Igepal CO-710 on sand (*6*) and generally are of the Langmuir type. As a result of more extensive study, it is concluded that the final increase in adsorption reported for this detergent is not valid and is a reflection of the large experimental error caused by the suspension of fine calcite particles identified in the sand sample.

The effect of electrolyte concentration on the adsorption of these detergent series is similar to the effect on the critical micelle concentrations of the Igepals (*7*). The maxima in adsorption are not increased markedly, but they occur at much lower concentrations. High electrolyte concentrations decrease the hydrophilicity of these detergents. Therefore, for comparable results, detergents used in saline water should have a higher ethylene oxide content than those used in fresh water. These results indicate that the detergents could be used effectively in strongly saline water, as well as in fresh water.

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Comparison of Brazilian and Colorado Shale Oils

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Lack of uniformity of retorting operations on shales from various localities has made it difficult to separate the effects of retorting from those contributed by the nature of the oil shale. Analyses of oils obtained from Colorado shale by various retorting methods and of oils from a number of countries have been published (*11*). These latter oils in general resulted from commercial retorting, so did not give information as to the range in product composition obtainable by different retorting methods or different operating conditions in the same retort. In the present investigation, oils obtained by retorting Paraiba Valley shale from Brazil in six experimental retorts have been analyzed. Comparison of selected properties with those on a similar series of Colorado oils affords an opportunity to distinguish between the effects of shale composition and retorting conditions.

The content of low-boiling distillate in oils from Colorado or Brazilian shale showed substantial differences, which depended largely on retorting method. The quantity of residuum in an oil from Colorado shale was always greater than in the corresponding oil from Brazilian shale, an indication of an effect of shale composition. The structure of the organic matter in the two shales differs with respect to the nitrogen linkages present, as evidenced by data on the oils produced from the shales. The proportion of nitrogen in the organic matter in Colorado shale that appeared in the oil was substantially higher than for the Brazilian shale. The nitrogen in all the Colorado oils analyzed was concentrated in the higher-boiling fractions, as has been found for other oils, but its boiling range distribution in four of the Brazilian oils was relatively uniform. The sulfur contents did not show an effect of shale composition similar to that observed for nitrogen. When produced under equivalent conditions, the Colorado oils contained more saturated and correspondingly less aromatic hydrocarbons than the Brazilian oils.

EXPERIMENTAL

The analyses discussed were obtained by the Bureau of Mines method (*11*) for the analysis of crude shale oil. The composite fractions indicated in the outline (Figure 1) are designated for ease of discussion as naphtha (fractions 1 to 7), light distillate (fractions 8 to 10), and heavy distillate (fractions 11 to 14). A summary of results pertinent to the present discussion is given in Table I for eight oils from Brazilian (Paraiba Valley) shale and four oils from Colorado shale. Complete analytical data on these oils have been published (*1, 11*).

The Brazilian oils for this work were obtained from experimental operations in six different retorts which may be grouped into three types according to the method of heating used. The Union (*7*) and Gas Combustion (*2*) retorts were internally heated; the entrained solids (*9*) and Fischer assay (*10*) retorts, and for one run the Parry (*6*) retort, were externally heated. The remaining runs on the Parry retort and the Otto (*4*) retort used a combination of these methods of heating. The Union, Gas Combustion, and Otto retorts have lump shale moving countercurrent or transverse to the gas phase. The entrained solids and Parry retorts treat finely ground shale in the entrained state. The Fischer assay retort is a small laboratory unit in which a charge of shale,

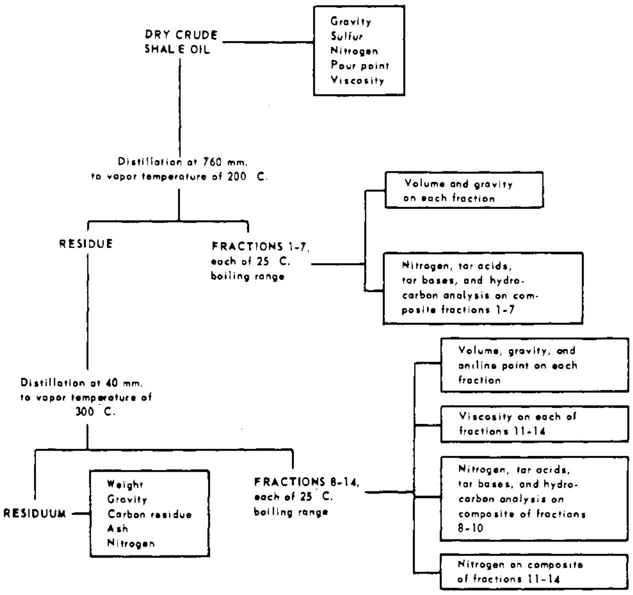

Figure 1. Properties determined in crude shale oil analysis

ground to minus 8-mesh per inch, is heated at a controlled rate.

