Relationship of Asphalt Properties to Chemical Constitution

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SOME OF THE most important rheological properties of asphalt depend on chemical constitution. Systmatically reblending chemical type components shows the influence of composition on penetration, softening point, penetration index, viscosity, viscosity-temperature slope, shear susceptibility, and complex stress-strain modulus.

A study of the constitution of asphalt in terms of distributions of molecular sizes and definite chemical classes of compounds led to the development of a group of separation procedures (*6*). These procedures were applied to a representative group of paving asphalts, and the individual fractions have been characterized with regard to molecular weight, hydrocarbon type composition, elemental composition, viscosity, viscosity-temperature slope, and durability (*3*). The Venezuelan asphalt referred to in that study is the basis for the work reported here.

PROPERTIES OF ASPHALT

The most important properties of the Venezuelan asphalt are as follows:

Penetration at 77° F., mm./10	
Softening point, ring and ball, ° F.	
Penetration index	
Viscosity, poises	
32° F.	4.17×10^8
77° F.	3.65×10^5
140° F.	1.60×10^3
285° F.	2.04
Viscosity-temperature slope, Walther	−3.59
Aging index, 2 hours at 225° F., 5-micron film	2.9
Saturates, %	15.8
Aromatics, %	53.7
Resins, %	10.0
Asphaltenes, %	20.5

This material has a relatively flat viscosity-temperature slope as well as good resistance to hardening in use, as indicated by the low value of the aging index. The asphalt was molecularly distilled into a group of distillate fractions and an extremely hard residue. These fractions were separated chromatographically into saturates, aromatics, and resins, and the amounts and properties of each of these fractions have been presented in detail (*3*). Saturates from all of the molecularly distilled fractions were recombined in the proportions in which they occurred to yield a single saturate fraction. Aromatic fractions were similarly combined to produce a single fraction, as were the resins. Thus, four major fractions consisting of saturates, aromatics, resins, and asphaltenes were available in the amounts listed above for reblending in a variety of ways to produce asphalts with a broad range of flow properties. Since the separation operations are conducted on relatively limited amounts of materials, the characterization of the products is greatly facilitated by the existence of a number of testing procedures which require only small amounts of asphalt. A fairly complete study of the properties of a given blend can be conducted on as little as 10 grams of material.

Graphical Representation of Results. The composition of the four-component system consisting of saturates, aromatics, resins, and asphaltenes is represented by a tetrahedron with each apex being 100% of one of the four ingredients, as shown in Figure 1. A point on the surface of the tetrahedron represents the composition of any three-component blend, while a point within the interior of the tetrahedron represents the composition of any four-component blend. If the concentration of one of the components in the blend is held constant, then all of the points representing the compositions of the blends will fall on a single plane with a triangular configuration, as shown in Figure 1,*B*. In all of the blends discussed here the asphaltene content has been held constant at 25%, while relative proportions of saturates, aromatics, and resins in the remaining 75% of the blend have been varied. In the triangular diagrams the influences of relative amounts of saturates, aromatics, and resins on properties of asphalts are presented in the form of contour lines. Each line represents a constant level of one physical property, while the position of the lines represents composition of the blends.

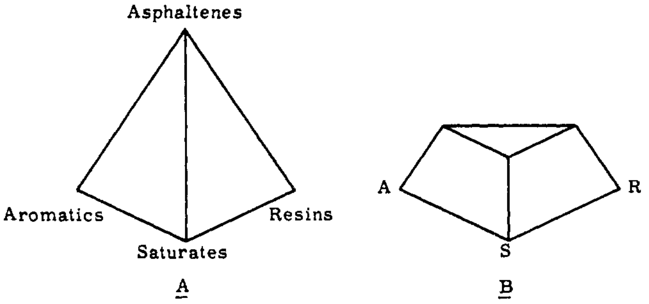

Figure 1. Graphical representation of the composition of a four-component system

Penetration. At a fixed level of asphaltene content (25%) the penetration of an asphalt may be varied over a wide range by varying the saturate, aromatic, and resin content as shown in Figure 2, where lines of constant penetration have been drawn through the results obtained on a series of blends. If the saturate to aromatic ratio is held constant and the resin content of the blend is increased—for example, by passing along the line *A*–*B* in Figure 2—a series of progressively harder asphalts is produced as indicated by the decreasing penetration. At a fixed resin to aromatic ratio, increasing the saturate content—passing along the line *C*–*D* in Figure 2—leads to production of a series of softer asphalts

