CORRELATION OF CHEMICAL CONSTITUTION AND OXIDATION SUSCEPTIBILITY OF LUBRICATING OIL COMPONENTS.*

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Abstract.

This paper presents a study of the influence of chemical constitution on the susceptibility to oxidation of the several general types of components in petroleum lubricating oils. A fractionation of a Pennsylvania lubricating oil-stock has been effected by distillation and extraction. The physical properties of the fractions and their chemical constitutions as calculated by Waterman's method are reported. Selected fractions were oxidized, and the extent of oxidation was measured by the acidity developed and by the increase of viscosity.

Similar treatment was then applied to a different stock; fractions from the two stocks gave the same behaviour on oxidation.

From the collected data, some generalizations have been made concerning the dependence of oxidation susceptibility on chemical constitution.

Introduction.

Although a great amount of research has been done on the oxidation of petroleum oils, most of it, of necessity, has been of empirical nature. Thus, it is generally believed that paraffinic oils form acidic oxidation products more readily than do more cyclic oils, while the opposite is true with regard to sludge precipitation. Aromatic compounds, at least in high concentrations, are easily oxidized, yet there are indications that natural traces of them may act as anti-oxidants. Nearly all the broad knowledge of this kind is purely qualitative in character.

The recent development of highly efficient methods of fractionation and the establishment of correlations between physical properties and chemical constitution now enable the preparation and recognition of very homogeneous fractions. The recording of findings concerning the behaviour of such fractions on oxidation is the principal object of this paper.

Unfortunately, no oxidation tests permit clean-cut interpretation. The oxidation can be carried out under a great variety of conditions, and many of its results can be measured, but all indications are of functional rather than basic significance. The two types of effects selected for investigation here, development of non-volatile acidity and increase in viscosity, appeared to be the most nearly fundamental of the simple changes to be recognized.

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Both alterations concern the oil molecule itself, not fragments broken off by the action; the first change may roughly be taken as a measure of attack on the side-chains, and the second, even more roughly, as an indication of consequent condensation.

FRACTIONATION OF THE OILS.

The fractionation of the lubricating oil-stock followed, in an abbreviated fashion, the fractionation of " water-white oil " by Rossini and his co-workers at the National Bureau of Standards, under A.P.I. Project No. 6.[8] The oil was first subjected to systematic fractional distillations, and the distillate cuts, in turn, were subjected to fractional extraction. The outcome is a square array of many fractions, arranged in one direction by molecular size (distillation) and in the other by molecular type (extraction). Details of the apparatus and procedure follow.

Distillation.

As the lightest components of the stock fractionated had molecular weights of over 300, all distillations were performed under high vacuum. Simple pot-stills were used up to a temperature of 300° C., corresponding to a molecular weight of about 500, and beyond that point molecular distillation was employed.

Pot-Stills. The type of pot-still employed is illustrated in Fig. 1; it is of all-glass construction and conventional design. The still-pot is a 1-litre spherical flask provided with filling and vapour tubes. The former has a ground-glass stopper carrying a thermometer well.

The pot was heated electrically by ring-heaters bolted on the underside of a solid aluminium block, the upper surface of the latter being machined to fit the bottom of the pot. This arrangement gives very uniform heating to the charge, reducing local and " skin " overheating. The entire pot and heater assembly was enclosed in an air-bath. The fairly uniform temperature established in this space prevents condensation on the upper parts of the pot.

Strictly speaking, no rectifying column is provided in the vapour line; at the pressures employed no appreciable enrichment can be obtained by any type of countercurrent contacting of vapour and reflux. The vapour line, however, does carry three thin bulbs enclosed in a silvered evacuated jacket. This device serves merely as a vapour riser to separate the condenser from the hot air bath around the pot; the bulbs act to give sufficient mechanical flexibility to tolerate the difference in expansion between the jacket and the column proper.

Above the jacket there is an off-set to catch entrained distilland. Of the several devices studied in this laboratory, this one is by far the most satisfactory for suppressing entrainment in high-vacuum distillations. The problem is important because the vapour velocities are always exceedingly high, and the vapour tends to carry with it large amounts of spray. In the arrangement shown, the large vapour velocity is used to advantage, for the swiftly moving droplets are thrown against the walls of the tube at the bend. Such an off-set, however, offers little resistance to the flow of the vapour itself; most other devices, such as baffles and Vigreux points,

introduce large pressure drops at high vapour velocities. The off-set is not of convenient shape for jacketing, so it is provided with a light winding of nichrome wire electrically heated to maintain it in approximately adiabatic condition.
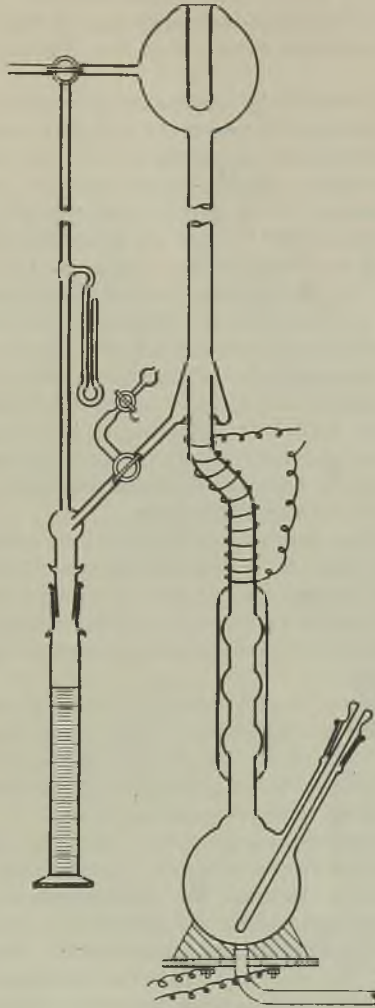

FIG. 1.
HIGH VACUUM POT STILL.

The condenser is merely a vertical air-cooled tube. Vapour rises in it, and the condensate runs down the inner surface to an annular trough.

From the collecting trough the distillate runs to the receiver. The receiver system has three stopcocks, so that the receivers may be changed without breaking the vacuum or interrupting the distillation, a conven-

tional arrangement.   At the top of the condenser a 1-litre bulb serves as a surge tank to maintain the vacuum while a new empty receiver is being evacuated ; a manometer indicates the course of this evacuation, revealing when the receiver, the still and the vacuum line may again be connected together.

A re-entrant tube in the surge-bulb serves as a trap ; it may be filled with a dry ice-acetone mixture during runs, but this precaution is scarcely necessary.

The vacuum was not controlled, but was merely the best that the pump used could produce ; it ranged between 0·1 and 0·01 mm. Hg.

Little need be said about the operation of the pot-stills other than the mention of a few precautions, principally the necessity of low-temperature degassing.   After regreasing all stopcocks and charging, the pot may be heated rapidly up to about 100° C., but must be held at this temperature under vacuum until all bubbling ceases.   As is well known, oils dissolve large amounts of air.   This air is released rather slowly even at high vacuum and high temperature, and unless it is completely removed before the high distillation temperatures are reached, oxidation may occur to a serious extent.   Incomplete degassing has frequently been observed to yield distinctly coloured distillates from water-white distillands.

The heat input to the stills was regulated to give a distillation rate of about 5 ml./min.   Some trial runs on relatively wide cuts showed that, at least as far as viscosity is concerned, the separations obtained are not dependent on distillation rate in this region.

At no time was the pot temperature allowed to exceed 300° C.   Trial runs on several oils of varied types demonstrated that none underwent pyrolysis (as indicated by gas formation) at this temperature, but that many did appear to break down at slightly higher temperatures.   Oils of high sulphur content present an exception, some of them producing gas at much lower temperatures.

Test of thermal stability is easily made by closing the stopcock in the main vacuum line during a distillation.   If an appreciable amount of gas is being evolved, it collects in the surge-bulb, increases the pressure, and quickly stops the distillation ; below pyrolysis temperatures distillation will continue almost indefinitely without pumping.

A word about temperature measurement and its significance in high vacuum distillation may be in place here.   The thermometer in the pot of such a still is used only to indicate the attainment of a safe maximum temperature, and, therefore, when the distillation should be stopped. These temperatures are definitely not reproducible ; they will frequently differ as much as 15° C. for successive runs on the same material with the same percentage taken overhead, a consequence of superheating, which is always present to a large extent in vacuum pot-stills.   The amount of superheat depends critically on the distillation rate and the pressure ; it cannot be reduced to even a small value, and the most accurate control of pressure and heat input will not hold it approximately constant or reproducible.

No effort was made to measure vapour temperatures.   Here, of course, superheating does not interfere, but, on the other hand, radiation is apt to be so large that equilibrium is not achieved, and pressure effects are still as

large as for liquid temperatures. Consequently vapour temperatures were considered to be of no significance.

Experience has shown that an operator can run three of these stills simultaneously.

Molecular Still. The molecular still used (Fig. 2) was of the conventional

A - Evaporator
B - Condenser
C - Mercury Boiler
D - Leveling Bulb for Temperature Control
E - Distillate Line
F - Residuum Line
G - Distilland Reservoir
H - High Vacuum Line
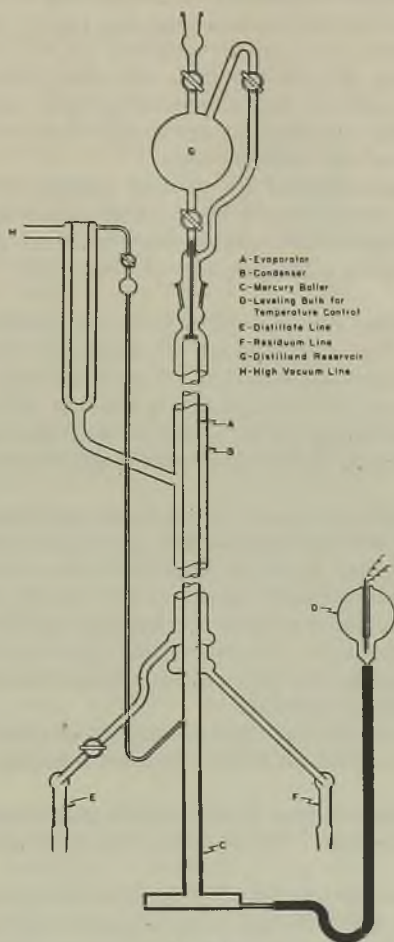
Fig. 2.
MOLECULAR STILL.

concentric tube, flowing film type; the radial clearance between the evaporator (inner tube) and the condenser (outer tube) was 1·0 cm.; the evaporator was 100 cm. long and 2·5 cm. o.d.

Perhaps the only novel feature of this still was the method of heating the evaporator with mercury vapour. The inside of the tube communicated with a welded steel boiler by a Kovar glass-metal seal. A side arm on the boiler led through a rubber hose to an evacuated levelling bulb, and another

side arm carrying a U-shaped trap connected the system with the vacuum line. The levelling bulb contained electric contacts for controlling the heat input to the boiler through a relay.

In operation the entire apparatus was first evacuated. Then the heat was turned on the mercury boiler. Soon after the mercury started to vaporize, sufficient liquid condensed to fill the trap of the glass side arm, sealing off the whole mercury system from the rest of the apparatus. As heating was continued, the vapour pressure of the mercury increased, forcing liquid mercury up into the glass side arm, which served for temperature indication, and also into the levelling bulb, which provided temperature control. The temperature was easily set at any desired value by changing the height of the levelling bulb.

Degassing was accomplished by radiant heaters with reflectors (not shown in the figure) directed on the charge-bulb at the top of the apparatus. Experience has indicated that satisfactory removal of air can best be achieved by maintaining a temperature of about 100° C. overnight under high vacuum.

Two additional bulbs, identical with the charge-bulb as illustrated, were used as receivers. The arrangement of stopcocks thereon enabled successive distillations on a single batch without breaking the vacuum over the oil. After a charge had been placed in the top bulb and degassed, and the run made, the residuum receiver and the charge-bulb were interchanged, with all stopcocks closed, and another pass could be accomplished without further degassing.

The amount of distillate removed on a single pass depends, of course, on the temperature and the flow rate as well as on the nature of the charge. Conditions for producing a cut of desired volume were found by trial. Usually the temperature could be set rather closely by approximation, and fine adjustment could be made by changing the flow rate as the first few millilitres ran through. Drop-counting tips were provided on the lines to the two receivers, and by watching them the distillate : residuum ratio could be determined quickly.

The distilland throughout rate was usually set at about 100 ml. per hour, but this rate could be doubled for the lightest fractions or halved for the heaviest ones.

Distillation Procedure.—Four cycles of systematic fractional distillation were applied to the stocks. Twelve litres of stock oil was used in each case.

The 12 litres of stock was distilled in several batches to give fifteen approximately equal distillate cuts, and corresponding cuts were combined. The fifteen primary fractions so obtained were in turn distilled into about ten cuts each, for which viscosities were determined at 100° F. After rearranging these secondary fractions in order of ascending viscosity, they were combined to give a new set of fifteen primary fractions of approximately equal volume. This cycle was repeated four times; thus the fifteen large primary fractions were distilled to afford ten small secondary fractions each, and the latter were then blended back, on a viscosity basis, to again give primary fractions; after four such cycles the overlap of properties among the fractions was practically nil, except for the two lightest ones.