Colorado oils were available from four of these same retorts: the Gas Combustion, Union, entrained solids, and Fischer assay. Published analyses (*11*) on Colorado oils from other retorts also were utilized in establishing the effect of nitrogen.

DISCUSSION

The crude shale oil analysis method is not a comprehensive composition study, but gives some data that can be correlated with the variables of production. For the present comparison, boiling range distribution, nitrogen content, sulfur content, and hydrocarbon composition were considered.

Boiling Range Distribution. Crude shale oil is usually obtained by thermal conversion, at a temperature of 400 °C. or higher, of the insoluble, nonvolatile organic matter occurring in oil shale. Oils obtained from the same shale by different retorting methods show differences in boiling range distribution (Figure 2), which are most evident for the naphtha fraction, boiling below 200 °C. For both Brazilian and Colorado oils, the Gas Combustion, Union, and Otto retorts give products containing 5% or less of this fraction. The low value may be due in part to failure to condense all the low-boiling material produced. These retorts have a moving bed of lump shale and large volumes of sweep gas that presumably remove the oil as soon as it is formed. When oils are produced by retorting in the entrained state or by the Fischer assay, which depends entirely on distillation of the pyrolysis products for their removal from the retort, the crude shale oil contains substantially greater amounts of naphtha. These results are in agreement with the concept that the first products of conversion of the organic matter in the shale are high-boiling materials and low-boiling constituents are produced largely by secondary reactions.

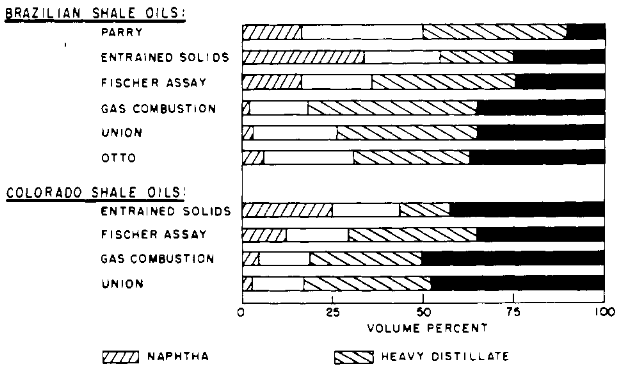

Figure 2. Distillation data

The Colorado oil from any given retort has a substantially greater quantity of residuum than the corresponding Brazilian oil. This consistently greater value may result from differences in composition of the organic matter in the shale which affect the characteristics of the oils rather than from the conditions used in retorting. A possible explanation is the higher content of nitrogen compounds in Colorado oils as these compounds are difficult to degrade thermally to lower-boiling materials.

Nitrogen Distribution. The crude shale oil analysis gives the nitrogen content of the crude oil and of each of the four composite fractions. It is therefore possible to determine both the variation in nitrogen content among different oils and the distribution of nitrogen with respect to boiling range for a given oil.

