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COMPOSITION OF OIL SHALE

Report of Work
Conducted under cooperative agreement
with
Standard Oil Company of Indiana

COMPOSITION OF SHALE OIL

by

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U. S. Department of the Interior
Bureau of Mines
Oil-Shale Demonstration Branch
Rifle, Colorado December 1951

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ABSTRACT

Shale oil, produced at Rifle, Colorado, by the Bureau of Mines through NTU retorting of oil shale, has been examined by a combination of the following techniques: distillation, extraction with a solution consisting of a metal chloride dissolved in concentrated hydrochloric acid, silica-gel percolation, extraction with urea, and infrared spectrometry.

Hydrocarbons constitute 39% of the shale oil, and compounds of nitrogen, sulfur, and oxygen account for the remaining 61%. The hydrocarbons are 6% normal paraffins, 6% normal olefins, 5% isoparaffins plus naphthenes, 12% isoolefins plus cycloolefins, 4% monocyclic aromatics, and 6% polycyclic aromatics. The non-hydrocarbons are 36% nitrogen compounds, 6% sulfur compounds, and 19% oxygen compounds.

The composition data suggest that some hydrocarbons are formed during retorting of oil shale via the steps: kerogen → nitrogen compounds → isoparaffins plus naphthenes → isoolefins plus cycloolefins → aromatics.

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INTRODUCTION

The oil-shale deposits of the United States are a potential source of tremendous quantities of petroleum substitutes. The most important deposit is located in Colorado, Utah, and Wyoming and is called the Green River formation (17). The Mahogany Ledge of this formation covers 1000 square miles in western Colorado, is about 100 feet thick, assays 25 or more gallons of oil per ton, and contains 126 billion barrels of oil (2). It is this Mahogany Ledge that is being worked by the Bureau of Mines at Rifle, Colorado, in its program of mining and retorting oil shale and refining shale oil.

Because shale oil is unlike crude petroleum, specific knowledge of its composition is essential for the production of usable products. The composition of shale-oil naphtha has been reported by Ball and associates (1, 5); they have also reported progress in the analysis of shale-oil fractions in the 200-325°C range (6). Nottes and Mapstone have analyzed the gas-oil fraction, boiling from 240 to 320°C, of Australian shale oil (13). Fragmentary data on individual organic compounds and hydrocarbon isomers or types in various shale oils exist (3). No comprehensive information on the composition of shale oil has yet been published.

The shale oil used in this study was obtained by retorting Mahogany Ledge oil shale in an NTU retort (8) at the Bureau of Mines Oil-Shale Demonstration Plant at Rifle (17). Inspection data are tabulated in Table I. This oil is considered to be characteristic of the product that may some day be produced in large quantities.

EXPERIMENTAL

The analysis of shale oil involved six steps:

a. Distillation of moisture-free shale oil at high vacuum into five successive 10% fractions and a 50% residue;

b. Extraction of the fractions and residue with ferric or zinc chloride dissolved in concentrated hydrochloric acid;

c. Silica-gel percolation of the raffinates from (b);

d. Urea extraction of the non-aromatic hydrocarbon eluates from (c);

e. Infrared analysis of some of the extracts and raffinates from (d), and of selected monocyclic-aromatic concentrates from (c);

f. Microfractionation under vacuum of the urea extracts from (d).

On the appropriate samples obtained during the six steps, tests were run for unsaturation by bromine number or iodine number and for conjugated diolefins by maleic anhydride addition. Essentially all samples were analyzed for nitrogen, sulfur, and oxygen. Modified micro-Kjeldahl methods (4, 10) were used for nitrogen analysis, the conventional bomb

method for sulfur, and a modified Untersaucher technique (7) for oxygen. Molecular weights of many samples were determined by boiling-point elevation in either a Menzies-Wright apparatus (12) or a semi-micro apparatus described by Matteson (11). Determinations of refractive index, specific gravity, and specific dispersion were made on most of the samples.

a. Distillation. A partial separation by molecular weight was effected by distillation. After removal of about 0.5% water by heating to 205°C., six kilograms of shale oil were distilled at 0.1 to 0.3 mm. into five successive 10% fractions and a 50% residue. There was no evidence of decomposition; the recovery was 99.4%. The specific gravities, molecular weights, and elemental analyses of the fractions are presented in Table II. Nitrogen content increased with molecular weight; sulfur was almost uniformly distributed; maximum oxygen content occurred in the 20-30% fraction.

b. Extraction with Metal-Chloride Solution. The distillation fractions were treated with a metal-chloride solution to separate the hydrocarbons from the compounds containing nitrogen, sulfur, or oxygen (14). These non-hydrocarbons are referred to as NSO compounds. Raffinates from metal-chloride extraction are called hydrocarbon concentrates.

The extraction reagent was a concentrated hydrochloric acid solution containing either 30% zinc chloride or 33% ferric chloride. (A number of other metal chlorides were found to be less effective.) Batch extractions were performed on 25 grams of the 20-30% fraction, and on 200 to 500 grams of the other fractions. For ease in handling, the 0-10% and 10-20% fractions were diluted with three volumes of technical-grade pentane; the other fractions were diluted with seven volumes. In each case, two volumes of the resulting solution was treated with one volume of the metal-chloride reagent.

Yields, molecular weights, elemental analyses, and compositions of the hydrocarbon concentrates are listed in Table III. The extraction proved to be most specific for the nitrogen compounds. The compositions of the hydrocarbon concentrates from the five 10% fractions were relatively constant; the 50-100% concentrate contained less than half as much hydrocarbon as the five 10% concentrates. Hydrocarbon content of the distillation fractions declined as molecular weight increased. No attempt was made to identify the compounds that formed adducts with the metal chlorides.

c. Silica-Gel Percolation. The silica-gel percolations of the hydrocarbon concentrates accomplished three separations: (1) hydrocarbons from the NSO compounds not removed by the metal-chloride extraction; (2) non-aromatic hydrocarbons from aromatics; and (3) monocyclic aromatics from polycyclic aromatics.