The pot-stills were applicable for slightly over half of the distillations.

In each instance, as mentioned, the distillation was transferred to the molecular still, where the temperature reached 300° C.   The residue from the pot-stills, boiling about 300° C., started distilling rapidly in the molecular still at 175° C.; and taking the temperature up to 300° C. in that still left only a few per cent. as residuum, which was not further treated or examined.

Solvent Extraction.

The extractors, of which two were built, are illustrated in Fig. 3.   They differ principally from conventional models [3] by being longer; the length of the columns proper was 100 feet.   After difficulty had been experienced from bumping, a side tube was sealed into the upper part just below the boiler, through which a slow, fine stream of dry carbon dioxide was bubbled.

In operation, the solvent was boiled off at the top, and, after condensation, was allowed to rise through the charge in the reservoir at the bottom. As this fresh solvent dissolves some of the oil, it rises again through the column to the boiler.   Removal of the solvent there causes precipitation of dissolved oil as a fine emulsion, and the precipitated droplets then fall down the column, countercurrent to the fresh extract phase.

Use of apparatus of this type considerably limits the choice of solvent.   In addition to being low-boiling, the solvent must have a lower density than the oil, or, more strictly, it must form systems with the oil in which the extract phase always has a lower density than the raffinate phase, even after processing through many effective transfer units. This requirement is stringent, because highly aromatic oils may yield extracts of relatively high density.

Acetone was selected as the basic solvent.   It has nearly ideal properties for extraction of the intermediate distillate fractions.   Apparently no one unmixed solvent exists which is suitable for all the varied close cuts which were studied; the lightest cuts were almost wholly miscible with acetone, and the heaviest almost insoluble.   Solvent modifiers

Fig. 3.
SOLVENT EXTRACTOR.

were therefore employed to produce mixed solvents.   Anhydrous methanol was found to be excellent for reducing solubility, and a hexane cut equally good for increasing it.   The latter was a 5–25 per cent. fraction of a commercial hexane, rich in 2 : 3-dimethylbutane.   The three solvents boil at nearly the same temperature, and even tend to form azeotropes boiling only slightly lower, so that little change in composition is induced by the simple distillation which removes solvent from the boiler.

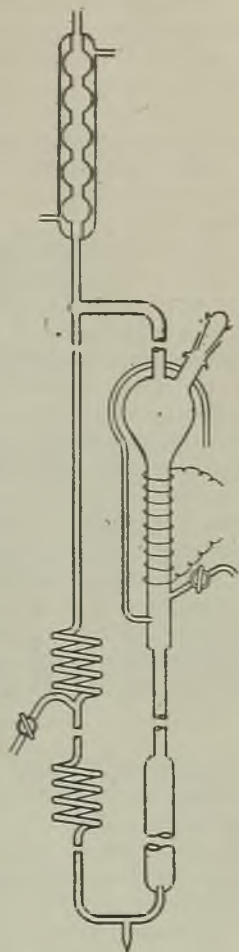Thus, for the lightest distillate the solvent used was pure methanol;

for the succeeding cuts acetone was introduced in increasing amounts; for the sixth through the tenth pure acetone was employed. Finally, for fraction eleven, 3 per cent. of the hexane cut was added, and for the fifteenth fraction a 15 per cent. addition was necessary.

The great length of the extractors made them very efficient, but a considerable time was required for them to reach equilibrium, as found by a semi-micro aniline-point determination. A steady state was assumed to prevail twenty-four hours after the aniline point of the solvent-free extract failed to fall more than $0.5°$ C. in twenty-four hours. This period was always several days, often ten days at the extreme of the series.

After equilibrium had been attained, the entire contents of the boiler were removed and the solvent was stripped from it with a small continuous tube-still.

A few trial tests showed that, with materials such as the final distillates from the stocks examined, the overlap of properties for successive extract fractions was nil. This trial was made by a simple extraction, in a separatory funnel, of two successive extract fractions. The amounts of solvent were so chosen that the raffinate phase of the first and the extract phase of the second fraction were very small portions of the whole. The aniline points of these " initial " extract and raffinate oils proved to be identical, proving that, under the conditions employed, the efficiency of the extractors was limited only by the size of the fractions. Since the compositions of the cuts produced by one pass through the extractor were nearly mutually exclusive, no successive fractionation was required, as had been necessary in the case of the distillation separations.

Each of the final distillate fractions, therefore, was passed through an extractor once, and was so divided into about ten fractions of nearly equal volume. These extracts were the principal materials studied with respect to physical properties, chemical constitution, and oxidation characteristics; each of the two stocks yielded about 150 such final extract fractions.

Physical Properties.

The usual physical properties were determined on a number of the final extract fractions, emphasis being placed on those known at the time that the work was done to be specifically correlated with chemical constitution. Several series of " key fractions " were selected for intensive study in this respect; they were chosen at the two ends and the middle of both the distillation and the extraction sequences, respectively.

Methods. Because the final fractions were small in amount, only a few cubic centimetres, semi-micro tests were devised for the determination of their physical properties. Descriptions of the methods for viscosity [1] and molecular weight [5] have already been published; densities and refractive indices were measured by conventional procedures. Aniline points were determined on 0.50-ml. samples, the volumes being obtained indirectly by weighing, the density having previously been determined.

Data. The physical property data for the final extract fractions of the principal stock studied are given in Table I.

In the code of notation, the first number is the ordinal number of the distillate; unextracted distillates have only this symbol. The extracts carry a second number, separated by a hyphen, which is the ordinal number

TABLE I.

Physical Properties of the Long Residuum Stock and its Fractions.

Oil	Sp. gr. 60°/60° F.	Aniline point, °C.	Mol. wt.	Viscosity 100° F.	Viscosity 210° F.	Refractive Index	K.V.I.	V.G.C.	Waterman analysis: C atoms/molecule Aromatic	Naphthene	Paraffin
LR-0	0·8963	108·7 a	510	194·2	16·03	1·4956 a	92	0·820	3·1	6·6	27·0
LR-1	0·8695	86·2	315	14·3	3·12	1·4813	80	0·822	2·7	3·5	16·4
LR-2	0·8746	92·6	362	26·2	4·41	1·4840	75	0·819	2·9	4·3	20·3
LR-3	0·8783	94·1	381	33·4	5·14	1·4851	86	0·816	3·2	4·5	21·4
LR-4	0·8790	96·6	406	42·33	5·93	1·4863	88	0·816	3·3	5·3	20·6
LR-5	0·8813	99·2	425	53·89	6·88	1·4877	89	0·815	3·3	4·9	22·2
LR-6	0·8837	101·4	445	69·18	8·08	1·4892	90	0·815	3·4	4·7	25·6
LR-7	0·8861	103·5	490	91·04	9·56	1·4907	89	0·816	4·2	5·4	27·6
LR-8	0·8891	105·1	514	123·4	11·58	1·4925	87	0·820	4·5	5·5	28·4
LR-9	0·8942	107·1	545	173·4	14·08	1·4955	83	0·824	4·6	6·3	30·4
LR-10	0·9014	109·0	574	267·4	18·19	1·5000	79	0·822	4·9	6·1	33·0
LR-11	0·9023	110·4	624	359·6	22·22	1·5004	82	0·822	4·6	5·9	35·2
LR-12	0·9045	113·6	674	486·2	27·12	1·5017	84	0·823	6·5	6·8	38·0
LR-13	0·9085	114·6	745	749	35·76	1·5042	85	0·823	8·5	6·3	41·6
LR-14	0·9132	116·6	800	1,251	49·84	1·5069	88	0·824	9·7	6·7	45·0
LR-15	0·9197	119·8	940	2,485	80·35	1·5106	79	0·826	4·4	8·1	
LR-R	0·9406	—	1500	29,620	417·5	—	106	0·832	—	—	
LR1-1	0·9063	17·9	(278) b	33·77	4·01	1·5498	107	0·944	11·8	0·4	8·6
LR1-2	0·9497	32·0	(288)	31·40	4·01	1·5371	71	0·922	10·2	1·2	9·9
LR1-3	0·9259	49·7	300	26·35	3·87	1·5185	18	0·892	7·8	2·8	11·4
LR1-4	0·9028	63·7	(310)	22·17	3·77	1·5010	36	0·862	5·7	4·2	12·6
LR1-5	0·8793	78·8	(320)	17·58	3·41	1·4850	59	0·836	3·4	5·5	14·2
LR1-6	0·8570	92·1	329	14·06	3·08	1·4719	78	0·816	1·8	4·9	16·9
LR1-7	0·8518	96·3	(335)	14·14	3·14	1·4690	88	0·807	1·3	4·3	18·4
LR1-8	0·8473	99·5	(340)	14·06	3·14	1·4666	90	0·801	0·9	4·4	18·9
LR1-9	0·8424	102·1	(347)	14·26	3·21	1·4650	98	0·792	0·9	4·3	20·4
LR1-10	0·8414	104·3	353	14·55	3·28	1·4637	103	0·787	0·7	4·6	20·4
LR1-11	0·8382	106·5	(364)	14·75	3·38	1·4623	115	0·783	0·7	3·6	21·8
LR1-B	0·8394	106·4	(366)	15·20	3·40	1·4630	109	0·784	0·7	3·4	22·0
LR2-1	0·9905	5·1	291	212·5	9·41	1·5642	102	0·954	14·3	0·6	6·9
LR2-2						1·5453					
LR2-3						1·5269					
LR2-4						1·5093					
LR2-5						1·4967					
LR2-6						1·4881					
LR2-7						1·4788					
LR2-8						1·4740					
LR2-9	0·8635	98·4	361	23·77	4·28	1·4700	90	0·805	1·3	5·2	19·4
LR2-10						1·4668					
LR2-11						1·4640					
LR2-R	0·8421	109·6	383	19·02	3·06	1·4633	119	0·779	0·1	5·7	21·6

TABLE I—*continued.*

Oil	Sp. gr. 60°/60° F.	Aniline point, °C.	Mol. wt.	Viscosity 100° F.	Viscosity 210° F.	Refractive Index	K.V.I.	V.G.C.	Waterman analysis: C atoms/molecule Aromatic	Naphthene	Paraffin
LR3-1	1.0064	-9.7	316	775	16.98	1.5738	-169	0.964	18.5	0	5.4
LR3-2	—	—	—	—	—	1.5592	—	—	—	—	—
LR3-3	—	—	—	—	—	1.5818	—	—	—	—	—
LR3-4	—	—	—	—	—	1.5062	—	—	—	—	—
LR3-5	—	—	—	—	—	1.4901	—	—	—	—	—
LR3-6	—	—	—	—	—	1.4821	—	—	—	—	—
LR3-7	—	—	—	—	—	1.4768	—	—	—	—	—
LR3-8	0.8615	108.7	390	28.44	4.86	1.4725	+101	0.798	1.1	5.9	20.4
LR3-9	—	—	—	—	—	1.4696	—	—	—	—	—
LR3-10	—	—	—	—	—	1.4674	—	—	—	—	—
LR3-11	—	—	—	—	—	1.4661	—	—	—	—	—
LR3-12	—	—	—	—	—	1.4643	—	—	—	—	—
LR3-R	0.8433	112.5	410	22.46	4.46	1.4637	126	0.776	0.3	4.7	24.6
LR4-1	1.0074	—	(340) b	2,068	20.88	1.5709	-447	0.961	—	—	—
LR4-2	0.9879	—	360	875	16.50	1.5600	-239	0.940	—	—	—
LR4-3	0.9458	49.6	(377)	213.3	10.87	1.5277	-143	0.892	11.4	4.2	12.1
LR4-4	0.9106	73.2	(389)	87.69	7.94	1.5042	-44	0.851	7.2	5.3	15.8
LR4-5	0.8914	88.4	(401)	56.84	6.64	1.4902	+67	0.830	4.2	6.9	17.7
LR4-6	0.8733	100.8	412	41.76	5.84	1.4800	86	0.808	2.2	6.8	20.5
LT4-7	0.8600	104.5	(413)	37.54	5.55	1.4707	90	0.804	1.4	7.3	20.0
LR4-8	0.8612	107.9	(417)	33.24	5.28	1.4727	98	0.795	0.9	6.9	22.0
LR4-9	0.8554	110.6	(418)	30.25	5.08	1.4607	105	0.789	0.3	6.9	22.7
LR4-10	0.8495	113.4	418	27.54	4.96	1.4672	117	0.781	0.1	5.4	24.5
LR4-11	0.8452	115.3	(418)	26.60	4.93	1.4655	122	0.776	0	4.7	25.1
LR4-R	0.8440	116.4	(418)	26.72	5.03	1.4652	128	0.774	0	4.4	25.4
LR5-1	1.0112	—	367	3,000	29.31	1.5756	-286	0.955	—	—	—
LR5-2	—	57.8	—	—	—	1.5493	—	—	—	—	—
LR5-3	—	—	—	—	—	1.5188	—	—	—	—	—
LR5-4	—	—	—	—	—	1.4967	—	—	—	—	—
LR5-5	—	—	—	—	—	1.4825	—	—	—	—	—
LR5-6	0.8666	108.0	433	43.97	6.34	1.4757	101	0.798	1.2	6.2	22.9
LR5-7	—	—	—	—	—	1.4738	—	—	—	—	—
LR5-8	—	—	—	—	—	1.4712	—	—	—	—	—
LR5-9	—	—	—	—	—	1.4690	—	—	—	—	—
LR5-R	0.8479	117.3	449	32.38	5.03	1.4665	124	0.776	0	5.2	27.0
LR6-1	0.9924	—	392	2,519	29.54	1.5624	-206	0.985	—	—	—
LR6-2	—	81.0	—	—	—	1.5290	—	—	—	—	—
LR6-3	—	—	—	—	—	1.5042	—	—	—	—	—
LR6-4	—	—	—	—	—	1.4880	—	—	—	—	—
LR6-5	0.8644	112.5	456	50.09	6.91	1.4790	+102	0.793	0.8	7.2	24.8
LR6-6	—	—	—	—	—	1.4749	—	—	—	—	—
LR6-7	—	—	—	—	—	1.4726	—	—	—	—	—
LR6-8	—	—	—	—	—	1.4708	—	—	—	—	—
LR6-9	—	—	—	—	—	1.4692	—	—	—	—	—
LR6-10	—	—	—	—	—	1.4680	—	—	—	—	—
LR6-R	0.8489	120.8	484	40.33	6.58	1.4682	124	0.774	0.1	4.5	30.1

TABLE I—continued.

