

# Rheology of Asphalts and Its Relation to Behavior of Paving Mixtures

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Pavement performance associated with binder properties can be best correlated with laboratory tests which are not only of a fundamental nature, but duplicate film thicknesses encountered in the pavement. This necessity of matching geometry of testing to geometry of end use results from changes in viscoelastic behavior with film thickness. The Shell Parallel Plate Microviscometer offers a simple laboratory means for studying thin films.

● **BITUMENS** vary from Newtonian to highly viscoelastic materials. It has been known for years that the greater the deviation from Newtonian behavior, purely viscous flow, the greater the inability of empirical laboratory tests to define behavior and predict performance.

There are many papers, dating from before 1938, dealing with this subject. Two authors in particular, Traxler of Texaco and Mack of Imperial Oil, advocate the use of fundamental tests. They have indicated that empirical tests, such as float, fluidity factor, penetration at high and low temperatures, ring-and-ball softening point, and ductility, are not adequate for quantitative evaluation of flow properties.

At the beginning of the work on asphalts and rubberized asphalts reported here, the usual empirical test data, which gave conflicting results, were collected. Fundamental data were then collected, which cleared much of the confusion.

## THIN FILM STUDIES

Recently an approach to testing has been brought to light which it is believed is as important as the first step in going from empirical to fundamental methods. This approach is to match the geometry of testing with the geometry of end use. For example, in order to predict performance of a binder in a pavement where film thickness is in the 5- to 10-micron range, laboratory tests should be made in instruments which duplicate these thicknesses.

Mack (4) has published a paper which deals with tensile properties. The author's laboratory has found the same dependency of shear properties on film thickness which Mack reports on tensile properties, and herein discusses these data and the merits of the geometry-matching approach. The Shell parallel-plate microviscometer is used in this work on thin films.

To illustrate the geometry-matching approach, consider the behavior of two samples of Venezuelan asphalt obtained from the same supplier and which met identical specifications. Penetration values were 114 and 116, softening point was 118 F in both cases, and all other specification test data showed the two asphalts to be identical. However, these two asphalts showed marked differences in performance when used in pavement sections.

As already indicated, the usual empirical specification tests showed no difference in the asphalts. The fundamental approach was then tried.

The two lower curves in Figure 1 were obtained. The points on these curves were obtained using several of the usual type fundamental viscometers, such as capillary, rotational, and falling cylinder. In such instruments the film thickness of the binder is much greater than in a pavement.

Even the fundamental approach, although being able to answer many questions unanswerable by empirical tests, does not seem to help here.

The two upper curves in Figure 1 were obtained with the microviscometer.

In going from thick to thin films, the viscosity of asphalt No. 1 has increased and

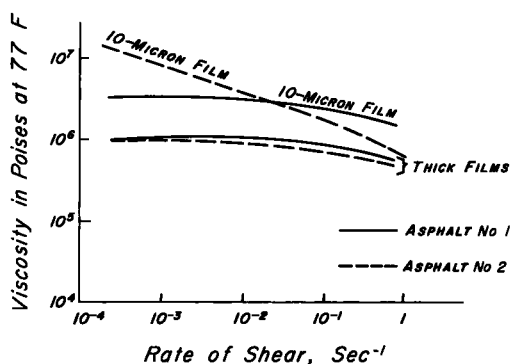


Figure 1. Thick-film and thin-film viscosity.

thick for polar liquids, to which class asphalts belong.

Even though these two Venezuelan asphalts are from the same source, there must be enough difference in molecular composition to account for the difference in behavior in thin films.

The Sternberg-Rostler (5) method of physical and chemical fractionation of asphalts is one of several methods which gives a good indication of molecular composition.

Variations in the asphaltene, resin, and saturated oil content of these two asphalts point to their differences in behavior.

#### PERFORMANCE OF PAVEMENT SECTIONS

Without elaborately discussing viscoelastic behavior, it can be said that the slope of the viscosity-versus-rate-of-shear curve tells a great deal about the performance of an asphalt.

The greater the slope, the more elastically the asphalt behaves. Both asphalts are from steamed-vacuum refined Venezuelan crudes so their differences are not sufficiently great to adversely influence wetting, adhesion, and aging characteristics. The performance of pavement sections made with asphalt No. 2 is better than those made with No. 1 because of greater elastic response. Greater load bearing capacity, flexibility, and resistance to impact at low temperatures, etc., can be shown in the laboratory by simple tests on small pavement sections.