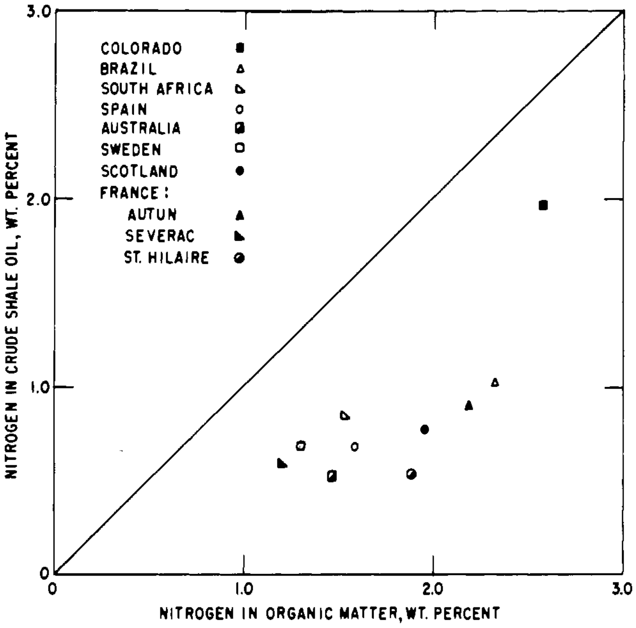

Figure 3. Relation of nitrogen in crude shale oil to organic matter in shale

The total nitrogen contents of both the Colorado and Brazilian oils show a range of values as illustrated in Table I. This variation may be due to retorting method, but no correlation with class of retort seems evident. Although the retorting method can cause a substantial difference in nitrogen content, the general level of the values for the Colorado oils is about twice that for the Brazilian oils. The difference may be attributed primarily to variations in the structures of the organic materials of the two shales, as the nitrogen contents of the organic materials are about equal, being 2.58 for the Colorado shale and 2.32 for the Brazilian shale. Colorado shale oils may be considered to differ in this regard also from all other shale oils on which analyses have been published by this laboratory (*3, 5, 8, 11-13*). As shown in Figure 3, the nitrogen contents of oils from various parts of the world range from about 0.5 to 1.0%, corresponding to a range of 1.0 to 2.3% of nitrogen in the organic material from which they were derived. Several interpretations

Table I. Summary of Analytical Results on Brazilian and Colorado Shale Oils

			Brazilian (Paraiba Valley) Shale Oils								Colorado Shale Oils			
			Parry Run			Entrained solids, 1120 °F.	Fischer assay	Gas Combustion	Union	Otto	Entrained solids, 1100 °F.	Fischer assay	Gas Combustion	Union
			1	2	3									
Properties of crude oil														
Gravity, 60/60 °F.			0.911	0.912	0.928	0.951	0.888	0.919	0.930	0.906	1.069	0.918	0.943	0.945
Sulfur, wt. %			0.35	0.48	0.46	0.69	0.41	0.68	0.73	0.68	0.56	0.64	0.69	0.71
Nitrogen, wt. %			0.78	0.70	0.74	1.22	0.98	1.06	1.43	0.79	1.94	1.95	2.13	1.89
Pour point, °F.			65	35	15	<5	80	90	80	80	<5	70	85	75
			Volume of Distillation Fractions, %											
No.	Temp., °C.	Pressure, mm.												
1	50	760				0.5								
2	75	760				3.2	0.1				3.4			
3	100	760				6.3	0.4				4.0	1.7		
4	125	760	0.4	0.3	0.9	5.7	2.1				4.4	1.0		
5	150	760	1.3	1.7	3.6	5.9	3.2				4.6	2.5		
6	175	760	3.9	4.4	6.0	4.9	4.2			0.6	3.5	3.5	1.5	0.1
7	200	760	8.7	8.9	9.4	6.8	6.4	1.4	2.7	4.9	4.9	5.0	2.9	2.6
8	150	40	6.9	11.0	10.6	9.4	4.0	1.9	4.2	7.2	7.9	4.8	3.2	3.3
9	175	40	10.5	12.5	12.5	5.3	7.1	6.2	8.9	8.5	6.4	5.8	5.7	6.0
10	200	40	12.2	12.7	11.7	6.3	8.4	8.6	9.7	9.1	5.1	6.2	5.7	5.0
11	225	40	10.7	13.8	10.5	5.5	8.7	9.6	9.1	10.0	3.9	6.9	5.9	7.8