Oil	Sp. gr. 60°/60° F.	Aniline point, °C	Mol. wt.	Viscosity 100° F.	Viscosity 210° F.	Refractive Index	K.V.I.	V.G.C.	Aromatic	Naphthene	Paraffin
LR7-1	1·0010	—	400	6,787	44·73	1·5087	-274	0·941	—	—	—
LR7-2	—	—	—	—	—	1·5246	—	—	—	—	—
LR7-3	—	—	—	—	—	1·5084	—	—	—	—	—
LR7-4	—	—	—	—	—	1·4871	—	—	—	—	—
LR7-5	—	—	—	—	—	1·4807	—	—	—	—	—
LR7-6	—	86·7	—	—	—	1·4704	—	—	0·7	7·8	26·0
LR7-7	—	—	—	—	—	1·4762	—	—	—	—	—
LR7-8	—	—	—	—	—	1·4736	—	—	—	—	—
LR7-9	—	—	—	—	—	1·4718	—	—	—	—	—
LR7-10	0·8054	115·8	494	61·86	8·07	1·4708	+100	0·792	—	—	—
LR7-11	—	—	—	—	—	1·4692	—	—	—	—	—
LR7-R	0·8516	123·1	512	49·97	7·58	1·4690	123	0·774	0	5·5	31·0
LR8-1	0·9898	—	453	6,498	50·0	1·5549 a	-177	0·924	—	—	—
LR8-2	—	—	—	—	—	1·5228	—	—	—	—	—
LR8-3	—	—	—	—	—	1·5081	—	—	—	—	—
LR8-4	—	—	—	—	—	1·4889	—	—	—	—	—
LR8-5	—	83·0	—	—	—	1·4827	—	—	1·0	8·1	28·0
LR8-6	—	—	—	84·17	9·73	1·4781	—	—	—	—	—
LR8-7	—	—	—	—	—	1·4759	—	—	—	—	—
LR8-8	—	—	—	—	—	1·4749	—	—	—	—	—
LR8-9	—	—	—	—	—	1·4742	—	—	—	—	—
LR8-10	0·8702	116·7	510	—	—	1·4730	+102	0·795	—	—	—
LR8-11 lc	—	—	—	—	—	1·4715	—	—	—	—	—
LR8-R	0·8568	124·0	539	74·62	8·85	1·4707	100	0·778	1·0	10·8	28·2
LR9-1	1·0200	—	453	10,020	71·99	1·5843 a	—	—	—	—	—
LR9-2	—	—	—	—	—	1·5505	—	—	—	—	—
LR9-3	—	—	—	—	—	1·5245	—	—	—	—	—
LR9-4	—	—	—	—	—	1·5048	—	—	—	—	—
LR9-5	—	—	—	—	—	1·4995	—	—	—	—	—
LR9-6	—	80·1	—	—	—	1·4800	—	—	—	—	—
LR9-7	—	—	—	—	—	1·4832	—	—	—	—	—
LR9-8	0·8758	116·5	547	117·8	11·84	1·4810	+96	0·797	1·0	11·0	30·3
LR9-9	—	—	—	—	—	1·4780	—	—	—	—	—
LR9-11	—	—	—	—	—	1·4769	—	—	—	—	—
LR9-12	—	—	—	—	—	1·4752	—	—	—	—	—
LR9-R	0·8630	124·8	567	88·36	10·61	1·4726	111	0·782	0	6·5	34·0
LR10-1	1·0118	—	(490)	4,078	252·4	—	37	0·938	16·3	5·2	16·7
LR10-2	0·9556	50·3	518	655	56·28	1·5410	40	0·890	9·2	8·1	21·5
LR10-3	0·9244	87·2	(587) b	311·3	26·44	1·5192	71	0·847	5·5	0·3	24·8
LR10-4	0·9041	102·2	(553)	198·0	19·12	1·4977	86	0·890	3·0	0·0	29·0
LR10-5	0·8887	112·7	571	149·2	15·00	1·4885	97	0·890	1·3	7·8	31·9
LR10-6	0·8775	119·9	(574)	—	13·89	1·4810	—	0·790	—	—	—

TABLE I—continued.

Oil	Sp. gr. 60°/60° F.	Aniline point, °C.	Mol. wt.	Viscosity		Refractive Index.	K.V.I.	V.G.C.	Waterman analysis : C atoms/molecule.		
				100° F.	210° F.				Aromatic.	Naphthene.	Paraffin.
LR10-7 d	0·8742	121·8	(575)	136·5	13·46	1·4796	101	0·792	0·4	8·6	31·9
LR10-8 d	0·8758	120·9	576	142·0	13·61	1·4812	90	0·794	1·3	7·4	32·5
LR10-9	0·8701	124·6	(586)	123·6	12·85	1·4779	104	0·788	0·3	7·5	33·0
LR10-10 k	0·8694	126·8	(596)	118·1	12·63	1·4767	100	0·787		8·1	34·4
LR10-11 k	0·8652	128·2	607	114·6	12·62	1·4754	109	0·781		7·0	36·4
LR10-R k.	0·8639	130·0	(624)	112·4	12·80	1·4752	113	0·779		6·7	37·9
LR11-1	1·0284					— c					
LR11-2						— c					
LR11-3		88·5				— b					
LR11-4						1·5142					
LR11-5						1·4999					
LR11-6						1·4889					
LR11-7	0·8842	119·9	622	219·7	17·46	1·4869	93	0·801	2·4	9·1	36·4
LR11-8						1·4868					
LR11-9						1·4842					
LR11-10						1·4789					
LR11-11 k						1·4765					
LR11-R	0·8852	132·0	643	136·3	14·48	1·4702	111	0·779		7·4	38·0
LR12-1	0·9845	87·5	585		166·5	— c		0·903			
LR12-2						1·5210					
LR12-3						1·5000					
LR12-4	0·8897	118·8	655	306·7	21·02	1·4899	89	0·805	3·5	10·1	36·7
LR12-5						1·4845					
LR12-6						1·4828					
LR12-7						1·4810					
LR12-8						1·4807					
LR12-9						1·4792					
LR12-10 k						1·4782					
LR12-R	0·8692	134·5	704	179·4	17·35	1·4780	110	0·781		7·0	43·2
LR13-1	0·9846	93·3	639		217·2	— c		0·896			
LR13-2						1·5195					
LR13-3						1·5020					
LR13-4	0·8955	119·9	703	492	28·50	1·5010	89	0·808	3·8	12·4	37·8
LR13-5						1·4875					
LR13-6						1·4848					
LR13-7						1·4847					
LR13-8						1·4840					
LR13-9						1·4800					
LR13-10						1·4800					
LR13-R	0·8727	136·9	783	252·2	21·75	1·4709	109	0·782	0·8	6·7	48·7

TABLE I—continued.

Oil	Sp. gr. 60°F/60°F	Aniline point, °C	Mol. wt.	Viscosity 100° F.	Viscosity 210° F.	Refractive Index.	K.V.I.	V.G.C.	Waterman analysis: C atoms/molecule. Aromatic.	Naphthene.	Paraffin.
LR14-1	1·0030	—	714	—	567	c	—	0·912	—	—	—
LR14-2	—	—	—	—	—	c	—	—	—	—	—
LR14-3	—	104·9	—	—	—	1·5001	—	—	—	—	—
LR14-4	0·9021	120·6	810	793	40·47	1·4953	95	0·811	8·2	9·9	40·8
LR14-5	—	—	—	—	—	1·4918	—	—	—	—	—
LR14-6	—	—	—	—	—	1·4855	—	—	—	—	—
LR14-7	—	—	—	—	—	1·4828	—	—	—	—	—
LR14-8	—	—	—	—	—	1·4822	—	—	—	—	—
LR14-9	—	—	—	—	—	1·4812	—	—	—	—	—
LR14-R	0·8759	140·2	860	352·0	28·40	1·4820	112	0·782	2·7	10·7	51·2
LR15-1	1·0056	—	817	—	—	c	—	—	—	—	—
LR15-2	0·9552	92·2	(910) b	393¼	68·75	c	—	—	—	—	—
LR15-3	0·9307	112·9	952	1721	64·77	c	88	0·836	11·1	4·8	53·8
LR15-4	0·9101	126·0	(965)	1458	60·49	1·5009	94	0·815	10·5	12·4	46·9
LR15-5	0·9049	128·9	(970)	1326	57·81	1·4979	97	0·808	9·8	15·3	45·2
LR15-6	0·9032	129·9	975	933	50·70	1·4947	98	0·807	9·9	12·7	48·8
LR15-7	0·8981	132·7	(930)	771	45·56	1·4920	104	0·802	7·9	12·4	53·2
LR15-8	0·8893	139·1	(1004)	695	44·7	1·4870	106	0·792	6·3	13·2	54·1
LR15-9	0·8841	143·7	1023	716	46·8	1·4846	109	0·786	—	—	—
LR15-R	0·8825	148·4	—	—	—	c	111	0·783	—	—	—
LRR-1	1·0088	c	—	—	404·4	c	—	—	—	—	—
LRR-2	0·9665	—	—	—	295·5	—	—	—	—	—	—
LRR-3	0·9418	—	1390	—	217·9	—	—	0·834	—	—	—
LRR-4	0·9383	—	—	—	226·3	—	—	0·834	—	—	—
LRR-5	0·9228	—	—	—	193·7	—	—	0·817	—	—	—
LRR-6	0·9180	—	1625	—	227·5	—	—	0·810	—	—	—
LRR-7	0·9138	—	—	—	261·5	—	—	0·807	—	—	—
LRR-8	0·9043	—	—	—	550	—	—	0·702	—	—	—
LRR-9	0·9257	—	—	—	—	—	—	0·819	—	—	—
LRR-R	0·9285	—	2273	—	—	—	—	0·813	—	—	—

a This value uncertain because of the dark colour of the oil.
b Molecular weight values in parentheses were not determined experimentally but interpolated from a graph of the experimental values.
c This value not determined because of the danger to the prisms of the refractometer from sticking.
d The break in the value of all the properties at this point is insignificant and is caused by the extractor not being quite at equilibrium for the LR10-7 fraction.
e Sample too dark.
k Data does not fit into Waterman's method. These values were calculated by assuming the aromatics to be zero and calculating solely on the basis of specific refraction.

of the extract cut from the distillate first indicated.   The distillate series are begun at the more volatile end, and the extract series at the more soluble end.   For example, fraction LR8-9 is the ninth extract from the eighth distillate.   The stock itself is indicated by 0, and residue from extraction or distillation by R.

Chemical Constitution.

Waterman analyses,[9] calculated from the physical properties shown, are also presented in Table I, together with values for kinematic viscosity index (K.V.I.) [4] and viscosity-gravity constant (V.G.C.).[6]

This experimental work was completed and the calculations made several years ago. Since that time several papers have appeared giving improved correlations between chemical constitution and physical properties.[2] The Waterman analysis, though now recognized as somewhat inaccurate, has the advantage of being widely known and used.   Until much more is learned about the chemical constitution of oils, it will probably remain the best method of characterizing close-cut oil fractions, even if regarded only as empirical. Consequently the results at hand are presented at this time rather than to delay the preparation of this paper by the determination of other properties and by calculation along more modern lines.

The Waterman analyses are reported, not conventionally as percentages of carbon atoms in aromatic, naphthene and paraffin structures, but as number of carbon atoms in the respective structures.   This effectively introduces a third parameter, the molecular weight;   the device is convenient in comparing different fractions.

Several conclusions may be drawn from the calculated results.   The stock appears to be a typical wide-cut, rather highly paraffinic lubricating-oil fraction;   its paraffinic content remains remarkably constant at about 73 per cent. throughout the distillation range.   The aromatic content is rather high, as is to be expected in an unrefined oil, and increases slightly towards the high end of the distillation range.

