Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Characterization of Thermal Diffusion Fractions of Petrolenes from a Mid-Continent Asphalt

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Methods previously used for the fractionation of asphalts have utilized solvents (*4*, *19*, *20*), adsorption (*10*), and chemical reaction (*17*), as well as various combinations of these (*5*, *15*). Most of the work has been directed toward intercomparison of a variety of asphalts, and ultimately toward correlation of the amounts of the fractions with service characteristics. Thermal diffusion sorts molecules on a different basis from methods previously applied to asphalts—namely, on the basis of molecular shape (*7–9*). It was of interest, therefore, to determine whether or not materials having viscosities as high as those of asphalts could be fractionated by thermal diffusion and if so, what molecular shapes would be sorted out in the process.

The thermal diffusion fractionation of petrolenes (*n*-pentane-soluble fraction) from a typical mid-continent asphalt prepared from a distillation residuum, has been accomplished. Ten fractions having widely different properties have been produced. The characterization of these fractions by elemental analysis, viscosity measurements, infrared spectrometry, nuclear magnetic resonance, and electron paramagnetic resonance reveals some properties which shed new light on the nature of the most viscous part of petroleum.

EXPERIMENTAL

Most applications of thermal diffusion to the fractionation of petroleum liquids have been concerned primarily with materials that are reasonably free flowing at room temperature. O'Donnell (*15*) used thermal diffusion to separate further some saturate oil fractions obtained from asphalt waxes. In general, the more viscous a material is, the more difficult it is to fill a conventional thermal diffusion column with it and to remove the fractions after separation has been accomplished. Therefore, the number of thermal diffusion experiments dealing with materials such as asphalt petrolenes has been limited.

An important factor not generally realized by many investigators is that a given thermal diffusion column has greater separating ability for more viscous materials than for less viscous ones, other conditions being equal. Debye (*1*) has presented an excellent discussion of this as related to apparatus dimensions and charge-stock properties.

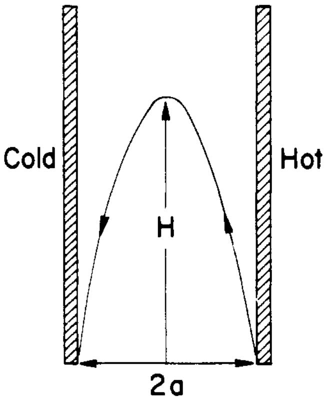

Figure 1. Diffusion path

Figure 1 illustrates the path a molecule takes in an idealized thermal diffusion column, when that molecule is the type which concentrates in the direction of the cold wall. The maximum height the molecule travels in the column before starting its downward path is designated by H. H may be determined from the relationship:

$$H = \frac{\alpha \rho g a^4}{24 \eta D}$$

α = coefficient of cubical expansion
ρ = density
g = gravity constant
a = 1/2 slit width
D = thermal diffusion constant
η = viscosity

The smaller the value of H, the greater is the separating ability of the column for that type of molecule. Therefore the separating ability of a given column is proportional to the viscosity of the liquid medium being processed. This enhancement of separating ability should make possible the effective fractionation of highly viscous materials such as asphalt petrolenes by thermal diffusion within a reasonable time.

However, the upper temperature limit of thermal diffusion column operation is determined by the thermal stability of the material being processed. Asphalts which are produced by solvent precipitation methods may be so hard that temperatures high enough to make them free flowing in the thermal diffusion column might cause degradation of the asphalt by thermal cracking.

The thermal diffusion apparatus used in this study is similar to that previously described (*9*) but differs in that it is made from smaller diameter tubing and its annulus contains a volume of 11 ml. instead of 22.5 ml. The annulus is essentially the same (0.010 inch). The column height is 56 inches. The inner tube of the concentric pair is cooled by water maintained at 185 °F. by means of a heat exchanger. The outer hot wall is electrically heated and was kept at 255 ° F. for this experiment. The column is equipped with 11 withdrawal ports located 5.6 inches apart to permit the removal of the annulus contents into 10 separate fractions. Each fraction has a volume of 1.1 ml.

