The hypothetic aliphatic chains in the oil-shale kerogen are cracked during the distillation of oil shale to give products of lower molecular weight. This would explain the fact that in the oxidation of shale oil, acids of similar nature are obtained, but with a lower average molecular weight.

If it is proved that the nonvolatile acids obtained by oxidation of shale oil contain aromatic rings, it can be presumed that these are formed during the distillation of oil shale or else that they are present in that part of the kerogen which is not oxidized, under the authors' experimental conditions, when the oil-shale concentrate is subjected to the action of potassium permanganate.

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Nitrogen in Petroleum Asphalt

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Nitrogen content is a property of asphalts that has not received the attention that its importance merits. Asphalt chemistry often is considered an extension of hydrocarbon chemistry, and the characteristics that are associated with the low-boiling fractions of petroleum are assumed to be slightly modified for asphalt. Asphalt, however, is composed essentially of nonhydrocarbon compounds containing sulfur, oxygen, and nitrogen.

This paper shows the importance of the nitrogen content through development of three concepts:

1. Most of the nitrogen in petroleum is found in the asphaltic fractions. Some asphaltenes contain as much as an average of two atoms of nitrogen per molecule.
2. Nitrogen not only forms an integral part of the high molecular weight compounds, but is so firmly combined that, upon pyrolysis, most of the nitrogen remains in the coke.
3. Nitrogen, and consequently asphalt, has significance geochemically as an indication of the degree of maturation or age of an oil.

These concepts have been developed from the results of the work of American Petroleum Institute Research Project 52b on the Nitrogen Constituents of Petroleum, as well as other Bureau of Mines projects. Project 52 is concerned chiefly with the distillable portions of the oil (*2, 4*); however, some information that applies to the asphaltic portions of the oil has been obtained. The project is studying intensively an oil from the Wilmington, Calif., field. A description of this oil has been published (*4*).

NITROGEN CONTAINED IN ASPHALT

A high percentage of the nitrogen content of a crude oil is normally found in its asphaltic fractions. For the purposes of this article, it is convenient to consider the residuum produced from the Bureau of Mines routine crude-oil analysis (*8*) as asphalt. This residuum (which is left after distillation to 300° C. at a pressure of 40 mm. of mercury) often is close to 100 penetration asphalt. Some comparisons taken from the data of Stanfield (*10*) are shown in Table I and indicate how well this relationship may be expected to hold. The nitrogen in a crude-oil residuum amounts to more than 85% of that in the crude oil, according to a study of 15 crude oils (*3*). For the Wilmington crude oil, the residuum amounts to 46.4 weight % and contains 1.20 weight % of nitrogen. Based on the crude oil nitrogen value of 0.65%, 85.7% of the nitrogen in the crude oil is found in the residuum.

A more detailed examination of the Wilmington residuum

Table I. Comparison of Yields of Residuum with Those of 100-Penetration Asphalt

Crude Oil	Yield of Residuum, Vol. %	Yield of 100-Penetration Asphalt, Vol. %
Byron, Wyo.	43.1	26.8
Frannie, Wyo.	49.8	42.6
Garland, Wyo.	42.2	43.8
Grass Creek, Wyo.	37.6	31.6
Irma, Ark.	57.9	49.7
Kern River, Calif.	56.5	54.6
Maverick Springs, Wyo.	43.5	32.6
Oregon Basin, Wyo.	44.4	44.6
Poison Spider, Wyo.	40.2	51.2
Smackover, Ark.	47.5	27.7
Tampico, Mexico	56.0	73.6
Urbana, Ark.	50.5	35.6

shows how this nitrogen is distributed. A deasphaltening procedure, using *n*-pentane (*4*), was employed for the first separation. The properties of the resulting fractions are shown in columns 2 and 3 of Table II. The asphaltenes have a nitrogen content of 2.28% and contain an average of two nitrogen atoms per molecule. On the other hand, only about one third of the molecules in the deasphaltened residuum contain nitrogen. The ratio of basic to total nitrogen is fairly constant for the various fractions and conforms to the ratio proposed by Richter and others (*7*).

Propane deasphaltening of the pentane-deasphaltened crude oil resulted in a precipitated fraction containing 14.5 weight % of the crude oil (*4*). This fraction, which approximates resins in the usual separation of asphalts into asphaltenes, resins, and oils, contained 1.7% of nitrogen and an average of 1.1 atoms of nitrogen per molecule. Another approach on the pentane-deasphaltened crude oil was to concentrate heterocyclic compounds by adsorption on Florisil. This resulted in a fraction comprising 32% of the crude oil and having the properties shown in the last column of Table II. This fraction contains resinous as well as distillable material.

