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CHEMISTRY OF THE ASPHALTS.
(Review of Literature)
M. Pier's files.

Asphalt bitumens are colloidal system in which the asphaltenes (hard asphalts) form the dispersed phase, and the malt ones (oily contituents) are the dispersion medium. According to Nellenstayn, the difficultly soluble asphalts are not hydrocarbons in mutual solution but carbon dispersed in oil. There exists a continuous transition series between the oily constituents of the asphalts to the free carbon. The molecular weight increases steadily and the system passes uniformely from solutions through colloidal dispersions to coarsely dispersed particles. Mineral oil resins form the first transition stage from petroleum hydrocarbons to asphalts. In a small proportions they are already present in most lubricating mineral oils. Larger amounts of them are formed during the oxidation of the oils in the air. Unlike the lubricating oils they are but little soluble in acetone. The asphaltenes are formed by further oxidation of the petroleum resins, and they are insoluble in benzol. Asphaltenes may however be formed without the presence of air. The high sulfur content is characteristic for the asphaltenes of the natural asphalts.

From the standpoint of chemical compositions, asphalts may be subdivided into natural asphalts, petroleum residues and cracking residues.

The older the asphalts, the more they contain of difficultly soluble constituents. Oxidation changes result in an increase in the hard asphalt contents. The oxidation behavior of the petroleum residues is similar to their distillation behavior. In the different bitumens produced from the same mineral oil,
the higher melting point asphalts are stable, and they become enriched at the cost of the soft asphalts, resins and the paraffin free oil constituents. Unlike the distillation process, the soft asphalts decrease during oxidation as the melting points rise, while resins increase up to a certain melting point, and then decrease. The soft asphalts are therefore converted during oxidation into hard asphalts, the paraffin-free constituents into resins, and the latter are in turn converted into hard asphalts.

The paraffin present in the bitumen during the oxidation or distillation does not enter into the process, but remains in a colloidal dispersion in the bitumen.

Almost nothing is known about the chemical structure and the relationship between the chemical composition and the physical properties of the hard asphalts and the residues obtained in distillation. The reason for it is that in the distillation residues we are dealing with the most difficult constituents of petroleum to study chemically, because they can hardly be separated and analyzed by the usual chemical methods. Hydrocarbons are the principal constituents of asphalts and the petroleum residues, and as the molecular weight rises, the differences in the boiling point decrease, while the number of the possible isomers increases tremendously.

The tendency to polymerize and to condense also increase with increasing number of carbon atoms. The chemical reactivity of the different kind of hydrocarbons is not very different. There is no great difference in the proportion of carbon to hydrogen determined by chemical analysis. On the other hand, the determination of the individual elements has brought certain results. Thus, petroleum asphalts have been found the more similar to natural asphalts, the more sulfur they contain. But there are exceptions even to this rule.

Should one use, however, physical methods of testing, one would find processes particularly suitable to certain intended applications (softening point, drop point, penetration, and other characteristic viscosity properties.)

Colloid chemical methods of study furnish us a third means for acquiring information on the ultimate make up of the asphalts. They inform us, chiefly from the work of Nellensteyn, that bitumens are colloidal systems, with dispersed phases composed principally of carbon or of high molecular weight hydrocarbons, absorbed on the surface of low molecular weight hydrocarbons. This dispersed phase is dispersed in an oily medium. The hardness depends on the proportion of the grainy and oily components, and the rheological behavior is conditioned by the adhesion of the different constituents. Precipitation methods, chromatographic separations may be used for the separation of the asphalts into different classes of materials, the most important of which are the hard asphalts or asphaltenes, the resins, and the oily constituents, or maltenes. One may arrive at conclusions on the colloid-chemical structure of particular bitumen from the proportion of the classes found. A comparison may also lead to conclusions on other properties.