Samples of 100 to 300 grams of each of the five hydrocarbon concentrates were dissolved in 0.5 to 1 liter of technical-grade pentane. The solutions were passed first through a tapered column containing 1000 grams of 28-200-mesh silica gel and then through a smaller tapered column containing 400 grams of the same type of silica gel. The samples were eluted successively by 7 to 11 liters of pentane, 4 to 5 liters of benzene, and 1.5 to 4.5 liters of methanol. Eluates, in multiples of 0.4 liter, were collected. The eluants were removed by distillation and the refractive indices, specific gravities, and specific dispersions of the residues were determined. Hydrocarbons were composited by type as indicated by refractive index and specific dispersion.

In most cases, a sharp separation of high-purity non-aromatic hydrocarbons was achieved. The aromatic composites were essentially free of nitrogen compounds, but they contained some oxygen compounds and higher concentrations of sulfur compounds than were present in the hydrocarbon concentrates. Good separation of monocyclic aromatics from polycyclic aromatics was obtained. A typical adsorptogram is shown in Figure 1 in which refractive index and specific dispersion are plotted as functions of the weight of product eluted. The eluants employed are also indicated. The breaks in the curves when about 60% of the sample had been eluted are due to the appearance of monocyclic aromatics; the transitions in the vicinity of 70% indicate a shift from monocyclic to polycyclic aromatics.

The 20-30% and 50-100% fractions were handled differently than the other four fractions. In the case of the 20-30% fraction, a time-consuming silica-gel percolation on a large scale had been completed before the metal-chloride studies were begun. The benzene eluate, consisting of aromatic hydrocarbons, had been further percolated through Florisil, a synthetic magnesium silicate (16), to complete the separation of the aromatics from the nitrogen and oxygen compounds and to separate the monocyclic aromatics from polycyclic aromatics. The 68% of the fraction eluted from silica gel by pentane and benzene was considered equivalent to a hydrocarbon concentrate as obtained from metal-chloride extraction. The 50-100% hydrocarbon concentrate was subjected to an additional percolation through 500 grams of Florisil in series with the silica gel in order to separate a dark material -- persumably nitrogen and oxygen compounds -- from the non-aromatic hydrocarbons.

The distributions of the adsorption composites by hydrocarbon types are presented in Table IV. Most of the adsorption composites contained NSO compounds.

d. Urea Extraction. Straight-chain hydrocarbons were separated from branched-chain and cyclic hydrocarbons by urea extraction (18). Samples of 40 to 170 grams of the non-aromatic hydrocarbons from the percolation experiments were diluted with 0.5 to 2 liters of pentane and reacted for 2.5 hours with 100 to 900 grams of urea in the presence of 50 to 150 ml. of methanol activator. The urea adducts were removed by filtration and decomposed by hot water. The diluent and activator were removed by distillation.

The results of the urea extractions are summarized in Table V. In the five successive 10% fractions, the straight-chain-hydrocarbon content almost doubled; the unsaturation of the branched and cyclic hydrocarbons remained constant, and the unsaturation of the straight-chain hydrocarbons was essentially constant in the first four fractions and lower in the 40-50% fraction. The 50-100% fraction differed unexpectedly in that it contained less straight-chain hydrocarbon than the three preceding fractions; furthermore, the unsaturation of the branched and cyclic hydrocarbons was only half that of the 0-50% fractions.

Hydrocarbons containing 20 or more carbon atoms and having a methyl branch near the end of the chain also form adducts with urea (15). Inasmuch as the hydrocarbons in the 20-100% portions of shale oil contain more than 20 carbon atoms, urea extracts of these portions might be expected to contain methyl-branched hydrocarbons. Results of infrared analysis indicated that methyl-branched hydrocarbons were absent from the adducts.

e. Infrared Analysis. Selected straight-chain hydrocarbons and the corresponding branched plus cyclic hydrocarbons from the urea extractions were examined to determine the olefin types present. Certain of the monocyclic-aromatic concentrates from the silica-gel percolations also were examined to determine the types of ring substitution. Except for the straight-chain terminal and trans-internal olefins, infrared analysis yielded only qualitative data because of the complexity of the samples.

Qualitative results of the examination of the straight-chain hydrocarbons of the 0-10%, 20-30%, 40-50%, and 50-100% fractions are summarized in Table VI. Terminal and trans-internal olefins were present. Tertiary-terminal and tertiary-internal olefins were not detected and would have been present only if appreciable quantities of branched hydrocarbons had been extracted by urea. Conjugated diolefins were not detected; this result agrees with the values previously reported for the metal-chloride raffinates (Table III). Of the three olefin types that cannot be identified by infrared, non-conjugated diolefins may have been present, quaternary olefins would not be expected in urea extracts, and cis-internal olefins probably were present. Thermodynamic equilibrium data (9) indicate that the concentrations of cis- and trans-internal olefins should be about equal.

Quantitative data on the distributions of terminal and trans-internal olefins in the straight-chain hydrocarbons are shown in Table VII. With a doubling of molecular weight, the trans-internal-olefin content increased and the terminal olefin content decreased, so that the ratio of trans-internal to terminal olefins increased three fold. The total olefin contents from infrared analysis agreed very well with those calculated from bromine numbers; both methods showed a maximum in the 20-30% fraction.

This agreement indicates that cis-internal olefins were present in relatively small amounts that were far from thermodynamic equilibrium.

Examination of the branched plus cyclic hydrocarbons yielded the following qualitative observations: In comparison with the spectra of the corresponding straight-chain hydrocarbons, the intensity of the absorption at 13.8 μ, which is characteristic of long straight chains, was weaker; at 7.3 μ, characteristic of methyl groups, it was stronger; and at 10.0 and 11.0 μ, which are characteristic of terminal olefins, it was weaker. The observed absorption in the region of 8.5 μ was due to branched structures, and that in the region of 12 μ could be due to tertiary-internal olefins.