The Wilmington asphalt was produced from a high-nitrogen crude oil, and the nitrogen pattern may not be the same for other asphalts. In Table III, the distribution of nitrogen in Oregon Basin (Wyo.) and Tampico (Mexico) asphalts are compared with that for the Wilmington asphalt. Although the separations were made by different techniques and the Wilmington crude oil has almost twice as much nitrogen as the Oregon Basin crude oil, the similarity of pattern of nitrogen distribution is significant. The concentration of nitrogen is greatest in the asphaltenes and decreases in fractions of less molecular weight.

Table II. Properties of Wilmington Asphalt

	Residuum	Fractions from Residuum: Deasphaltened residuum	Asphaltenes	Nitrogen concentrate
Crude oil, wt. %	46.4	39.0	7.4	32
Total nitrogen, wt. %[a]	1.20	1.03	2.28	1.5
Nitrogen based on crude oil, %	85.7	61.8	26.0	73.8
Basic nitrogen, wt. %[b]	0.32	0.26	0.54	0.41
Basic nitrogen–total nitrogen ratio	0.27	0.25	0.24	0.27
Average molecular weight	. . .	475	1225	600
Nitrogen atoms per molecule, av.	. . .	0.35	2.00	0.64

[a]By Kjeldahl method (*5*).
[b]By perchloric acid titration (*6*).

Table III. Distribution of Nitrogen in Three Petroleum Asphalts

	Nitrogen, Wt. %: Tampico	Oregon Basin	Wilmington
Crude oil	. . .	0.35	0.65
Residuum	. . .	. . .	1.20
100-penetration asphalt	0.50	0.64	. . .
Oils	0.05	0.13	0.6
Resins	0.78	0.89	1.7
Asphaltenes	1.06	1.18	2.28

Values for Tampico and Oregon Basin asphalts from (*3*).

Although the number of oils for which data are available is small, it is apparent that the bulk of the nitrogen in a crude oil can be concentrated in the asphaltic fractions. This conclusion is substantiated further through work on the nitrogen-Conradson carbon-residue relationship discussed later.

THERMAL DECOMPOSITION STUDIES

The stability of nitrogen compounds was tested by subjecting a residuum from Wilmington crude oil to pyrolysis experiments. Similar experiments were made on a sample of asphaltenes and the deasphaltened residuum from the same oil. Material balances, sulfur balances, and nitrogen balances were used to gain some insight into the reactions.

Experimental. To obtain residua similar to those from Bureau of Mines routine crude-oil analyses, crude and deasphaltened Wilmington oils were topped to a vapor temperature of 300° C. at 40 mm. of mercury. This was done in an all-glass system under a sweep of purified nitrogen. A Vigreux column 12 inches long was used to increase the efficiency of the distillation. The materials remaining in the flasks were used for coking experiments. Asphaltenes from the separation with *n*-pentane also were coked.

The three samples were coked in a stainless steel reactor. The reactor temperature was controlled by means of a Celectray controller connected to electrical heaters. During coking the reactor temperature was gradually raised until a temperature of 500° was reached. The temperature was maintained until no more gases or distillate was obtained. All operations were protected by a sweep of purified gas.

Results. The results of the thermal treatment are shown graphically in Figure 1. The yields of coke and oil are shown in weight-percentages on the lines connecting the boxes. The percentages in the boxes represent the percentages of nitrogen and sulfur in the product based on the coking charge. Reliable values could not be obtained for basic nitrogen on the samples of coke. The losses to gas in each experiment are shown to the right of the product boxes.

Discussion. The results presented in Figure 1 demonstrate that the nitrogen tends to become fixed in the coke and that losses to gas are relatively small, except for the asphaltenes. Even there, the amount lost is not as great as the percentage figure would imply, because the asphaltenes are a small portion of the asphalt. The sulfur balances also are shown for comparison, and around 40% of the sulfur evidently is eliminated in each of the coking runs. The distribution of the sulfur between oil and coke results in about equal sulfur contents for all products. However, the oils produced are relatively low in nitrogen. The basic-nitrogen to total-nitrogen ratios shown for the coker distillates are considerably higher than those found for uncracked distillates.

