Influence of Composition of Paving Asphalt on Viscosity, Viscosity-Temperature Susceptibility, and Durability

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The separation of petroleum residues on the basis of molecular size and chemical type is a complex study in which many problems remain unsolved. The residues may be subdivided into broad groups of compounds at various molecular weight levels. The composition of paving asphalts is described in terms of molecular weight and molecular type distribution; composition is related to viscosity, viscosity-temperature susceptibility, and durability or resistance to hardening.

SEPARATION OF ASPHALTS

The four asphalts studied were separated in terms of molecular size and definite chemical classes of compounds. Most methods of separation into chemical types lose sharpness when applied to mixtures with a broad distribution of molecular weights. The asphalts studied contain material ranging from 350 to 5000 molecular weight. To enhance the sharpness of separation into chemical types, a separation on the basis of molecular size is first made by molecular distillation. The individual distillation fractions having fairly narrow molecular weight spreads are separated by chromatography over silica gel into three type fractions: saturated hydrocarbons, aromatic hydrocarbons, and heterocyclic and polar compounds containing most of the sulfur, nitrogen, and oxygen which has been designated as "resins" for convenience. The residue from the molecular distillation is generally a very hard material of high molecular weight; it is separated into an oil fraction and a solid powder (designated as asphaltenes) by solvent precipitation with 40 volumes of 2-methylbutane (isopentane). The oil fraction may be further molecularly distilled or separated directly by silica gel chromatography into saturates, aromatics, and resins as were the distillation fractions. The asphaltenes consist in a large part of high molecular weight aromatic and heterocyclic compounds whose further separation into distinct classes of compounds is beyond the scope of a routine separation. A schematic diagram of the separation is shown in Figure 1.

The experimental details of these separation procedures have been published (7), and only a brief description is given here. The molecular distillations are carried out in 14- or 5-inch cyclic stills manufactured by Distillation Products, Inc., which permit distillation of high molecular weight material with minimum thermal hazard. In the chromatographic separation, silica
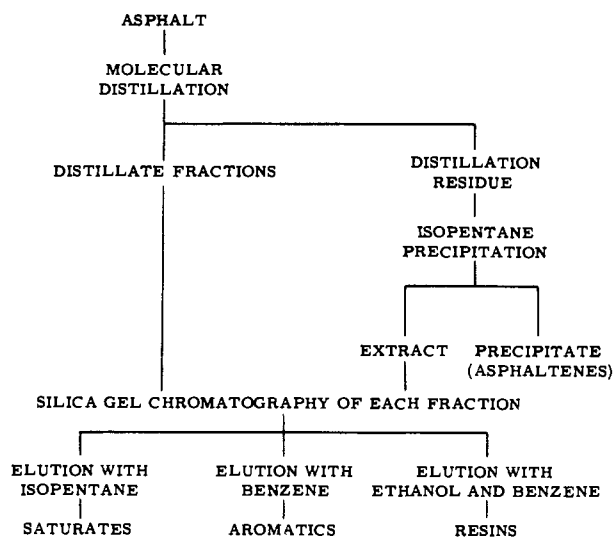
gel to oil ratios up to 50 to 1 are needed to obtain sharp separation, the highest ratios being required for the high molecular weight materials. The split between saturate and aromatic fractions is made by observing the ultraviolet absorption spectrum of the eluate at a wave length of 2650 A. When aromatics begin to be eluted, a rapid rise in absorption at this wave length occurs. By making the split when the extinction coefficient of the effluent is 0.1 liter per gram cm., an aromatic content of less than 0.2% is assured in the saturates.

The aromatics are removed with benzene, eluting until the benzene comes through colorless. Then a mixture of equal volumes of ethanol and benzene is used to remove the resins. Total recoveries generally amount to 98 to 100% by weight of charge. During the chromatographic separation of fractions above about 500 molecular weight, the eluate is protected from excessive exposure to oxygen and light to prevent oxidation of the aromatic and resin fractions.

In many cases when the separated fractions have been recombined; examination of the reconstituted product confirms that these separation procedures do not lead to changes in the properties of the asphalt.