Monocyclic-aromatic concentrates from the silica-gel percolations of the 0-10%, 20-30%, and 50-100% fractions were also examined in the regions of 11 to 15 μ for benzene-ring substitution. Of the substituted ring types, the para-substituted were predominant and lesser amount of the meta-substituted were present; the complexity of the sample spectra precluded the possibility of estimating the ortho-substituted rings. Mono-substituted rings were present to about the same extent as meta-substituted. As expected, the aromatic-ring content decreased with increasing molecular weight; the corresponding increase in side-chain carbons is accounted for primarily by an increase in the length of a side chain rather than by an increase in the number of short side chains. No substitution on the alpha carbon of the side chain on the mono-substituted aromatic ring was found in any fraction; this indicates that aromatics are not alkylated during the retorting process. All the monocyclic-aromatic concentrates analyzed contained trans-internal olefin bonds in about the

same volume concentration; an increase in the molecular concentration of aromatics having trans-internal-olefinic side chains seems to occur with increasing molecular weight.

f. Microfractionation. The boiling ranges of the shale-oil fractions gave only an approximation of the carbon-number distributions. The molecular weights of the hydrocarbon concentrates were of limited assistance in further defining the average molecular weight, because of the NSO compounds that were also present. However, straight-chain hydrocarbons obtained by urea extraction were suitable materials for determination of the carbon-number range of shale-oil hydrocarbons.

The straight-chain hydrocarbons from the five 10% fractions were fractionated in miniature Hyper-Cal, Podbielniak concentric-tube, or Piros-Glover spinning-band columns. Samples of about 35 ml. were charged to columns operating at 1-20 mm, the pressure depending on the fraction being distilled. At total reflux and atmospheric pressure, these columns have an efficiency equivalent to about 60 theoretical plates. From the distillation data and the molecular weights of related fractions, the carbon-number distributions of the urea extracts were estimated, with the results presented in Figure 2; the yields and average carbon numbers of the distillation residues are also shown. As their molecular weight increased, the fractions covered a wider carbon-number range. Adjacent fractions overlapped extensively.

METHODS OF CALCULATION

From the data obtained, the hydrocarbon contents of shale oil and its fractions can be calculated with considerable certainty, the type compositions of the hydrocarbons with reasonable assurance, and the distributions of aromatics according to ring content with less assurance.

Although the total NSO-compound contents of shale oil and its fractions are known with considerable accuracy, the distributions of the nitrogen, sulfur, and oxygen types are uncertain.

To calculate the composition of shale oil it was necessary to make numerous assumptions concerning the separation processes, methods of calculation, molecular-weight relationships of hydrocarbons and NSO compounds, and the concentration of poly-NSO compounds. Those assumptions related to separation processes or to the methods of calculation are tabulated and discussed in Table VIII.

Initially it was arbitrarily assumed that the hydrocarbons and NSO compounds in the same fractions had the same molecular weight, but this yielded inconsistent results. The molecular weights of the shale-oil distillation fractions (Table II), of the hydrocarbon concentrates (Table III), and of the non-aromatic hydrocarbons (Table V) were determined experimentally. Molecular weights of the NSO compounds were then calculated from the results of these experiments. It was assumed that the aromatic and non-aromatic hydrocarbons in a given fraction had the same molecular weight. The molecular weights of the hydrocarbons, of the NSO compounds, and of the total fractions are shown in Figure 3. NSO compounds in the 0-50% fractions had much lower molecular weights than the corresponding hydrocarbons, but, for the 50-100% fraction, the NSO compounds had a much higher molecular weight than the hydrocarbons.

In the preliminary calculations of the NSO-compound contents, it was assumed that the NSO compounds contained only one atom of nitrogen, sulfur, or oxygen per molecule. However, when the molecular weights of

the NSO compounds and the elemental analyses of the samples were used to calculate the percentage of these compounds present, the calculated values were always higher than the experimentally observed values. The calculated values could be high only if poly-NSO compounds were present. Therefore, it was necessary to express the non-hydrocarbon contents in terms of mono-NSO and poly-NSO compounds.

To arrive at the poly-NSO content, two assumptions were made. The poly-NSO compounds could contain two, three, or more atoms of nitrogen, sulfur, or oxygen, but in the absence of specific knowledge concerning these materials, it was assumed that they contained only two of these atoms per molecule. Such di-NSO compounds could contain nitrogen, sulfur, or oxygen atoms in like or unlike pairs. It was also assumed that the nitrogen, sulfur, and oxygen atoms doubled up to an equal extent. From these assumptions, the percentage of di-NSO compounds in any sample was calculated by subtracting the experimentally observed percentage of NSO compounds from the calculated percentage, since the following relationships hold:

% NSO compounds (calc.) = % mono-NSO + 2 (%di-NSO)

because the calculated percentage of NSO compounds counts all di-NSO molecules twice, and

% NSO compounds (expt.) = % mono-NSO + % di-NSO.

SHALE-OIL COMPOSITION

Shale Oil - On the basis of the present studies, the composition of shale oil is as given in Table IX. With increasing molecular weight, the non-hydrocarbon content of shale oil increases and the hydrocarbon content decreases. The increase in the non-hydrocarbon content is due primarily

to the nitrogen compounds. In the first five 10% fractions the increase in nitrogen compounds is almost exactly matched by the large decrease in isoolefins plus cycloölefins and the small decrease in isoparaffins plus naphthenes; n-paraffins, n-olefins, and total aromatics are essentially constant.

Shale oil contains 61% non-hydrocarbons, of which about 60% are nitrogen compounds, 10% sulfur compounds, and 30% oxygen compounds. Only 39% of shale oil is hydrocarbons. Isoolefins plus cycloolefins are predominant and constitute one-third of the total hydrocarbons. The remaining two-thirds is divided almost equally among the other types.