The above observations lead to the suggestion that the sulfur and nitrogen combinations must be different. From analogy with the lower boiling compounds of sulfur and nitrogen that have been found in petroleum, most of the nitrogen probably is present in ring compounds. On the other hand, the sulfur may be present as hydrogen sulfide or other low molecular weight compounds that are either adsorbed on the large molecules, or, because of their acidity, are bound to the basic centers of the

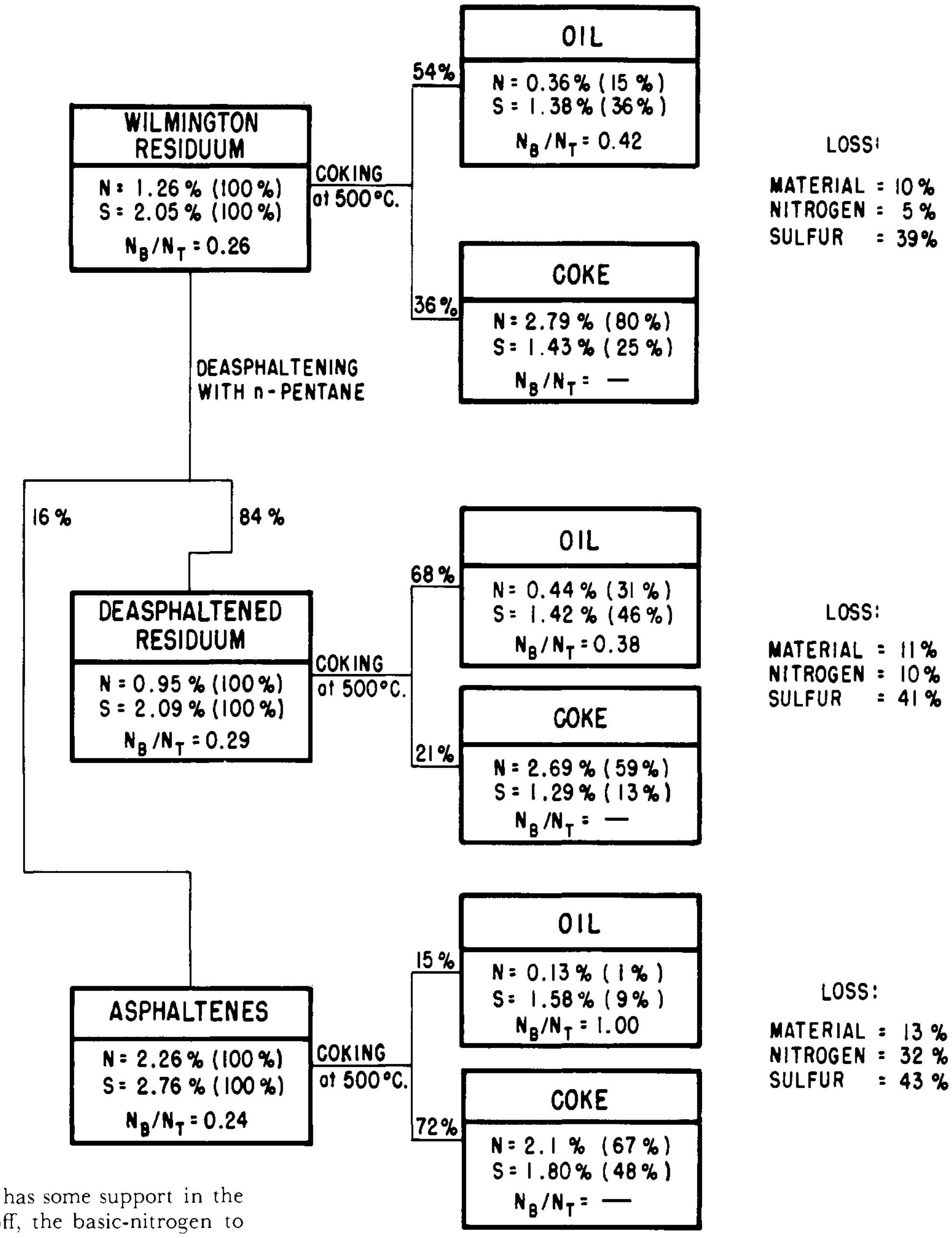

Figure 1. Coking experiments on fractions from Wilmington crude oil

nitrogen compounds. This latter view has some support in the fact that, when the sulfur is driven off, the basic-nitrogen to total-nitrogen ratio increases.

NITROGEN-CARBON RESIDUE RATIO

The Conradson carbon-residue content is sometimes used as a measure of the asphalt contained in a crude oil. A correlation has been developed (*9*) for estimating the yield of 100-penetration asphalt from a crude oil. This yield equals 4.9 times the weight per cent of carbon residue. Another correlation has been suggested (*3*) between nitrogen content and carbon residue. The value for this ratio is 0.050 and is obtained by averaging the results for 1002 oils from widely distributed origins within the United States (*7*). Thus the asphalt content is approximately 100 times the nitrogen content.

The nitrogen-carbon residue relationship has been studied from the standpoint of the geological formation from which the oil originated. Such a breakdown of the 1002 oils, arranged in order of increasing age of formation, is shown in Figure 2. It is evident that the ratio is an approximation, and it must be used with caution for individual oils. However, it appears to have some validity when averaged for a large number of oils, and existence of such an approximation points again to the relationship between asphalt and nitrogen. It further suggests a generality of the premise that the bulk of nitrogen compounds in a crude oil are associated with the asphaltic fractions.