Impact resistance can be shown by molding a typical aggregate-binder hot mix into rectangular blocks  $1\frac{1}{2}$  in. thick, 2 in. wide, and 6 in. long and measuring the number of drops of a steel ball required to fracture the specimen at various temperatures. Temperatures between 0 C and 15 C are chosen as representing Spring thaw conditions. The rectangular blocks are end-supported on  $\frac{1}{2}$  in. square steel bars. A 150-gram steel ball is dropped 20 in. on an anvil, which distributes the load. Impact results for asphalts No. 1 and No. 2 are shown in Table 1.

Using the same rectangular blocks, load bearing capacity can be compared by standing the blocks on end, applying a fixed load (2,500 grams) on top and measuring the time required for the blocks to crumble or sag. Typical results at 140 F are shown in Table 1.

the two curves are almost parallel. In the No. 2 asphalt, not only has the viscosity increased, but the slope of the curve also has changed.

Mack (4) and Henniker (2) have given a suggested explanation for the differences in behavior of liquids in thin films as opposed to behavior in mass.

Molecules at the surface of a wettable solid have a free surface and are exposed to a stronger field of forces than molecules in the interior. These forces are responsible for adhesion. The distance over which these forces act varies for polar and non-polar liquids. The distance may be only a few molecules thick for non-polar liquids and thousands of molecules

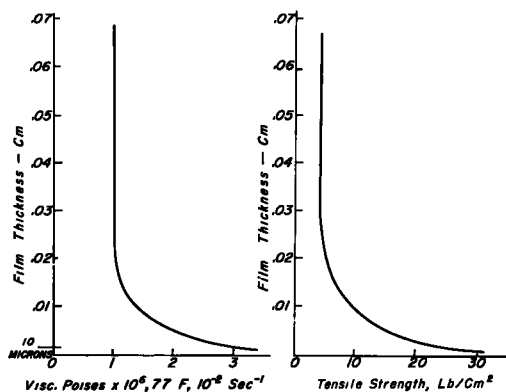


Figure 2. Effect of film thickness on viscosity (left) and tensile strength (right).

TABLE 1  
IMPACT RESULTS

Asphalt	No. of Ball Drops to Fracture			Load Bearing Capacity <sup>a</sup>
	0 C	10 C	15 C	
Venez. No. 1	4	11	16	11 min
Venez. No. 2	15	31	40	25 min
Air Blown	50	130	b	300 min
5% Rubberized	180	b	b	480 min

<sup>a</sup> Blocks on end; 2,500-g loading at 140 F; time to sag  $\frac{1}{8}$  in.  
<sup>b</sup> No failure at 250 ball drops.

Empirical and thick-film fundamental tests did not indicate differences in the asphalts. The superior performance of asphalt No. 2 could have been predicted from the curves in Figure 1. The effect of a wide range of film thicknesses on viscosity in shear is shown in Figure 2.

Bitumens have what might be called an infinite thickness region, above which the viscosity becomes constant for a given rate of shear. In this particular asphalt, above 0.04-cm thickness the viscosity is constant at a given rate of shear, regardless of the fundamental type of viscometer used.

In Figure 2, it is apparent that an infinite thickness region is also encountered for bitumens under tensile stress. The magnitude of infinite thickness varies with the bitumen and is determined by molecular composition.

Asphalt producers now blend various lots of asphalts to meet specifications based on empirical tests. Blending to give a more uniform product based on fundamental thin-film tests, or even molecular composition, seems possible.

#### BLOWN ASPHALTS

It has been shown that asphalt No. 2, having the curve of greater slope, gave the best pavement sections.

Asphalts from certain crudes, or produced by methods such as air blowing or phosphorus pentoxide oxidation, may have much greater curve slopes than encountered with Venezuelan asphalts. The curve of one such asphalt, air blown, is shown in Figure 3 along with the curves of asphalt No. 1 and lower penetration grades made from the same crude as No. 1. In these and following curves the viscosity is measured at 140 F.

The steep slope indicates much greater elastic response of this asphalt as com-

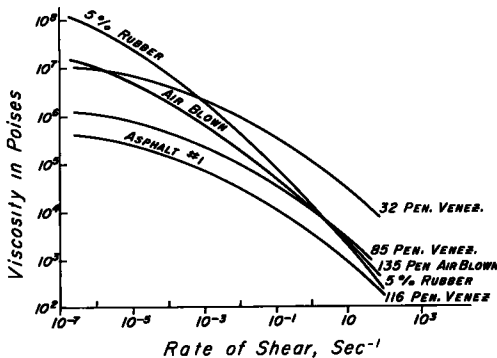


Figure 3. Steady-state viscosity at 140 F.