MOLECULAR WEIGHT DISTRIBUTION

Ebullioscopic determination of the average molecular weights of molecular distillation fractions in benzene reveals interesting molecular weight distribution differences between asphalts of the same viscosity but from different crude sources. Figure 2 shows the molecular weight distribution in four asphalts having a nominal penetration of 200 mm./10 at 77° F. These asphalts are from a California coastal crude from the Santa Maria area, a California valley crude from the Bakersfield region of the San Joaquin Valley, a Venezuelan crude from the east coast of Lake Maracaibo, and a mid-continent lube crube from West Texas. All were manufactured by distillation of the crude without further processing or blending and are commercial products with the exception of the mid-continent asphalt. The average molecular weight of the first distillation fraction from these asphalts ranges from about 350 for the California coastal crude to about 1150 for the mid-continent crude, while the average molecular weight of the asphaltenes ranges from 2500 for the California valley asphalt to 4800 for the Venezuelan asphalt. This large difference in the molecular weight to which various crudes must be distilled to yield an asphaltic residue of a given viscosity is a result of differences in concentrations of the components which are reflected in the viscosity of the materials.
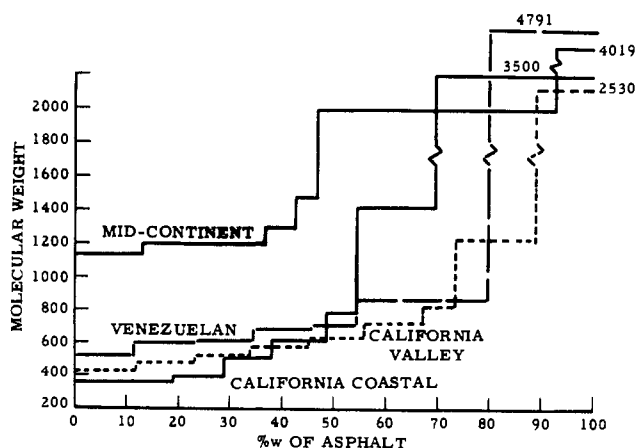

Figure 1. Schematic diagram of separation scheme

Figure 2. Molecular weight distribution

Elemental Composition. The sulfur content rises rapidly with increasing molecular weight in the case of the California coastal asphalt, less rapidly in the Venezuelan asphalt and hardly at all in the other two asphalts, as shown in Figure 3. Nitrogen content rises with increasing depth of distillation except in the case of the mid-continent asphalt as shown in Figure 4. The atomic ratio of hydrogen to carbon decreases from a level of 1.5 to 1.6 rather slowly with increasing depth of distillation, but drops to a level of 1.1 to 1.2 in the highest molecular weight fraction (distillation residue).

Viscosity of Asphalts. The flow properties of asphalts at various temperatures are among the most important characteristics of these materials with respect to conditions required for application as well as performance in use. Specification tests which are commonly used in asphalt testing describe the dependence of viscosity on temperature. Table I shows the results on the four asphalts discussed.

All of these specification tests give results in different units at different temperatures; hence, it becomes difficult to compare the flow properties of asphalt in this manner. Therefore, the authors measured viscosity in fundamental units over the temperature range from 32° to 285° F. At temperatures up to 140° F., all measurements were made with the sliding plate microviscometer (5) manufactured by Hallikainen Instruments, Berkeley, Calif. At high temperatures, viscosities were determined in a Lantz-Zeitfuchs reverse flow capillary viscometer (1).

Table II shows the viscosities of the four asphalts between 32° and 285° F. The variation of asphalt viscosity over this wide temperature range is plotted using the Walther (9) equation:

$$\text{Log log } (V_k + 0.7) = M \log T + b$$

where V_k is viscosity in centistokes, T is temperature in degrees absolute, and M and b are constants of the liquid. This equation is the basis for the ASTM viscosity-temperature charts for petroleum products which extend to 2×10^5 stokes. By extending the charts to 10^{12} stokes they are suitable for asphalts. The absolute viscosity in poises is obtained by introducing the density.

The viscosities of the four asphalts shown in Table II were plotted on the viscosity-temperature charts and the slope of the straight line obtained for each asphalt is shown in Table III. The California coastal asphalt, with a slope of –3.52 is the least temperature susceptible, and the California valley, with a slope of –4.20, is the most susceptible.

Viscosity of Distillation Fractions. The extremely wide range of viscosities covered by the distillation fractions of asphalts is demonstrated by the data for the fractions of the California coastal asphalt shown in Figure 5 which range from 0.3 poise to 130 billion poises at 140° F. The linear relation between log viscosity and molecular weight for the fractions of a given asphalt has been found to hold reasonably well for all asphalts examined, the slope and intercept of the line depending on the composition of the asphalt. This type of relation also holds for members of a homologous series of organic compounds (3). Only large differences in chemical constitution of the fractions with the same molecular weight but from different crudes can account for the variation in viscosity (Figure 5).

