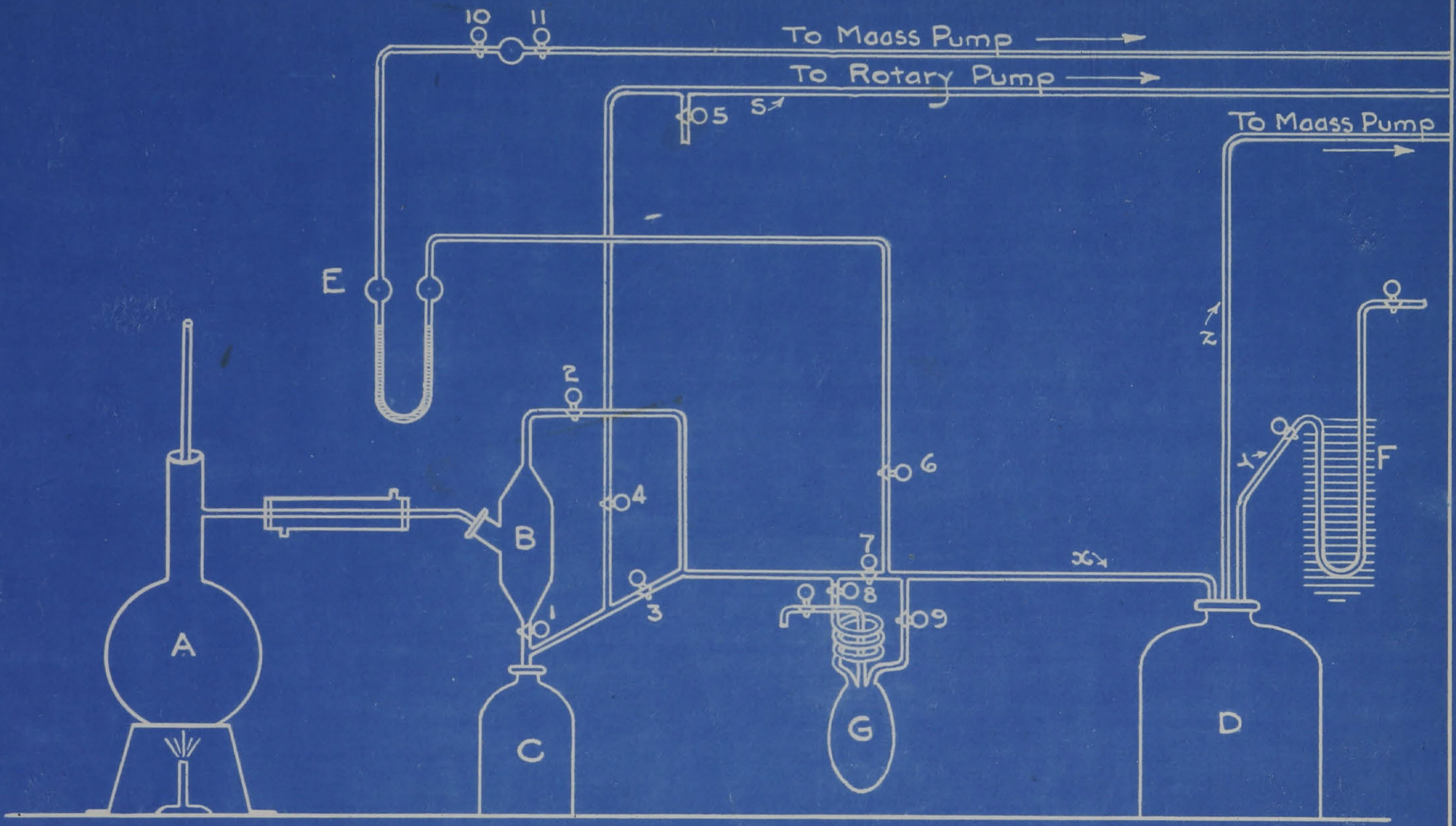
Spec. Gravity	20°C	0.927.
Refractive Index	20°C.	1.5000.
Optical activity		Dextro-.15-1.6.
Viscosity at 25°C.		20.
Molecular Weight		350.
Sulphur		1.87.
Carbon		85.76.
Hydrogen		12.19.
Iodine no.		2.1.

