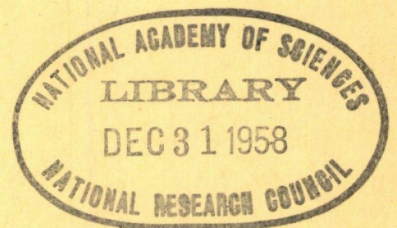# HIGHWAY RESEARCH BOARD

Bulletin 192

Rheological and Adhesion Characteristics Of Asphalt

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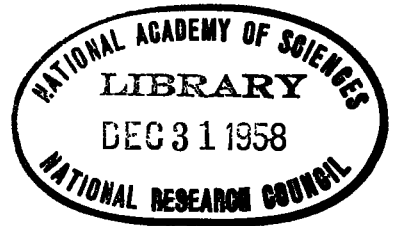2101 Constitution Avenue   Washington 25, D. C.

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Contents

Use of Rheological and Other Data in Asphalt Engineering Problems

JOHN G. BRODNYAN, Research Engineer, Franklin Institute Laboratories, Philadelphia, Pa.

The performance in service of asphalts in various systems depends both on the influence to which the material is subjected and the intrinsic properties of the asphalt itself. A wide variety of asphalts has been investigated with respect to (a) their rheological behavior under both static and dynamic load, (b) their breaking properties, and (c) other properties such as water permeability, photochemical decomposition, etc.

The rheological data are condensed to generalized curves of both the dynamic storage and loss moduli versus frequency, the temperature dependence of these curves, and the dependence of the initial viscosity on temperature. By the use of the softening point and penetration, it is shown how, with the aid of the stated curves and empirical relationships, to find the whole rheological behavior of an asphalt.

Several prototype examples of engineering problems are solved, and are evidence that asphalts, no less than metals, can be dealt with as engineering materials. A flow problem is solved with the aid of the curves of initial viscosity versus temperature. Use of the two rheological moduli in solving engineering problems is shown for the case of the attenuation of vibrations. Also the method of extending classical elastic theory to these visco-elastic materials is outlined, with the particular case of a bending beam given in detail. Finally, the problem of whether thermal changes will cause cracking of an asphalt is investigated.

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MATERIALS INVESTIGATED

The asphalts investigated were chosen to give as wide a variety as could be obtained. The conventional tests of these NARC asphalts, when they were received, are given in Table 1. Three years later, when A. S. Orr had the asphalts checked at Gulf Oil's Refinery Technology Laboratory in Philadelphia, most had not changed much, but the MD and GC asphalts had hardened significantly. The results of a Sternberg-Rostler (5) analysis provided by F. G. Gzemski of the Atlantic Refining Company are given in Table 2.

1

The gel asphalts were Mid-Continent air-blown stocks, the Medium asphalts were Venezuelan air-blown asphalts and the Sol asphalts were straight-run distilled residues from Santa Maria Valley, California crude, except that Sol D is propane extract asphalt from a different crude which is essentially the resin fraction alone.

The different types can be distinguished by their softening point—penetration ratios. If the log of the penetration for 100 g acting for 5 sec at 77 F is plotted against the softening point in degrees Fahrenheit straight lines (Fig. 1) with different slopes for each family are obtained.
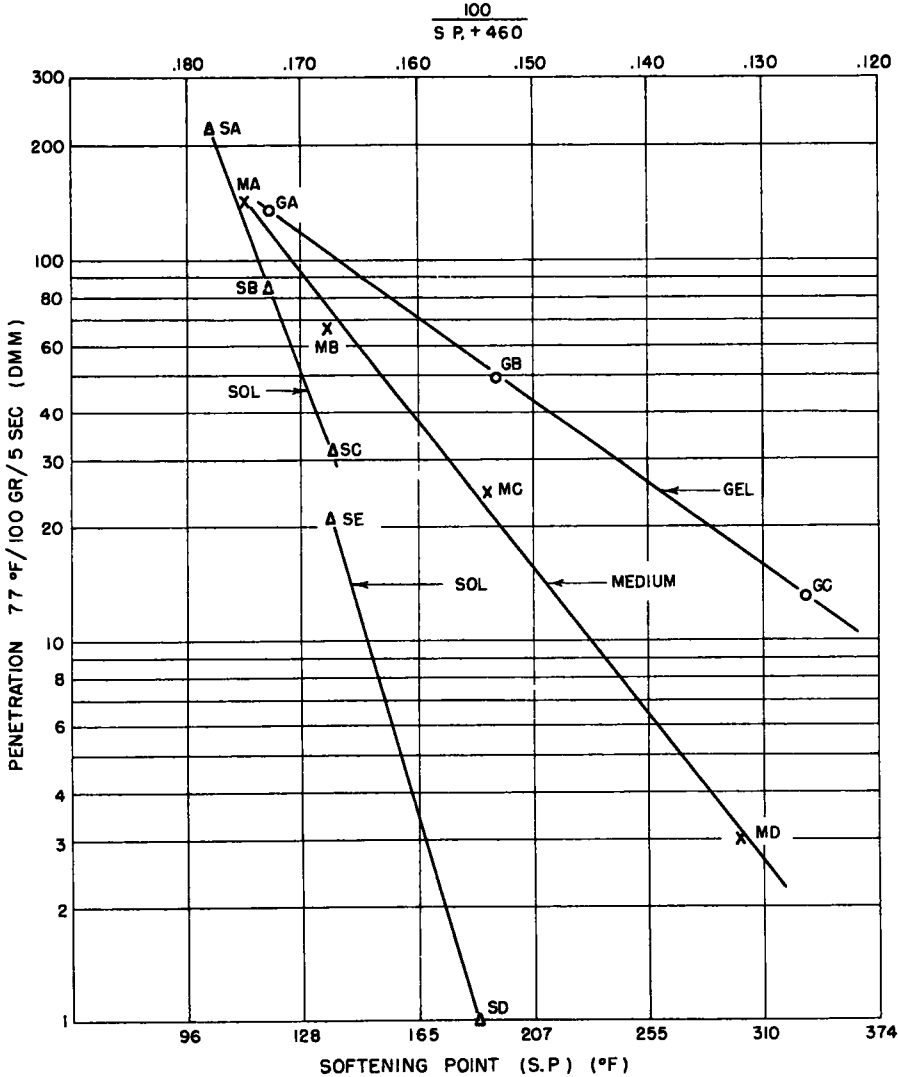

Figure 1.   Softening point—penetration relationships of NARC standard asphalts (log penetration vs 100/(460 + softening point)).