The Waterman analyses of the extracts show several rather surprising characteristics of the stock (Fig. 4).   Fractions LR4 and LR10, the intermediate " key " distillates, all the extracts of which were examined completely, appear to have pure aromatics as the limiting start of the extract series;   both the paraffin and napthene contents apparently extrapolate to zero, and the aromatic to 100 per cent.   The presence of even traces of unalkylated aromatics in a high-molecular-weight oil which had undergone essentially no chemical change is at least somewhat remarkable. This is definitely not true of the lightest distillate examined, LR1 ;   in it, the limiting composition is aromatic, naphthene-free but strongly alkylated.

The heaviest fraction, LR15, could not be completely examined in this way, because the range of the method of Waterman has not been extended to materials of such high molecular weight and aromatic content.

The paraffin contents of all the members of the extract series increase regularly in the direction of percentage extracted, but at a rapidly decreasing rate, levelling off very uniformly at about 85 per cent.   This fact gives excellent confirmation of the now generally accepted view [7] that wax-free oils are quite free of acylic hydrocarbons.   The present work allows an

even stronger statement : a single naphthene ring apparently cannot hold more than about forty carbon atoms in aliphatic side-chains.

Additional support for the absence of pure paraffins is the fact that within the experimental error no fraction showed less than five cyclic carbon atoms per molecule.
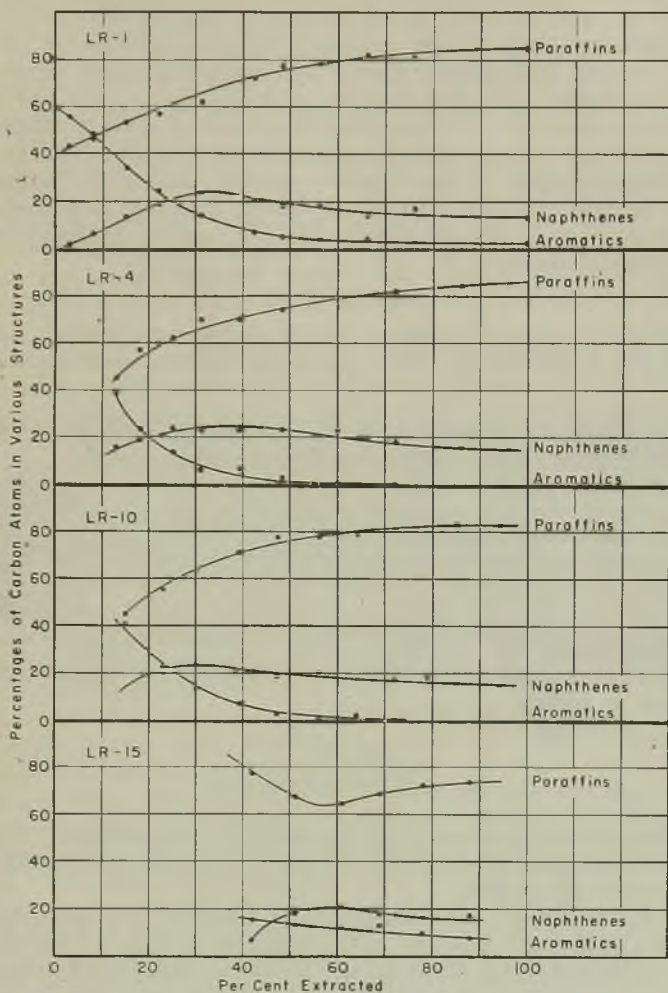

Fig. 4.

COMPOSITION OF EXTRACTS FROM KEY DISTILLATES.

For all the extract series, the naphthene content extrapolates to zero at the more soluble end. In the case of the low-molecular-weight distillates, this finding is not surprising, for these materials may not contain more than one ring per molecule, and if both naphthenes and aromatics are present, they must occur in different component compounds. Unfortunately, the

converse cannot be verified experimentally; slightly alkylated naphthenes cannot be separated from strongly alkylated aromatics of the same molecular weight by the fractionation methods used in this work.

The naphthene content passes through a broad but definite maximum in each extract series; this maximum occurs at about the 25 per cent. extracted point and amounts to about 25 per cent. naphthenes. The peak is not unexpected, because the solubilities of the naphthenes are intermediate between those of the aromatics and the paraffins of the same molecular weight, and therefore they should concentrate at an intermediate point in the series. The fact that the peak is broad on the less soluble side indicates that much of the naphthene content is strongly alkylated.

The analyses show remarkable homogeneity for the less soluble halves of the distillate fractions. Thus there is a definite limit to the paraffinicity of oils obtainable from such a stock by physical methods, as is well known in refinery practice. Oils of extreme high V.I. can be produced only by drastic chemical methods.

Oxidation Tests.

Unfortunately none of the many tests described for oxidation susceptibility of oils is suitable for the examination of the close-cut fractions
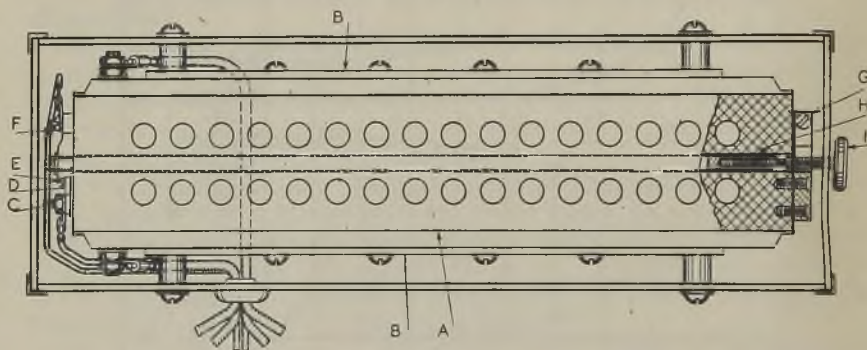
Fig. 5.
OXIDATION TEST THERMOSTAT.

obtained in this work, because all require relatively large samples. The final fractions were so small in volume that a semi-micro method was developed; it will be described in detail.

Method of Oxidation. The samples were oxidized in a specially built thermostat, illustrated, with the cover removed, in Fig. 5. Its essential part is a solid aluminium block having thirty-two holes, drilled part way into it, to accommodate the samples, and " Chromalox " strip heaters bolted to its sides. Temperature control is provided by the expansion of the block itself; a " Kovar " rod, having a low coefficient of thermal expansion, passes through a hole in the axis of the block, and the difference in expansion actuates contacts which control the voltage applied to the heaters through an electronic relay. A differential screw is provided for adjustment. The whole assembly is enclosed in an air-bath.

The temperatures in the holes used were found to be the same to within

less than $0 \cdot 2°$ C., and the amplitude of the regulation cycle was less than even this amount.

The samples, $1 \cdot 0$ g. each, were contained in 10×75 mm. standard test tubes, which fitted snugly in the holes in the block to a depth twice that of the oil layer.

In all runs, a control oil was oxidized along with the specimens being investigated. Testing of this oil served as an indication that conditions were maintained constant at the normal values throughout the oxidation. The control experiments served also to bring out the reproducibility of the tests.

The duration of the oxidation was ninety-six hours in all tests. In the non-volatile acidity tests the temperature was $160°$ C.; in the viscosity-increase tests it was $155°$ C.

In some preliminary trials air was bubbled through the samples at different rates during the oxidation. This action did not affect the results, and consequently an air stream was not used in the later runs. The lack of effect of the air-stream is a good indication that the samples were always saturated with air and that the volatile acids were lost as fast as formed, as might be expected from the small size of the sample and the slow oxidation rate.

Determination of Neutralization Number. Examination of the oil fractions after oxidation also required the development of a new procedure which was devised along the lines of the A.S.T.M. neutralization number method, but adapted to small samples and single-phase titration.

A sample of about $0 \cdot 05$ g. of oil was weighed into a 50-ml. Erlenmeyer flask, dissolved in 5-ml. anhydrous *t.*-butyl alcohol, and titrated to a thymolphthalein end-point with a $0 \cdot 005$N solution of tetramethylammonium hydroxide in *iso*propanol.

Each of these details was given consideration. The *t.*-butyl alcohol was by far the best of many solvents tried. It has excellent solvent power for all oils, being even completely miscible with the lighter ones. It is also a good solvent for the gums and sludges formed during oxidation. Finally, it is not only wholly miscible with water, but appears to be a powerful mutual solvent for water, oils, and their oxidation products. With some of the other liquids tried, the minute amount of water formed by the neutralization caused a troublesome turbidity.

A curious effect was noted with some other solvents, especially dioxane and the mono-butyl ether of ethylene glycol. Though these liquids have fairly satisfactory solvent power, they appear to inhibit the neutralization reaction. The end-points were very broad and drifted badly.

Tetramethylammonium hydroxide proved to be the best of several bases tried; it is a strong, stable alkali, freely soluble in the systems used. The standard solution in *iso*propanol remains clear and requires recalibration only about once a week. *t.*-Butyl alcohol was first used as solvent, but the solutions darken on standing, and will not remain at constant strength.

Sodium *t.*-butylate was also studied, but it is not convenient because the metal reacts very slowly with pure *t.*-butyl alcohol, and the neutralization is rather slow, causing a drift in the end-point. Results with this base, however, checked those with the tetramethylammonium hydroxide to within the experimental error. Aniline in *t.*-butyl alcohol is not satisfactory because the calibration is not stable and the end-point is broad.

L L

The standard base solutions were calibrated with benzoic acid weighed into *t*.-butyl alcohol, using thymolphthalein.

Thymolphthalein was found to be the best of seventeen indicator dyes tested ; it gives a pale salmon colour in acid solution, and an intense blue where alkaline.   The acid colour is almost wholly masked by the solutions of oxidized oils, but the alkaline blue stands out very sharply even with dark media because it presents absorption in a spectral region to which all oils and their oxidation products are nearly transparent.   Thus, in the extreme case, the solution changes, by transmitted light, from a deep red or brown to a muddy green.   A photo-electric photometer was constructed for observation of the end-point ; filters rendered it sensitive only to the red region, but it proved to be unnecessary, as the end-point could be observed nearly as well visually.

One of the most important details of the technique of this method is the rigorous exclusion of carbon dioxide.   The alcohols for the standard solutions and also the solvent alcohol are boiled for some time, without reflux, in their own storage bottles, and those bottles are then provided with siphons and soda–lime tubes.   Even the titration flask is similarly protected ; a jet, in the form of a hooked glass tube, is hung over the neck and inside the flask and supplied with a steady stream of CO_2-free air.   The jet is connected with a long light rubber hose, which does not interfere with the manual swirling of the contents of the flask.

Extraction of alkali from the glass of the storage bottles and siphons caused much difficulty at first, which was corrected by coating them with Vinylite lacquer, baked on.   With these precautions, the standard solutions are very stable, and large stocks can to advantage be made up at one time.

Viscosity Measurements.   Several runs were made in which the course of the oxidation was followed by the increase of viscosity.   The viscosities were determined by the semi-micro method previously mentioned, and the results were expressed by the percentage increase of the original values.

Results of the Oxidation Tests.

Data are presented in Fig. 6 on the non-volatile acidity developed on oxidation of the final distillate fractions.   The curves are of peculiar shape, showing a distinct minimum in susceptibility slightly below the molecular weight of 400, and an equally broad maximum near 550.   These effects, however, are probably individual characteristics of the stock examined, and are of little general significance.

Fig. 7 sets forth the results of the same oxidation tests on the extracts obtained from the first, fourth and tenth distillate fractions.   For convenience in comparison, the data are plotted on the basis of mol. fraction of monobasic acid.   As is evident from the curves, the development of acidity on this molar basis is nearly independent of the molecular weight, being a function only of the oil type.

These results show, further, that the naphthene-rich fractions are more stable in this respect than either the aromatic or paraffin-rich components ; the broad minimum in each curve is at the point of maximum naphthene content, as can be seen by comparison of Fig. 4 and Table I.   From this minimum, the curves show a slight and gradual increase in oxidation susceptibility towards the aromatic-rich end, and a much stronger and sharper

rise towards the paraffin-rich end; the tendencies of naphthenes, aro-
matics, and paraffins to develop non-volatile acid on oxidation therefore
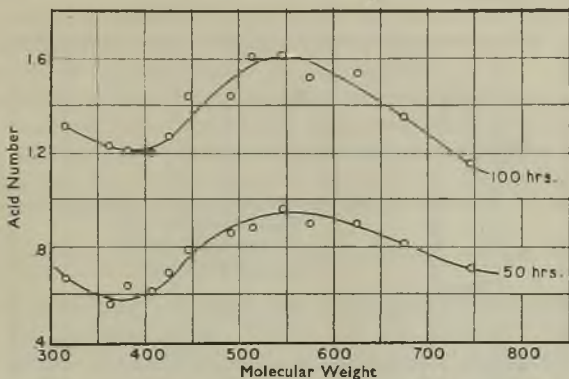increase in that order.

FIG. 6.