The column was filled with petrolenes which were extracted from a standard 85 to 100 penetration paving material prepared from a blend of Illinois and Oklahoma crudes by oxidation of a 200 penetration vacuum distillation residuum. Inspections of the asphalt are shown in Table I. The petrolenes were extracted by using a 50 to 1 volume ratio of *n*-pentane to asphalt.

In order to facilitate filling of the thermal diffusion column with the petrolenes the entire apparatus was preheated to 212 ° F. Petrolenes were fed to the second port from the top through a heated funnel and connecting tubing.

Table I. Inspections of Asphalt Used

Specific gravity, 77°	0.997
Viscosity, SF	
at 300°	110
at 250°	443
Soft point R & B, °F.	119
Penetration,	
77°—100 grams—5 sec., DMM	88
32°—200 grams—60 sec.	21
Loss on heating, 325°, 50 grams, 5 hours, %	0.005
Flash point (COC), °F.	660
Fire point (COC), °F.	710
Asphaltenes, wt. %	17.6
Resins, wt. %	52.8
Oils and waxes, wt. %	28.6

After 2 days the column was completely full, as evidenced by a steady flow of petrolenes from the uppermost port. The inner tube was then connected to the hot water supply (185 °) and the temperature of the outer tube was raised to 255 ° F. These conditions were maintained for 22 days. At the end of this time 10 fractions were removed from the apparatus, starting from the top of the column. The material representing the bottom four fractions required infrared heating of the sampling ports in order for it to flow out of the column. Four days were required to empty the apparatus.

Infrared spectra were obtained with a Perkin-Elmer Model 21 double beam spectrophotometer. Fractions 1 to 8 were run as viscous liquids in a demountable cell, using a spacer of 0.05-mm. thickness. Variations in cell thickness were checked and corrected by using relative absorbances of C—H bands (*14*). Fractions 9 and 10 were run in a 0.1-mm. fixed cell as 43.6 weight % solutions in carbon disulfide, using a solvent blank. Viscosities were measured by the sliding-plate microviscometer of Labout and Van Oort (*11*). Thermal diffusion separation and the above measurements were made by The Standard Oil Co. (Ohio) research personnel.

Humble Oil and Refining Co. research personnel made molecular weight measurements by ebullioscopic methods, carbon-hydrogen determinations by standard combustion methods, and nuclear magnetic resonance (NMR) and electron paramagnetic resonance measurements. A Varian Model V-4300B high resolution NMR spectrometer was used. The electron paramagnetic resonance spectrometer was assembled in their laboratory.

DISCUSSION

Analytical data for the thermal diffusion fractions are summarized in Table II. Fractions are numbered from the top of the column downward. Because of the limited amount of sample (1.1 ml.), oxygen, sulfur, and nitrogen were not determined separately, but are lumped together in a single figure, obtained by difference. The relative proportions by weight of these elements in the feed were 2.0/1.0/0.4. For purposes of subsequent calculations, the same proportions were assumed to hold in each of the thermal diffusion fractions. Figure 2 shows that there is a distinct decrease in hydrogen content from fraction 1 to fraction 10. This decrease is balanced by a comparable increase in the sum of oxygen, sulfur, and nitrogen, and a very slight increase in carbon content.

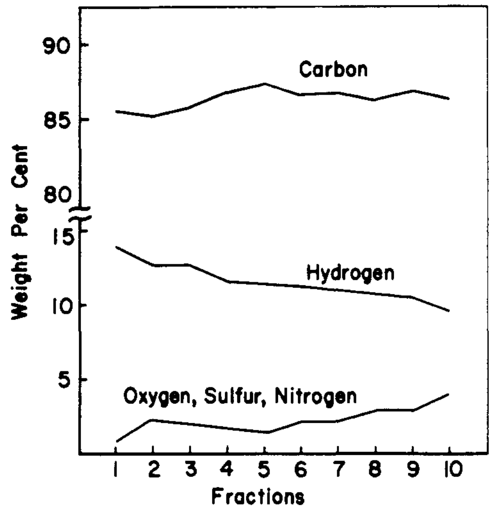

Figure 2. Elemental analyses

The molecular weights of the fractions listed in Table II illustrate the difficulty of obtaining good values from small samples in this range of molecular weight. Variations by a factor of 2 in replicate determinations are not unusual. As a result of the large variability, not too much reliance should be placed in the data shown here. They are useful in showing the order of magnitude of molecular weights of the various fractions but should not be used to draw conclusions concerning the degree of mass fractionation obtained in the experiment. When narrow boiling range lubricant fractions are thermally diffused in the type of apparatus used here, there is essentially no fractionation of molecular weight (*7, 13*). In general, in complex mixtures such as this petrolene fraction, shape differences between molecules may be expected to be more important in governing the separation than are mass differences.