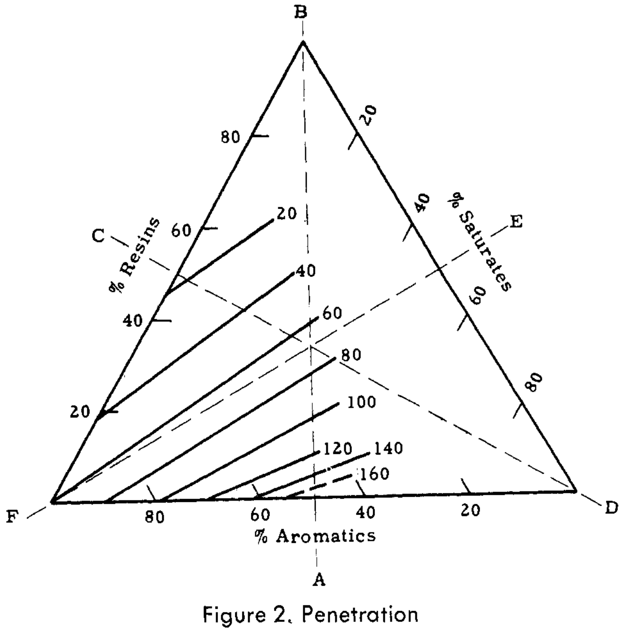

Figure 2. Penetration

of increasing penetration. At a fixed saturate to resin ratio increasing the aromatic content—passing along the line *E-F* in Figure 2—has very little influence on the penetration of the asphalt, the line passing essentially parallel to the lines of constant penetration.

The experimental procedure for determination of penetration on small amounts of material involved the use of a special receptacle, consisting of a cylindrical cup 18 mm. i.d. and 28 mm. deep. The molten asphalt was allowed to cool in this receptacle for 10 minutes in air, then 10 minutes in the 77° F. water bath. The small samples reached the temperature of the water bath within this period of time. Penetration determinations were made with a standard penetrometer and the result designated a "quick pen." The relationship between standard penetration values and quick pen values was as follows for asphalts of 20 pen and softer:

$$\text{Standard penetration} = (\text{quick pen} - 4) \times 1.2$$

No correction is required for asphalts harder than 20 pen.

Softening Point. Figure 3 shows that an increase in resin content at constant saturate to aromatic ratio leads to progressively higher softening points. Increasing the saturate content at a constant aromatic to resin ratio lowers the softening point. Increasing the aromatic content at a constant saturate to resin ratio produces practically no change in softening point, because such changes in composition proceed along lines essentially parallel to the constant softening point lines. The softening points were determined by the normal ring and ball method.

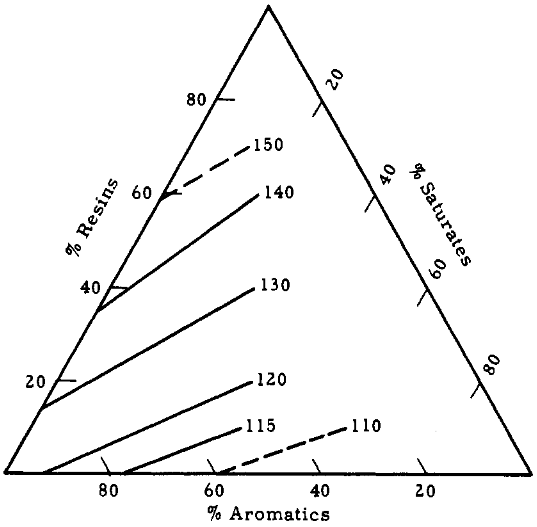

Figure 3. Softening point, ° F.