Slightly over 7½ litres of this oil were extracted. This was considered to be sufficient for the fractional distillation as the intention was to get only a knowledge of the series of hydrocarbons present without actually isolating any one constituent.

Fractional Distillation of the Oil at Reduced Pressures.

It was impossible to distil the oil at atmospheric pressure. When the distillation apparatus was made air tight and the pressure reduced to 40 m.m. by means of water suction pump, a small amount of a colorless oil could be removed however, when the temperature at which the oil came over reached 150^{o}C. cracking began, which could be detected by the appearance of a fog in the condensing tube and the rank odor of the distillates which now possessed a deep red color. The pressure was then reduced to 18 m.m. with the result that a slightly higher temperature could be reached before cracking began. It was next decided to lead in carbon dioxide during the distillation, as it was thought this might prevent the decomposition of the oil. This was of no avail for the decomposition even under 18 m.m. pressure was so great at 165^{o}C. that it was useless to try and get any separation in this manner. All but the distillates below a 100^{o}C. had a red color and a rank odor. Those distilling below a 100^{o}C. were clear limpid oils with a strong turpentine odor.

Obviously the only ~~the~~ successful way of distilling the oil lay in a still further reduction of the pressure. This could not be done by a water pump and as there were always small amounts of gases given off, Sprengel or Gaede pumps were of no use. The difficulty was overcome by Dr.O.Maass of this University, consenting to the use of a special pump devised by him. By means of this pump



— VACUUM DISTILLATION APPARATUS —

based on an entirely new principle it was possible to reach as low as 0.1 m.m. even when there was a slight evolution of gas. Distillation at such low pressures required the construction of a special distillation apparatus which is described below.

The flask (A) was of pyrex glass and it connected with a receiver (B). By means of taps 1, 2, & 3 the bottle (C) could be entirely separated from the rest of the apparatus and removed. (G) was a bulb which could be immersed in Dewar flask cooled with solid carbon dioxide. This permitted the collection of the most volatile substances. (D) was a strong bottle of 5 litres capacity this acted as an equilizer of the pressure. From this led three tubes, X to flask, Z to pump and V to a mercury manometer.

The tube (S) led to a large rotary pump. By means of it the pressure in the bottle (C) could be rapidly reduced to about 20 m.m. so when the tap was opened connecting the bottle (C) with the apparatus there was only a very slight change in the pressure.

(E) was a sulphuric acid manometer. As this was seven times as sensitive as the mercury one, changes in pressure of .1 m.m. could be readily detected. The tube (R) connected with the pump and after the vacuum at which the distillation was to be carried out had been reached the taps 13 and 14 were closed. The pressure could be controlled to within 0. 1 m.m. by simply connecting or disconnecting the pump.

A litre flask was used for the first distillation. It was filled to 2/3 of its capacity with oil. The pressure during the distillation was reduced by steps, as at the low pressure the first distillates were fairly volatile even at room temperatures. The distillates were collected first over 25°C. intervals, then over 10, then 5 and finally over 3 or less as the quantity of oil determined. After the first distillation the oil fell into the following fractions.

Temperature.	Pressure.	Amount.
0-80	10	160
80-110	10	395
110-135	5	530
135-160	1	300
160-185	0.5	550
185-195	0.4	220
195-213	0.4	400
213-230	0.4	430
	Condensed in carbon dioxide.	
	bulb.	400
	total.	3385

After the third distillation the distillates tended to collect in quantity about certain temperatures. These fractions were subjected to two further distillations.

The distillates were all clear and transparent. The lower ones possessed a strong terpene odor while the higher ones had a slight disagreeable odor. No attempts were made to fractionate any of the oil distilling above 230°, although it was possible to do so up to 300° without any signs of cracking, providing, the pressure was kept below 0.4 m.m. An increase of pressure of only .2 m.m. was sufficient at these temperatures to cause cracking of the oil.

Purification of the Distillates.