Viscosity measurements obtained by the sliding-plate microviscometer (Figure 3) show a considerable increase in viscosity in going from the top fractions to the bottom. Fraction 10 is about 30,000 times more viscous (at 100 ° F.) than fraction 2. This difference in viscosity is primarily a result of the difference in the average shapes of the molecules in the respective fractions, rather than their size. The optical and magnetic measurements, discussed below, characterize to a large extent the types of molecular structures which are responsible for these large differences in viscosity.

Results of infrared examination of the fractions are shown in Figure 4. Because of their high viscosity and intense color, fractions 9 and 10 were run under different conditions as to cell thickness and concentration than

Table II. Analytical Data

Fraction	Carbon, %	Hydrogen, %	O.S.N. by Diff., %	Mol. Wt.	Viscosity at 100 °F., Poises (5×10^{-2} Sec.$^{-1}$)
1	85.31	13.99	0.70	1070	....
2	85.11	12.65	2.24	950	2.5×10^2
3	85.37	12.66	1.97	1150	2.7×10^2
4	86.77	11.60	1.63	1560	1.2×10^3
5	87.30	11.40	1.30	1695	2.1×10^4
6	86.59	11.25	2.16	760	3.9×10^4
7	86.87	10.98	2.16	1160	2.8×10^5
8	86.41	10.73	2.86	...	1.8×10^6
9	86.96	10.41	2.69	3000	3.4×10^6
10	86.37	9.52	4.11	3800	7.0×10^6

were fractions 1 to 8. Absorbances were corrected on a linear basis to the same conditions, but curves are shown in dotted lines to indicate that the results may not be strictly comparable.

Absorbance curves of three bands at 11.45, 12.30, and 13.42 microns were of similar magnitude and essentially parallel; so only one is shown in Figure 4. These bands are attributed to substituted aromatics (*2, 12, 18*). Their positions suggest 1,2-di-, 1,2,4-tri-, 1,2,3,4-tetra-, 1,2,4,5-tetra-, and 1,2,3,4,5-penta- substitution, as listed by Friedel and Queiser (*2*). The substituent groups could be alkyl chains, methyl groups, co-condensed aromatic nuclei, or co-condensed saturated cyclic nuclei.