EXPERIMENTAL METHODS AND RESULTS

Rheological Investigations

As asphalts are visco-elastic materials the mechanical behavior depends on the time of loading ("frequency" or rate of shear) and temperature.   The usual viscous response

has been investigated by using a coni-cylindrical (rotational) viscometer described elsewhere (6) as well as a high-pressure capillary viscometer described in another publication (7). As asphalts are non-Newtonian liquids it was expected and proved, after an initial period of loading, during which the elastic strains are brought to equilibrium, their properties depend only on the rate of shear and not on the amount of shear. The dynamic properties have been investigated in The Franklin Institute's vibration tester which has been described by Philippoff (8). In this instrument a sinusoidal stress is imparted to a visco-elastic material and the deformation follows in a sinusoidal manner, but will lag

TABLE 1
IDENTIFICATION OF ASPHALTS

Code Name	Penetration °F/gm/sec Decimillimeters ASTM D 946-47T						Softening Point	Ductility (cm) ASTM D113-44 °F/cm/min		Flash Point ASTM D92-46 C.O.C. Fire Point		Loss on Heating 5 hr at 325 F	Penetration of Residue ASTM DG-39T	Solubility in CCl₄	Solubility in DS₂	Insoluble in n-hexane	Ash Content	Specific Gravity
	$\frac{32}{200}$ $\frac{}{60}$	$\frac{77}{100}$ $\frac{}{5}$	$\frac{115}{50}$ $\frac{}{5}$	$\frac{115}{200}$ $\frac{}{5}$	$\frac{150}{100}$ $\frac{}{5}$	$\frac{185}{50}$ $\frac{}{5}$	F	$\frac{77}{5}$ $\frac{}{1}$	$\frac{39.2}{1}$ $\frac{}{1}$	F	F	%	dmm.	%	%	%	%	
Gel A	77	135	301+	---	---	---	127	8.6	2.8	520	600	.036	134	99.6	---	18.5	.05	.977
Gel B	34	50	77	---	---	---	193	2.1	1.9	530	605	.016	51	99.6	---	25.5	.08	.983
Gel C	11	13	18	---	---	---	335	non-ductile		585	620	.004	14	99.4	---	36.4	.01	1.004
Med A	42	141	300+	---	---	---	112	150+	26.4	490	575	.054	109	99.8	---	22.5	.005	1.014
Med B	27	67	234	---	---	---	134	31.5	5.1	500	575	.052	50	99.8	---	27.0	.009	1.017
Med C	13	25	49	---	---	---	191	4	0.7	510	625	.038	16	99.8	---	35.1	.006	1.031
Med D	< 1	3	5	12	21-23	31	299	non-ductile		550	640	.0032	< 1	99.8	---	49.2	.009	1.057
Sol A	86	225	300+	---	---	---	102	150+	150+	365	455	1.015	94	99.9	---	28.4	.01	1.016
Sol B	31	85	300+	---	---	---	118	150+	150+	420	510	.334	60	99.9	---	23.7	.005	1.044
Sol C	16	32	114	---	---	---	137	104	1.1	480	570	.065	29	99.9	---	31.9	.015	1.045
Sol D	0	1	6	23	110	290+	184	non-ductile		695	755	0	< 1	99.8	---	18.1	.015	1.056
Sol E	1	21	168	---	---	---	137	---	---	---	---	---	---	----	---	----	---	1.039

behind the stress by an angle δ. The ratio of the maximum stress to the maximum strain gives the absolute value of the complex modulus $G^* = G' + iG''$ where $i = \sqrt{-1}$. The in-phase component of stress divided by the strain is called the storage modulus, G', because it is a measure of the energy stored. The component of the stress 90 deg out of phase divided by the strain is called the loss modulus, G'', because it is a measure of energy loss. By the methods of complex variables it can be shown that the following relationships hold true:

$$G' = |G^*| \cos \delta \tag{1a}$$

$$G'' = |G^*| \sin \delta \tag{1b}$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \tag{1c}$$

$$\frac{G''}{G'} = \tan \delta \tag{1d}$$

This instrument gives both the complex modulus G^*, which is comparable to one-third the stiffness as defined by van der Poel, and the loss angle δ thereby enabling the separation of the complex modulus into G' and G'' which is related to the dynamic viscosity η by the relationship $G'' = \omega \eta'$ where ω is the circular frequency ($2\pi f$). The curves of G' and G'' give more information than the "stiffness" which is essentially an envelope of these two curves. Isothermal curves of the moduli, G' and G'', were obtained over

TABLE 2
STERNBERG-ROSTLER ANALYSIS OF NARC ASPHALTS

Code Name	Asphaltenes	N-Base Resins	Group 1 Resins	Group 2 Resins	Saturated Hydrocarbons
Gel A	17.0	12.3	13.5	26.9	30.3
Gel B	23.1	10.0	12.2	25.1	29.6
Gel C	33.3	5.0	13.7	21.1	27.0
Med A	18.1	18.4	15.6	28.8	19.1
Med B	20.2	19.7	16.0	27.4	16.8
Med C	29.3	14.5	14.8	24.2	17.1
Med D	42.8	12.3	12.6	21.3	11.0
Sol A	24.6	31.2	21.5	15.8	6.9
Sol C	21.9	36.9	21.4	14.5	5.4
Sol D	6.5	38.0	27.7	24.7	2.6

a wide range of temperatures and frequencies (Fig. 2) and were shifted together, using Ferry's method of reduced variables: (9) a superposition principle, which set up an equivalence between temperature and frequency, to obtain a large reduced curve (Fig. 3). The fundamental relationships of this method are:

$$G'(\omega) = \frac{T\rho}{T_0\rho_0} \, G_0'(\omega a_T) \qquad (2a)$$

$$G''(\omega) = \frac{T\rho}{T_0\rho_0} \, G_0''(\omega a_T) \qquad (2b)$$

$$\eta'(\omega) = a_T \left(\frac{T\rho}{T_0\rho_0}\right) \eta_0'(\omega a_T) \qquad (2c)$$

$$\eta = a_T \frac{T\rho}{T_0\rho_0} \eta_0 \qquad (2d)$$

where the quantities without subscript refer to the absolute temperature T and those with subscript $_0$ refer to the reference temperature T_0. η' is the apparent viscosity and η is the initial viscosity, which is a constant; ρ is the density. The initial viscosity is the highest one exhibited by a non-Newtonian liquid and is at any given temperature found at lowest rates of shear or frequencies. It is seen that the function a_T gives essentially the temperature dependence of the initial viscosities.

TABLE 3
ASPHALT IMPACT TEST
1 in. -lb = 0.700 ergs/cm^2 x 10^6

Asphalt	Temperature		Impact Energy (in. -lb) Uncorrected
	F	C	
Gel A	-20	-28.9	1.36 $\pm$ .25
Gel C	-20	-28.9	1.39 $\pm$ .25
Gel C	32	0	2.46 $\pm$ .29
Med D	-20	-28.9	1.71 $\pm$ .22
Med D	- 9	-22.8	1.63 $\pm$ .12
Med D	80	26.7	1.80 $\pm$ .32
Sol D	-20	-28.9	1.44 $\pm$ .25
Sol D	80	26.7	1.38 $\pm$ .25
Sol D	32	0	1.52 $\pm$ .25

In practice, the isothermal curves of G' and G" versus frequency are plotted on a log-log scale. To reduce the curves, each pair of isothermal curves is first shifted vertically by the factor $\dfrac{T\rho}{T_0\rho_0}$ and then moved along the frequency axis by the same amount until the points line up with the reference curves (25 C) to give continuously smooth graphs. The amount of horizontal shift necessary to bring coincidence (log a_T) is a measure of the temperature dependence of the material. These shifts for asphalts are given as a function of temperature in Figure 4.

The method of reduced variables makes possible the reduction of the properties of visco-elastic bodies to only two general curves: (a) the dependence of G' and G" (or η') on the reduced frequency, and (b) the temperature dependence of log a_T. As the asphalt families react qualitatively in the same manner with only the time scale transposed, all the reduced curves have been superposed to give three generalized reduced curves, which were then combined to give one large curve with three "sections" (Fig. 5).

The validity of the method of reduced variables for asphalts has been checked by measuring the mechanical properties at 20 kilocycles with a torsion crystal arrangement.
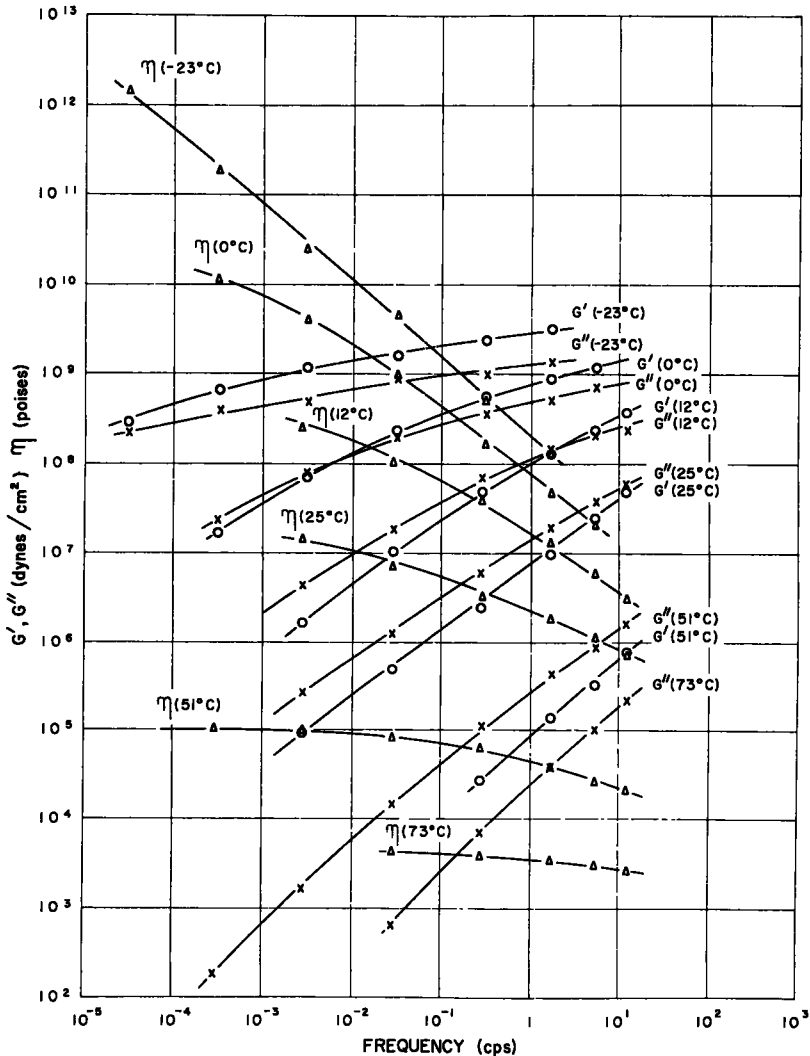

Figure 2. Mechanism of reduction (isotherms—Sol C asphalt).