All previous investigators of heavy hydrocarbon oils, Mabery, Kraft, and Marcusson used sulphuric acid to purify the distillates. The acid served to remove the unsaturated, sulphur and nitrogen compounds. The value of sulphuric acid as purifying agent for hydrocarbon oils has been much questioned. It has long been known that sulphuric acid attacks the higher saturated hydrocarbons with the production of tars. It was found that all the distillates although they were only slightly unsaturated would dissolve completely in concentrated sulphuric even when these oils were dissolved in petrol ether. Once these oils had been dissolved they could not be recovered from the acid as it slowly converted them into tar like substances. Liquid sulphur dioxide at-10°C. has been used for a number of years in the separation of saturated and unsaturated hydrocarbons on a commercial scale. The saturated compounds are insoluble in the oxide while the unsaturated ones dissolve. So far only the very light hydrocarbons have been purified in this manner.* However it has been found that even the heavy hydrocarbons can be separated by the use of liquid sulphur dioxide. There appears to be only one factor which tends to limit its use to the heavy ones and that is their viscocity at-10°C. This disadvantage could be overcome by simply dissolving the oil to be purified in petrol ether which had previously been treated with sulphur dioxide until all unsaturated compounds had been removed.

The whole proceedure was very simple. The oil to be purified was placed in a burette with taps at each end. The burette was then immersed in an ice bath and cooled to-10°C. Liquid sulphur dioxide was then run in. After shaking and allowing the burette to remain in the bath for 15 min., two layers could be observed, the upper one, the oil, was

* Met.& Chem. Eng. p.396 Vol. XVIII No. 1918.

clear, the lower one, the sulphur dioxide, layer was red. The lower layer was allowed to run off and the oil treated with more reagent. This was continued until the sulphur dioxide layer remained colorless. It was noticed that upon the first addition of sulphur dioxide, crystals formed in the oil which sank and were later redissolved in the lower layer. It was also observed that the sulphur compounds could be removed by this method, as the oil which contained almost 1% before treament contained only a faint trace afterwards.

The amount removed by the sulphur dioxide varied with the different distillates, being on the average about 2%. After purification the oils distilling below 162° were completely colorless and those above that which had become slightly discolored upon standing, possessed a light yellow color and had no longer the disagreeable odor they formerly had.

The combustion analyses of the oils had to be done with a great deal of care as they were exceedingly difficult to burn. Even then the results were somewhat low.

The molecular weight determinations were done by the freezing point method in benzene. In making these determinations advantage was taken of a devise first used by Dr. O. Maass and described in the"Proceedings of The Royal Society of Canada" for 1919. Instead of adding a crystal of benzene from some external source to start crystallization, he simply touched a platinum wire, sealed in the inner freezing tube with a copper rod, one end of which had been cooled in a solid carbon dioxide ether bath. This caused the formation of crystals about the platinum wire inside the tube. In this manner the degree of super cooling could be accurately controlled. Also the difference between the freezing point of benzene and the temperature of the cooling bath could be reduced, thus decreasing the magnitude of the error from this source. The difference between these two temperatures it was found, should never be less than 1 degree and never greater than 1.5. If the difference is less and the cooled rod is applied there is an immediate supercooling of as much as 0.3 degree before crystals appear. When,however it is greater than one degree crystals appear immediately and there is no supercooling. About 0.05 degree of supercooling should be allowed. The benzene was regularly stirred by means of a magnetic stirrer.* The outer bath was kept constant by means

* Maass.O. Magnetic Stirrer. Jour.Amer. Chem. XLI 1. 1919.

of an electric stirrer, the temperature being lowered to correspond with the depression of the freezing point of the solution as the concentration increased. With care the determinations would check within 1%. Thus the molecular weights for the lowest fraction were, 154, 156,155, with varying concentrations while for the highest fraction they were, 346,346,347,.

Physical and Chemical Properties of the Distillates.

All the distillates except the first were optically active. The amount of rotation was not large, about that of the petroleums examined and like them was dextro active. The activity was slightly increased by purification. The optical activity of petroleums has been questioned by some authorities, especially Mabery, who claims to have examined a number of distillates but found no sign of any activity.* It is possible that in his case the oils had been racemized during the distillation. The optical activity proves clearly that the asphalt in its formation has not passed through a temperature above 450°C., as it has been found that all activity is destroyed at this temperature.

* Jour. Amer. Chem. Soc. Vol. XLI 1. 1919.