Non-hydrocarbons - Little is known of the nature of the non-hydrocarbons. Ball has shown that nitrogen may be present as pyrroles, pyridines, and quinoline homologues; sulfur as thiophene homologues; and oxygen as phenols and fatty acids (1). Distribution of non-hydrocarbons according to elemental and molecular types is given in Table X. The lower-boiling half of shale oil contains 34% of the NSO compounds and, according to the calculations, all of the mono-NSO compounds and 7% of the di-NSO compounds. There appears to be a maximum in the concentration of di-NSO compounds in the 20-30% fraction. Because the higher-boiling half apparently contains only di-NSO compounds, there must be a distinct increase in the percentage of these materials as the molecular weight increases. It is less likely that the higher-boiling half actually contains exclusively di-NSO compounds than that mono-, tri-, and tetra-NSO compounds are also present. In total shale oil, the non-hydrocarbons appear to be 30% mono-NSO compounds and 70% di-NSO compounds.

Hydrocarbons - The distribution by weight of the hydrocarbon classes in the shale-oil fractions, exclusive of NSO compounds, is shown in Figure 4. In the first five 10% fractions, the normal paraffins double, the normal olefins and polycyclic aromatics increase slightly, the isoolefins plus cycloolefins decrease by 40%, and the isoparaffins plus naphthenes decrease slightly. The 50-100% fraction reveals an unexpected increase in isoparaffins plus naphthenes and decreases in the isoolefins plus cycloolefins and polycyclic aromatics. In total shale oil, only the monocyclic aromatics are constant.

CONCLUSIONS

The observation that the isoolefin plus cycloolefin and the isoparaffin plus cycloparaffin contents of the first five 10% fractions of shale oil decrease as the nitrogen contents increase leads to the conclusion that, in the degradation of kerogen during the retorting of oil shale, the yield if iso- plus cyclic compounds depends primarily upon the denitrogenation of nitrogen compounds, and that this is less complete for compounds of higher molecular weight. However, in the higher-boiling half of shale oil, an unexpected increase in the isoparaffins plus naphthenes and the decreases in isoolefins plus cycloolefins and in polycyclic aromatics suggest that the sequence of steps in the degradation of the nitrogen compounds originally formed from kerogen during retorting is as follows: nitrogen compounds to isoparaffins plus naphthenes, to isoolefins plus cycloolefins, to aromatics. These results also suggest that the polycyclic naphthenes of higher molecular weight do not dehydrogenate as readily as those of lower molecular weight.

The constancy of the hydrocarbon composition of the lower-boiling half of shale oil leads to the conclusion that kerogen consists predominantly of homologues of a complex structure that upon degradation yield hydrocarbons having the same distribution of structural types.

The trends in molecular-weight distribution of the hydrocarbons, the NSO compounds, and the total shale-oil fractions suggest that there are no hydrocarbons in the higher-boiling portion of the 50-100% fraction of shale oil. If the hydrocarbon molecular-weight curve in Figure 3 is extrapolated to 490, which is the average molecular weight of the hydrocarbons found in the 50-100% fraction, this molecular weight corresponds to a distillation point of 60% and all these hydrocarbons would be contained in a 50-70% fraction. Therefore, approximately the highest-boiling 30% of shale oil must contain essentially no hydrocarbons.

ACKNOWLEDGEMENT

The sample of shale oil studied was obtained through a cooperative agreement between Standard Oil Company (Indiana) and the U.S. Bureau of Mines.

The authors are grateful for discussions with A.P. Lien and for the infrared analyses and interpretation by P.J. Launer.

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TABLE I

Inspection of Colorado Shale Oil

Specific Gravity, 15.6/15.6°C.	0.934
Distillation, °C.	
Initial	182
10%	262
20%	304
30%	345
40%	380
50%	413
60%	445
70%	470
80%	483
Elemental analysis, wt. %	
Carbon	84.25
Hydrogen	11.41
Nitrogen	2.02
Sulfur	0.72
Oxygen	1.61
Total	100.01
H/C Atomic ratio	1.61

TABLE II

Characterization of Distillation Fractions

Fraction, wt.%	Specific Gravity, 15.6/15.6°C	Molecular Weight	Elemental Composition, wt.% N	S	O	C	H
0 - 10	0.851	192	1.14	1.00	1.40	85.04	11.42
10 - 20	0.881	221	1.33	0.80	1.72	84.76	11.39
20 - 30	0.902	250	1.84	0.80	1.88	84.19	11.29
30 - 40	0.919	280	1.99	0.77	1.50	84.41	11.33
40 - 50	0.922	330	1.94	0.68	1.12	84.87	11.39
50 - 100	0.984	586	2.42	0.75	1.22	84.30	11.31

TABLE III

Characterization of Hydrocarbon Concentrates

Fraction	Metal Chloride	Yield, wt. %	Molecular Weight	Elemental Analysis, wt.%			Unsaturation[a], wt.%	Conjugated Diolefins, wt.%	Calculated Composition[b], wt.%			
				N	S	O			N cpds	S cpds	O cpds	Hydrocarbons
0 - 10	$ZnCl_2$	84	200	0.13	0.88	1.13	81	0.3	1	4	11	84
10 - 20	$ZnCl_2$	79	235	0.10	0.90	1.14	86	0.0	1	5	12	82
20 - 30	$ZnCl_2$	63	280	0.15	0.75	0.65	92	1.0	2	4	8	86
30 - 40	$FeCl_3$	62	325	0.11	0.94	0.99	100	0.0	2	6	14	78
40 - 50	$FeCl_3$	59	375	0.13	0.78	1.12	100	0.0	3	6	19	72
50 - 100	$FeCl_3$	34	540	0.18	0.94	1.02	101	0.0	8	18	33	36

(a) From bromine numbers.

(b) Assuming one N, S, O atom per molecule.