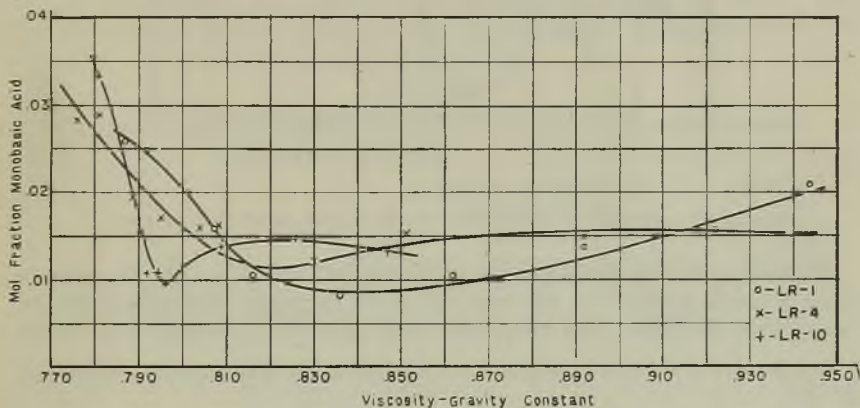ACIDITY DEVELOPED ON OXIDATION—LONG RESIDUUM DISTILLATES.

FIG. 7.

COMPARISON OF ACIDITIES AFTER OXIDATION—EXTRACTS OF KEY DISTILLATES—
LONG RESIDUUM.

The relative increase in viscosity on oxidation for a series of extracts is
illustrated in Fig. 8. This curve has the minimum of susceptibility at
maximum naphthene content even more strongly marked. In this case,
however, the paraffin-rich components are less susceptible than the aro-
matic-rich ones. One point was obtained for an exceedingly aromatic oil,
the first extract fraction in the figure, which indicates a considerably
greater resistance to oxidation than the slightly less aromatic ones, probably
a consequence of the presence of some natural anti-oxidants in it.

Summarizing these results, naphthenes are the most resistant to oxida-
tion of all the natural components in the stock, paraffins tend to form acids

without much condensation to yield viscosity increase, and aromatics are subject to the formation of condensation products, presumably of high molecular weight, which increases the viscosity, but only moderate amounts of acid are generated.
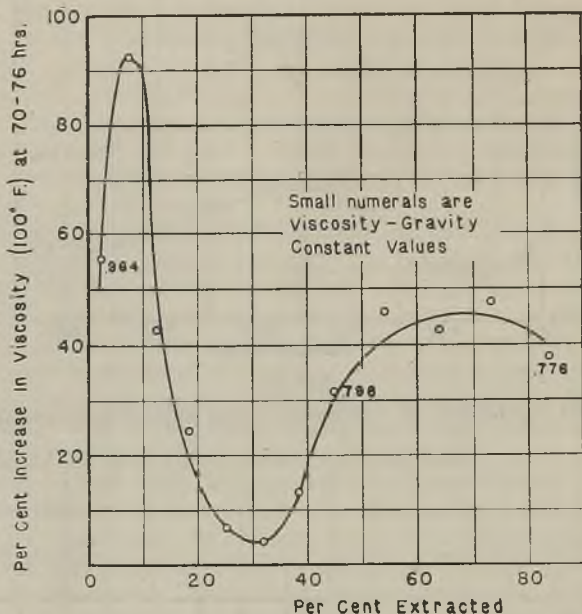
FIG. 8.

PER CENT. INCREASE IN VISCOSITY ON OXIDATION—EXTRACT OF LR-3.

Returning to the development of non-volatile acidity, Fig. 9 presents data indicating that, for the series of most paraffinic raffinates from the respective distillates, the monobasic acid equivalent formed is a nearly
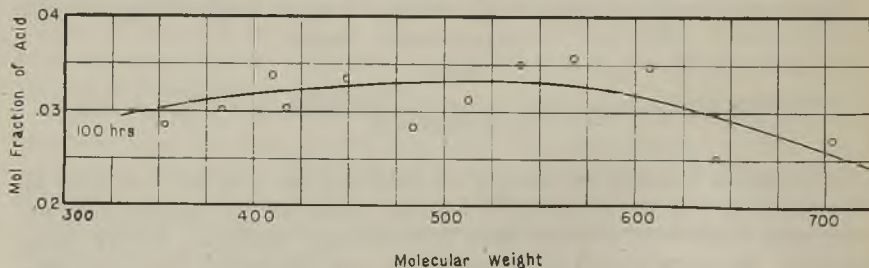
FIG. 9.

ACIDITY DEVELOPED ON OXIDATION—FINAL EXTRACTS OF LONG RESIDUUM.

constant mol fraction. If it is assumed that acid groups are only produced at or near the ends of side-chains, this result gives some indication that the number of chain ends per molecule is constant for this series. In other

words, as the molecular weight is increased, the chains are merely lengthened, without additional branching.   As the constancy appears to extend uniformly to the low end of the series, a moderate extrapolation of reasoning suggests that the chains may be normal.   Consequently there is a likelihood that the most paraffinic components in the oil are poly-*n*-alkyl *cyclo*-paraffins—a condition that, if true, may in some way be related to the curious absence of *iso*-paraffins in lubricating oils.

As has been noted, the Waterman analyses indicate that a single naphthene ring can hold only about forty carbon atoms in side-chains, at least in the materials studied.   This point, at a molecular weight of slightly less than 500, appears as a feeble break in the curve of Fig. 9, but the effect is scarcely larger than the experimental error.

Oxidation Characteristics of a Refined Oil.

A refined lubricating oil-stock was examined by essentially the same method as the long residuum.   This stock was prepared from one similar to the long residuum by a rather drastic commercial refining process.   The data obtained are too extensive to report here, but certain general results can be gleaned from them.

From the properties of the fractions of the refined oil on oxidation there is good indication that both stocks contain essentially the same components, but in different proportions.   Table II gives a comparison of four

TABLE II.

Comparison of Oxidation Susceptibilities of Fractions from Different Stocks.

	Oil.	Waterman analysis, C atoms/molecule.			Neutralization Number after Oxidation.
		Aromatic.	Naphthene.	Paraffin.	
Not refined . .	LR 1–10	0·7	4·3	20·4	4·25
Refined . .	X 2–6	0·5	4·9	20·4	4·61
Not Refined .	LR 4–4	7·2	5·3	15·8	2·20
Refined . .	X 2–2	6·2	3·2	14·0	2·34
Not refined . .	LR 9–12	0·0	6·5	34·0	3·34
Refined . .	X 11–9	0·0	6·4	39·0	3·40
Not refined . .	LR 14–4	8·2	9·9	40·8	0·72
Refined . .	X 13–2	8·2	9·2	33·8	0·32

pairs of fractions, each pair being composed of cuts respectively from the two stocks, having as nearly as possible identical compositions.   Close matching is difficult because three variables are concerned.   These data indicate that the susceptibility to oxidation of close cuts under the present test conditions is apparently dependent on the features of chemical constitution indicated by the Waterman analysis, rather than on any possible characteristic dependent on source, such as " natural antioxidants."

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THE CHEMISTRY AND CONSTITUTION OF ASPHALTS.

By B. A. MURPHY (Student).

Occurrence of Asphalts.

IN this paper the term " asphalt " is used in the American sense to include native and rock asphalts and all bitumens or asphaltic bitumens produced from crude petroleum.

Deposits of native asphalts, of which the best known is from Trinidad Lake in South America, have probably been formed from liquid asphalt. The latter, originally formed in the substrata, was probably forced to the surface through fissures in the surface crust by gas pressure. Bitumens (sometimes called pyrogenous asphalts) are manufactured from naphthenic or " asphaltic " types of petroleum residues which remain after fractional distillation of the lighter fuel and lubricating oils. The most suitable crudes for the production of pyrogenous asphalts occur in America (California and Mid-Continent), Mexico, Russia and Persia.

Production of Asphalts.

Native asphalts, which usually contain a percentage of water and mineral matter, require only to be dehydrated by heating to 160° C. before use; in some cases, however, where the percentage of mineral matter is excessively high, the asphalt is solvent extracted. The solvent is then removed by distillation.

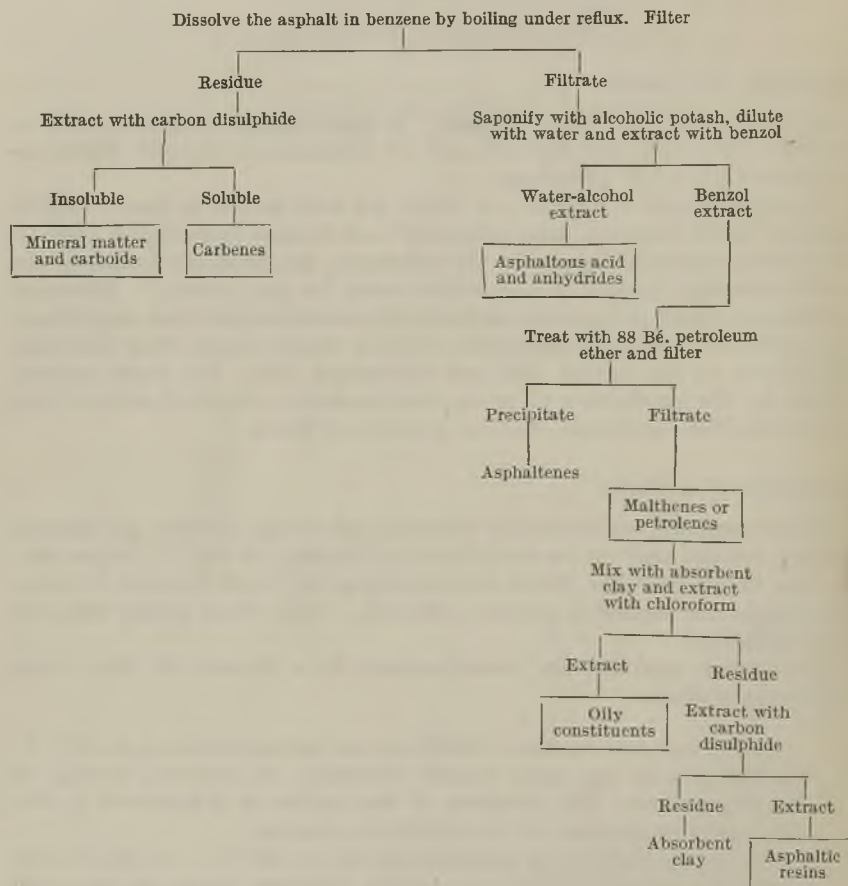Pyrogenous asphalts are manufactured in a variety of ways from petroleum residues :

(i) By vacuum or steam distillation at temperatures up to 625° F. In this process the more volatile fractions are removed, leaving an asphalt residue. The hardness of this residue is determined by the time and temperature of the distillation process ;

(ii) By air blowing at temperatures up to 625° F. In this process distillation of some of the more volatile fractions occurs, but the main production of asphalt is due to dehydrogenation and polymerization. This method of refining gives a high yield of asphalt which is also more " rubber-like " than that produced by other methods ;

(iii) By cracking at temperatures up to 900° F. and under a pressure of about 250 lb. This method of refining, often coupled with air-blowing, is particularly suitable for semi-asphaltic residues, since it increases the yield of gasoline and asphalt at the expense of the lubricating-oil fraction. Dehydrogenation is the main reaction, resulting in a product similar in physical properties to coal tar pitch.

Components of Asphalts.

Since asphalt is essentially a high-boiling-range product, it is possible to achieve only partial fractionation by distillation, even under high vacuum, and hence the method of analysis commonly employed is one of solvent fractionation using a series of solvents of increasing surface tension— a process outlined by Abraham.[1]

Method of Analysis.

Dissolve the asphalt in benzene by boiling under reflux. Filter

```
                    Residue                              Filtrate
        Extract with carbon disulphide        Saponify with alcoholic potash, dilute
                                                with water and extract with benzol

      Insoluble          Soluble              Water-alcohol            Benzol
                                                 extract               extract
   ┌──────────────┐   ┌──────────┐
   │Mineral matter│   │ Carbenes │         ┌────────────────┐
   │and carboids  │   └──────────┘         │Asphaltous acid │
   └──────────────┘                        │and anhydrides  │
                                           └────────────────┘

                                      Treat with 88 Bé. petroleum
                                             ether and filter

                                   Precipitate              Filtrate

                                   Asphaltenes
                                                  ┌──────────────┐
                                                  │ Malthenes or │
                                                  │  petrolenes  │
                                                  └──────────────┘

                                              Mix with absorbent
                                              clay and extract
                                              with chloroform

                                       Extract              Residue
                                   ┌────────────┐      Extract with
                                   │   Oily     │        carbon
                                   │constituents│       disulphide
                                   └────────────┘
                                                  Residue        Extract
                                                  Absorbent   ┌──────────┐
                                                    clay      │ Asphaltic│
                                                              │  resins  │
                                                              └──────────┘
```

Survey of Typical Analyses.

Typical analyses of asphalts by Baskin,[2] Abrahams,[1] and others are shown in Table I.   The wide variation of the asphaltene content of asphalts from various sources will be noticed, ranging from 4·6 per cent. for Californian to 22 per cent. for the corresponding Mexican grades, and in addition it will be generally found that the asphaltene content depends on :

(i) The penetration (or hardness) and softening point of the asphalt. The asphaltene and asphaltic resin content increases with increasing

TABLE I.