Degree of Rotation in 1 d.m. Tube.

Fraction	B.P.	Pressure	α
1.	75-80	10	0.0
2	95-99	10	0.14
3	93-98	2	0.18
4	139-135 ?	1.5	0.25
5	143-147	1.	0.30
6	153-156	1	0.35
7	158-162	0.5	0.48
8	183-184	0.4	0.36
9	220-225	0.4	1.24

Refractive Indices of the Distillates.at 20.5°.

Fraction	B.P.	Pressure	Refractive Index.
1	75-80	10 m.m.	1.4450
2	95-99	10	1.4580
3	93-98	2	1.4722
4	133-35	1.5	1.4768
5	143-47	1	1.4859
6	153-56	1	1.4911
7	158-62	0.5	1.4942
8	183-84	0.4	1.5011
9	220-225	0.4	1.5180

This high refractive index points to unsaturation or cyclic structures, as the unsaturated compounds have been removed, it can only be due to the latter. A high refractive index is a general characteristic of all lubricating oils.

Density of the Distillates.

Fractions	B. P.	Pressure	Density at 20°C.
1	75-80	10 m.m.	.8186.
2	95-99	10	.8395.
3	93-98	2	.8709.
4	133-35	1.5	.8989.
5	145-47	1	.9178.
6	153-56	1	.9350.
7	158-62	0.5	.9439.
8	183-84	0.5	.9556.
9	220-225	0.5	.9598.

The molecular weight determination and results of the combustion analysis showed the presence of nine hydrocarbons. As only five distillations were made it is not assumed that the different fractions were absolutely pure, as the original intention was to merely obtain the series present. It is evident, never-the-less that quite pure hydrocarbons can be obtained by this method providing distillation is repeated five or six times. Then too, a much better separation is possible at pressures of 1 m.m. than at atmospheric pressure as a consideration of the vapor pressure curve will show.

Hydrocarbons Found.

Molecular weight and combustion analysis of fraction 1. distilling at 75-80 at 10 m.m. indicated the hydrocarbon $C_{11}H_{22}$. .1078gm. gave .1394gm. H_2O and .3374gm. CO_2.

Found.			Calculated.		
H.	C.	M.W.	H.	C.	M.W.
14.40	85.20	155	14.30	85.70	154.

This hydrocarbon is apparently the same as those isolated by Mabery and Takano * from Japanese petroleum, and Mabery and Hudson ** from California petroleum, and by Markownikoff and Ogloblin from Apscheron naphtha ***

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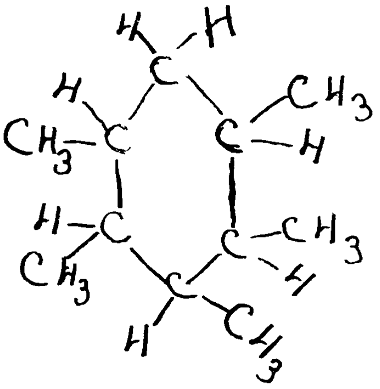
* J. Soc. Chem. Ind., 29, 614 (1900).

** Proc. Am. Acad. Arts Sci., 35 (1900).

*** Ber., 16, 1983 (1873).

It was also found by Pictet and Bouvier* in the Loire coal who showed that this compound was a naphthene having the following structural formula.



The refractive index (1.4231 at 20°) and spec. gravity (.7832 at 20°C) of this hydrocarbon corresponded to that one which Mabery and Quaqle ** fonnd in Canadian petroleum, being lighter than the one in the Californian petroleum. The hydrocarbon found in the Alberta asphalt as will be seen from the tables (p. 39 & p. 40) has also a higher refractive index and spec. gravity than Pictet's had. However the molecular refractive index is the same for both compounds.

<u>Molecular Refractive Index</u>.

Found	Calculated.
50.55.	50.56.

* Ber., 46, 3342 (1913)

** Proc. Amer. Acd. XXXII 121. 1897.

The fraction No. 2 distilling between 95-99°C. 10 m.m. appeared to be $C_{12}H_{24}$. .1368 gm. gave . 1798 gm. of H_2O and .4237 gm. CO_2.