The composition of the natural asphalts is entirely different from that of the petroleum asphalts. The hard asphalt contents of the latter is much higher, their soft asphalt content is low, and their resin content is particularly low. As the softening point of the petroleum asphalts is higher, the hard and the soft asphalt content is increased, and the oil content becomes correspondingly lower. One may readily understand the reason for the oil content not increasing when the hard asphalt content decreases, but actually becoming lower in some cases, while the proportion of the soft asphalts and the resins actually increase, because otherwise it would automatically be reduced at lower hard asphalt contents. It appears that the contents of the different constituents are less important than the proportion of the constituents of the class.

Different values are obtained by different methods of breaking down into classes.

Breaking the asphalts down into these classes tells us nothing about the chemical constitution. Identification of hydrocarbons and their preparation in the pure state from petroleum oil has been done successfully only in case of the lower boiling fractions. With higher boiling fractions, greater difficulties are to be overcome with increasing molecular weights. It has accordingly become customary to be satisfied with the determination of the characteristic classes of materials, such as the aromatics, naphthenes, paraffins, olefins. The methods used here are ring analysis of Waterman and a few physico-chemical processes which have recently come into use, such as the ultraviolet absorption and the Raman spectrum.

July

Changes in the classes of Materials Produced by Distillation and Oxidation of Hard and Soft Asphalts of the Ebano Bitumen (Mexico)

	Distillation					Oxidation				
	Melting point with rise 1° (Kramer)					Melting point with rise 1° (Kramer)				
	27°	35°	45°	55°	60°	55°	70°	85°	115°	100°
Asphalts: Hard	16.8	17.6	16.35	19.3	19.9	30	33.7	39	40	35.9
Soft	20.8	24.2	23.95	21.2	23.6	8	7.7	7.5	7.0	16.7
Resins	22.4	20.76	18.1	18.0	17.9	29	27.6	25.7	22.3	18.3
Paraffin free oil proportion	39.2	36.7	33.0	29.87	27.8	32.1	30.2	27.9	23.8	27.14
Paraffin	1.08	1.11	1.17	1.22	1.25	—	—	—	—	—
Changes in the Hard Asphalts		+0.8	+1.55	+2.5	+3.1	+13.2	+16.9	+21.2	+29.2	+20.0
Soft Asphalts		+3.4	+8.15	+10.4	+12.8	−12.8	−13.1	−13.3	−13.8	−4.1
Changes in the Resins		−1.68	−4.3	−4.4	−4.6	+6.6	+5.2	+3.3	−0.1	−3.9
Paraffin free oil constituents		−2.5	−6.2	−9.3	−11.4	−7.1	−9.0	−11.3	−15.4	−12.1

(Manhelmer, Petroleum 28 (1932) Nr. 16)

Obviously, the ring analysis can not be used for the total petroleum residue, but only for the oil constituent. The composition of the other components must be similar in principle to the oil component because of the organic relationship of the individual components and their means of formation. Moreover, the petroleum oil component is the largest in quantity.

Natural asphalts contain little paraffins and correspondingly much aromatic rings, so that the amount of aromatics and of naphtenic hydrocarbons is much greater in them than found in petroleum residues.

The asphaltic base petroleum oil residues approach the natural asphalts in their chemical composition, and the statement is justified, that the higher the asphalt content of the petroleum from which the residues were obtained, the more similar these residues are to the natural asphalts. The more paraffinic the mineral oil, the more does the residue differ in composition from the natural asphalts.

The composition of the petroleum asphalts differs depending on whether they are asphaltic base bitumens, or paraffinic base bitumens. The former contain 40 - 50% of ring compounds and 50 - 60% paraffins, and the latter 30% ring compounds and 70% paraffins. The mixed base bitumens occupy an intermediate position with 30-35% ring compounds and 65 - 70% paraffins.

One may prove a relationship between the chemical composition and the physical properties. The great adhesive power of the asphaltic base bitumens results from their high ring compound contents.

As a rule, the specific gravity of the petroleum residues is the higher, the more asphaltic base in the crude oil from which they were obtained. The picture becomes however clearer when the specific gravity of the oil constituents alone are considered, and a grouping according to the specific refraction produces a series in agreement with the results of the ring determinations.