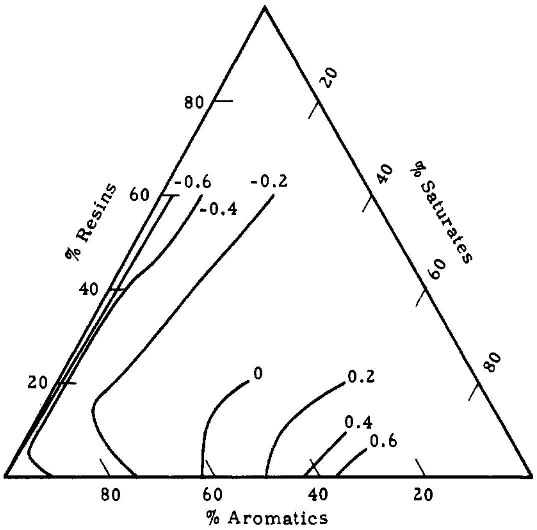

Figure 4. Penetration index

Penetration Index. The penetration index is a property of an asphalt derived from the penetration and softening point as described by Pfeiffer and van Doormaal (7) and is a useful means of classifying asphalts according to major rheological characteristics. Asphalts with penetration indices less than −2 are generally Newtonian materials with high viscosity-temperature susceptibility. Asphalts with penetration indices between −2 and +2 are of the normal type; most paving asphalts fall in this category. Asphalts with penetration indices greater than +2 have relatively lower temperature susceptibility of viscosity and include all of the air-blown asphalts used for roofing and other industrial purposes. Figure 4 shows lines of constant penetration index for a group of asphalt blends. All of these penetration indices are in the range expected for normal paving grade asphalts. Increasing the resin content at constant saturate to aromatic ratio leads to a decrease in penetration index. Increasing the saturate content at constant aromatic to resin ratio leads to an increasing penetration index. Increasing the aromatic content at constant saturate to resin ratio produces practically no change in penetration index until very high aromatic concentrations are reached, and the penetration index then decreases slightly.

Viscosity and Viscosity-Temperature Slope. The viscosity of the asphalt blends has been investigated over a wide range of temperatures with two micro instruments, the sliding plate microviscometer (*1*) and the microcapillary viscometer. An example is shown in Figure 5, where lines of constant viscosity at 77° F. are shown in a triangular plot with saturate, aromatic, and resin content as the composition variables. There is increasing resin content at a constant saturate to aromatic ratio leads to an increasing viscosity over a range of about 0.7 to 40 megapoises. Increasing the saturate content at constant aromatic to resin ratio leads to a decreasing viscosity in the same range. Increasing the aromatic content at a constant saturate to resin ratio produces practically no change in viscosity, the composition lines being essentially parallel to the lines of constant viscosity.

The temperature susceptibility of viscosity of asphalts can be most nearly expressed in terms of a single number by application of the Walther equation (*11*). In this expression the viscosity-temperature susceptibility is the slope of the plot of log log viscosity against log temperature and a small negative value indicates a low change of viscosity

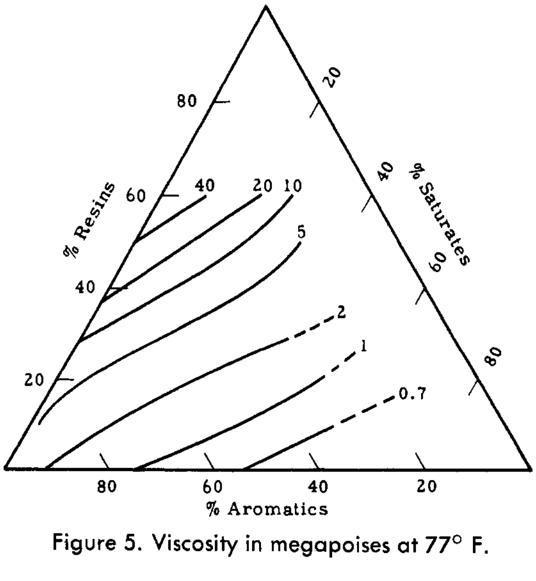

Figure 5. Viscosity in megapoises at 77° F.

with changing temperature. Figure 6 shows lines of constant viscosity-temperature slope obtained from a series of asphalt blends. Increasing the resin content at a constant saturate to aromatic ratio leads to a slight increase in the value of negative slope (greater temperature susceptibility) followed by a slight drop in this value. Increasing the saturate content at constant aromatic to resin ratio leads to a flatter or lower value of viscosity-temperature slope. Increasing the aromatic content at a constant saturate to resin ratio leads to a steeper viscosity-temperature slope. At high temperatures (275° F.) the changes in viscosity-temperature slope with changes in composition cover a relatively narrow band (−3.45 to −3.65) in the composition area investigated.