TABLE IV

Distribution of Adsorption Composites by Hydrocarbon Types

Fraction	Hydrocarbon Types (a), wt. %					
	Non-aromatics	Mixed	Monocyclic Aromatics	Mixed	Polycyclic Aromatics	NSO Compounds
0 - 10	62.3 (100)(b)	5.5 (98)	8.0 (77)	--- ----	15.8 (66)	8.4 (0)
10 - 20	59.2 (100)	3.2 (92)	7.4 (78)	4.8 (77)	15.8 (60)	9.6 (0)
20 - 30	60.8 (100)	--- ----	--- ----	21.4 (81)	9.0 (69)	8.8 (0)
30 - 40	54.6 (100)	5.2 (89)	8.2 (84)	1.3 (81)	24.3 (67)	6.4 (0)
40 - 50	56.8 (99)	5.6 (88)	7.5 (72)	--- ----	25.2 (50)	4.9 (0)
50 - 100	47.8 (97)	--- ----	10.4 (56)	--- ----	22.9 (21)	18.9 (0)

(a) Based on refractive-index and specific-dispersion data.

(b) Parenthetical figures indicate the actual concentration of hydrocarbons in the composite.

TABLE V

Urea Extraction of Non-aromatic Hydrocarbons

Fraction	Charge		Extract (Straight-chain hydrocarbons)		Raffinate (Branched plus cyclic hydrocarbons)	
	Molecular Weight	Unsaturation, wt. %	Yield, wt. %	Unsaturation, wt. %	Yield, wt. %	Unsaturation, wt. %
0 - 10	220	73	34	54	66	81
10 - 20	257	71	36	55	64	80
20 - 30	315	71	45	59	55	81
30 - 40	359	69	57	58	43	81
40 - 50	415	60	58	46	42	80
50 - 100	490	42	42	47	58	40

TABLE VI

Infrared Examination of Straight-Chain Hydrocarbons

Olefin Type	Formula	Identifying Absorption Band, μ	Result
Terminal	$R\text{-}CH{=}CH_2$	10.0, 11.0	Present
Trans-internal	trans $R\text{-}CH{=}CH\text{-}R_1$	10.35	Present
Tertiary-terminal	$R\text{-}C(R_1){=}CH_2$	11.25	Not detected
Tertiary-internal	$R\text{-}C(H){=}C(R_2)\text{-}R_1$	11.8 to 12.5	Not detected
Conjugated diolefin	$R\text{-}CH{=}CH\text{-}CH{=}CH\text{-}R_1$	6.2	Not detected
Non-conjugated diolefin	$R\text{-}CH{=}CH\text{-}(CH_2)_n\text{-}CH{=}CH\text{-}R_1$	None	-----
Quaternary	$R\text{-}C(R_2R_3){=}C\text{-}R_1$	None	-----
Cis-internal	cis $R\text{-}CH{=}CH\text{-}R_1$	None	-----

TABLE VII

Olefin Contents of Straight-Chain Hydrocarbons

		Olefin Content[a], mole %			
		Infrared			Bromine Number
Fraction	Mol. Wt.	Trans-internal[b]	Terminal[b]	Total	
0 - 10	220	16	37	53	54
20 - 30	315	26	37	63	59
40 - 50	415	24	27	51	46
50 - 100	490	25	21	46	47

(a) Calculated as monoolefins.

(b) Estimated accuracy of $\pm$ 10% of the value reported.

TABLE VIII

Assumptions Required for Calculating Shale-Oil Composition

Separation Process	Assumption	Comment
1) Distillation - - - of total shale oil. of urea adducts.	Proportional distribution of losses.	Wt. % recovery of 99.43. Vol. % recoveries of 92.0 to 97.7.
2) Extraction with metal-chloride solution.	100% recoveries.	No recovery of extracts. Demonstrated experimentally.
	No extraction of hydrocarbons.	
	Negligible chemical reaction with the hydrocarbons.	Low chloride contents of raffinates.
3) Silica-gel adsorption.	Proportional distributions of losses or gains.	Wt. % recoveries of 96.5 to 100.9.
4) Urea extraction.	Proportional distributions of losses.	Wt. % recoveries of 88.8 to 99.9.
Method of Calculation		
1) Experimental NSO-compound contents of distillation fractions.	NSO-compound content equals sum of: (1) material removed by metal chloride; (2) compounds separated by percolation; (3) compounds found in mixed percolation fractions.	
2) Distribution of N, S, and O compounds in non-hydrocarbon portions of distillation fractions.	N, S, and O compounds are present in atomic ratio of N, S, and O.	
3) NSO-compound contents of fractions from adsorption experiments.	All NSO compounds have the same molecular weight calculated for the total NSO compounds in the particular distillation fraction.	
	Oxygen contents of non-aromatic fractions equal zero.	Infrared spectra show no $C{=}O$, O-H, or $-CH_2-O-CH_2-$.
	Nitrogen contents below 0.05% equal zero.	Represents lower limit of sensitivity of method.

TABLE VIII (Cont'd.)

Method of Calculation	Assumption	Comment
4) Hydrocarbon content of any fraction.	100% - % NSO compounds.	Always gives a minimum value.
5) Straight-chain-hydrocarbon contents.	Urea extracts consist only of straight-chain hydrocarbons.	Extraction of some methyl-branched hydrocarbons is possible.
6) Olefin contents of urea charges, adducts, and raffinates.	Only monoolefins present. Molecular weights of extracts and raffinates same as those of charges.	High values if diolefins are present.
7) Non-aromatic and monocyclic-aromatic contents of mixed adsorption fractions.	Based upon average refractive indices and specific dispersions, some literature and some experimental.	
8) Isoolefin plus cycloolefin contents of certain mixed adsorption fractions.	Non-aromatics are isoolefins plus cycloolefins.	Unsaturations of the fractions range from 92 to 133%.
9) Monocyclic-and polycyclic-aromatic contents of mixed aromatic adsorption fractions.	Monocyclic-polycyclic splits based on literature values of refractive index and specific dispersion of mono- and dicyclic aromatics. Effect of NSO compounds on physical properties of aromatic fractions eliminated by calculation.	