GEOCHEMICAL CORRELATIONS

The presence of the large amount of nitrogen in the heavy fractions probably has geochemical significance, but widely different interpretations may be made. For those who believe that asphaltic oils are young oils, the process of maturation includes elimination of nitrogen, and the asphalt is the less mature portions of the oil, which contain the expected high

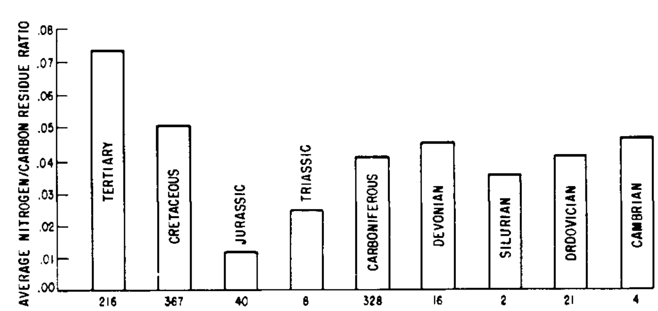

Figure 2. Nitrogen-carbon residue relationship in petroleums from different geological strata

content of nitrogen. For those who wish to take the opposite view, asphalt may result from polymerization or condensation of the more reactive parts of the oil, and nitrogen would be expected to join these reactions.

Figure 2 depicts averages of the nitrogen-carbon residue ratio for oils produced from formations of different geologic ages. The number of oils entering into the averages for each period is given below the bar representing the ratio, so that greatest importance can be attached to those bars representing a large number of oils. It is apparent that oils from younger formations (Tertiary and Cretaceous) have higher ratios than those from the older formations, and oils from formations older than Triassic have a fairly constant value. This suggests that the ratio is significant in assessing the age of a petroleum.

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Neopentane and Cyclobutane in Western Venezuelan Crude Oils

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The presence of neopentane in crudes has been reported (*3*) and a quantitative method of analysis has been published (*4*). However, its presence is rarely reported in crude analyses and it is generally believed that the compound does not occur in most crudes. Cyclobutane has never been reported and probably does not occur naturally. A thorough investigation of straight-run refinery isopentane stream obtained from a western Venezuelan crude rich in naphthenes has shown that neopentane and/or cyclobutane are present in small amounts in certain crudes.

DETECTION AND QUANTITATIVE DETERMINATIONS

The routine gas chromatographic analysis of a virgin refinery isopentane stream derived from Bachaquero crude revealed two unidentified peaks in very low concentration. The chromatogram, presented in Figure 1, shows these two peaks, *A* and *B*, relative to the known constituents in the sample. This chromatogram was obtained with a standard Perkin-Elmer vapor fractometer. Resolution of the components was obtained using two columns in tandem. The columns consisted of 2 meters of tetraisobutylene on Celite followed by 2 meters of

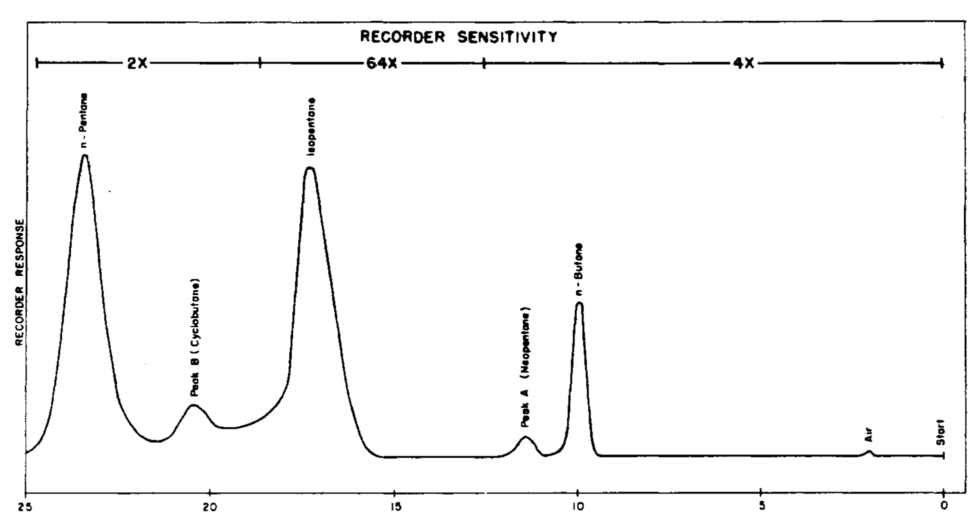

Figure 1. Gas chromatogram of refinery virgin isopentane using a two-stage column at 75° F.