Analyses of Typical Asphalts.(a)

Source.	Soften-ing point (R. & B.), ° F.	Pene-tration 100 gm., 25° C./ 5° C.	As-phaltous acids, per cent.	As-phaltous an-hydrides, per cent.	As-phaltenes, per cent.	As-phaltic resins, per cent.	Oily con-stituents, per cent.
Natural							
Trinidad Lake	132	4	6·4	3·9	37·0	23·0	31·0
Residual asphalts							
Californian	131	39	—	—	4·6	59·0	36·4
Venezuelan	133	34	—	—	16·0	35·0	49·0
Mexican	134·5	38	—	—	22·0	34·0	44·0
Blown asphalts							
Mexican	148	40	—	—	26·84(a)	28·36	44·88
Californian	133	30	—	—	18·32(b)	—	52·80
Cracked asphalts							
High press. C.C. tar	105	150	—	—	14·43	—	76·15
Low press. C.C. tar	105	183	—	—	11·56	—	74·52

(a) Free from associated mineral matter.
(b) The difference between asphaltenes, resins, etc., and 100 per cent. is apparently saponifiable constituents.

softening point and hardness. This may be clearly seen in Table II;

TABLE II.

Effect of Blowing on Asphaltic Constituents.[1]

	Soften-ing point (R. & B.), ° F.	Fusing point of as-phaltene. ° F.	As-phaltous acids and an-hydrides, per cent.	As-phaltenes, per cent.	As-phaltic resins, per cent.	Oily consti-tuents.	Ash, per cent.	Total, per cent.	Mol. wt. of as-phaltene.
Original	93	313–324	1·85	24·2	15·0	55·0	4·3	100·35	2219
Blown	219	491–505	0·87	47·8	9·3	37·8	4·5	100·27	2560
Blown	272	579–587	0·64	48·4	8·4	39·2	4·2	100·84	3130
Blown	336	680–695	0·42	57·8	8·0	29·1	4·38	99·70	4690

(ii) The method of processing. Blown asphalts contain more asphaltenes and less oily constituents than the corresponding steam-refined grades, and the ratio of asphaltenes to resins is higher for blown asphalts. Cracked asphalts also have a relatively high asphaltene–resin ratio, and a high content of oily constituents.

Nature of Benzol-soluble Constituents.

In order to ascertain the chemical relationship between the various asphaltic constituents, some of their properties have been described below. It is apparent that evidence of close similarity between the various components will make information on each component additive.

Asphaltous Acids and Anhydrides.—These are tar-like, resinous masses, soluble in alcohol and chloroform. On heating they are converted into unsaponifiable products similar in appearance to asphaltenes.

On the assumption that asphalts are derived from petroleum hydrocarbons by oxidation or sulphurization, Gruse [3] regards the acids as products which have increased in molecular weight according to a type of oxidation-condensation reaction. They are considered too closely related to the asphaltenes, except that they have become acidic by production

of convential carboxylic groups. The action may be illustrated diagramatically as follows :

$$
\begin{array}{ll}
\text{R–CH}_3 & \text{R–COOH} \\
\text{H} & \\
\text{H} & \xrightarrow{\text{(O)}} \\
\text{R–CH}_3 & \text{R–COOH}
\end{array}
\qquad + \text{ water.}
$$
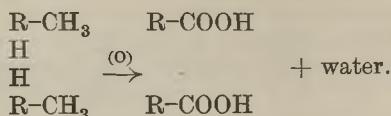
The anhydrides are probably produced by dehydration of the acids.

It is of interest that, in contrast to native asphalt, pyrogenous asphalts do not contain any appreciable amount of these acids or anhydrides, possibly due to the high temperatures used in the production of pyrogenous asphalt.

Asphaltic Resins.—These are dark-coloured products with the following properties :

(*a*) Their fusing point is below $100°$ C.;

(*b*) They are soluble in 88 Bé.'petroleum ether, chloroform, carbon disulphide, and benzol, but only sparingly soluble in hot or cold acetone ;

(*c*) Their molecular weights are dependent on the molecular weights of the oily constituents, and are lower than those of the asphaltenes.[5] This may be seen by reference to Table III ;

(*d*) They can be oxidized to asphaltenes, and can be produced from the oily constituents by heating for some time at $120°$ C. in the presence of oxygen ; [1]

(*e*) The ratio of the percentage carbon to hydrogen is about $8 : 1$ for uncracked asphalts. The ratio is somewhat higher for cracked asphalts ;

(*f*) The percentage of sulphur or oxygen is usually high.

Oily Constituents.—Oily constituents from natural asphalts contain a small percentage of solid paraffins (< 1 per cent.), and are fluid and sticky at $20°$ C.; those from the petroleum asphalts appear non-fluid and have a consistency of vaseline. These ingredients have the following properties :

(*a*) They are optically active and usually fluorescent, with a specific gravity of less than unity ;

(*b*) They have the same iodine value as viscous lubricating oils derived from petroleum ;

(*c*) As previously mentioned, heating, oxidation, or sulphurization converts them into asphaltic resins ;

(*d*) The percentage C : H ratio is about $7 : 1$ for uncracked asphalts and somewhat higher than this for cracked asphalts ;

(*e*) Sulphur or oxygen content is usually high, although it is always lower than that of the resins.

Asphaltenes.—Asphaltenes are usually dark-brown solid powders with the following properties :

(*a*) They melt at a high temperature with decomposition and swelling ;

(b) They are soluble in benzol, chloroform, and carbon disulphide, almost insoluble in alcohol and petroleum ether, and only sparingly soluble in ether and acetone ;

(c) On hydrogenation they are converted into resins ;

(d) The percentage C : H ratio ranges from 10 : 1 for uncracked asphalts to 12 : 1 for cracked asphalts (Tables III and IV);

(e) Their sulphur or oxygen content is generally high.

TABLE III.

Analysis of Asphalts.[7]

Source and constituents.	Total, per cent.	Carbon, per cent.	Hydro-gen, per cent.	Sulphur, per cent.	Oxygen nitrogen by dif-ference,* per cent.	Ash, per cent.
Mexican asphalt of 170 penetration .	—	82·93	10·37	6·20	0·50	—
Asphaltenes	18·60	83·45	7·37	8·83	0·35	—
Asphaltic resins	39·74	82·7	9·87	6·99	0·40	—
Oil	41·22	83·75	12·01	4·27	—	—
	99·63					
Mexican asphalt of 238 penetration .	—	85·05	10·38	6·10	—	0·27
Asphaltenes	28·0	79·60	7·79	8·09	3·92	0·50
Asphaltic resins	37·7	82·45	10·63	7·07	0·81	—
Oil	34·0	85·39	11·39	4·04	—	—
	99·7					
Russian asphalt						
Asphalt	—	85·3	6·4	0·6	9·7	—
Resins	—	84·12	9·92	0·64	5·32	—

* A blank in this column indicates that carbon, hydrogen, sulphur and ash add to more than 100 per cent.

TABLE IV.

Analyses of Asphaltenes from Various Sources.[8]

Source of asphaltenes.	Soft Mexican Asphalt 238 pene-tration.	Air-blown Mexican (a).	Vacuum-reduced Mexican (b).	Air-blown Gulf Coast (c).	Air-blown cracked (c).
Carbon, per cent. . . .	79·61	81·31	79·70	83·99	90·73
Hydrogen, per cent. .	7·79	7·91	7·83	8·26	6·30
CH ratio	10·2	10·4	10·2	10·2	14·4
Sulphur, per cent. . .	8·09	7·79	8·25	1·70	0·89
Ash, per cent. . . .	0·59	0·24	0·34	1·25	0·06
Oxygen, per cent. (by diff.) .	3·92	2·75	3·88	4·80	2·02

(a) Softening point (R. & B.) 220° F.
(b) Softening point (R. & B.) 200° F.
(c) Softening point (R. & B.) 201° F.

Nature of Benzol Insoluble Constituents.

Carbenes and Carboids.—These constituents form only a very minor part of asphalts, and are usually present only when severe cracking of the asphalt has occurred during processing. They have a high oxygen content (present as an ester) [8] and a high molecular weight. In other

respects they are similar to asphaltenes, from which they can be formed by oxidation. The sulphur content appears to be the same as for the parent asphaltene.[8]

The above properties of the constituents as well as rheological studies of asphalts (temperature susceptibility, etc.) by Mack,[10] Pfeiffer and Van Doornal [9] and others indicate that these components are closely related structurally, apparently differing only in C : H ratio and molecular weight (Tables III and IV). Rheological properties also indicate that asphalt is a colloidal system with the asphaltenes dispersed in the malthene (resins and oils) fraction.

Therefore, in view of the close relation of components, the chemistry of individual fractions can be related to the whole, and the known chemical composition of " simpler " petroleum fractions such as lubricating oils can be used to elucidate the composition of the more complex asphalt constituents.

Chemical Composition of Asphalts.

Cyclic Character.—The following reactions of asphalt and its constituents show evidence of the presence of an unsaturated cyclic structure.

1. In the presence of sulphuric acid, formalin reacts with asphaltic constituents to yield insoluble " formalite." This reaction has been found [1] to be typical of unsaturated cyclic hydrocarbons, whereas paraffins, olefins, naphthenes, polynaphthenes, ketones, and sulphur compounds remain unchanged. The unsaturated nature of the structure is also shown by their reaction with halogens and halogen acids. Since slightly more halogen is evolved as the acid than is retained by the residue, the main reaction appears to be substitution.

2. Asphaltenes react with fuming nitric or mixed acid to give a brown or yellow oil which is soluble in acetone, although the original residue is practically insoluble in this solvent. The nitrated product may be precipitated from acetone solution by mercuric bromide or ferric chloride dissolved in ether. Alkalies convert the nitrated product into water-soluble salts. Spielman [11] claims that the nitrated product is a cyclic nitrogen derivative (containing 4 to 6 per cent. nitrogen), and suggests a compound of the phenyl nitromethane type. It is considered, however, that since any solid paraffins originally present with the asphaltenes remain unnitrated and insoluble in acetone, nitration conditions are not suitable for the preparation of nitro-paraffins. Unfortunately no information is available on the effect of reduction on this type of nitrated compound.

3. The high molecular C : H ratio (from 1 : 1·7 for the oily constituents to 1 : 1 for asphaltenes) indicates that the hydrocarbons are of cyclic character, although obviously different from highly condensed benzene ring hydrocarbons which are crystalline solids of high melting point.

Aromatic Character.—In confirmation of the unsaturated cyclic character of asphaltic constituents, there is definite evidence that these cyclic compounds are in part, at least, of an aromatic type. This applies particularly to the asphaltenes.

1. Hilmann and Bernett [12] have found that, like aromatic coal-tars, " pure " asphaltenes are readily sulphonated by fuming sulphuric acid

and rendered completely water soluble. Cracked malthenes can also be sulphonated to almost complete solubility in water (only a trace of tarry matter remains), although only part of the straight-run material is attacked.

2. Waterman analyses * of malthene fractions of cracked and uncracked asphalts (Table V) shows aromatics, naphthenes, and paraffins to be present. The aromatic content is greater for the cracked material than for the

TABLE V.

Waterman Analysis of Malthene Fractions.[12]

Grade of asphalt.				Molecular weight.	Aromatics, per cent	Naphthenes, per cent.	Paraffins, per cent.
Straight-run * .	.	.	.	293	14	35	51
,,	.	.	.	448	27	24	49
,,	.	.	.	616	53	1	46
Cracked .	.	.	.	270	36	16	48
,,	.	.	.	344	47	1	52
,,	.	.	.	350	51	2	47

* The term " straight-run " is used to designate vacuum- or steam-refined asphalts.

uncracked, and increases with increasing molecular weight, mainly at the expense of the naphthenes. The percentage of paraffins appears to be the same for all molecular weights and for cracked and uncracked residues.

This suggests that the oil fraction of asphalt consists of naphthene and aromatic rings with paraffinic side-chains. In the processing of asphalt, hydrogen or the naphthene rings is apparently lost as water or hydrogen sulphide. This is in agreement with experimental evidence.

3. In support of the above conception of the structure of the asphalt molecule, Mair and co-workers,[14] after examination of a Mid-Continent lubricating oil, reached the following conclusions for the basic ring structure of the molecules :

(a) about 60 per cent. consists of naphthenes with one to three rings per molecule ;

(b) about 15 per cent. consists of molecules with one aromatic ring and from one to three naphthenic rings/molecule associated with a small amount of sulphur and oxygen compounds ;

(c) about 14 per cent. consists of molecules with two aromatic rings (linked through two common carbon atoms) and about two naphthenic rings per molecule associated with a small amount of oxygen and sulphur compounds ;

(d) about 11 per cent. consists of molecules with more than two aromatic rings (each probably linked through two common carbon atoms) associated with some sulphur, oxygen, and nitrogen compounds.

Reference to Tables III and IV suggests that, in view of the high percentage of sulphur or oxygen in asphaltic constituents, these elements may be an important part of the structure of asphalt molecules. More-

* The Waterman analysis [13] determined the percentage of carbon atoms present in the molecule as paraffins, naphthenes, and aromatics, by specific refraction measurements before and after hydrogenation.

over, although only a small percentage of nitrogen is usually present, this element may also occur in the structure.