TABLE IX

Composition of Shale Oil

Fraction	0-10	10-20	20-30	30-40	40-50	0-50	50-100	0-100
Non-hydrocarbons, wt. %								
N Compounds	12	14	21	26	33	21	51	36
S compounds	5	4	4	5	5	5	7	6
O compounds	12	17	18	17	16	16	22	19
Total	29	35	43	48	54	42	80	61
Hydrocarbons, wt. %								
n-Paraffins	8	8	8	8	10	8	3	6
Isoparaffins plus naphthenes	7	6	4	3	3	5	5	5
n-Olefins	10	9	11	11	9	10	3	6
Isoolefins plus cycloolefins	31	25	19	14	12	20	5	12
Monocyclic aromatics	6	8	6	6	5	6	2	4
Polycyclic aromatic	9	9	9	10	7	9	2	6
Total	71	65	57	52	46	58	20	39

TABLE X

Non-hydrocarbons in Shale Oil

Fraction	Elemental Type Distribution, wt.%			Molecular Type Distribution, wt.%	
	N	S	O	Mono-NSO	Di-NSO
0 - 10	41	17	42	97	3
10 - 20	40	11	49	94	6
20 - 30	49	9	42	79	21
30 - 40	54	10	36	81	19
40 - 50	61	9	30	87	13
0 - 50	50	12	38	87	13
50 - 100	64	9	27	0	100
0 - 100	59	10	31	30	70