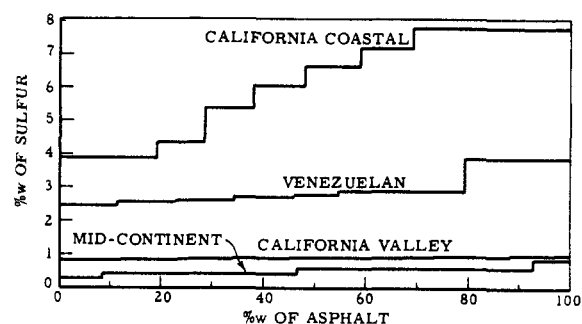Figure 3. Sulfur distribution

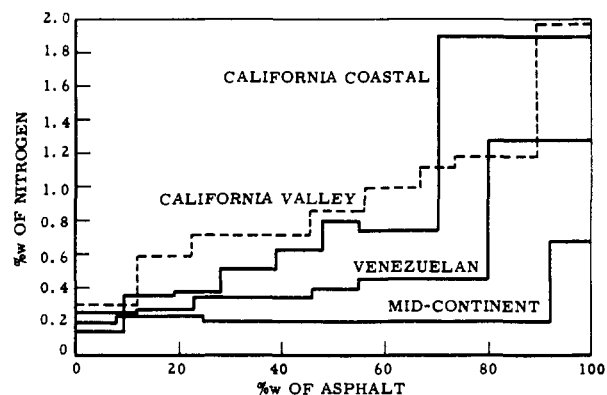

Figure 4. Nitrogen distribution

Table II. Measured Viscosities of Asphalts Over a Wide Temperature Range

(Viscosities in poises)

Temp., °F.	Venezuelan	California Coastal	California Valley	Mid-Continent
32	4.17×10^6	1.09×10^8	1.95×10^8	4.16×10^8
77	3.65×10^5	1.95×10^5	9.4×10^4	1.70×10^5
140	1.60×10^3	1.21×10^3	3.09×10^2	1.00×10^3
225	11.9	12.0	5.09	15.9
285	2.04	2.11	0.93	2.80

Viscosities at 140° F. and lower by sliding plate microviscometer at a shear rate of 5×10^{-2} sec.$^{-1}$.

Viscosities at higher temperature by reverse flow Lantz-Zeitfuchs capillary viscometer.

Table III. Slopes of the Viscosity-Temperature Plots Between 32° and 285° F.

	Venezuelan	California Coastal	California Valley	Mid-Continent
M from Walther equation	–3.59	–3.52	–4.20	–3.64

Table I. Asphalt Specification Tests Dealing with Flow Properties at Various Temperatures

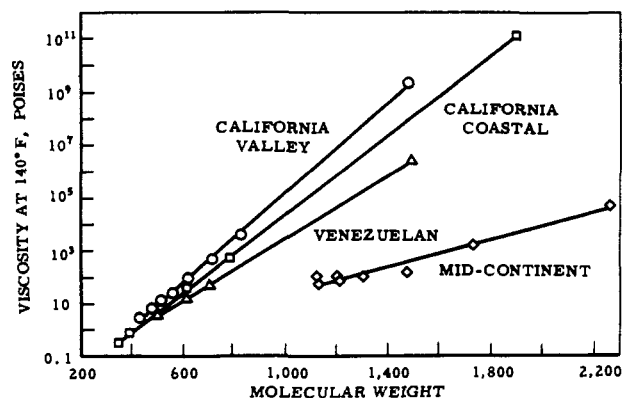|	Vene-zuelan	California Coastal	California Valley	Mid-Continent
Penetration at 77° F., mm./10 100 g. for 5 sec.	183	194	224	200
Softening point, ° F. ring and ball	103	105	97.5	102
Penetration index	–0.6	+0.1	–1.2	–0.5
Penetration at 39.2° F., mm./10 200 g. for 60 sec.	67	71	63	60
Pen. ratio = $\dfrac{\text{Pen. at } 39.2° \text{ F.} \times 100}{\text{Pen. at } 77° \text{ F.}}$	36.6	36.6	28.0	30.0
Saybolt-Furol viscosity at 275° F., seconds	125	129	58	175

Figure 5. Viscosity of distillation fractions

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The slopes of the viscosity-temperature plots calculated by the Walther equation for the molecular distillation fractions from these four asphalts are shown in Figure 6. In general, the susceptibility of viscosity to change with temperature decreases with increasing molecular weight, the most striking variance with molecular weight being shown by the Venezuelan asphalt fractions. The distillation fractions from the mid-continent asphalt show a low viscosity temperature susceptibility with practically no change with increasing molecular weight.

Microfilm Durability Test. One of the main factors determining the life of a paving asphalt is its ability to resist hardening as a result of oxidation and loss of volatile components. The degree to which an asphalt resists such changes is an indication of its durability relative to other asphalts when used under the same conditions. As a result of theoretical and experimental studies of the phenomena which lead to hardening of asphalts, Van Oort (8) devised an accelerated durability test designed to allow prediction of the hardening which an asphalt may be expected to undergo in use. The ratio of the final viscosity to the original viscosity is used as an aging index to express the durability of the material. A modification of this durability test (4), correlates reasonably well with field performance (6) of asphalts under identical conditions, and has been used to study the contribution of molecular size and type distribution to the durability of asphalts. The test consists of aging films of asphalt 5 microns thick on glass plates in an oven at 225° F. for 2 hours; the hardening which occurs is determined by measuring the viscosity of the material before and after with the sliding plate microviscometer. If the aging is carried out in a nitrogen atmosphere, the hardening observed is attributable to loss of volatiles only, while aging in air gives a measure of hardening due to oxidation as well as to loss of volatiles. The aging is conducted in the absence of light, because most of the asphalt films between mineral particles in road construction are in a dark environment.