It is also significant that although these elements are present in all asphaltic fractions, the percentage increases from oils to asphaltenes—*i.e.*, the sulphur content increases as the molecular weight increases.   In view of the close relation between the chemical properties of these fractions, it suggests that sulphur and oxygen may be linking units, as in vulcanized rubber.   Oxygen and sulphur are probably interchangeable, while nitrogen is probably present as a separate compound.
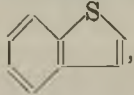
The evidence supporting these hypotheses is as follows :

(*a*) Generally when the sulphur content is high, the oxygen content is low (Table III) and vice versa ;

(*b*) The product obtained by air blowing of asphaltic oils is very similar in physical properties to that produced by heating with sulphur ;

(*c*) Gruse,[3] Spielman [11] support the contention that sulphur or oxygen occurs in ethereal, ketonic, or bridge positions because of the reactions of asphaltic constituents with ferric chloride, mercuric chloride, and sulphuric acid, to give oxonium type compounds ;

(*d*) Garner [7] reports that thiophenes have been isolated from the malthenes, while Spielman [11] found that oxidation of asphaltenes high in sulphur with more persulphuric acids, yields sulphoxides and sulphones, and oxygen-containing compounds are produced from those low in sulphur.   This suggests that sulphur (or oxygen) occurs

in units something like thio naphthene , or more probably

as a sulphide.

The work of Friedman [15] on the reactions of hydrocarbons with sulphur gives further support for the sulphur in asphalts occurring in the form of complex thiophenes or sulphides.   Gruse [3] considers that the first products in Friedman's experiments were probably sulphides of successive polymers of the original hydrocarbons, which then lost hydrogen as hydrogen sulphide.   For example, octylene can be vulcanized to " asphalt " in the following way :—

$$\text{Octylene (S)} \begin{array}{c} \longrightarrow \end{array} \left. \begin{array}{c} C_8H_{15}S \\ C_{16}H_{32}S \\ C_{24}H_{42}S \end{array} \right\} \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} \left. \begin{array}{c} C_{24}H_{24}S_2 \\ C_{64}H_{32}S_5 \end{array} \right\} \text{`` Asphalt ''}$$
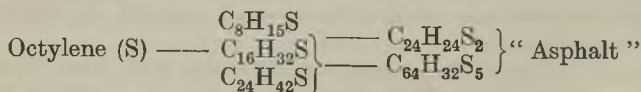
(*e*) The percentage of nitrogen present in asphaltic constituents is usually very low, and is only about one-half to one-third of the percentage of oxygen present.   Ellis [16] and Bailey [17] report that the nitrogen occurs as isolated nitrogen bases containing quinoline, pyridine, and *cyclo*pentane rings.

Spatial Configuration of the Molecular Structure.—Although some authors, such as Abraham,[1] consider that the asphaltic molecules are present in
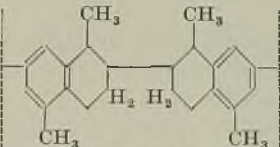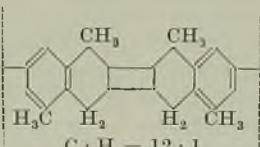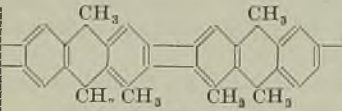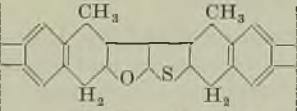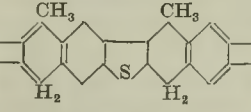
the form of condensed nuclei, there is considerable evidence to show that this is unlikely.   For example :

(1) The C : H ratios are not high enough for the high molecular weights found.   Asphaltenes with a percentage C : H ratio of 10 : 1 have a molecular weight of 2400, whereas a condensed polycyclic hydrocarbon such as decacyclene has a molecular weight of only 450 for a C : H ratio of 24 : 1 ;

(2) There is a close similarity between the bromide and sulphonate derivatives of the various fractions.   Moreover, the calcium sulphonates of all fractions are qualitatively identical,[12] having the same appearance, soap, qualities, and extreme solubility in water.   Solutions of these salts all exhibit the same curious behaviour on evaporation, first becoming syrupy, and finally drying rapidly to a powdery consistency.   It seems unlikely that the sulphonic acid salts of a compound of molecular weight of 2400—namely, asphaltenes—would have the same qualitative properties as salts of oils, which have a molecular weight of 400, unless the asphaltene unit is broken down during sulphonation into simpler units ;

(3) Pure polycyclic compounds, such as picene, crackene, and truxene, are insoluble in most solvents, whereas asphaltenes readily dissolve in benzol, carbon tetrachloride, etc.

TABLE VI.
Structures of Asphaltenes and Asphaltic Resins.[12]

Type I	CH_3 CH_3 / H_2 H_2 / CH_3 CH_3 / C : H = 10·3 : 1	CH_3 CH_3 / H_3C H_2 H_2 CH_3 / C : H = 12 : 1
Type II	CH_3 CH_3 / CH_3 CH_3 CH_3 CH_3 / C : H = 14·6 : 1	
Type III	CH_3 CH_3 / O S / H_2 H_2 / C : H = 12 : 1	
Type IV	CH_3 CH_3 / S / H_2 H_2 / C : H = 13·5 : 1	

It therefore appears that the molecular units do not exist in a highly condensed form, but rather as chains, although rheological properties suggest a compact three-dimensional structure in which the units are probably superimposed.

Molecular Structure.—Hillman and Barnett [12] have suggested the types of structures shown in Table VI to account for some of the known facts. These structures showing methyl groups on the rings are indicative of cracked rather than straight-run malthenes, whose side-chains are considered to be longer, and therefore less susceptible to sulphonation. As further support for those structures, the authors show that Type I can theoretically be converted by cracking and condensation, etc., into picene, which has been isolated from Californian cracked asphalts.

Conclusions.

Although there are still many gaps in the information on the chemistry and constituents of asphalts, it is clear from the foregoing evidence that any proposed structure for molecules of the asphaltic constituents must meet the following specifications :—

(1) The ring type of the asphaltene must be predominantly aromatic, and must be susceptible to hydrogenation to produce naphthene rings which are apparently the main constituent of straight run malthenes.

(2) The malthene fractions should be susceptible to dehydrogenation of the ring structure, without causing any appreciable change in the paraffin side-chains.

(3) Oxidation of the asphaltenes, probably the paraffin side-chains, to saponifiable products [8] under conditions more severe than those encountered in processing should be possible.

(4) Sulphur (or oxygen) should be present as a fairly stable compound, probably as a bridge unit.

(5) Approximately half the total number of carbon atoms present in the molecule should occur in naphthene or aromatic rings, and half as paraffin side-chains. This relation should hold, independent of the molecular weight.

(6) Hydrogenation and sulphonation should be capable of rupturing the asphaltene macromolecules into simpler units.

Tentative Structure of Asphaltic Molecules.

Although the typical structures suggested by Hillman and Barnett (Table VI) for the constitution of asphaltenes and cracked resins explain some af the known properties of asphaltic constituents, they fail to meet certain of the above specifications, namely :

(1) In Table VI the number of carbon atoms present in the molecules as paraffins is considerably less than the number of present in rings ;

(2) If sulphur is present in thiophene rings, we can only conceive the Type IV structure being formed between two similar units. If sulphur is initially present as a Type IV structure and the main

action of any excess sulphur during sulphurization is dehydrogenation and polymerization, then it would be anticipated, either that the sulphur content of the fractions should remain sensibly constant or should decrease with increasing molecular weight. In fact, the sulphur content increases with increasing molecular weight.

Therefore as a basis for further thought and investigation, the following structure for asphaltenes and resins may be suggested :

Asphaltenes.
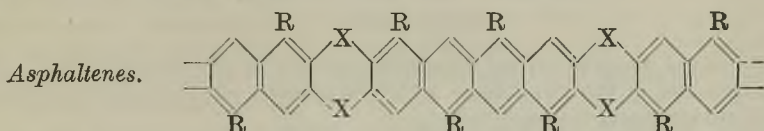
Where R represents paraffin chains of 3 or 4 carbons and X represents sulphur or oxygen.

Resins.—On hydrogenation the four or more membered rings shown above would probably break up into simpler naphthene units of two or three rings. Some of the rings would be of a mercaptan or sulphide type, while some of the sulphur linkages would be lost as hydrogen sulphide.

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OIL MIGRATION.

By James Frost (Student).

Introduction.

This paper aims at giving a general account of the phenomena of oil migration and of the hypotheses which have been put forward to explain these fluid movements in the rocks.

Oil migration may be divided into three phases. These are :—

(a) *Primary Migration—i.e.*, migration of oil from the source rock (usually a clay, but sometimes a limestone) into the reservoir rock. The reservoir rocks being those of high porosity and high permeability, such as sands, sandstones, dolomites, etc.;

(b) *Secondary Migration—i.e.*, the segregation of oil into pools within the reservoir rock;

(c) *Tertiary Migration* or the *dispersal* of oil.

The subject of migration of oil necessitates some reference to the origin of oil, since the times in the sedimentary cycle at which migration can occur will depend on the time in that cycle at which the oil is generated.

It is generally accepted to-day that the formation of oil is by no means as rare, and does not require the special conditions for its formation that were once thought necessary. Oil formation is believed to be a process common in the sedimentary cycle, although commercial accumulations of the fluid remain in the nature of freaks. Most oil geologists subscribe to the organic origin theory, and believe that oil has been generated from sediments similar to those now being laid down on the Continental Shelf in waters deeper than 600 feet. Sediments in this area are almost completely free from interference due to wave action and water circulation. In these circumstances stagnant (*i.e.*, anærobic) conditions easily arise, and organic matter deposited on the sea-bed is capable of being entombed and preserved. Reducing conditions are essential for preservation, but high organic content does not seem to be necessary.

Sediments typical of this environment are the blue and black muds. These muds are very common, and the dark colour, which is due to the presence of sulphides, notably iron, testifies to the reducing nature of the environment.

From sediments of this type oil is believed to be generated, but the mode of generation is a problem which is the cause of much discussion. The difficulty lies in the fact that while blue and black muds have been observed and sampled, and their organic content analysed, and while beds of exceptionally high organic content have been recorded, there is, as yet, no record of an observation of petroleum *being* formed from organic matter. The formation of methane is very common in nature, but the formation of the higher paraffin homologues has not been recorded on a

scale even remotely commensurate with the formation of methane, let alone with the requirements of the formation of petroleum.

To account for the generation of oil and gas from the organic matter two major hypotheses have been put forward. They are :—

(i) The low-temperature or bacterial hypothesis, and
(ii) The high-temperature or thermal distillation hypothesis.

The first states that oil is generated fairly early after the entombment of the organic matter, chiefly by the action of bacteria working at low temperatures. The second states that when the rocks have compacted into consolidated sediments, oil is generated from the source rock by means of temperature distillation, the heat being supplied by mountain-building movements, radioactivity, etc.

For the purpose of this paper the low-temperature hypothesis will be accepted, chiefly because it gives a better explanation of primary migration than does the high-temperature hypothesis.

Primary Migration.

The problem of primary migration may be summed up as follows :

Clays are, in general, impervious to fluids, and make the best cap rocks needed for sealing the oil and gas in the reservoir rock. If these clays, which are now impervious, have acted as the birthplace of petroleum, how have the fluids generated in the clays been able to escape from them into the porous reservoir rocks ?

There is only one answer to this problem, and that is that the fluids were expressed from the clays before they (the clays) were compacted and consolidated and rendered impervious to fluids.

This means that oil must be generated fairly early in the geological history of the source-bed, and for this reason the low-temperature hypothesis for oil generation is favoured here.

We must now consider how the generated oil, widely disseminated through a relatively unconsolidated clay bed, is expressed into the porous reservoir rocks.

There are numerous theories which have been advanced to explain this movement of the oil through the clay. They are considered below.

The Effect of Gravity.

This theory which has been applied to primary and secondary migration alike, states that the oil globules in the water-saturated clay will separate out from the water by reason of their lower density compared with that of water. That is the buoyancy effect will cause separation just as if the fluids were in a beaker.

In fact this is not likely to occur. It has been shown experimentally that oil will not separate from water in coarse sands, let alone in clays where the pores are very much smaller.[1]

The Effect of Capillarity.

The capillarity theory has been advanced by Washbourne.[4] It states that the dominant cause of primary migration is the fact that the average

pore in the reservoir rock is much larger than that in the source rock, and the interfacial tension forces will tend to make the oil pass from the fine to the coarse capillaries. (The surface tension of water/air is 72 dynes/cm., compared with 20–25 dynes/cm. for an oil/air surface.) This effect will undoubtedly occur at the junction of the coarse and fine pores in the two rocks, but there seems no reason to suppose that an oil globule several feet away from this junction should be affected especially when the globule would have to travel along a very tortuous path within the clay before reaching the sand. In travelling along this path the shape of the globule would have to be distorted many times, and this would mean that work would have to be done on the globule. Capillarity cannot provide the energy required, since capillarity tends to promote static conditions rather than to initiate flow. Further, it has been shown experimentally that oil globules under conditions approximating to those described above show no desire to move to the finer pores.[1]

McCoy's Adhesion Hypothesis.[3]

This adhesion hypothesis is based on the fact that oil has a superior adhesion for quartz than for amorphous clay particles, and that water has a superior adhesion for clay than for quartz grains. On this basis, say the theorists, primary migration is simple. The oil in the clay moves into the sand and is replaced in the clay by the water which leaves the sand. Thus there is a continuous exchange of fluids across the coarse-fine junction. This theory is subject to the same objections as were offered against the capillarity hypothesis. Further, if the clay and sand are initially water saturated, as they will be, being marine sediments, only limited fluid transfer will be possible unless there is some initial pressure difference between the two beds to cause the movement. Large volumes of gas will undoubtedly be generated with the oil, and this would cause an expulsion of fluids from the clay rather than an exchange.