FIGURE 1

SILICA-GEL PERCOLATION OF THE 10-20% HYDROCARBON CONCENTRATE

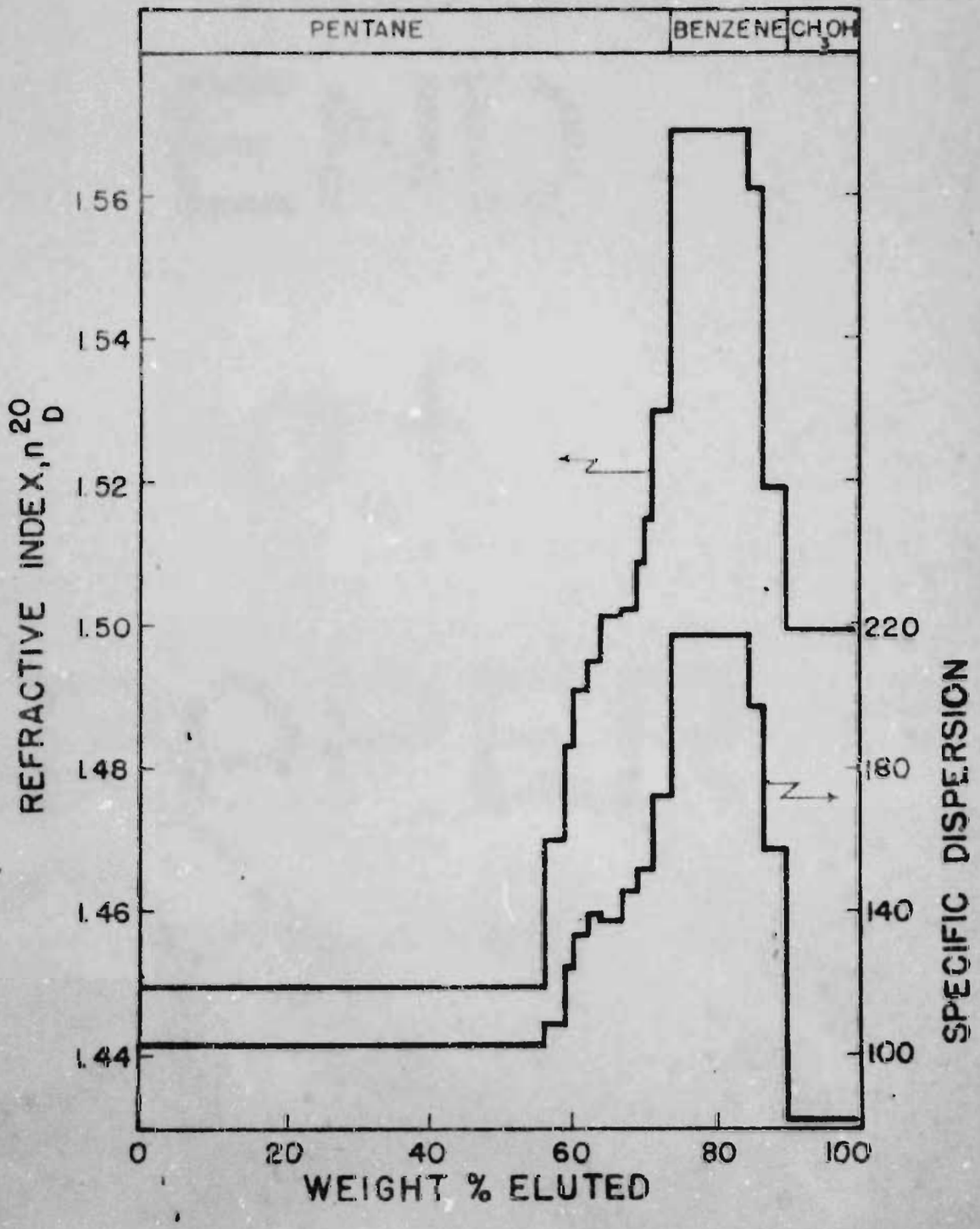


FIGURE 2

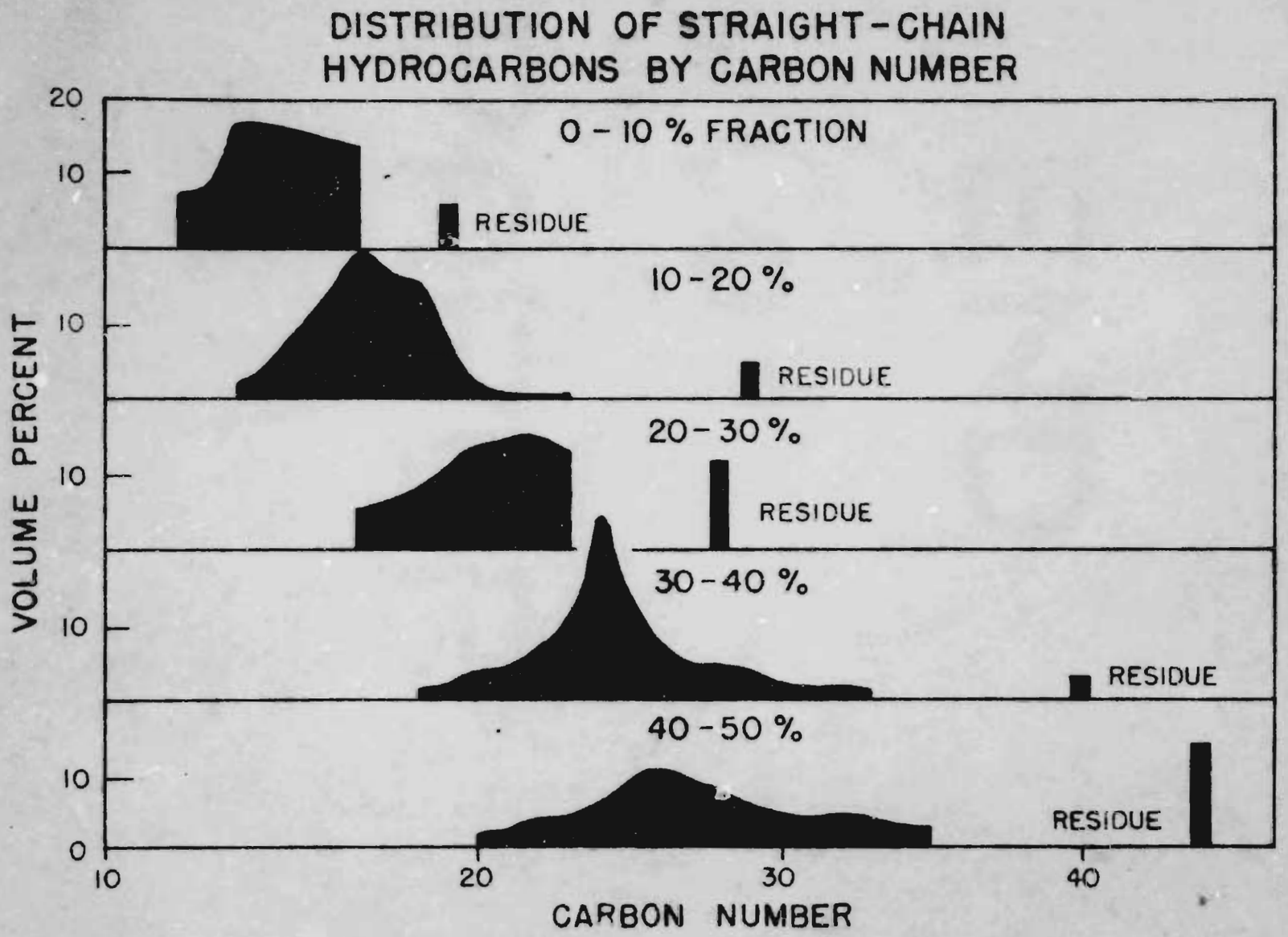

DISTRIBUTION OF STRAIGHT-CHAIN HYDROCARBONS BY CARBON NUMBER
0 - 10 % FRACTION
RESIDUE
10 - 20 %
RESIDUE
20 - 30 %
RESIDUE
30 - 40 %
RESIDUE
40 - 50 %
RESIDUE
VOLUME PERCENT
20
10
10
10
10
10
0
10
20
30
40
CARBON NUMBER