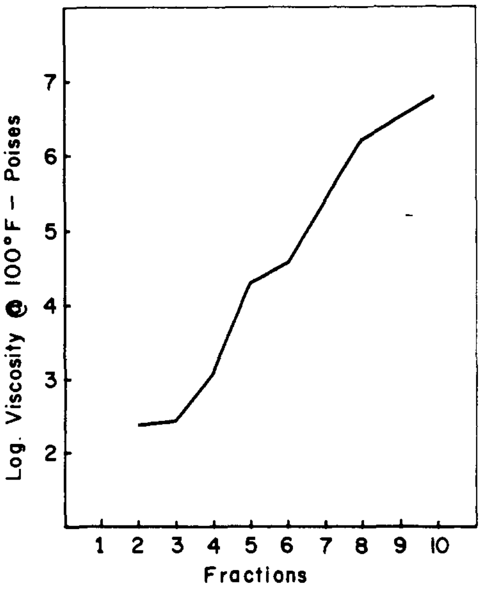

Figure 3. Viscosity of fractions

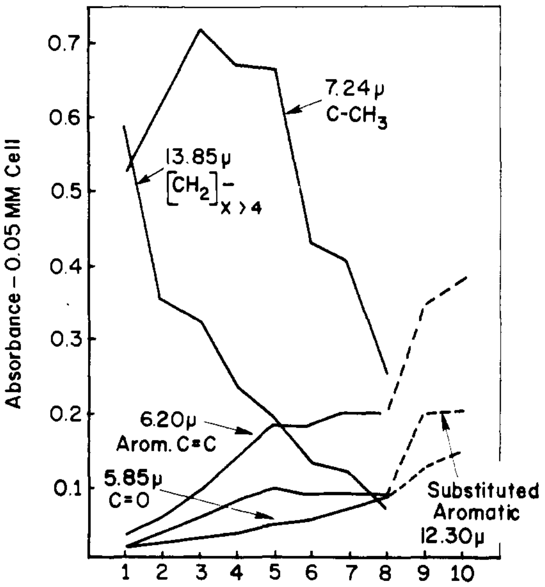

Figure 4. Infrared absorptions

The infrared data indicate that fraction 1 contains small amounts of aromatic, and a very small concentration of carbonyl compounds. It contains a large proportion of polymethylene chains and of CH_3 groups. Using a method similar to that of Hastings and others (*3*), but based on peak absorbances, it is estimated that the polymethylene chains contain not less than 13 methylene units, and that there is present about one CH_3 group per each eight carbon atoms.

In going down the column, the absorbances indicate a rapid diminution in the concentration of polymethylene chains, accompanied by an increase in highly substituted aromatics and carbonyl compounds. The CH_3 absorption first increases, then very sharply decreases. For fraction 5 there is estimated on the above basis to be present about one CH_3 group for each six carbon atoms. Polymethylene chains still contain at least six methylene units. Evidence was also noted, but is not plotted, for very small concentrations of OH groups in the heavier fractions.

Nuclear magnetic resonance data, shown in Table III and Figure 5, give a more quantitative picture of the composition of the fractions. Because of the presence of large concentrations of saturates in admixture with aromatics in most fractions, alkyl groups alpha to aromatic rings could not be resolved. Two types of measurements were possible, the alkyl branchiness index and the relative concentrations of aromatic ring hydrogen and total alkyl hydrogen. To calculate carbon in aromatic rings, it was necessary to assume that the carbon-hydrogen ratio for saturates in fractions 2 to 10 was constant and the same as for fraction 1, in which no aromatic material was detected. Car-

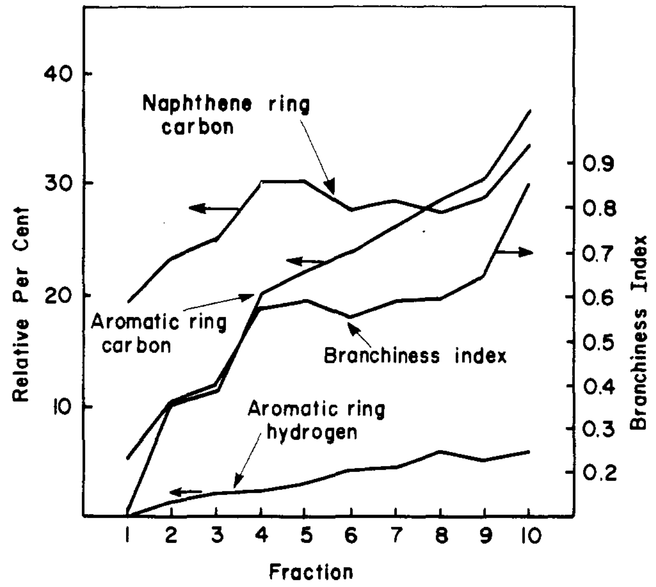

Figure 5. NMR derived data

Table III. NMR and EPR Data

Fraction	Branchiness Index	Branchiness Ratio	Relative % C in Naphthene Rings: Aliphatic portion	Relative % C in Naphthene Rings: Total sample	Relative % C in Aromatic Rings	Relative % Hydrogen: Total alkyl	Relative % Hydrogen: Aromatic	Unpaired Electrons per Carbon Atom
1	0.229	−0.270	19.5	19.5	0.0	100	0	Nil
2	0.358	−0.004	26.4	23.7	10.2	99	1.0	Nil
3	0.397	0.076	28.5	25.3	11.4	98	2.0	2×10^{-7}
4	0.575	0.442	38.0	30.2	20.2	97.7	2.3	1.2×10^{-6}
5	0.590	0.473	38.8	30.2	22.2	97.0	3.0	7.3×10^{-6}
6	0.553	0.397	36.8	27.8	24.0	95.8	4.2	1.3×10^{-5}
7	0.587	0.467	38.7	28.6	26.2	95.6	4.4	1.9×10^{-5}
8	0.592	0.477	38.9	27.7	28.7	94.1	5.9	3.9×10^{-5}
9	0.646	0.588	41.8	29.0	30.4	94.8	5.2	4.2×10^{-5}
10	0.860	1.029	53.3	33.7	36.7	94.1	5.9	4.8×10^{-5}

bon in naphthene rings was estimated through its correlation with branchiness index (*22*). This involves the further assumption that the correlation holds for aromatic alkyl groups as well as for saturates. This assumption leads to only minor errors where the aromatic concentration is relatively low.