According to Abraham (Asphalts and Allied Substances, 1929), the hard asphalts (asphaltines) are polycyclic in character and have largely a naphthenic structure.

Mack (Colloid Chemistry of the Asphalts, Colloid Symposium Monograph, vol. 10, 1932, p. 53) discusses the polycyclic compounds containing oxygen or sulfur in the bridges or in the unlike rings. Sachanen and Tilichajew believe that naphthenic derivatives and other condensed aromatic ring system must be present in the asphaltenes. (Die Chemie and Technologie des Krackens, 1932). They are of the opinion that still higher condensed ring systems are formed during cracking.

On the other hand, Nillman and Barnett claim, that the highly condensed aromatic hydrocarbons are insoluble in the solvents in which the asphaltenes are dissolved. This leads them to the conclusion that the distillation asphalts as well as those obtained from the cracking residues contain not too highly condensed ring systems, in spite of their higher aromatics content. The more highly condensed systems break down during cracking into simpler systems which manifest itself only in such rheological properties which may be attributed to higher dispersed lyophilic colloids.

Asphaltenes can not be readily sulfurized, because they are protected by the adsorbed oil. The purified asphaltenes can only be sulfurized after extraction, and thus converted into water soluble products.

Cracked malthenes can also be sulfurized, but not the uncracked. This means, that the uncracked malthenes contain whole paraffin molecules as well as paraffin chains as side chains of aromatics and naphthenes, while the cracked maltenes contain no more free paraffin molecules.

All the constituents of cracking residues (except the carbenes and the carboids) are closely related chemically, and are formed from simple structural units.

A structure of these building blocks of the bitumens must take into consideration whatever is known about their closest relatives, i.e. the heaviest lubricating oils. The U.S. Bureau of Standards has established that the heavy lubricating oils contain principally naphthenes and hydrocarbons with a single ring or with several condensed rings with or without paraffinic side chains.

It is generally assumed, that the least soluble cracked fractions contain no long side chains. The C:H proportion is not high enough in these fractions, so that highly condensed ring system may be assumed corresponding to the molecular weight. We must assume therefore units of relatively small ring systems, chained to each other. This follows from the molecular weights and the C:H proportion:

	molecular weight	C:H
Decacyclene	≈ 450	24.0
Cracking asphalt	700–890	13.5
Distillation asphalt	2400	11.1

We may conclude from the similarity of the bromide and sulfonates of different fractions, that the building blocks of the larger molecules may be limited to but a few similar types.

The process which takes place during mild cracking consists in the breaking down of complicated structures into smaller fragments. In addition, the side chains are split off (formation of CH_4) and a gentle inner dehydrogenation occurs with a liberation of a small amount of H_2. Many cracking products are not merely less aliphatic in character, but also more highly condensed, which explains the difficult solubility of some of the fractions. A de-polymerization is not excluded as a first step of a cracking process. The side chains are split off later. As a result, distillation and cracking asphalts differ from each other only in molecular weight, density and length of the side chains. The lower solubility of the cracking asphalt than of the distillation asphalt may be attributed to the lower paraffin and paraffinic side chains. The small amounts of the heavy fractions (carbenes, carboids) are attributed to the condensation reactions described above.

We may, accordingly, represent the structure of the asphaltenes as follows:

or
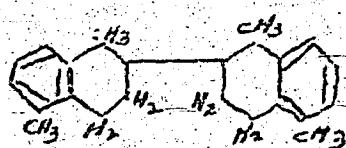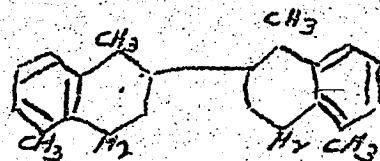
$C : H = 10.3$ $C : H = 12.0$

Longer side chains may probably be present in the distillation asphalts. The side chains are split off during cracking, with an additional condensation.
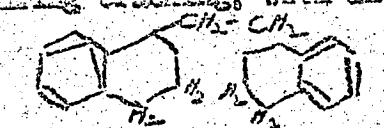
The naphthene ring is simultaneously dehydrogenated.