Found			Calculated.		
H.	C.	M.W.	H.	C.	M.W.
14.58	85.10	167.5	14.30	85.70	168.

This as the former is thus also a naphthene of the series C_nH_{2n}.

<u>Molecular Refractive Index.</u>

Found	Calculated
55.07	55.15

A similar compound has also been found in the petroleums mentioned above, except that it has both a higher refractive index and spec. gravity. Mabery found a compound of the same formula in Gilsonite and Grahamite.*

Fraction No.3 distilling between 93-98°C. and 1 m.m. was found to be $C_{15}H_{30}$. This also belongs to the C_nH_{2n} series. .261 of oil gave .1580 gm. H_2O and .3975 gm. CO_2.

Found			Calculated.		
H.	C.	M.W.	H.	C.	M.W.
13.92	85.97	209	14.30	85.70	210.

Molecular refractive index found was 68.10

The fraction No. 4 distilling between 133-135°C. and 1.5 m.m. pressure was much larger than the first three. Almost 75 c.c. were obtained which distilled between the two temperatures stated. Unlike the former this fraction no longer possessed a terpene odor. Upon combustion .1395 gm. of the oil gave .1363 gm. of H_2O and . 4481 $C\,O_2$ it is probably $C_{18}\,H_{32}$

Found			Calculated		
H.	C.	M.W.	H.	C.	M.W.
12.61	87.60	242	12.90	87.10	248.

The molecular refractive index found was 76.03, calculated 78.37. This hydrocarbon was found by Mabery in Utah Gilsonite. The low molecular weight obtained would indicate that this fraction still contained a good deal of a lower hydrocarbon probably $C_{17}\,H_{30}$. These are most likely members of the dicyclic naphthenes of the $C_n\,H_{2n-4}$ series.

The fraction No. 5 distilling between 145-47° C. at 1 m.m. proved to be, upon combustion and molecular weight determination $C_{19}\,H_{34}$. .1361 gm. of material gave .1680 of H_2O and 42.51 of $C\,O_2$.

Found			Calculated.		
H.	C.	M.W	H.	C.	M.W.
13.72	86.09	265	12.98	87.02	262

The above results agree much closer with the ratios calculated for $C_{19}H_{36}$. The carbon and hydrogen ratios in this are 86.36 and 13.64. But this fraction like all the others was insoluble in liquid sulphur dioxide, consequently one cannot consider it as being unsaturated.* The molecular refractive index was found to be 81.91 and as the theoretical was 82.98 without assuming the existence of an unsaturated bond the evidence is clearly on the side of the $C_{19}H_{34}$ compound.

The fraction No. 6 distilling between 153-156°C. at 1 m.m. appeared to be the hydrocarbon $C_{20}H_{36}$. 1307 gm. of oil gave .1567 gm. of H_2O and .4132 of CO_2.

Found			Calculated		
H.	C.	M.W.	H.	C.	M.W.
13.34	86.38	272	13.05	86.95	276.

The molecular refractive index found was 84.24 which agrees with the theoretical 84.46. Similar arguments to those brought forward in discussing the formula for the

* After purification the distillates no longer decolorized a permanganate solution as they did formerly.

hydrocarbon $C_{19}H_{36}$ are applicable here.

The fraction No. 7 distilling between 158-162° C. at 0.5 m.m. after analysis proved to be $C_{21}H_{38}$..1183 gm. gave .1394 gm. H_2O and .3688 gm. CO_2

Found			Calculated.		
H.	C.	M.W.	H.	C.	M.W.
13.10	85.42	288	13.11	86#89	290.

The molecular refractive index found did not agree as well with the theoretical as the others have so far, the two being 92.17 and 88.86 respectively.

The fraction No. 8 distilling between 183-184°C. at 0.4 m.m. appeared to be a very pure specimen as 85 c.c. come over within 1 degree. This oil was viscous and possessed a yellow color, even after purification with the liquid sulphur dioxide. Upon combustion .1491 gm. of the oil gave .1778 gm. of H_2O and .4735 gm. of CO_2 which proved that this fraction was $C_{23}H_{42}$.

Found			Calculated.		
H	C	M.W.	H.	C.	M.W.
13.12	86.69	314	13.21	86,79	318.