Durability of Asphalts and Distillation Fractions. Application of the microfilm durability test to four asphalts yields the results shown in Table IV. Aging of the asphalts in nitrogen caused the viscosity to increase by only a very small factor in all but the California coastal asphalt in which it increased by a factor of 20, indicating that hardening by loss of volatiles is a serious problem in this asphalt. The actual viscosity of this asphalt increased during the test from 1.95×10^5 to 4.03×10^6 poises at 77° F. The relative vulnerability of this asphalt to hardening by loss of volatiles is indicated by the molecular weight distribution data.

Results of the microfilm durability test in air show that the California coastal asphalt hardens by a factor of 84 because of the combined effects of loss of volatiles and oxidation, but the others harden by a factor of 2.5 to 3.

The ratio of the air aging index to the nitrogen aging index is a measure of the hardening due to oxidation. This ratio for the California coastal asphalt is 4.1 while for the other three asphalts it varies from 1.9 to 2.5, showing that the California coastal asphalt also hardens more from oxidation than the others do.

The tendency of the individual molecular distillation fractions to volatilize under the conditions of the microfilm durability test was measured by determining the weight loss of the fractions of the California Coastal asphalt during the test in nitrogen as shown in Figure 7. The weight loss due to volatility amounts to 25 to 30% in the lowest molecular weight fractions.

To demonstrate the influence of the initial molecular weight on the durability of asphalt the molecular distillation residue of the California coastal asphalt was blended back with the distillation fractions to yield a series of products all with viscosities of about 8×10^5 poises but with successively higher initial molecular weights as a result of leaving out low molecular weight fractions. The aging indexes of these asphalts in air as a function of initial molecular weight are shown in Figure 8. From data of this type, it is concluded that the hardening of asphalts by the loss of volatile components may be effectively
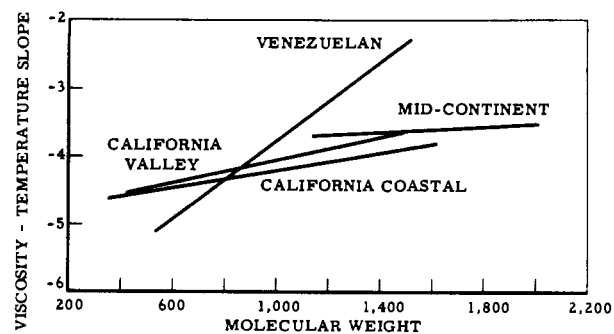

Figure 6. Viscosity-temperature slope of distillation fractions

controlled by eliminating components lower than 400 molecular weight from the products.

CHEMICAL TYPE DISTRIBUTION

The type distribution for a California valley asphalt, shown in Figure 9, is fairly typical of the decline of saturated hydrocarbon content with increasing molecular weight and the corresponding rise in both aromatic hydrocarbons and resins. At high molecular weights, the concentration of aromatics decreases because of the rapid rise of compounds containing sulfur,

Table IV. Hardening of Asphalts in the Microfilm Durability Test

	Venezuelan	California Coastal	California Valley	Mid-Continent
Aging index, nitrogen[a]	1.17	20.7	1.35	1.40
Aging index in air	2.91	84.5	2.50	2.80
Air aging index / nitrogen aging index	2.5	4.1	1.9	2.0

[a]Film 5 microns thick aged 2 hr. at 225° F.; viscosity determined at 77° F. in sliding plate microviscometer. Ratio of viscosity after aging to initial viscosity designated as aging index.
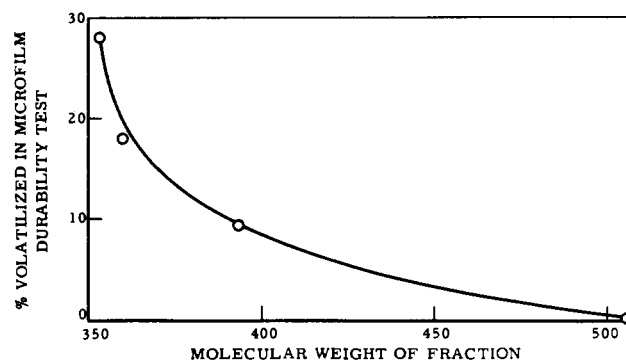