Shear Susceptibility of Viscosity. With the sliding plate microviscometer it is possible to study the influence of rate of shear on viscosity of the asphalt. For most asphalts a plot of log viscosity *vs.* log shear rate gives a straight line and the slope of this line is defined as the shear susceptibility of viscosity. A large negative slope indicates a highly susceptible asphalt. The shear susceptibility of viscosity at 59° F. is shown in terms of lines of constant shear susceptibility in Figure 7. Increasing the resin content at constant saturate to aromatic ratio leads to a decrease in shear susceptibility. Increasing the saturate content at a constant resin to aromatic ratio leads to an increasing shear susceptibility. Increasing the aromatic content at constant saturate to resin ratio leads to a decrease of shear susceptibility in a narrow region of about 25 to 35% of aromatics, after which further increases of aromatic content have very little influence on shear susceptibility.

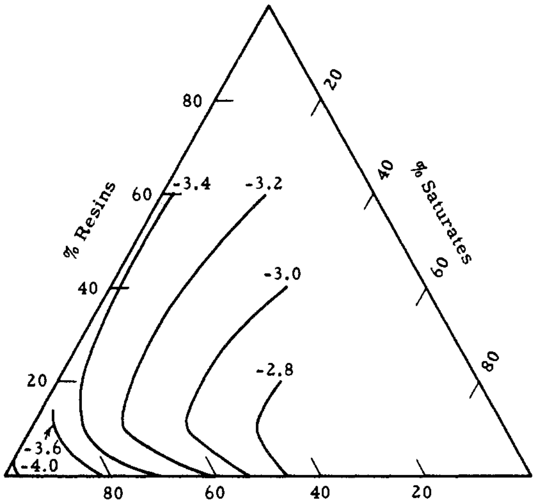

Figure 6. Viscosity-temperature slope below 77° F.

Stress-Strain Modulus (Stiffness). Since asphalt is a viscoelastic material, its response to an applied stress consists of both viscous and elastic responses. The relative amounts of each are determined by the temperature and duration of load application and by the rheological characteristics of the asphalt. The complex behavior of all types of asphalts over wide ranges of loading times and temperatures have been represented by van der Poel (*8*) in a single nomograph. The complex stress-strain modulus or stiffness of an asphalt may be determined from the nomograph with a knowledge of the penetration, softening point, and penetration index of the asphalt or, alternatively, may be determined experimentally by means of the microelastometer described by Labout (*5*). The influence of asphalt composition on the stress-strain modulus (stiffness) at low temperatures and short loading times is shown in Figure 8, where lines of constant stiffness have been drawn. In this example, increasing the resin content at constant saturate to aromatic ratio leads to an increase in stiffness from about 10^9 to over 10^{10} dynes per sq. cm. Conversely, increasing the saturate content at constant resin to aromatic ratio leads to a decrease in stiffness from about 10^{10} to 10^9 dynes per sq. cm. under these conditions of loading time and temperature. Increasing the aromatic content at constant saturate to aromatic ratio produces very little effect on stiffness at low temperature and short loading time, the direction of composition change being parallel to the lines of constant stiffness. Similar plots of stiffness at other temperatures and loading times can easily be derived from the nomograph of van der Poel by means of penetration, softening point, and penetration index data given in previous figures.