This arrangement gave essentially the same values as reduced curves measured at much lower frequencies and temperatures. The validity of the method has also been checked with a solution of polyisobutylene (10).
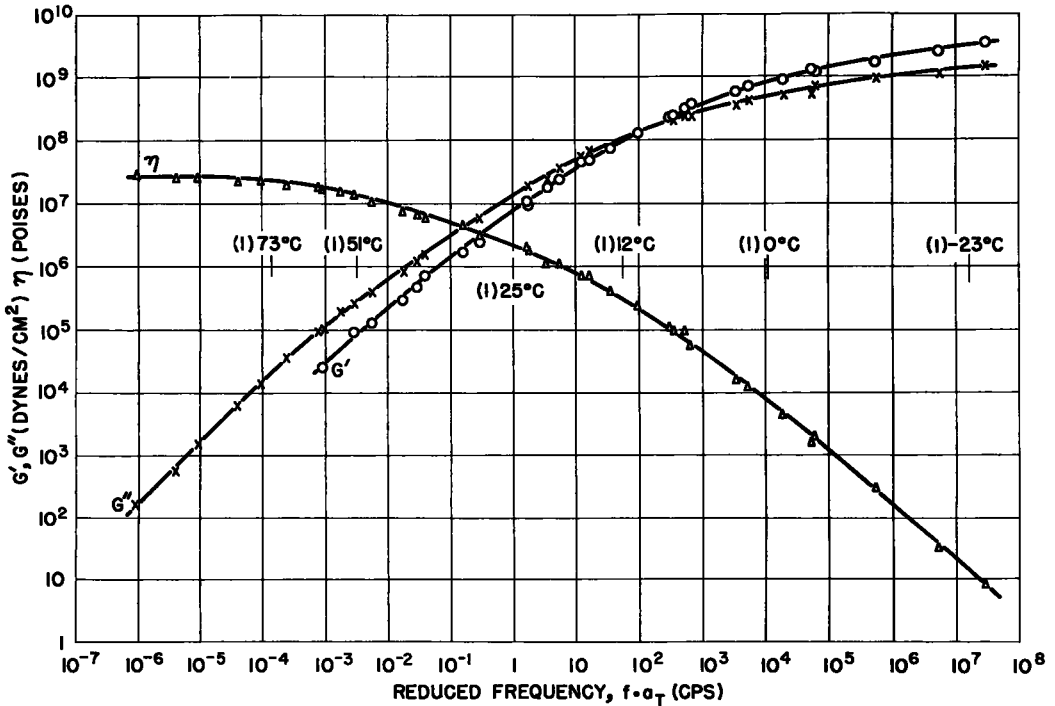

Figure 3. Mechanism of reduction (reduced curves—Sol C asphalt).

In addition, the steady state viscosity data has also been condensed. As the asphalts are non-Newtonian liquids, the viscosity varies with the rate of shear; but they behave like Newtonian bodies below a certain rate of shear; that is, they have a viscosity that is independent of both rate of shear and shearing stress. This is the initial viscosity defined earlier. Actually, it has been found that the upper limit for Newtonian behavior at low rates of shear is determined primarily by the shearing stress. The rate of shear is determined by the viscosity of the asphalt at that particular shearing stress (about $3,000 \, \text{dynes/cm}^2$). This initial viscosity has been plotted as function of temperature on a plot (Fig. 6) based on the empirical relationship of Walther; $\log \log (\nu + 0.8) = m \log T$, where ν is the kinematic viscosity and T the absolute temperature.

As the viscosity at very low frequencies is equal to this initial viscosity, by the use of the time-temperature reduced plots the initial viscosity at very low temperatures could be obtained by extrapolation and plotted as in Figure 6. This has been done to extend the initial viscosity data down to -23 C.

Recently it was shown experimentally (8) that the change in viscosity with rate of shear for visco-elastic bodies is very similar to the decrease of the viscosity with the circular frequency of vibration. This has also been shown to be true for asphalts. This means that, to a first approximation, rate of shear (D) and circular frequency ($\omega = 2\pi f$) can be interchanged.

Limited experience with coal tar and rubberized asphalt did not show any major qualitative departures from the behavior of the NARC normal asphalts.

The coal tar curves appeared to be similar to those for hard Sol asphalts, whereas the rubberized asphalts are typical of those for medium asphalts. Of course the properties of the rubberized asphalt may change with large changes in concentration and methods of incorporation and this would have to be ascertained by extensive experimentation.

An important consideration in engineering use is the effect of filler on the rheological behavior of asphalt. C. van der Poel (4) has found that the stiffness of an asphalt-mineral mixture is determined only by the stiffness of the asphalt alone since, by comparison, the filler is "infinitely" stiff and the volume concentration of the mineral aggregate. This is the same as the results of Nielsen, Wall and Richmond (11) on another visco-elastic material, polystyrene. They found that the storage modulus $\overline{G}'$ is approximately a linear function of the volume fraction up to at least 40 percent filler with mineral aggregates in polystyrene.

Breaking Properties and Impact Resistances of Asphalts

The breaking strength of asphalt is important as it limits the stresses that can be applied in use. The stresses may be limited in two ways: (a) if a certain stress is imposed, it must be less than the breaking stress, and (b) if a certain deformation in a given time is imposed, it must be less than the breaking stress divided by the stiffness at this rate of loading.

The second limitation assumes that there is a constant stiffness at a given rate of loading up to the point of fracture. It has been found experimentally that this linearity occurs up to the point where brittle fracture occurs.
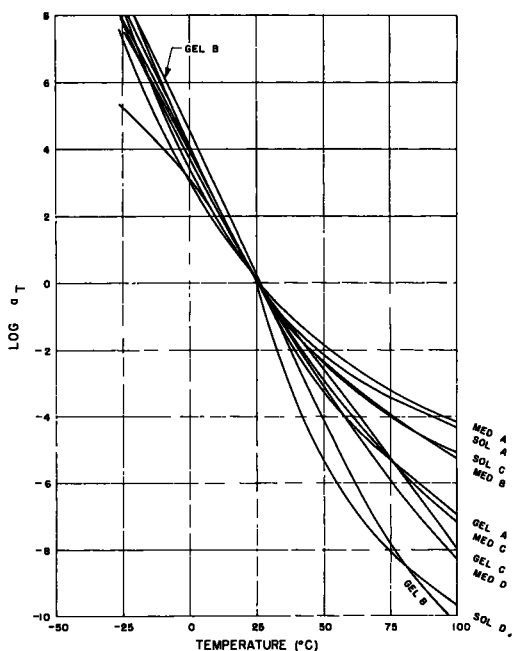

Figure 4. Temperature dependence of a_T values.