FIGURE 3

MOLECULAR WEIGHTS OF SHALE-OIL FRACTIONS AND COMPONENTS

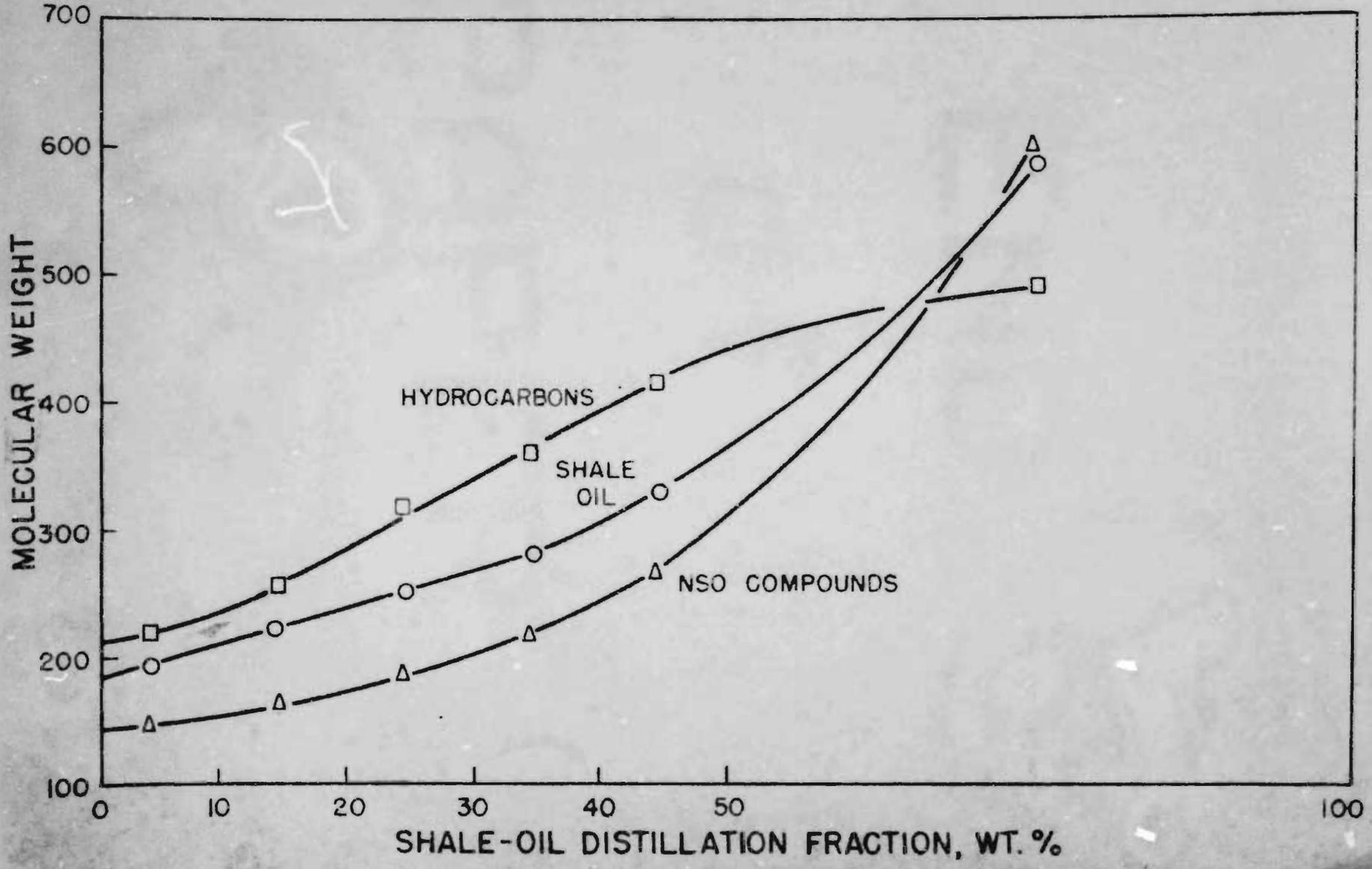
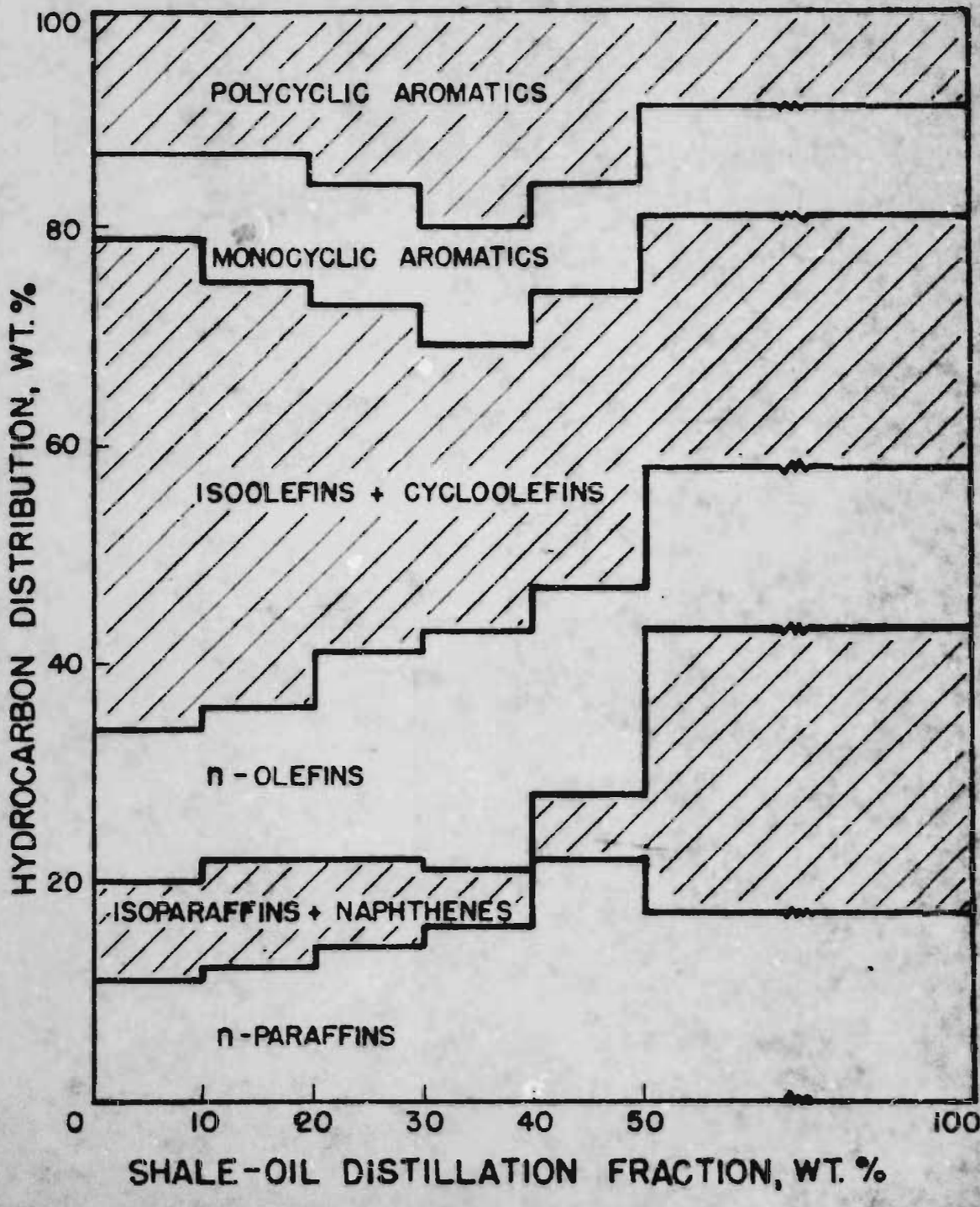


FIGURE 4

HYDROCARBON COMPOSITION OF SHALE-OIL FRACTIONS



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