In fraction 1, about 20% of the carbon is indicated to be present in naphthene rings. In going down the column, naphthene ring carbon increases fairly regularly. Aromatic ring carbon is shown to increase from zero in fraction 1 to some 37% of the total carbon in fraction 10. This is a considerably more rapid increase than that of aromatic ring hydrogen, an indication that the aromatics are highly condensed, highly substituted, or perhaps both.

Values for the concentration of unpaired electrons as determined by electron paramagnetic resonance (*21*), are plotted in Figure 6. The existence of free radicals in samples similar to these has been reported (*6*, *16*). From a structural point of view, compounds capable of existence as extremely stable free radicals are condensed polymeric ring structures (*16*). This then is additional evidence for the presence of condensed aromatic ring structures in fractions 5 to 10.

Because so little is actually known about the compounds present in asphalt, it is of interest to go one step further and postulate what structures best represent the present data. Empirical formulas and other pertinent information calculated from the data of Tables II and III are shown in Table IV. Infrared results were used to estimate the total number of methyl groups.

Figure 7 shows structures which agree well with the data for fraction 1. These structures are drawn with the full realization that they represent merely possible average structures, and that individual molecules may differ widely from those shown. Nevertheless, they serve better than words or numbers to illustrate the relative proportions of alkyl chains and naphthenic rings, as well as the probable average degree of branching and substitution. The picture, then, for fraction 1 is that of lightly branched paraffin chains and heavily branched naphthene rings. A small fraction of the molecules contains sulfur or nitrogen in unknown configuration, and nearly one third contain oxygen, probably in ketonic form.

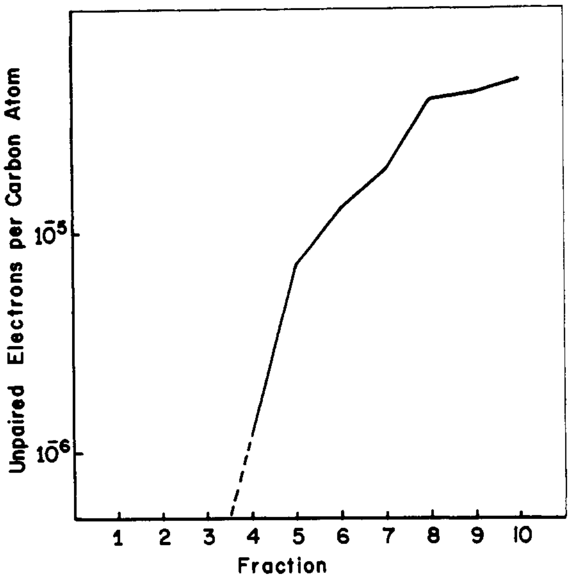

Figure 6. EPR data

The structure shown in Figure 8 represents closely the data for fraction 5. Earlier data of Williams (*22*) have been used to indicate the number of aromatic nuclei per molecule. In conformity with infrared results, alkyl chains are pictured as mostly normal, with most of the methyl group branches being on rings. A lesser degree of substitution or condensation of aromatic nuclei would give too high aromatic ring hydrogen content. About four molecules in ten contain either a sulfur or nitrogen atom, possibly in heterocyclic rings. About eight molecules in ten contain an atom of oxygen.