Durability. A convenient means of evaluating the ability of a paving asphalt to resist hardening during application and use is the microfilm durability test (*2, 10*). 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 this exposure with the sliding plate microviscometer. The ratio of the viscosity of the aged

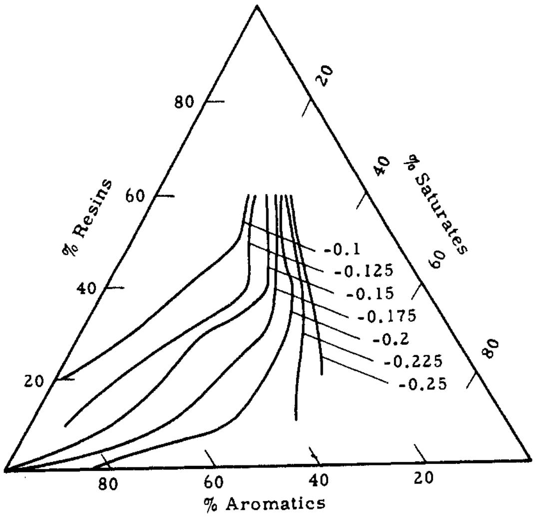

Figure 7. Shear susceptibility of viscosity at 59° F.

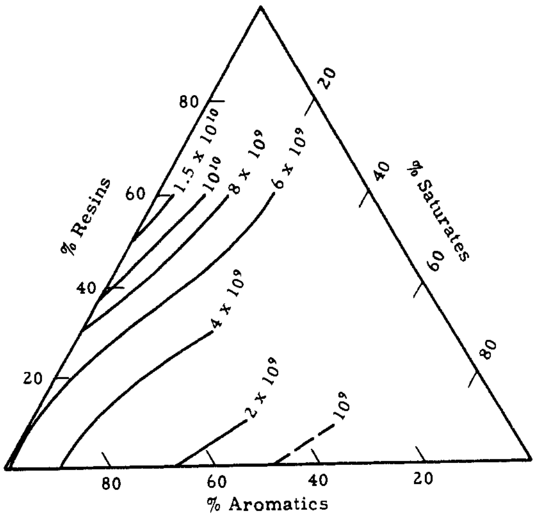

Figure 8. Complex stress-strain modulus at 32° F. and 0.001-second loading time in dynes per square centimeter

asphalt to that of the original asphalt is used as an aging index to express the durability of the material. The microfilm durability test correlates well with the relative field performance of asphalts when used under identical conditions in test roads (*4*, *9*). The blended asphalts described here were examined by this technique. The aging index was influenced to only a very small degree by changes in hydrocarbon-type composition. Variation of aging index over the range of compositions studied was very narrow (aging index 3 to 5.75). This conclusion is in agreement with previous findings (*3*) that saturates, aromatics, and resins from asphalts of different geographical origins behave similarly with respect to hardening by volatility and oxidation. While the tendency of asphaltenes to harden by oxidation depends somewhat on geographical origin, it has been shown (*3*) that very satisfactory durability (aging index of 10 or less) can be obtained by limiting the initial molecular weight of asphalts to 400 or higher.

APPLICATION OF THE DATA

To obtain a clear picture of the changes in the various physical properties which accompany a change in hydrocarbon-type composition it is useful to plot the data of Figures 2 through 8 on transparent material, so that by overlaying one set of properties with several others a simultaneous view of the changes in all the properties is possible. For example, to produce a group of paving grade asphalts with the best possible viscosity-temperature slope, the simultaneous plot of lines of constant penetration and lines of constant viscosity-temperature slope (Figure 9) can be used as a guide. The lines of constant penetration indicate that an asphalt of a given penetration may be made over a wide range of composition, but to have the best viscosity-temperature slope, a preferred composition becomes apparent for a product of any given penetration. A 100-penetration asphalt may be produced from a blending stock consisting of 80% of aromatics and 20% of saturates with a viscosity-temperature slope of -3.6. While this is a very acceptable viscosity-temperature slope, it is possible to produce an asphalt with a very superior viscosity temperature slope of −2.8 by moving along the line of constant penetration (Figure 9) toward the curve of lowest viscosity-temperature slope. Thus, a blending stock consisting of 40% of saturates, 40% of aromatics, and 20% of resins would produce a far superior asphalt. For harder paving grade asphalts the blending procedure offers somewhat less flexibility in choice of viscosity-temperature slope. Asphalts of 40 penetration grade may be produced with viscosity-temperature slopes in the range from about −3.6 to about −3.1. Improvements in viscosity-temperature slope (Figure 9) are generally the result of increasing both saturate and resin content while decreasing aromatics. By such simultaneous consideration of all properties of the asphalt considered to be of most importance, it is possible to arrive at an optimum composition leading to the most desirable combination of properties.