Effect of Compaction.

Athy [5] has shown in his studies on compaction that the process of compaction begins with the birth of a sediment and is continuous throughout its life in varying degrees of intensity. His results may be summarized briefly as follows : In any sediment the percentage of water present will be a logarithmic function of the depth of burial to which that sediment has been subjected. For example, for one shale analyzed the sediment had been compacted by more than 20 per cent. of the original volume at 1000 feet depth of burial, and the corresponding figures for 2000 feet and 3000 feet were 35 and 40 per cent. respectively. 50 per cent. of the original fluids had been expressed at 1000 feet, 70 per cent. at 2000 feet, 85 per cent. at 3000 feet, and 90 per cent. at 6000 feet. That is, compaction at 1000 feet is only one half of what it is at 6000 feet. It is apparent from these figures that as a sediment becomes buried deeper and deeper it is being continuously robbed of its fluids, and that there is a continuous flow of fluids upwards.

In the compaction of the clays these movements will be almost entirely vertical. In all cases the fluids will find the lines of least resistance to flow,

and these lines will, in general, be upwards to the less compacted sediments, where the pore spaces will be larger.

The pores in the reservoir rocks will not suffer so sharp a reduction in size as those in the clayey rocks. The sands, which will rapidly adopt their most economical packing, will act as collectors of fluids, by reason of their high porosity, and the fluids will tend to remain in them, especially if there is lateral egress along the sand for the excess fluids given up by the clays. Further, at depth, compaction will reach a stage such that fluids entering a sand-bed will be unable to penetrate the next clay bed above, owing to the low permiability of the clay bed at that depth. The fluids will then be forced to remain in the porous bed and be subject to the horizontal flow-lines in that bed.

Applying this process to the migration of oil and gas, it is apparent that the oil and gas will be expressed from the source clays together with much connate water. While the water has an excellent scavenging effect in stripping the source rock of its oil, it must be stressed that most of the oil and gas will be expressed as a result of the change in volume demanded by the increasing weight of sediments above the source rock. Athy's figures seem to suggest that most of the oil will have been expressed from the source rock by the time the sediment has been buried 2000 feet, since 70 per cent. of the original fluids will have been expressed from it by that time.

The Effect of Gas.

Johnson has attempted to explain the whole process of primary migration by the vehicular action of gas. He suggests that the gas separates out by reason of its very low density compared with that of water, and that in its upward movement it carries the oil with it, an oil globule being attached to each gas bubble. This theory should really be considered under the Effect of Gravity, since it is subject to the same criticism—namely, that the pores in the source rock will be too small to permit of gravity separation, even the separation of gas.

The effect of gas should, however, not be minimized. When one considers the vast amounts of gas (chiefly methane) which are being formed to-day, the vast amounts of natural gas in the oil and gas fields of the world, and, further, when the facility with which gas can escape is taken into account, then it is apparent that enormous quantities of gas must have been evolved with the smaller volumes of oil which it accompanies. It is contended here that the effect of this gas in migration has been much minimized in the literature. It appears possible that most of the oil is transferred from the source rock to the reservoir rock either as gas, or as small films of oil surrounding gas bubbles within the water. Segregation of the oil from the gas probably does not occur until the fluids are in a coarse medium, when coalescence of gas bubbles causes the small films of oil to unite, until a drop of oil grows sufficient in size to exist in its own right. The effect of gas will be considered further under secondary migration. It is mentioned here to stress the importance of gas.

Conclusions.

It appears then that the major force operative in the expulsion of oil and gas from the source rock to the reservoir rock is the fluid movements

from the source rock caused by the compaction of that sediment, and that the transference of the oil and gas is greatly aided by the presence of vast quantities of gas and by the high mobility of this fluid.

SECONDARY MIGRATION.

Secondary migration concerns itself with the movements of the petroleum fluids within the reservoir rock and with the causes of these movements.

Consider a globule of oil just expressed or forced into the reservoir rock from the source rock. The globule will still be subjected to the same compactive forces and water drive which caused it to be expelled from the source rock, and thus it will tend to continue its upward movement—in fact, it will move upward with greater facility, due to the larger pores in the reservoir rock compared with those in the source rock. The pores in the sand reservoir rocks will reach a minimum size early in the geological history of the sediment, since a re-arrangement of the sand-grains to give the most economical packing is all that compaction can achieve. (This does not, of course, take into account the possibilities of the sand being cemented by solutions, etc.)

Due to the presence of these relatively large pores, the fluids will favour flowing within the reservoir rock rather than enter a bed containing pores of a smaller size. The flow lines will thus tend to be diverted from the vertical to an up-dip direction, and the fluids will seek egress at the outcrop of the reservoir rock (if one occurs) rather than force their way through the next clay bed in the succession.

The globule of oil under these conditions will tend to follow the direction of movement of the water. Its ability to do so will depend on several factors. These are :—

     (1) The rate of flow of the water;
     (2) The concentration of the oil (i.e., the oil/water ratio);
     (3) The viscosity of the oil;
     (4) The presence or absence of gas with the oil;
     (5) The porosity and permeability of the reservoir rock.

Under static conditions the globule will, from surface-tension considerations, tend to assume a spherical shape. That is, it will tend to occupy a pore large enough for it to do this.

Flow of water through a sand containing these oil droplets will have no effect on the oil as long as the rate of flow remains slow, since the water will be able to by-pass the oil, by reason of the initial water-wet condition of the sand, and due to the fact that each oil globule will be surrounded by water. As the rate of flow increases the oil will begin to act as a greater and greater hindrance to the flow of water. In other words, we may say that the oil globule experiences a pressure difference across itself which tends to move it in the direction of flow. To move the oil it will be necessary to change its shape so as to force it through any of the smaller channels leading from its pore. To produce a given change in shape (i.e., in curvature of the oil–water face) a finite pressure gradient is necessary, and until this is reached the oil will not move. The critical pressure gradient to initiate oil movement can be reached by increasing the rate of flow of water or

by increasing the oil/water concentration. When this pressure is reached the oil will move along with the water. The movement of the oil will not be smooth, it will move jerkily, since the shape of each globule will be changing continuously as the oil moves through the multi-sized pores in the rock.

Once oil movement has been initiated, the possibilities of an oil-pool resulting will depend on the type of structures which the oil encounters on its journey. If the fluid movements are dominantly upward, the oil will tend to be filtered off where the fluids enter a finer rock (*i.e.*, one containing pores smaller than those in the reservoir rock, since the critical pressure gradient to initiate oil flow in the fine rock will be much higher than for the coarser rock).

This filtration effect at coarse-fine interfaces is of great importance in oil accumulation, especially in the early stages, before compaction has rendered the cap rock completely impervious to fluids.[2]

When the fluid movements are dominantly up dip, the oil will, under flow conditions, tend to move towards the top of the reservoir rock, by reason of its lower density compared with that of water. It has been demonstrated that buoyancy is effective in producing separation in the fluids under conditions of flow, but that buoyancy has no effect under static conditions.[2] Oil will thus migrate towards the high spots in a structure, where it will remain unless the flow of water becomes fast enough to scour it from its position or some destructive interference disturbs the accumulation. Oil will be continuously added to the accumulation as long as the water flow carries oil from the source rock and as long as the oil does not take up too much room so as to hinder the flow of water. Equilibrium will be set up when there is just enough room for the water to flow past the oil. At this stage no further addition will be made to the accumulation, and any oil in the water will be carried on to the next structure.

The advantage of this hydraulic theory is that it explains almost every type of accumulation of oil, from the structural accumulations of the faulted and folded regions, such as the Rocky Mountain Region, California, Burma, etc., to the porosity traps, such as those in the Appalachian area, the " wedge " fields like East Texas, Glenn, etc., and to the freak shoestring fields of Kansas.

But there are several objections to be offered against the hydraulic-flow theory. The theory assumes that continuous expression of fluids is taking place from the rocks during their burial, and that even when compaction has ceased, water circulation continues. These assumptions are by no means universally accepted. How is it that some sands are dry ?, and how do sands become sandstones if they are always wet ? and how do clays become indurated and hard if they, too, are always wet ? If these water movements do, in fact, occur in the earth's crust, do the waters move at a rate sufficient to cause the oil movements outlined above ? Opponents of large-scale migration have objected to the hydraulic theory by pointing out that if water movements were so active, there would not be such large divergencies as are found in the chemical properties of underground waters from bed to bed, and within the same formation. At very least these divergencies testify to the slow rate at which the waters move.

Most recorded measurements of the rate of flow of underground waters

show that it is extremely slow, of the order of 1 to 2 miles per year, and this seems hardly adequate to accomplish the secondary migration processes outlined above. Rich,[6, 7] himself, one of the leading exponents of the theory, expresses doubt as to the ability of the known ground water currents to overcome the resistance offered by the globules of oil, and suggests that some factor has been overlooked in the problem of oil accumulation.

Some of these criticisms can be answered by the fact that, while oil generation and primary migration probably occur fairly early in the sedimentary cycle, secondary migration is often a much later phase, and may be initiated by fluid movements which have some cause other than compaction.

It seems that for the oil to flow freely, the globules must be smaller than the smallest pore in the reservoir rock. This would necessitate an extremely small oil droplet. Here again it appears that the effect of gas has been minimized, and it is suggested that tiny gas bubbles carry a small film of oil with them in their movements, and that even slow water currents can move these gas bubbles with ease compared with moving an oil globule. It appears possible that an accumulation of oil begins by an accumulation of these oil-carrying gas bubbles. Under flow conditions the bubbles will separate out from the water to the high spots of the reservoir rock, and coalescence of the gas bubbles will occur until a globule of oil separates out in its own right. Hereafter the globule will grow by the small additions given it by the carrier gas bubbles.

The oil will not move from its position unless the flow conditions become very rapid (and this is unlikely from field evidence), but should the accumulation be broken into, the entombed gas, being in contact with the oil, will once again pick up its film of oil before moving on. It has been recorded that the production of oil from a field is greatly enhanced by the presence of gas, not only for the pressure drive which gas so often gives, but also for the relative ease with which oil can be extracted when gas is present as compared with an oil of a low gas content.

The time at which secondary migration has occurred can often be accurately determined. Where accumulation is structural, migration must have occurred after the structures were formed, and if these can be dated, it should be possible to set the time of secondary migration to certain limits. For example, in anticlinal accumulations some competent bed is needed to form the structure, and this implies that compaction had ceased when the earth movements occurred, and as migration occurred after the structure was formed, it is obvious that the fluid movements would have their origin in the diastrophism rather than in compaction. In these cases fluid movements will be initiated by the squeezing effects of the diastrophism, and it seems that there will be a general expulsion of fluids from areas of high pressure—i.e., intense folding towards the areas of low pressure, i.e., gentler folding.[8] Temperature differences and irregularities may also set up small-scale convection currents within the earth's crust, which will have an effect in aiding water circulation.

Numerous other theories have been put forward to explain secondary migration. Some of them have been applied to primary and secondary migration alike, as if the two processes were exactly similar.

Separation under the sole influence of gravity cannot be accepted,

since the pores, even in a reservoir rock, are too small to allow the process to take place. Capillarity is a negative force, since it would require that water should flow into the finer rocks, and this would tend to make the oil reservoirs areas of low pressure, which is contrary to experience. Adhesion theories have no application to secondary migration, since the fluids are constantly flowing in the same surroundings in the reservoir rock, and are thus not subject to varying adhesion forces. The vehicular action of gas is of great importance under flow conditions, but of no value under static conditions, even in the coarse pores of the reservoir rocks.

Conclusion.

Whatever may be the cause of secondary migration—and the problem has yet to be fully investigated—it is reasonably certain that a heterogeneous mixture of the fluids, oil, gas, and water cannot be separated into pools as they are found in the oilfields of the world unless there is some means of agitating them directly by earth movements or by the initiation of water circulation.

Tertiary Migration.

Tertiary migration is the final phase in the movement of the oil and gas. It is the dispersive phase. Oil and gas seepages record nature's inability to retain any longer the elusive fluids.

Tertiary migration occurs where an oil structure has been broken into. The chief agents effective here are diastrophism and weathering. Diastrophism causes upheavals in the rocks, faulting and folding, etc., which fissures and weakens the seals which hold the oil in check. Weathering is the final agent which causes the trap to be opened up at the surface.

Apart from these direct causes of tertiary migration there is also deep-seated weathering, which can effect the pool long before normal surface weathering begins to play its part.

Relief of pressure in the rocks as the agents of weathering wear down the overburden causes a general loosening and fissuring in the cap rock, incipient joints and fissures become actual, and migration is easily initiated. Gas, being more mobile than oil, is the first to take advantage of any avenue of escape, and the pressure falls rapidly. Oil follows along any fault or fissure or plane of weakness, and all that remains of the accumulation is a viscous residue of pitch or bitumen. In time this, too, is removed, and Nature has to begin work afresh.

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