When asphalts are overloaded they fail in three different modes depending on the stress-strain, time and temperature conditions. It appears that when asphalts are essentially viscous, they fail in a ductile fashion; when essentially elastic, they exhibit brittle failure; and when their viscous and elastic responses are both important, they show a ragged break.

This indicates that the breaking strength cannot be taken to be a constant but is a function of time and temperature. This has been found experimentally. The dependence of breaking strengths on time is not as great as the dependence of the moduli G' and G'', on time and it appears to follow the reduced variable principle. At high rates or low temperatures the breaking stress is found to be $0.70 - 2.43 \times 10^7$ dynes/cm^2 and the deformation at break is found to go through a maximum.

In investigating the strength of films of asphalt, C. Mack (12) found that the film strength varied between 1.30 and 1.45×10^7 dynes/cm^2. It has been found, however, that the temperature dependence of the breaking strength is essentially the same as that of the non-destructive rheological behavior and accordingly composite curves could be formed for the breaking strength versus deformation rate similar to the ones of moduli versus frequency. This behavior is qualitatively like that of GR-S rubber as reported by T. L. Smith (13).

An important related phenomenon is that of impact resistance. The various asphalts were investigated with a Tinius Olsen Impact machine and the results are given in Table 3. The results show that the asphalts have very similar impact resistances which one would be led to believe from the similarity of the breaking properties.

In comparing two asphalts to see which would give the better impact resistance one finds that the one with the lower storage modulus and higher tan δ at the frequency of impact, approximately 10^2 to 10^3 cycles per sec, is the better.

Temperature Dependence of Asphalts

Since there is a similarity in shape between all the curves of G' and G'' versus frequency they can be superimposed by shifting along the frequency axis. It is then natural to ask, are there some similarities between the temperature dependences, curves of log a_T vs temperature, which will enable a superposition of these curves. The answer is yes.

Recently, Williams, Landel and Ferry (14) have found that upon choosing suitably a separate reference temperature, T_S, for each individual polymer system, and expressing a_T as a function of $T - T_S$, this function turns out to be identical for a wide variety of polymers and their solutions. That a_T is a function of $T - T_S$ has also been found true for all the NARC asphalts over a wide range of temperatures. The reference temperature T_S was chosen arbitrarily for one system, 243 K for a high molecular weight polyisobutylene, the same as that taken by Ferry as a reference. The plots of log a_T versus T for the asphalts were matched by shifting the curves (plotted on transparent paper) both horizontally and vertically for coincidence in shape. Upon finding
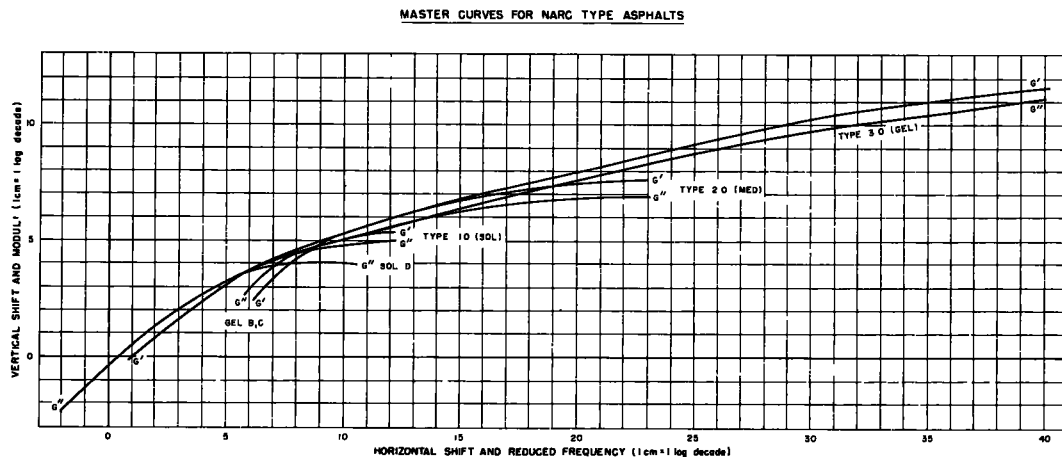
MASTER CURVES FOR NARC TYPE ASPHALTS

Figure 5. Master curves for NARC type asphalts.

coincidence in shape, the temperature which matches the point $T - T_S$ equal to zero on the log a_T versus T plot would be the T_S value. The reference temperatures, T_S, found are listed in Table 4 and it is seen that the softening points in degrees centigrade are very similar in value to those reference temperatures. Figure 7 shows that all the asphalts form one curve from $T - T_S$ equal to zero to $T - T_S$ equal to 150 C, but below $T - T_S$ equal to zero one has three distinct curves. The curves can be differentiated by using the penetration values at 77 F. The upper curve holds for the NARC asphalts with a penetration greater than 30 decimillimeters for 5 sec under a load of 100 g. The lower curve holds for a penetration of less than 15 decimillimeters under the same conditions. The middle curve holds for values of penetration between 15 and 30 decimillimeters.

Water Permeability of Asphalt

Although asphaltic materials have been used for a long time as barriers to hold back moisture, it is known that these materials have measurable permeabilities to water vapor and other gases.