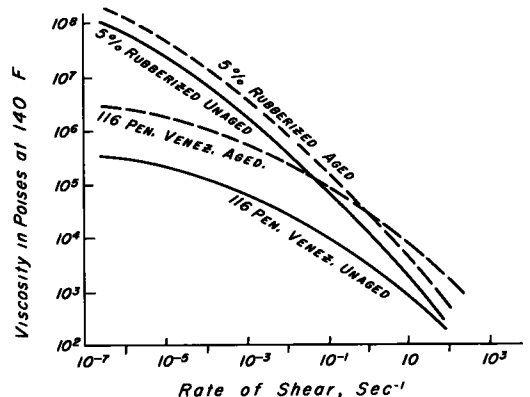


Figure 4. Viscosity before and after aging, five micron thick films two hours at 225 F.

**TABLE 2**  
**IMPACT TEST AFTER AGING**

Asphalt	No. of Ball Drops to Fracture at 15 C			
	Unaged	Aged 1 Day	Aged 2 Days	Aged 3 Days
85 Pen. Venez.	32	5	3	3
120 Pen. Venez	40	8	5	3
5% Rubberized	a	a	a	a

<sup>a</sup> No failure at 250 ball drops.

pared to the Venezuelan asphalt. This should result in a pavement having greater load bearing capacity and impact resistance. Such is the case, as shown in Table 1.

These improvements are desirable, yet it is well known that such asphalts do not give better pavements. In fact, pavement life may well be greatly reduced.

The reason is that although certain physical properties have been improved, it has been accomplished at the expense of other properties. These other properties deal with surface phenomena such as wetting, adhesion, and molecular compatibility. Such asphalts have a high degree of asphaltene micelle orientation throughout the film thickness, resulting in high elastic response.

Modification of asphalts by methods such as air blowing or phosphorus pentoxide oxidation is a chemical modification. Molecules in the original asphalt, which are necessary for good wetting, adhesion, and intra-molecular compatibility, are transformed into different type molecules that result in changes in certain physical properties and change in slope of the viscosity curve. This change in molecular composition can be observed by changes in the Sternberg-Rostler analysis.

It is unfortunate that the molecular composition changes, because the improvements in viscous and elastic response are very desirable.

### RUBBERIZED ASPHALT

A viscosity curve for a rubberized asphalt is also shown in Figure 3. This rubberized asphalt was made by adding 5 percent rubber to asphalt No. 1. The increase in slope, which is even larger than that of the air blown asphalt, should be noted. This increase in viscous and elastic response was brought about by the physical addition of a rubber to asphalt. The original molecules present in the asphalt have not been changed in any way. Instead, the rubber actually increases wetting ability, adhesion, and intramolecular compatibility.

For comparison, the effect of such a rubber-asphalt blend on impact strength and load bearing capacity is shown in Table 1.

### AGING STUDIES

Of the factors influencing the life of a pavement, the effect of weathering on the binder is one of the most important. Oxidation, which causes embrittlement, is perhaps the severest factor in weathering.

The ability of asphalts to resist weathering is usually determined by following the rate of hardening by the Lewis thin-film ( $\frac{1}{8}$  in.) test. Recent publications (1, 3) have shown that aging characteristics can be determined in very thin films, duplicating film thickness of binder on aggregate, using the Shell parallel plate microviscometer.

Van Oort (6) has shown that the rate of oxygen absorption in a given type asphalt decreases with increasing viscosity. Inasmuch as 5 percent rubber produces more than 100-fold increase in viscosity, one would expect a reduction in rate of oxygen absorption and rate of oxidation. This would be reflected by less increase in viscosity and more retention of flexibility.

The effect on viscosity after accelerated aging of an asphalt with and without rubber is shown in Figure 4. The Shell aging test was used. Films five micron thick were aged 2 hr at 225 F. The change in viscosity of the rubberized asphalt is much less than for the plain asphalt.

After aging, most interest is centered in the change in impact strength. To study this, aggregate-binder mixes were made and aged in an oven at 225 F. The mixes were aged in  $\frac{1}{2}$ -in. thick layers in trays and then molded into rectangular blocks for impact testing. Typical results are shown in Table 2. The ability of the rubberized asphalt to maintain flexibility longer is clearly shown.

It is beyond the scope of this paper to discuss further the ability of rubber to improve pavement performance and life, but it has been learned how to test such blends, both in binder tests and aggregate-binder mixes. These test methods, which can be run by any laboratory, are being published.

### CONCLUSIONS

The viscoelastic behavior of bitumens varies with film thickness under both shear and tensile stresses.

Fundamental tests on bitumens result in data which allow better correlation to pavement performance than is possible with conventional empirical tests.