12	250	40	11.8	10.3	9.5	5.2	8.8	9.8	9.6	10.1	3.8	7.8	7.6	6.5
13	275	40	8.8	7.3	7.1	4.4	9.6	11.5	12.3	12.3	4.1	7.7	7.6	8.9
14	300	40	10.1	8.9	8.4	4.6	12.0	16.4	7.4	[a]	1.3[b]	12.6	10.2	11.5
Residue			13.5	7.7	10.2	24.8	24.6	34.8	34.6	36.5	43.1	34.6	49.7	48.0
			Gravity of Distillation Fractions											
No.														
1						0.702								
2						0.710	[c]				0.709			
3						0.749	0.736				0.744	0.732		
4			[c]	[c]	0.781	0.782	0.758				0.773	0.756		
5			0.773	0.821	0.806	0.805	0.782				0.792	0.772		
6			0.813	0.829	0.834	0.826	0.807			0.807	0.814	0.798	0.806	[c]
7			0.849	0.853	0.862	0.859	0.833	0.843	0.837	0.827	0.846	0.820	0.831	0.823
8			0.871	0.876	0.884	0.906	0.852	0.861	0.862	0.854	0.879	0.854	0.849	0.854
9			0.884	0.892	0.899	0.918	0.865	0.870	0.877	0.867	0.901	0.868	0.867	0.869
10			0.896	0.904	0.912	0.929	0.877	0.881	0.891	0.879	0.923	0.889	0.889	0.882
11			0.906	0.915	0.927	0.944	0.887	0.888	0.901	0.891	0.942	0.905	0.899	0.891
12			0.920	0.931	0.947	0.961	0.897	0.899	0.911	0.903	0.964	0.926	0.915	0.912
13			0.926	0.938	0.961	0.973	0.900	0.905	0.927	0.908	0.975	0.939	0.935	0.930
14			0.935	0.958	0.993	0.985	0.902	0.907	0.932	[a]	0.980	0.951	0.945	0.943
			Nitrogen in Composite Fractions, Wt. %											
Naphtha (fract. 1-7)			0.85	0.70	0.73	0.49	1.17	1.06	0.84	0.89	0.63	0.74	1.17	[d]
Light distillate (fract. 8-10)			0.77	0.64	0.61	1.01	1.02	0.98	0.76	0.72	2.01	1.49	1.37	[d]
Heavy distillate (fract. 11-14)			0.71	0.65	0.72	1.41	0.93	0.99	1.14	0.74	2.69	2.04	2.03	[d]
Residue			0.92	1.10	1.10	2.03	0.91	1.16	2.18	0.82	3.12	2.34	2.47	[d]
			Analysis of Neutral Naphtha, Vol. %											
Saturates			15	12	11	6	19	[c]	[c]	25	11	33	27	21
Olefins			60	51	38	54	60	[c]	[c]	49	62	56	51	55
Aromatics			25	37	51	40	21	[c]	[c]	26	27	11	22	24
			Analysis of Neutral Light Distillate, Vol. %											
Saturates			12	9	10	12	18	23	11	16	33	23	27	[d]
Olefins			45	44	35	31	48	41	53	44	23	47	42	[d]
Aromatics			43	47	55	57	34	36	36	40	44	30	31	[d]
			Aniline Points of Fractions, °C.											
No.														
8			15.3	9.5	5.8	11.0	26.2	27.9	34.4	27.2	22.3	30.2	32.4	32.8
9			21.0	16.5	11.2	13.1	32.5	31.5	37.7	31.6	25.0	30.6	33.5	32.0
10			28.0	24.1	18.9	22.4	36.3	37.2	42.3	37.5	28.3	31.3	34.4	35.4
11			36.9	32.2	25.6	32.0	43.2	43.7	47.0	43.9	29.9	32.9	34.8	[d]
12			45.4	38.5	32.8	40.3	52.8	50.1	50.5	48.8	29.3	31.6	33.6	[d]
13			53.2	48.0	40.5	52.4	57.5	57.0	54.1	56.9	36.4	33.7	32.9	[d]
14			57.8	45.7	38.9	58.4	65.4	60.6	60.2	[a]	[c]	38.2	38.3	[d]