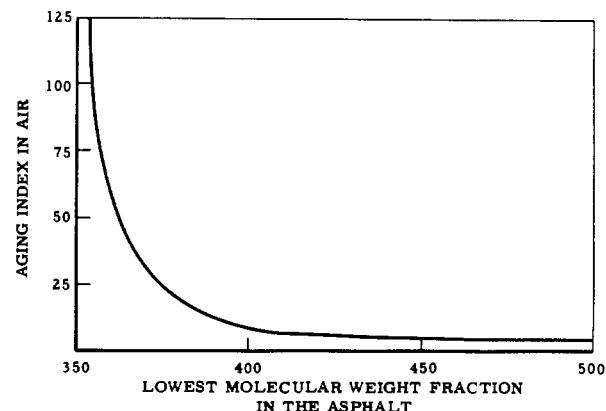Figure 7. Weight loss of distillation fractions of California coastal asphalt

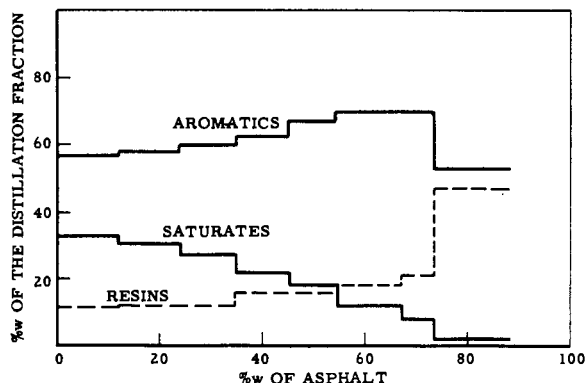Figure 8. Influence of initial molecular weight on durability

Figure 9. Hydrocarbon type composition of California valley asphalt

Table V. Average Hydrogen-Carbon Ratio (Atomic) of Chemical Type Fractions

Chemical Type Fraction	Hydrogen-Carbon Ratio			
	Venezuelan	California coastal	California valley	Mid-continent
Saturates	1.88	1.92	1.89	1.88
Aromatics	1.45	1.49	1.43	1.52
Resins	1.46	1.45	1.44	1.46

nitrogen, and oxygen which make up the resins. Although these trends are generally found, there are large differences between asphalts as demonstrated by the distribution curves for four asphalts shown in Figures 10 to 12. Note especially the low saturate content and high concentration of aromatics in the initial fractions of the mid-continent asphalt relative to the others.

From the data shown in Figures 10 to 12, a summary of the composition of each asphalt may be derived as shown in Figure 13. The outstanding differences between these four asphalts are the wide spread in asphaltene content ranging from 29.9% in the California coastal asphalt to 7.3% in the mid-continent asphalt, the predominantly aromatic character of the mid-continent asphalt, and the high saturate and resin content of the California valley asphalt.

The hydrogen-carbon ratio of the saturate fractions proved to be uniform over the wide molecular weight range represented in each asphalt. The average values of hydrogen-carbon ratio of saturate fractions from the individual asphalts are also very similar as shown in Table V. The only source of deviation from
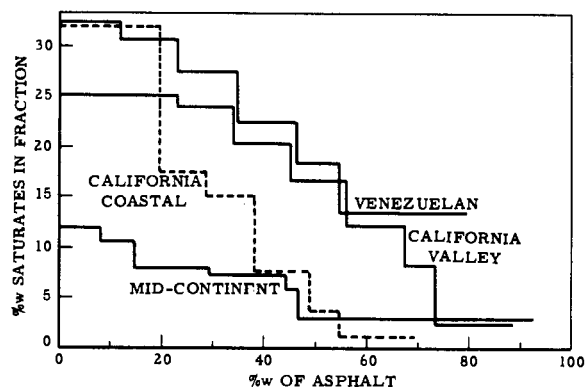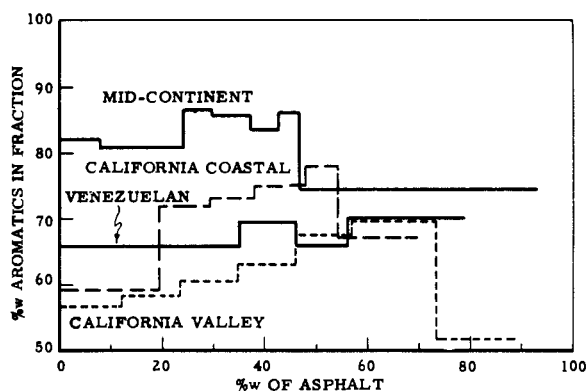
the hydrogen-carbon ratio indicated by $C_nH_{(2n+2)}$ would be expected to arise from cyclic alkanes and their alkyl derivatives (C_nH_{2n}). The data indicate that the California coastal asphalt would be expected to have a somewhat lower content of cyclic alkanes (naphthenes) than the other asphalts.

The average values of the hydrogen-carbon atomic ratio for the aromatic fractions are also shown in Table V. The mid-continent aromatics must contain more carbon atoms in saturated structures than the aromatics from the other asphalts studied.