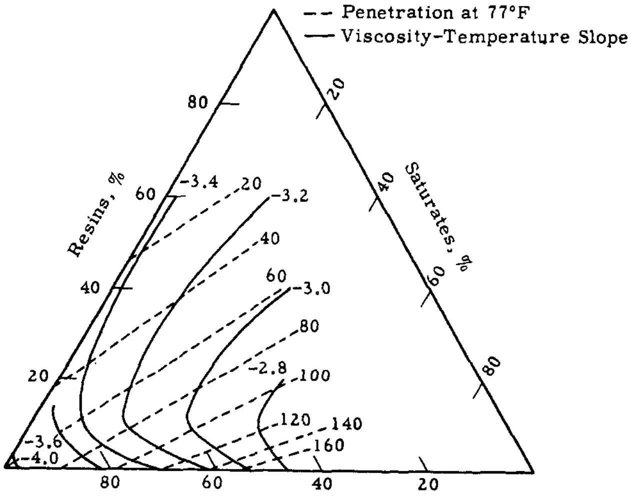

Figure 9. Choosing a composition for best viscosity-temperature slope at fixed penetration

While the results shown here were obtained by reblending of separated hydrocarbon-type fractions of asphalts, experience indicates that the principles are equally applicable to the production of asphaltic products by blending of hard distillation residues with judiciously selected distillates, extracts, and raffinates from petroleum refining operations. To operate within a framework of hydrocarbon type composition such as that shown here, a knowledge of the saturate, aromatic, and resin content of each blending stock is necessary. To assure adequate durability, the molecular weights must not be excessively low. All of the foregoing data apply to paving grade asphalts which can be produced at a single level of asphaltene content. It is easy to visualize how a great deal of additional information of the same type can be obtained at other levels of asphaltene content and that instead of plotting simply lines of constant physical properties it would be possible to draw planes or response surfaces for various properties within the tetrahedron defined by the four components, saturates, aromatics, resins, and asphaltenes. The graphical representation of this type of information is difficult and beyond the scope of this article.

CONCLUSION

These results show that variation of the hydrocarbon-type composition of asphalt in a systematic fashion can lead to products of widely varying physical properties. The principles demonstrated here with separated hydrocarbon-type fractions are also applicable to the blending of hard residues with raffinates, extracts, and distillates from conventional refining operations. Control of asphalt properties by such blending techniques is a valuable tool providing flexibility and quality control for the refiner in asphalt manufacture.

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LITERATURE CITED

(1) Griffin, R.L., Miles, T.K., Penther, C.J., Simpson, W.C., Am. Soc. Testing Materials Spec. Tech. Publ. No. **212**, 36 (1957).
(2) Griffin, R.L., Miles, T.K., Penther, C.J., *Proc. Assoc. Asphalt Paving Technologists* **24**, 21 (1955).
(3) Griffin, R.L., Simpson, W.C., Miles, T.K., J. CHEM. ENG. DATA **4**, 349 (1959).
(4) Heithaus, J.J., Johnson, R.W., *Proc. Assoc. Asphalt Paving Technologists* **27**, 17 (1958).
(5) Labout, J.W.A., *Rheologica Acta* **1**, 186 (1958).
(6) O'Donnell, G., *Anal. Chem.* **23**, 894 (1951).
(7) Pfeiffer, J.P., van Doormaal, P.M., *J. Inst. Petroleum Technol.* **22**, 414 (1936).
(8) Poel, C. van der, *J. Appl. Chem.* **4**, 221 (1954).
(9) Simpson, W.C., Griffin, R.L., Miles, T.K., Am. Soc. Testing Materials Third Pacific Area National Meeting, October 1959, Spec. Tech. Publ., No. **277**, 52 (1959).
(10) Van Oort, W.P., *Ind. Eng. Chem.* **48**, 1196 (1956).
(11) Walther, C., *Oel u. Kohle* **11**, 684 (1953).

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