$+ H_2$

These examples illustrate a relatively large molecule; it may be assumed that the compounds found in asphalts have more "balled to-gether" compounds, as also indicated by the Rheological properties (Refiner, vol. 16, 1937, p. 362)

/signed/ Henkels.

Translated at:

U. S. Bureau of Mines
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	Chromatographic Separation						Ring Analysis					
	Oils %	Petro Oil % Rosins	Soft asph. %	Hard asph. %	D 20	n D 20	AP	Aro- matics %	Naph- thenes %	Paraf. fins %	Paraf. H/C Ratio	Origin
Natural asphalts												
Selenizza	21.0	9.8	22.8	46.1	0.9765	1.5385	62.2	27.7	39.5	32.8	1.580	
Trinidad	20.9	10.7	19.1	49.3	0.9650	1.5307	64.4	23.9	43.0	33.1	1.593	Trinidad
Derna	44.8	9.2	18.1	27.9	0.9400	1.5161	88.5	6.1	44.8	49.1	1.596	Hungary
Petroleum asphalts												
M 200	40.0	16.0	51.6	32.4	0.9421	1.5220	95.0	18.6	29.5	52.1	1.699	Mex. asph. base
K 85	--	--	34.2	41.1	0.9377	1.5190	98.3	15.4	27.2	57.4	1.711	Calif.
K 150	38.9	17.8	34.2	41.1	0.9363	1.5162	95.0	13.7	20.8	57.5	1.712	"
V 65	43.8	12.2	27.3	40.7	0.9357	1.5170	106.1	24.2	25.8	50.0	1.705	Venezuela
V 300	47.8	17.1	26.4	9.4	0.9342	1.5168	101.7	10.9	28.9	60.2	1.700	"
D I 200	40.7	20.6	31.5	7.2	0.9374	1.5200	102.1	15.4	24.4	60.2	1.733	German Asph. base
D II 150	33.9	28.2	37.0	5.9	--	--	--	10.5	25.7	63.8	1.720	"
D IV 300	39.1	21.9	31.6	7.2	--	--	--	4.7	22.7	72.6	1.7	" paraff. base
D III 50	41.9	18.4	32.5	7.2	--	--	--	5.9	21.6	72.9	1.800	"
G 50	39.5	20.6	34.6	5.4	0.9200	1.5129	121.3	6.4	17.6	76.0	1.780	West Calif. "

This table presents the results of investigation of some natural and petroleum asphalts.
It is arranged in order of increasing paraffin content.
(Grader, GJ. und Monro 52, (1942) 057).

Oberbach und Psner, "Über die Zusammensetzung von Erdasphalten"

p. 90 Ultimate analysis of asphalt Ebano ND and its components:

	Ebano ND	petroleum fraction	petroleum resin	asphalt resin	hard asphalt
% carbon	82.93	83.87	82.76	83.01	78.51
% hydrogen	10.58	12.00	10.97	9.29	7.38
% sulfur	6.20	4.27	6.74	7.25	14.07

Tabulated Summary: Ultimate analysis and decomposition of some bitumens (Poll)

	German Bitumen	Galician Bitumen	Russian Bitumen	Gilsonite U.S.A.	Trinidad	Boston
% carbon	85.87	87.13	85.68	87.54	86.11	81.12
% hydrogen	10.31	10.60	11.43	10.76	10.87	9.32
% sulfur	1.13	0.71	0.61	1.45	2.74	5.07
% balance	2.69	1.56	2.38	0.25	0.28	4.49
Proportion petroleum oil	44.03	42.71	37.73	0.75	20.04	22.98
Oil resin	34.35	23.57	37.77	0.67	25.22	49.96
Asphalt resin	19.18	22.67	23.67	64.19	46.44	19.82
Hard asphalt	2.24	11.05	0.83	34.39	8.93	7.24