One of the interesting findings from the ultraviolet absorption spectra of the aromatic fractions is that the presence of catacondensed tricyclic and tetracyclic aromatic molecules is limited to a few per cent of the aromatic fractions.

The average hydrogen-carbon ratio of the resin fractions shown in Table V is about the same as the corresponding aromatic fractions in the case of the California valley and Venezuelan asphalts, thus indicating similar structures. However, the resin fractions of the California coastal and mid-continent asphalts have fewer saturated substituents than the aromatics from corresponding fractions. The average numbers of various heteroatoms per molecule in the resins shown in Table VI indicate the high sulfur content in the California coastal asphalt, high nitrogen content in the California valley asphalt, and high oxygen content in both the Venezuelan and mid-continent asphalts.

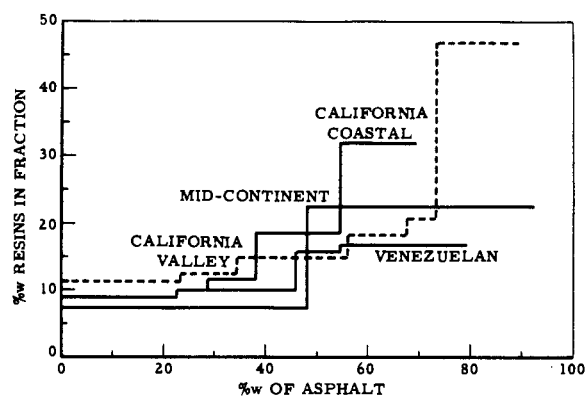The elemental composition of the asphaltenes is shown in

Figure 10. Distribution of saturates

Figure 12. Distribution of resins

Figure 11. Distribution of aromatics

Figure 13. Chemical type distribution

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Table VI. Heteroatom Content of Resin Fractions

Average Heteroatoms per Molecule	Venezuelan	California Coastal	California Valley	Mid-Continent
Sulfur	0.54	1.11	0.21	0.44
Nitrogen	0.55	0.78	0.98	0.95
Oxygen	1.50	0.77	0.89	2.03
Total	2.59	2.66	2.08	3.42

Table VII. Composition of Asphaltenes

	Molecular Weight	Empirical Formulas	H/C (Atomic)	Total Heteroatoms per Molecule
Venezuelan	4719	$C_{339}H_{385}N_{4.38}S_{5.72}O_{3.80}$	1.13	13.90
California coastal	3500	$C_{234}H_{295}N_{4.75}S_{8.46}O_{3.33}$	1.26	16.54
California valley	2530	$C_{184}H_{208}N_{3.56}S_{0.76}O_{1.93}$	1.13	6.25
Mid-continent	4019	$C_{298}H_{335}N_{1.95}S_{1.06}O_{2.76}$	1.12	5.77

Table VII. Very little is known about the degree of complexity of the aromatic ring systems involved, but it is clear from the relatively high hydrogen-carbon ratios that a considerable fraction of the carbon atoms present must be nonaromatic.

Viscosity of Chemical Type Fractions. The viscosities at 77° F. of the various type fractions obtained from the separation of the California valley asphalt shown in Figure 14 are typical of data generally obtained. At a given molecular weight level, the saturates are lowest in viscosity, the aromatics are intermediate, and the resins the highest. With such large differences in viscosity of the three types of components, it is easy to understand how varying concentrations could lead to different viscosities at a given molecular weight level (Figure 5) for the molecular distillation cuts from various asphalts.

The viscosity of the saturates from the four asphalts rises with increasing molecular weight; the data for all the saturate fractions fit within a narrow band as shown in Figure 15. The viscosity-temperature slopes in Figure 16 over the range 77° to 210° F. are also similar. The susceptibility of viscosity to change with temperature decreases with increasing molecular weight of the saturate fraction.

In contrast to the similarity of the saturate fractions, the aromatic fractions from the four asphalts have widely different viscosities at the same molecular weight as shown in Figure 17. The general level of viscosity of aromatics from the various sources appears to be associated with the amounts of saturated substituents, the California valley aromatics with the least alkyl substitution having the highest viscosity and the mid-continent aromatics with the greatest amount of saturated groups having the lowest viscosity. The viscosity of the aromatic fractions becomes less susceptible to change with temperature at higher molecular weights, as shown by the plots of slope of the viscosity-
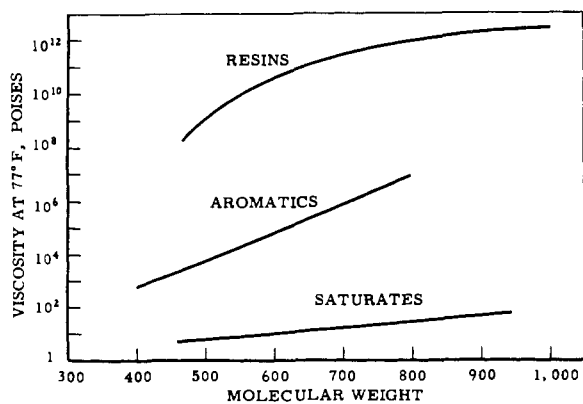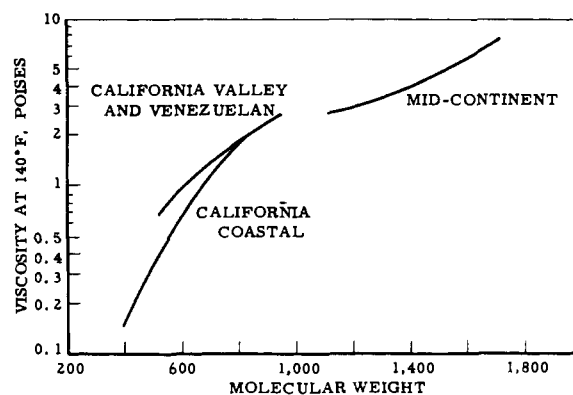