It is now evident that even the choice of the fundamental test instrument or method is important. The thickness of bituminous material under test in an instrument should match the thickness encountered in the end use.

The Shell parallel-plate microviscometer is an important contribution to the bituminous field. In addition to being a fundamental test, it offers a simple means of duplicating the extremely thin films encountered in pavements.

Air blowing of asphalts is a chemical means of modification which, although improving viscoelastic response, adversely affects wetting, adhesion, intramolecular compatibility, aging, etc.

The addition of rubber to asphalt is a physical means of improving viscoelastic response while at the same time improving the properties adversely affected by air blowing.

### REFERENCES

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2. Henniker, I. C., *Rev. Mod. Phys.*, 21:322 (1949).
3. Labout, J. W. A., and Van Oort, W. P., *Anol. Chem.*, 28:1147-1150 (1956).
4. Mack, C., "Physical Properties of Asphalts in Thin Films." *Ind. Eng. Chem.*, 49:422-426 (1957).
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### Discussion

W. C. SIMPSON, R. L. GRIFFIN, and T. K. MILES, Shell Development Co., Emeryville, Calif. --The writers would like to comment on a point raised by Mr. Wood concerning the viscosity of asphalts at various levels of film thickness. He indicates that the viscosity of an asphalt increases with decreasing film thickness. In the example shown, the viscosity was independent of thickness only when the films were 0.04 cm (400 microns) thick or thicker. This is an important point for discussion as it has a serious bearing on the behavior of paving mixtures. The writers' experience with the experimental determination of viscosity of paving asphalts has shown that viscosity is a characteristic of the material which is independent of its thickness. An example given by Griffin, Miles and Penther<sup>1</sup> is quoted to illustrate this point:

<sup>1</sup>"Microfilm Durability of Asphalt." *Proc. Assn. Asphalt Pav. Tech.*, 24:31 (1955) (see Fig. 7).

The following measurements were made with an air bath model of the sliding plate viscometer on a slightly non-Newtonian asphalt.

Film Thickness, microns	Viscosity, Poises at 77 F Shear Rate 0.05 sec <sup>-1</sup>
69.4	1.55 x 10 <sup>6</sup>
50.8	1.50 x 10 <sup>6</sup>
29.3	1.50 x 10 <sup>6</sup>
10.2	1.40 x 10 <sup>6</sup>

In order to investigate the influence of film thickness over a still wider range and to determine whether the use of a variety of viscometers has any effect, the following measurements were made by Griffin, Miles, Penther and Simpson<sup>2</sup>, which are quoted from the paper "Sliding Plate Microviscometer for Rapid Measurement of Asphalt Viscosity in Absolute Units." Another slightly non-Newtonian<sup>85/100</sup> penetration grade asphalt was used in this case.

Viscometer Type	Film Thickness, microns	Viscosity, Poises at 77 F, Shear Rate 0.05 sec <sup>-1</sup>
Covette conicylindrical	5,000	7.9 x 10 <sup>5</sup>
Open end ring viscometer	2,000	7.8 x 10 <sup>5</sup>
Sliding plate, air bath model	109	7.6 x 10 <sup>5</sup>
Sliding plate, water bath model	11	7.8 x 10 <sup>5</sup>

In the case of a third<sup>85/100</sup> penetration grade asphalt, the viscosity measurements were carried out on films as thin as 5 microns between metal gage blocks polished flat to within 50 Angstrom units. These data also show no influence of film thickness on viscosity.

Film Thickness		Viscosity at 77 F, Poises Shear Rate 0.05 sec <sup>-1</sup>
Microns	Inches	
9.25	0.000364	1.28 x 10 <sup>6</sup>
6.60	0.000260	1.37 x 10 <sup>6</sup>
4.85	0.000191	1.23 x 10 <sup>6</sup>

In view of the writers' repeated finding that the viscosity of paving asphalts is independent of film thickness at constant rate of shear, it is felt that the results reported by Mr. Wood can only be explained in terms of some systematic error in the determinations or by the presence of foreign matter in the sample.

PAUL R. WOOD, Closure—During his work on the influence of viscosity of asphalts with film thickness the author was well aware of the work done by the Shell Development Company. In fact, he has stated many times that their part in improving the parallel-plate microviscometer as originally worked on by Labout and van Oort has been perhaps the most significant work in the field of asphalt testing in many years.

The difference between the data probably is not due to an error in workmanship or thinking in either case, but is due to the distance and duration of pull in each viscosity measurement.

This point is clearly explained in another paper, submitted to "Analytical Chemistry" for publication.

<sup>2</sup> "Road and Paving Materials," Spec. Tech. Pub. No. 212, ASTM (1957) (See Table III).