The permeability measurements reported here were made by using the procedures developed by Beckman et al (15) but with a slightly modified apparatus. The data obtained at 99.5 and 77.8 F are given in Table 5. The diffusion constants do not vary as would be expected from viscosity and asphalt-water interfacial tension information. There is an indication that the results might correlate with the polarity or unsaturation
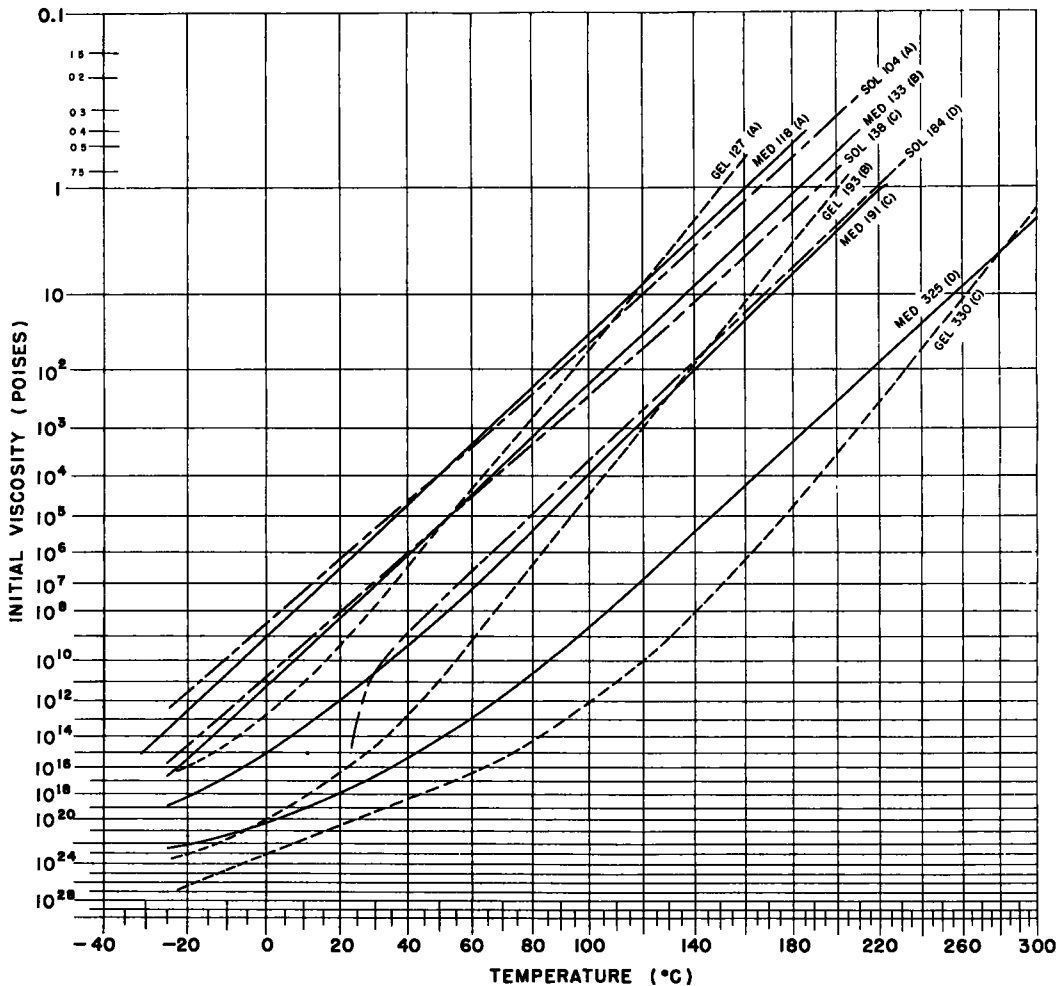
Figure 6. Initial viscosity of all NARC asphalts.

of the asphalts, which increases as they are airblown. The lesser diffusion at 77.8 F as compared with 99.5 F is believed to be due to the greater kinetic energy of the water vapor molecules at the higher temperature.

This permeability has been determined by the use of Fick's Law giving:

$$W = DAP \ \tau/L$$

in which,

W	=	weight of water passing through the film, grams
D	=	diffusion constant
A	=	area of film, cm^2
P	=	vapor pressure difference across the film
τ	=	time, hours
L	=	length of diffusion of path, cm.

The driving force, or difference in free energy, of course was the difference in pressure in this case. The driving force may be given by some other thermodynamic unbalance, that is, chemical reaction, etc., but a similar type of equation should hold as long

as P is replaced by the new driving force. These driving forces are discussed in E. Thelen's paper under the diffusion of water molecules through asphalt (21).

Photochemical Decomposition

Weathering is a complex phenomenon which depends upon many fundamental properties. As a first step it was decided to investigate the effect of ultraviolet radiation on asphalt surfaces. It was known that the contact angle of water droplets on polymers decreases markedly after exposure to high intensity Hanovia ultraviolet arc lamp for only a few hours. Therefore, it was decided to follow any chemical change on the surface of the asphalt by measuring the change of the contact angle of water droplets.

Three different asphalts were exposed to ultraviolet light for increasing periods of time. The contact angle of water droplets on these surfaces did decrease with increasing periods (Fig. 8). In addition, there were some easily visible changes in the samples. Wrinkles, cracks and bloom occurred to a degree which increased with the length of exposure.

Miscellaneous Properties of Asphalts

Properties such as tackiness, fatigue, mar resistance, etc., are also of great interest to the engineer dealing with asphalt. Some work has been done on these properties but it is only of a preliminary nature. Tackiness, that is, the resistance of liquid adhesive joints to fail in cohesion,

Figure 7. Master plot of log a_T vs T - T_s (NARC asphalts).

is determined by the rheology of the adhesives and is not affected by their adhesion to the substrates. In fact, the tack temperature as defined by McLaren, Rager and Mark (16) is the lowest temperature at which two polymer films fuse when under a pressure of 20 psi and is found experimentally to be a temperature of constant viscosity. Bekerman has found that if the adhesive is Newtonian, tackiness is governed by Stefan's equation $4S t \delta d^2 = 3 \eta r^2$; S is the applied stress, t time of separation, and d initial thickness of the liquid film, η its viscosity and r radius of the adhered plates used in the experiment.

There are indications (22) that fatigue resistance is enhanced by using materials with both higher storage moduli and higher tan δ. Here colloidal differences may be more important than rheological properties.

It is found that mar resistance is increased by using a material with a high storage modulus and a low viscosity. Here a thick film gives greater resistance.

CORRELATION WITH PRACTICAL TESTS

The practical tests mentioned throughout this paper are described in more detail here. The penetration (ASTM D946-47T) is defined as the depth, measured in multiples of 0.1 mm, that a standardized needle penetrates into an asphalt surface under a constant load (100 g) in a specified time (5 sec).