$C_{76}H_{150}S_{0.07}N_{0.06}O_{0.3}$

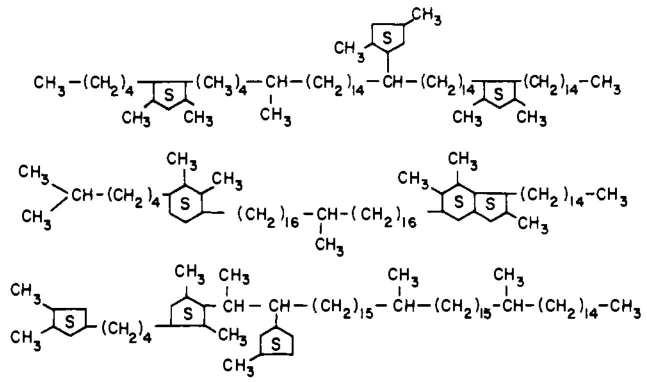

Figure 7. Hypothetical average structures in fraction 1

$C_{124}H_{194}S_{0.2}N_{0.18}O_{0.8}$

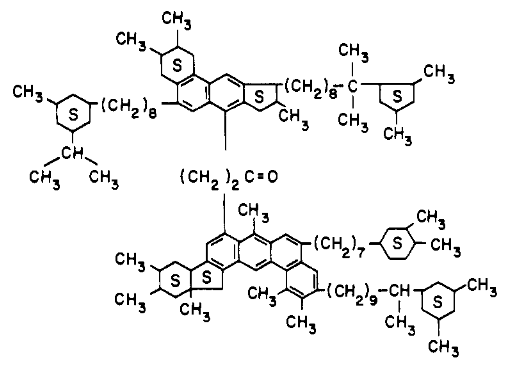

Figure 8. Hypothetical average structure in fraction 5

Table IV. Derived Structural Data

Fraction	1	5	10
Empirical formula	$C_{76}H_{150}S_{0.07}N_{0.06}O_{0.3}$	$C_{124}H_{194}S_{0.2}N_{0.18}O_{0.8}$	$C_{274}H_{362}S_{1.4}N_{1.3}O_{5.7}$
Carbon, atoms/molecule			
Aromatic ring	0	27	101
Naphthenic ring	15	37	92
Alkyl			
CH_3	9	21	81
Other	52	39	
Hydrogen, atoms/molecule			
Aromatic ring	0	6	21
CH_3	27	63	341
Other	123	125	

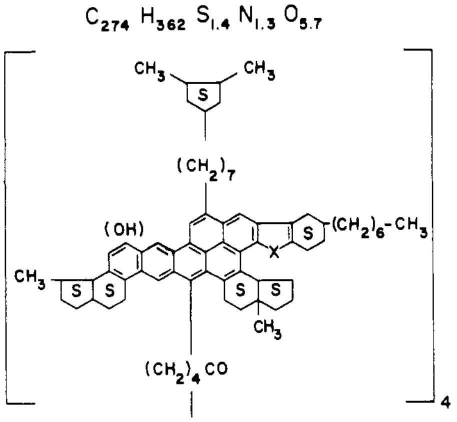

Figure 9. Hypothetical average structure in fraction 10

For fraction 10, a still higher degree of condensation of both aromatic and naphthenic rings would seem to be required, as shown in Figure 9. Most of the nuclei contain an atom of sulfur or nitrogen, and one or two atoms of oxygen are pictured as present per nucleus, either as carbonyl or hydroxyl groups.

These structures indicate that the degree of linearity of the molecules decreases from the top to the bottom fraction, in conformity with thermal diffusion results with less complex, lower molecular weight materials.

ACKNOWLEDGMENT

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Some Chemical Aspects of the Components of Asphalt

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Asphaltic bitumen is a colloidal dispersion of compounds of high molecular weight of varying composition in oils also of diversified constitution. Both the dispersed and dispersing materials contain, in addition to hydrocarbons, appreciable amounts of compounds containing oxygen, sulfur, and nitrogen. Traces of vanadium, nickel, and other elements are also present. Thus, because the types of compounds and their molecular weights cover wide ranges, it is difficult to learn much about the composition from tests on the entire asphalt. However, useful information is being obtained by solvent fractionation of asphalts followed by investigation of the chemical composition and physical properties of the separated components. This characterization of the fractions should be helpful in explaining differences in the properties of the asphalts.

PREPARATION OF COMPONENTS

In the work described, components from asphalts of 50 penetration at 77° F. were studied extensively. The three asphalts were prepared by airblowing vacuum reduced residua from typical Texas crudes and represent the following

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