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	

$C_{274}H_{362}S_{1.4}N_{1.3}O_{5.7}$

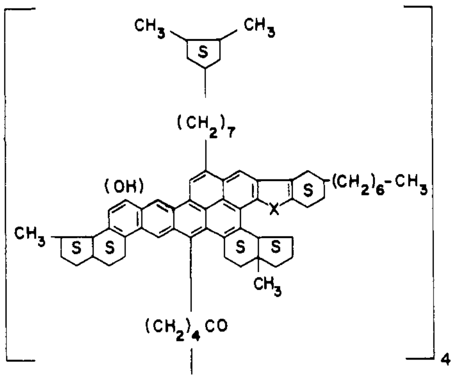

Figure 9. Hypothetical average structure in fraction 10

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.

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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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types: a gel-type asphalt which shows considerable non-Newtonian flow, a sol-type asphalt which is essentially a Newtonian liquid, and an intermediate type classified as sol-gel.

The physical and rheological properties are shown in Table I.

Table I. Properties of Asphalts

	Gel	Sol-Gel	Sol
Specific gravity at 77°F.	0.986	1.028	1.014
Softening point, R & B, °F.	149	140	128
Penetration			
At 32°F.	27	21	15
At 77°F.	51	50	49
At 115°F.	117	166	270
Viscosity at 77°F., megapoises	27	12	4.4
Degree of complex flow c *(3)*	0.55	0.75	1.0

Three components from each typical asphalt were obtained by solvent fractionation using a method proposed by Traxler and Schweyer *(4)*. The procedure consisted of the following steps:

Separating the asphaltics as the precipitate from a 1-butanol extraction at 122°F., using a solvent to sample ratio of 20 to 1. The asphaltics are black, and range in nature from semisolids to friable solids.

Removing the paraffinics as the raffinate from an acetone extraction of the 1-butanol extract using a solvent to sample ratio of 35 to 1 at −10°F. The paraffinics are dark colored viscous oils.

Recovering the cyclics from the acetone extract. The cyclics are also viscous oils and frequently are lighter in color than the paraffinics.

Yields of each component from the three asphalts are given in Table II.

Table II. Yields of Components

	Gel	Sol-Gel	Sol
Asphaltics, %	30	39	20
Cyclics, %	11	24	36
Paraffinics, %	59	37	44

CARBON TO HYDROGEN RATIOS

This ratio is an indication of chemical structure, since for hydrocarbons of a given molecular weight, naphthenic rings give a higher C/H ratio than paraffins, and aromatic rings have a higher ratio than naphthenic rings. From the data on C/H values given in Table III it appears that the aromatic content is largest in the "asphaltics" and smallest in the "paraffinics." The asphaltics and cyclics from the sol asphalt have high C/H ratios. The close agreement for the ratios found for the three components of the intermediate or sol-gel type asphalt may be significant.

Table III. Carbon to Hydrogen Ratios of Components

	C-H Ratio		
	Gel	Sol-gel	Sol
Asphaltics	8.6	7.7	8.9
Cyclics	7.5	7.5	8.6
Paraffinics	7.3	7.3	6.9

The sol asphalt is an essentially Newtonian liquid which indicates good dispersion or solvation of the high molecular weight compounds by the oils present. The powerful dispersing action of the oils in this asphalt probably is related to the high percentage of cyclics (36%) present and to their high aromaticity as indicated by the C/H value of 8.6. The low percentage of asphaltics (20%) possessing a high aromaticity as indicated by the C/H value of 8.9 may also contribute to the sol characteristics. On the other hand, the gel-type asphalt has a high asphaltics content (30%) with a C/H value of 8.6 and an extremely low cyclics content (11%) having a C/H value of only 7.5. Both of these facts may account for the poor dispersion in this asphalt resulting in gel characteristics (non-Newtonian flow).

SULFUR CONTENT

The sulfur contents of the three typical asphalts and each of their components are given in Table IV. The sulfur contents of the sol-gel asphalt and all of its components are high compared with the other two asphalts. Sulfur is concentrated in the asphaltics and usually is lowest in the paraffinics. The sol-gel asphaltics have a sulfur content which is equivalent to about 1.25 atoms of sulfur for each molecule. The importance of sulfur, as well as that of oxygen and nitrogen, is not fully understood, but more extensive investigations may clarify the significance of the compounds containing these elements in respect to the properties of the asphalts.

Table IV. Sulfur Contents of Asphalts and Components

	Per Cent Sulfur		
	Gel	Sol-gel	Sol
Asphalt	0.63	3.34	0.67
Asphaltics	1.02	4.84	1.03
Cyclics	0.66	3.56	0.51
Paraffinics	0.48	2.31	0.53

REFRACTIVE INDEX, SPECIFIC GRAVITY, AND MOLECULAR WEIGHT

From Table V it is evident that the components from the gel asphalt have the lowest specific gravities and refractive indices. The paraffinics and cyclics from the sol asphalt have the highest specific gravities and refractive indices, but the asphaltics from the sol-gel asphalt possess the highest specific gravities. Because of the high viscosity and dark color of the asphaltics, it was not possible to determine their refractive indices.

Mean molecular weights (Table V) were estimated from the viscosities of dilute solutions *(1)*. Although the values are not considered to be very accurate, the magnitude of the molecular weights is of interest.