The softening point, (ASTM E28-42) ring and ball, is determined as follows. A ring of given dimensions, filled with asphalt, is loaded with a steel ball (3.5 g). The whole is heated in a bath and the temperature at which the asphalt reached a certain deformation is reported as the ring and ball softening point.

It has been found experimentally that a certain penetration corresponds to a certain complex modulus, G*, at a rate of shear of 2.5 sec^{-1} or a frequency of .40 cps. Therefore a plot of complex modulus versus penetration for a number of asphalts (Fig. 9) should give a straight line. The figure shows a line drawn from van der Poel's data with
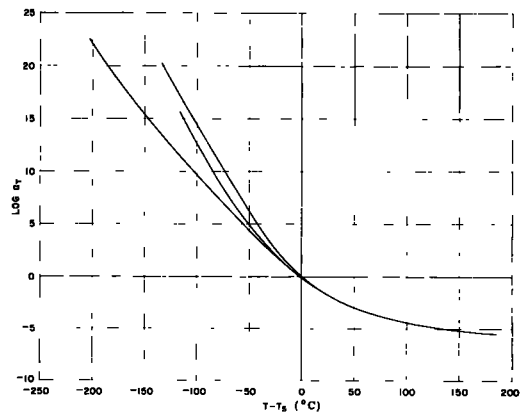
the points corresponding to the NARC standard asphalts. From these results, it can be seen that the determination of the penetration of an asphalt gives one a value of the complex modulus, G*, which is essentially an envelope of the G' and G" curves, at a frequency of 0.40 cps at 25 C (77 F).

PREDICTION OF RHEOLOGICAL BEHAVIOR FROM KNOWLEDGE OF THE SOFTENING POINT AND THE PENETRATION

The rheological properties of an asphalt are satisfactorily known if one has its reduced variable curves for G' and G" and its curve for initial viscosity as a function of temperature. Presented here is a means for obtaining a complete rheological description of an unknown asphalt, by running a minimum of laboratory measurements and utilizing the rheological curves for asphalts in general.

One first determines the softening point and penetration at 77 F, then looking at the figure (Fig. 1) for log penetration vs softening point the family in which the unknown asphalt belongs can be determined. Knowing this one knows which "section" of the generalized curve (Fig. 5) to use. Using again the softening point and penetration data and Figure 10, a vertical shift can be obtained which gives the point at which G' and G" are 10^6 dynes/cm^2 at 25 C, and a horizontal shift, which gives the point at which the frequency is one cycle per sec at 25 C. These shifts are measured from the origin (0,0) on Figure 5 and the axes of these points should be labelled 10^6 and 1 cps respectively.

If it is assumed that the softening point is equivalent to T_S, one can determine the proper curve of log a_T vs temperature (Fig. 7). Therefore, one now has the reduced curves of G' and G" vs frequency and their temperature dependence.

As $\omega\eta$ = G" at the lowest frequencies, it is possible to determine the initial viscosity at 25 C from the generalized curve given above; the log a_T vs temperature curve and Eq. 2 can be used to determine the viscosity at any other temperature. In this manner an initial viscosity vs temperature plot can be drawn for the unknown asphalt.

It must be stressed that these correlations are empirical and are derived from tests on NARC asphalts only. However, a check may be made on the positioning by obtaining the value of the complex modulus at 0.4 c/s and 25 C from the penetration at 77 F and the figure of log complex modulus vs log penetration (Fig. 9) and determining if it is the same as predicted by the generalized curve.

Sol C which has a penetration of 32 at 77 F and a softening point of 137 F (58.4 C) can be taken as an example of this method. From Figure 1 it can be seen that here is a member of the Sol family. By interpolating between the lines of Figure 10 a vertical shift of 1.00 and a horizontal shift of 3.65 are obtained. Making these shifts on the generalized curve (Fig. 5) one obtains the points for G', G" = 10^6 dynes/cm^2 and f = 1 c/s. At 0.4 c/s this generalized curve predicts G* = 3 x 10^7 as determined from Eq. 10. Figure 8 predicts G* = 0.80 x 10^7 dynes/cm^2. This agreement is probably good enough for engineering work and really is a small error considering that the values of moduli may easily change by several orders
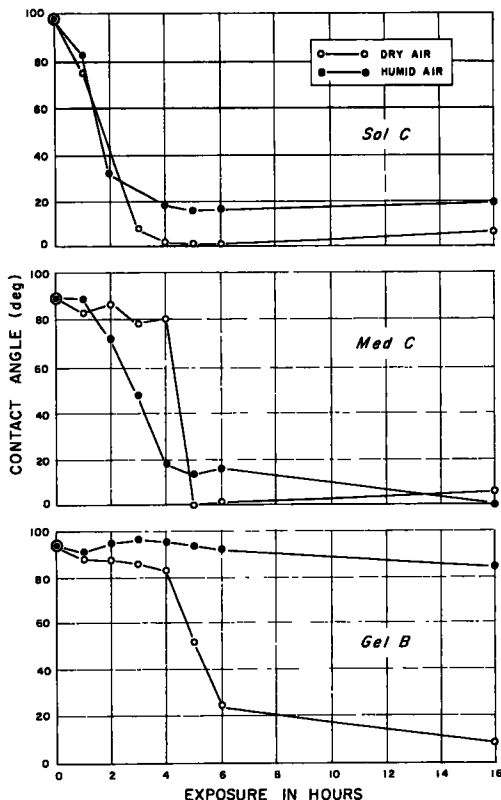

Figure 8.   Effect of ultraviolet radiation on contact angles.

TABLE 4
CORRELATION OF T_S WITH SOFTENING POINT

Code Name	T_S C	Softening Point C
Gel A	65.5	52.8
Gel B	106	89.5
Gel C	174	168.2
Med A	44	44.5
Med B	56	56.6
Med C	84	88.4
Med D	137	148.2
Sol A	34	38.9
Sol C	56	58.4
Sol D	86	84.5

TABLE 5
DIFFUSION CONSTANTS OF ASPHALTS
(Expressed in g/cm/mm Hg/hour x 10⁹)

Code Name	99.5 F	77.8 F
Gel A	14.9	9.6
Gel B	17.4	---
Gel C	22.2	---
Med A	---	---
Med B	---	---
Med C	16.4	10.0
Med D	21.4	12.8
Sol A	---	---
Sol C	16.6	---
Sol D	---	---

of magnitude with temperature and frequency changes.