[a] No fraction obtained because of foaming.
[b] Distillation stopped at 278 °C. because of cracking.
[c] Insufficient sample for analysis.
[d] Sample analyzed before these determinations were included in this method.

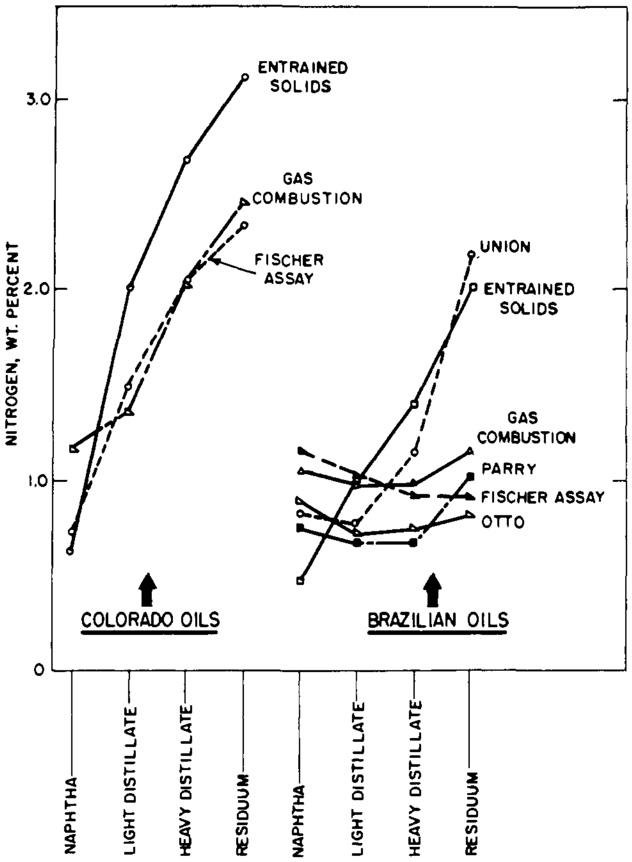

Figure 4. Nitrogen contents of fractions from crude shale oils

of these data are possible, but the simple one which assumes that the Colorado shale is unique seems preferable. For clarity of presentation and because in general the oils were not derived from exactly the same shale sample on which elemental analysis of the organic matter was made, a single average value for each shale is given in Figure 3.

The distribution of nitrogen with respect to boiling range shows some variation among the Colorado oils, but in all cases the slopes of the curves shown in Figure 4 are steep. Previously published (*11*) data from this laboratory show that this sharp increase in nitrogen content with increase in average boiling point of the fraction also is true for other oils from Colorado and from foreign countries. As indicated in Figure 4, only the entrained solids and Union oils from Brazilian shale show this same general nitrogen distribution and even the Union oil has about the same nitrogen content for the first two fractions, naphtha and light distillate. The curves for the other four oils are approximately level, with the Fischer assay oil actually showing a slightly negative slope. This distribution of nitrogen is particularly important from a refining standpoint, as the nitrogen content of a particular distillate to be processed rather than that of the total crude oil is significant.

Sulfur Distribution. The sulfur content of the crude shale oils also is shown in Table I. Relating the sulfur content of the oil to that of the shale is more difficult than with nitrogen, as the sulfur in the shale exists in both inorganic and organic forms. However, the sulfur contents of the Brazilian and Colorado oils are in the same general range, an indication that the structure of the organic matter in Colorado shale does not differ from that in other shales with respect to sulfur as it does with respect to nitrogen. Sulfur is usually distributed evenly throughout the boiling range in shale oils (*11*). A similar distribution was found for the Brazilian oils.

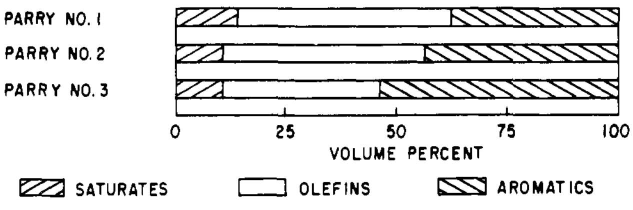

Figure 5. Hydrocarbon groups in combined naphtha and light distillate fractions from Brazilian shale oils

Table II. Conditions of Three Runs on Parry Retort

Run No.	Temp., °F.	Entraining Medium	Rate, S.C.F./Lb. Shale
1	900	Recycle gas	2.0
2	900	Air	2.0
3	950	Air	2.0

Table III. Hydrocarbon Analysis of Combined Naphtha and Light Distillate Fractions from Colorado and Brazilian Oils

		Hydrocarbon Composition, Vol. %		
Retort	Shale Source	Saturates	Olefins	Aromatics
Fischer assay	Brazil	18	54	28
	Colorado	27	51	22
Entrained solids	Brazil	9	46	45
	Colorado	20	46	34
Gas Combustion	Brazil	23	41	36
	Colorado	27	44	29

Hydrocarbon Composition. Results published (*11*) on Colorado oils have shown that retorting can have a pronounced effect on hydrocarbon composition. For example, a substantial increase in retorting temperature will give a highly aromatic oil. For the Brazilian oils only the Parry retort was operated under more than one set of conditions. Three of the oils were obtained by this retort under the conditions listed in Table II. These runs were designed to show the effect of temperature and type of entraining gas. The hydrocarbon analyses of the combined naphtha and light-distillate fractions from these oils (Figure 5) indicate that the oil ob-