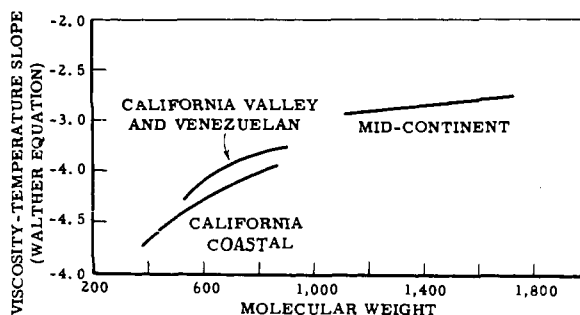Figure 15. Viscosity of saturate fractions

Figure 16. Viscosity-temperature slopes of saturate fractions

temperature lines (Walther equation) vs. molecular weight in Figure 18. The decrease of slope with increasing molecular weight is only slight in the mid-continent aromatics in which the atomic hydrogen-carbon ratio decreases slightly with increasing molecular weight. In the other asphalts there is a general upward trend of the hydrogen-carbon ratio with increasing molecular weight which may account in part for the general decrease in viscosity-temperature slopes.
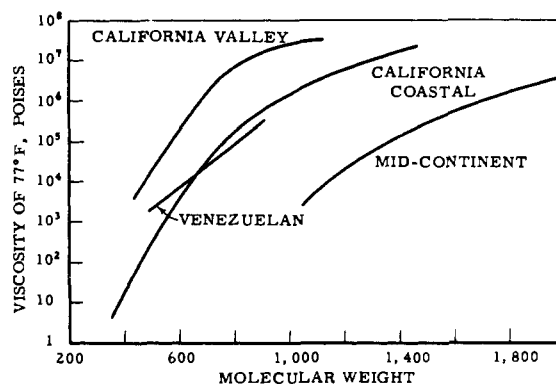

Figure 17. Viscosity of aromatic fractions

Figure 14. Viscosity of chemical type fractions of a California valley asphalt
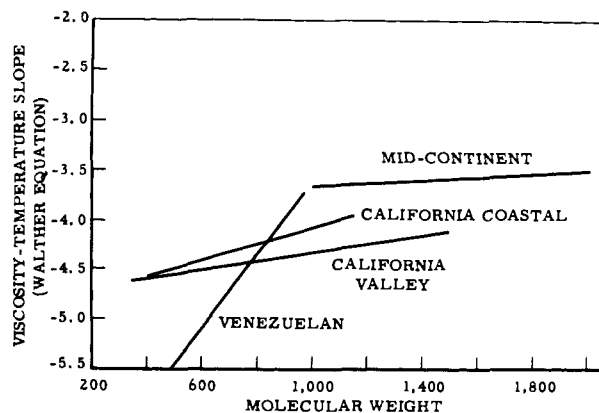

Figure 18. Viscosity-temperature slopes of aromatic fractions

Differences in viscosity of the resin fractions of the same molecular weight from various sources shown in Figure 19 are even greater than in the case of the aromatic fractions. The dependence of viscosity level on source is essentially the same as in the case of the aromatics, the resins from the California valley asphalt being the most viscous and those from the mid-continent asphalt the least viscous. The decrease of the viscosity-temperature slope with increasing molecular weight is greatest in the case of the resins from the California valley asphalt and least for the mid-continent resins as shown in Figure 20.