The molecular refractive index was found to be 96.9 which was somewhat lower than the calculated one 101.5.

The fraction No. 9 distilling between 220-225°C. at a pressure of .4 m.m. was a very viscous oil. It retained its yellow color after purification. After analysis and molecular weight determination this proved to be $C_{25}H_{46}$ .1179 gm. oil gave .1393 gm. H_2O and .3691 gm. ?

Found			Calculated.		
H.	C.	M.W.	H.	C.	M.W.
13.11	85.70	346	13.30	86.70	346.

The molecular refractive index found, 109.2, which agreed with the calculated one, 110.5.

There are two members of the $C_n H_{2n-4}$ missing $C_{22}H_{40}$ and $C_{24}H_{44}$. These will undoubtedly be found in the distillates between 167-183 and 184- 220. None of the $C_n H_{2n-4}$ series above the $C_{18}H_{34}$ have ever been isolated in such a state of purity as to enable one to identify them. It has, up to now been found impossible to distil them at all without decomposition. This failure has simply been due to the fact that the pressure had not been sufficiently reduced. With the Maass pump pressures as low as .1 m.m. can be maintained which is low enough for distilling hydrocarbons of the $C_n H_{2n-4}$ series even up to 30 carbon atoms.

Kraft found this number to be the limit in the distillation of paraffins.* However these oils cannot be removed from the asphalt directly by distillation even with a low pressure for two reasons. Firstly, it has been pointed out that asphalts are composed of asphaltenes, resins and oils of which the former are solids. These asphaltenes can scarcely be heated to their melting point which is about 150° before they decompose into gaseous and liquid products. Consequently upon distilling the asphalt as a whole, the distillates will be contaminated with these decomposition products. Secondly, the asphaltenes and resins seem to possess an extraordinary power of retaining lower hydrocarbons within themselves. It has been found necessary to heat the asphaltenes to a 100°C. for several days to remove all the petrol ether which had been used to separate them. This is not surprising, as Markownikoff found that to remove the last traces of butylene from a high boiling oil it was necessary to heat it to 280°C.* Nor does low temperature distillation for long periods of time avoid the difficulties, as it has been found that even the lowest distillates will, upon prolonged heating, be gradually

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* Ber. Deu. Chem. Ges.

** Comp. Rend. XCL 873.

polymerized into asphalt like substances.

The method outlined in this paper overcomes all the difficulties mentioned above. It is in fact the first and the only method of effectively dealing with this class of substances. Up to now the lower constituents are all that have been investigated, but there is no doubt that through further subdivision by solvents and fractional distillation at very low pressure one will be able to get an insight into the nature of the resins as well.

Sumary.

1. The physical and chemical properties of the asphalt in the Alberta sands have been determined.
2. Sulphuric and nitric acid react with the asphalt in a similar manner as they do with Caucasian petroleum, which indicates cyclic structures.
3. The asphalt can be separated into four fractions by means of alcohol, acetone ether and carbon bisulphide.
4. A practical method, based on Marcusson's analysis of asphalts has been devised for removing the oil from asphalts on a large scale.
5. The oil when fractionally distilled under a pressure of 20 m.m. still decomposed all the distillates except the

lowest having a red color.

6. When the oil was distilled at pressures less than 1 m.m. there was no decomposition and the distillates were clear, colorless oils.

7. Liquid sulphur dioxide has been used to purify the distillates for the first time. This produces no polymerization or decomposition of the distillates as sulphuric acid does which is therefore highly objectionable.

8. Hydrocarbons of the series $C_n H_{2n}$ and C_{2n-4} were isolated These were $C_{11} H_{22}$.

$C_{12} H_{24}$

$C_{15} H_{30}$

$C_{18} H_{32}$

$C_{19} H_{34}$

$C_{20} H_{36}$

$C_{21} H_{38}$

$C_{23} H_{42}$

$C_{25} H_{46}$

9. The first two hydrocarbons have been found in coals and petroleum.

10. The method given in this paper can be applied to any asphalt.

In conclusion I wish to express my gratitude to the following gentlemen for their help and suggestions, Dr.A.Lehmann of the University of Alberta, and Drs. V. Krieble and O. Maass of this University.

W. J. Seyer.

Ld. July 6-49