The relatively high molecular weight of the asphaltics from the gel asphalt may have a bearing on its colloidal properties. It has been found from other work that paraffinic oils (which have low refractive indices) are poor solvents or dispersing agents for asphaltics and are not strongly adsorbed to the heavy bodies in the asphalt. This could explain the colloidal characteristics of the gel asphalt, as it contains a relatively large amount of asphaltics of high molecular weight and a large percentage of paraffinics.

On the other hand, the sol-type asphalt contains a smaller percentage of asphaltics of relatively low molecular weight. Also, the paraffinics content of the sol-type asphalt is

Table V. Physical Properties of Components

	Gel	Sol-Gel	Sol
Asphaltics			
Yield, %	30	39	20
Specific gravity at 77°F.	1.063	1.096	1.076
Mean molecular weight	1150	850	750
Cyclics			
Yield, %	11	24	36
Refractive index, 158°F.	1.538	1.547	1.554
Specific gravity at 77°F.	0.989	0.998	1.016
Mean molecular weight	400	450	300
Paraffinics			
Yield, %	59	37	44
Refractive index, 158°F.	1.515	1.527	1.541
Specific gravity at 77°F.	0.948	0.966	0.981
Mean molecular weight	600	600	650

small as compared to that of the gel asphalt and has a higher refractive index than the paraffinics from the gel type. Finally, the cyclics content of the sol asphalt is high and the refractive index is the highest obtained for any of the components investigated.

PARAFFINICS COMPARED WITH EXUDED OIL

The staining of paper or other porous material by certain hard gel-type asphalt is caused by syneresis of a portion of the oil composing the continuous phase of the asphalt. A large number of cigarette paper disks stained by contact (2) with a hard gel asphalt were extracted with pentane to recover the oily material. Evaporation of the pentane solution gave a small amount of a dark red-brown very viscous liquid. Analysis of the oil is compared in Table VI with that of the paraffinics obtained by the component analysis method from the gel asphalt discussed above. It appears that the oil exuded by the asphalt in the stain test is even more paraffinic in its properties than the paraffinics obtained by solvent fractionation.

Ultraviolet analysis of the oil extracted from the paper indicated that aromatics were present only in small amounts. Infrared analysis also showed that the oil recovered from the stained papers was primarily saturated hydrocarbons. However, the presence of small amounts of aromatic hydrocarbons, and carbonyl groupings was also indicated.

Table VI. Properties of Oils

	Extract from Stained Paper	Paraffinics
Refractive index, 158 °F.	1.495	1.515
Specific gravity at 77 °F.	0.883	0.948
Viscosity at 210°F., centistokes	85	195

INFRARED ANALYSIS OF COMPONENTS

Infrared examinations were made of each component from the gel, sol-gel, and sol asphalts. Spectra of the three-component fractions from the three asphalts (nine samples) were recorded in the spectral region of 2.5 to 15 $m\mu$. Most of the spectral data were obtained with a modified Perkin-Elmer Model 12B spectrometer using a sodium chloride prism. The asphalt components were dissolved in C.P. grades of carbon tetrachloride or carbon disulfide. Comparison and structural interpretation of the spectra using correlations given in the literature made possible the following conclusions.

The asphalts can be distinguished and identified by the infrared spectra of their components.

The spectra of the components of a particular asphalt show different amounts of the same structural groups.

A particular component from different asphalts shows the presence of different structural types.

Asphaltics from a given asphalt have fewer CH_3 and CH_2 groups per unit weight than do the cyclics and paraffinics.

Dimethyl groups attached to a single carbon atom occur in all components but are more concentrated in the sol asphalt.

Table VII. Carbon Linkages in Fractions of Asphalt

	Gel	Sol-Gel	Sol
Asphaltics			
Carbon in aromatic rings, %	58	39	60
CH_3 groups, %	9	7	9
CH_2 groups (chains), %	30	25	26
Other carbon linkages, %	3	29	5
	100	100	100
Cyclics			
Carbon in aromatic rings, %	24	20	27
CH_3 groups, %	12	12	12
CH_2 groups (chains), %	36	33	27
Other carbon linkages, %	28	35	34
	100	100	100
Paraffinics			
Carbon in aromatic rings, %	14	14	21
CH_3 groups, %	12	12	13
CH_2 groups (chains), %	51	43	40
Other carbon linkages, %	23	31	26
	100	100	100

The results are in accord with the current concept that asphalts are composed of large molecules formed by alkyl-substituted, fused aromatic and naphthenic nuclei, such as Tetralin, joined by methylene chains. A considerable number of the molecules contain O, S, or N atoms. The data obtained by infrared analysis and presented in Table VII show the same general trend as the C/H ratio.

The per cent of carbon in aromatic rings indicates the highly aromatic nature of the asphaltics. The sol asphalt is highest in aromatic rings in each component.

The amount of CH_3 (terminal) groups is about the same for the paraffinics and cyclics from each of the asphalts. CH_3 groups are low in the asphaltics fraction from each asphalt.

Paraffinic CH_2 groups (side or connecting chains) are considerably higher in the paraffinics than in the asphaltics or cyclics. Generally, the amount of such CH_2 groups in all of the components tends to decrease in the order of gel, sol-gel, and sol asphalts.

The amounts of "other carbon linkages" shown in Table VII were obtained by difference. Naphthenic linkages probably account for most of this material, which is very low in the asphaltics from the gel and sol asphalts.

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