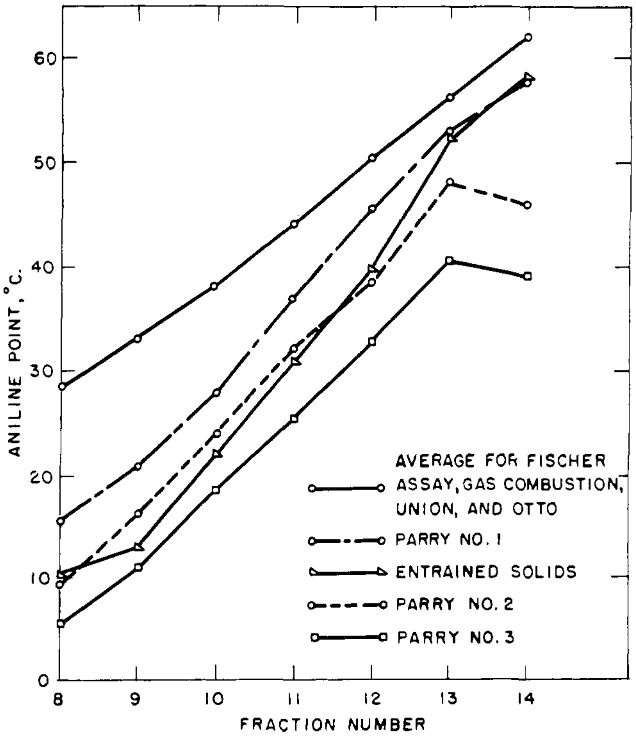

Figure 6. Aniline points of vacuum fractions from Brazilian oils

tained from run 1 at 900° F. using recycle gas for entrainment is the least aromatic. The oil from run 2 at the same temperature but using air for entrainment is somewhat more aromatic. The air decreased the over-all oil yield by 20 to 25% and this decrease may have been differential according to hydrocarbon type. The oil obtained at the higher temperature of 950° F. and also using air, is the most aromatic, showing the combined effects of these two variables. The oil yield on this last run was equivalent to the run using recycle gas. The aniline points of the individual fractions obtained in the vacuum distillations of these oils, plotted in Figure 6, show that the differences in composition of the oils are also evident in the higher-boiling fractions where hydrocarbon group determinations could not be made.

Figure 6 includes aniline points for the entrained solids oil and an average curve that is taken as representative of oils produced in the Fischer assay, Gas Combustion, Union, and Otto retorts. The curve for the entrained solids oil approximates that for the medium aromaticity oil from the Parry retort, although the entrained solids oil was from a run having a nominal retorting temperature about 200° F. higher. Although retorting temperature is an important variable that may be correlated with composition for a given retort, other factors such as residence time affect composition. Oils from retorts in which the products are removed by a sweep gas and from the Fischer assay retort have much higher aniline points, as indicated by the upper curve in Figure 6.

As the Brazilian and Colorado shales differ with respect to nitrogen content, the hydrocarbon compositions of several oils were compared to see if differences were indicated. The Fischer assay, entrained solids, and Gas Combustion retorts were used on shales from both sources. Hydrocarbon analyses of the combined naphtha and light distillate fractions after removal of tar acids and tar bases are shown in Table III. The saturates for the Colorado oils are consistently higher and the aromatics correspondingly lower, with only small differences in the olefin contents. This trend is apparent even if the tar acids and tar bases, which are generally higher for the Colorado oils, are considered as aromatics.

SUMMARY

Oils obtained from Brazilian and Colorado shale by several different experimental retorting methods have been analyzed by the Bureau of Mines method for crude shale oil. The proportion of lower-boiling distillates was primarily a function of the retorting method, but the Colorado oils always contained larger amounts of residuum. The retorting method caused a variation in the total nitrogen and sulfur contents of the oils. The average nitrogen content of the Colorado oils was about twice that of the Brazilian oils. This difference apparently results from variations in structure of organic matter, as total nitrogen contents were about the same. Most of the Brazilian oils had a different distribution of nitrogen with respect to boiling range than the Colorado oils. Oils produced from the two shales by the same retorting method showed regular differences in hydrocarbon composition, the Colorado oils having a greater content of saturates and a lower content of aromatics.

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Distribution of Nitrogen Compounds in Wilmington, Calif., Petroleum

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Nitrogen compounds in petroleum are known to have deleterious effects on cracking catalysts in refining operations (*6, 8, 12, 16*) and on the stability of petroleum products (*5, 15*). Knowledge of the occurrence, types, and properties of nitrogen compounds in petroleum is important in combating these undesirable effects. To procure fundamental data on the structure and properties of these compounds, the American Petroleum Institute Research Project 52 on nitrogen constituents in petroleum was established July 1, 1954. The initial studies of one phase of Project

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