The viscosity of a mixture of ideal liquids can be calculated from the viscosities of the components and their mole fractions (2). Using the measured molecular weights and viscosities of saturate, aromatic, and resin fractions, calculations of the viscosity of the mixture (the molecular distillation fraction) have been made. The calculated viscosities are in reasonable agreement with observed values at low molecular weight levels, but at higher molecular weights, the calculated viscosities are always lower than the observed values. This discrepancy between calculated and observed values is generally attributed to the occurrence of association between some of the various components.
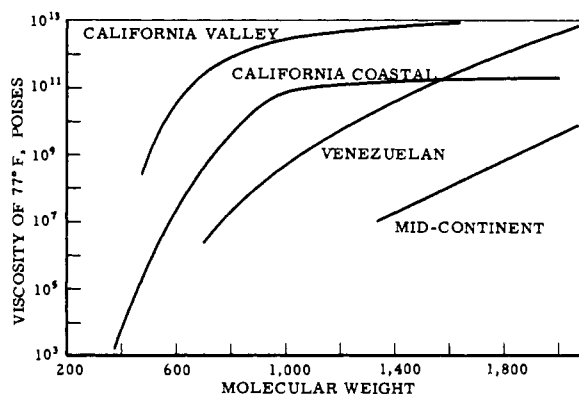

Figure 19. Viscosity of resin fractions

In spite of this nonideal behavior of the components in mixtures, it is possible to control the flow properties of asphalts by blending of selected fractions chosen on the basis of hydrocarbon-type composition. At the same time, the durability or resistance of the asphalt to change can be controlled to a very large degree by proper attention to initial molecular weight.

Durability of Chemical Type Fractions. The high aging index of all fractions of less than 400 molecular weight is due to volatility, and this overshadows any effect of chemical type. Above 400 molecular weight, volatility is insignificant, and oxidation is the important factor effecting the aging index. Accordingly, the aging index in air of the type fractions above 400 molecular weight was determined in the microfilm durability test and is summarized in Table VIII.

Saturates from the Venezuelan and California coastal asphalt showed no hardening (aging index 1.0), while saturates from
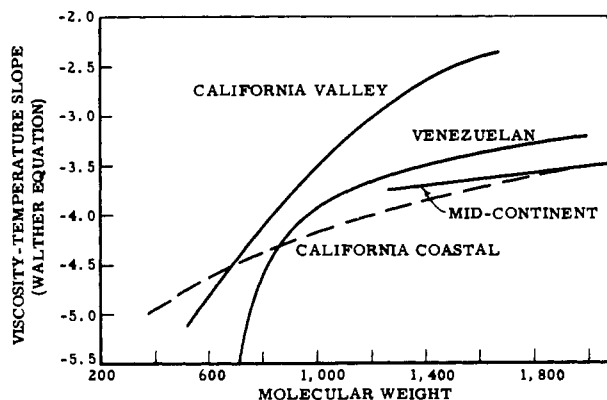

Figure 20. Viscosity-temperature slopes of resin fractions

Table VIII. Hardening of Hydrocarbon Types above 400 Molecular Weight in the Microfilm Durability Test

| Type Fraction | Aging Index in Air | | | |
	Venezuelan	California coastal	California valley	Mid-continent
Saturates	1.0	1.0	1.4–2.8	... [a]
Aromatics	1.3–1.8	1.2–1.9	1.8–4.0	1.0–2.0
Resins	1.3–4.1	1.6–2.6	1.6–4.2	1.0–2.2

[a] Too fluid for test.

the California valley asphalt had aging indexes which varied from 1.4 to 2.8.

Aromatics from the California valley asphalt had air aging indexes which varied from 1 to 4 while those from all the other asphalts had air aging indexes below 2.0.

In the type fractions from these asphalts, the resins had the highest aging indexes. The values for the Venezuelan and California valley resins varied from 1.3 to 4.2, while the mid-continent and California coastal had a maximum of 2.6.

The durability of the various asphalts as shown by the microfilm durability test is reasonably well accounted for by the data from the type fractions from the distillation cuts with the exception of the California coastal asphalt. The ratio of the air aging index to the nitrogen aging index for the California coastal asphalt was 4.1 (Table V), while the comparable ratio for the other three asphalts varied from 1.9 to 2.5. Because the air aging index for the type fractions from the California coastal asphalt is lower than that for some others, the question arises as to what is responsible for the high air aging index of the whole asphalt. The answer is found in the effect of the asphaltenes. The California coastal asphaltenes proved to be more susceptible to hardening by oxidation than any of the other asphaltenes. Synthetic asphalts prepared by blending the asphaltenes from one crude with the fractions from another crude showed high aging indexes whenever the asphaltenes from the California coastal asphalt were used. The flow properties of such asphalts prepared by blending of selected fractions are outside the scope of this article.

CONCLUSION

Composition data of the type shown here can be a valuable aid to the refiner in choice of crudes and blending stocks for the manufacture of asphalt and can provide flexibility in the control of flow properties and durability of the products. The chemical constitution of asphalts is far too complex to be used as a basis for simple specification tests, so the user would specify the desired flow properties and durability in the most precise and meaningful terms possible and rely on the refiner to apply his knowledge of composition of crudes and blending stocks as well as processing methods to produce materials meeting these well-defined properties.

ACKNOWLEDGMENT

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