By extrapolating to the lowest frequencies, where G' disappears, it is found that the initial viscosity determined from the generalized curve is 2.52×10^7 poises. To determine the initial viscosity at 100 C the log a_T vs T curve can be used (Fig. 7) and it is found that the shift from 25 C to 100 C is -5.50 or $a_T = 3.16 \times 10^{-6}$. As

$$\left(\frac{T_{100} \, \rho_{100}}{T_{25} \, \rho_{25}} \right) \simeq 1.20$$

Eq. 2 may be used to calculate the initial viscosity at 100 C. The Eq. $\dfrac{T \rho}{T_0 \rho_0} = 1 + (\dfrac{1}{T_0} - \alpha) \Delta T$ was used where $\alpha = 6.1 \times 10^{-4}$

$$\eta_{100} = a_T \left(\frac{T_{100} \, 100}{T_{25} \, T_{25}} \right) \qquad \eta_{25} = 3.16 \times 10^{-6}$$

$\times 1.20 \times 2.52 \times 10^7 = 95.5$ poises. This compares with the experimentally-determined value of 290 poises.

EXAMPLES OF USE OF RHEOLOGICAL DATA FOR ASPHALTS

After reduced variable curves for an unknown asphalt are obtained what can be done with them? Below are given a few examples of engineering questions which might be asked. The examples are selected to show the various aspects of asphalt behavior which may be ascertained from the data: (a) a flow problem, sliding on a slanted surface under the weight of granules; (b) damping, the attenuation of vibrations by asphalt; (c) a deformation problem, the bending of a beam under a concentrated load; and (d) a strength problem, the stresses set up by thermal change.

In the first example it is necessary to know the initial viscosities of the asphalts. In the second example the ratio of the loss modulus to the complex modulus is the determining quantity. This shows the necessity for separating the complex modulus into its components. The third example uses the whole complex modulus and the fourth example uses the information on the breaking properties of asphalt.

Sliding of Granules on a Roof

Sliding of granules or other loads on slanted decks can be calculated readily by means of the parallel plate viscometer as a model. The asphalt is visualized as a layer between the felt and the granules. It is sheared by the vertical component of the granule weight.

$$\eta = \tau \frac{tl}{d}$$

where

d	=	amount of flow,
l	=	thickness of asphalt film.

$$\tau = \frac{W \sin\theta}{A}$$

when

W = weight of granules,

A = area of granules,

θ = pitch of the roof, and

t = time in sec.

As a practical problem the ASTM softening point and penetration of a Medium asphalt that will permit a slide rate (d/t) of 0.01 in. per month at 135 F under a weight of granules of 60 lb/100 ft² will be determined. The thickness of the asphalt is 0.05 in. and the pitch of the roof is 1:5.

$$\sin\theta = \frac{1}{\sqrt{1^2 \times 5^2}} = 0.196$$

$$\tau = \frac{W \sin\theta}{A} = \frac{60}{100 \times 144} \ (0.196) = 0.000818 \text{ psi} = 56.3 \text{ dynes/cm}^2$$

Since this value of τ is well under 3,000 dynes/cm², the asphalt will behave as a viscous liquid (Sec 3A), whose initial viscosity at 135 F is desired.

$$\eta = \tau \frac{tl}{d} = \frac{56.3 \times 2.59 \times 10^6 \times 0.05}{0.01} = 7.3 \times 10^8 \text{ poises}$$

From Figure 6 it is known that the asphalts have these initial viscosities:

MED C, 191 SP = 2.9×10^7 poises, and
MED D, 325 SP = 1.8×10^{13} poises.

For a fair approximation the log of the initial viscosities vs the softening point is plotted. This relationship is approximately linear. Then by interpolation the softening point is found for which $\eta = 7.3 \times 10^8$. It is 224 F. From Figure 1 it is seen that the penetration is 11.3.

In passing it is noted that both the thickness of the asphalt layer and the weight of the granules enter directly into the calculations as first powers; doubling the thickness or doubling the weight of granules would also double the creep rate and double the required viscosity.

Attenuation of Vibrations

The basic manifestation of the absorption or attenuation of vibrational energy is the conversion of organized systematic motions of the particles of the medium into the uncoordinated random motions of thermal agitation. If it is assumed that the organized motion is sinusoidal and has the angular frequency $\omega = 2\pi f$, the velocity of a surface causing a shearing motion can be represented by
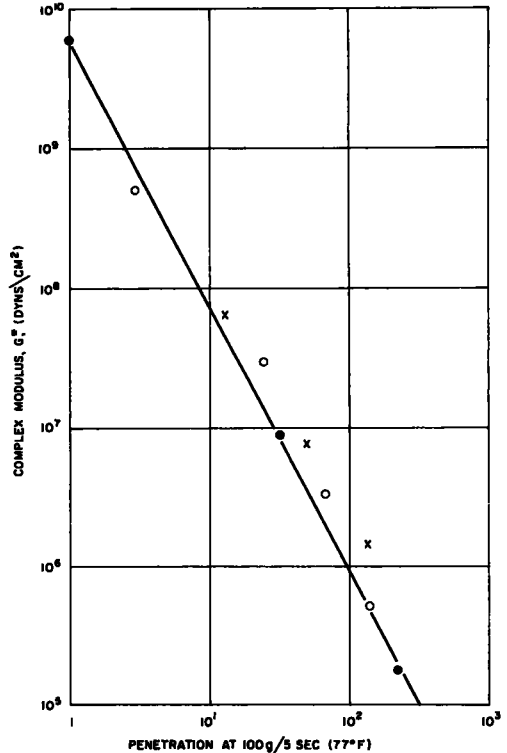
$$v_s = v_0 e^{i\omega t}$$

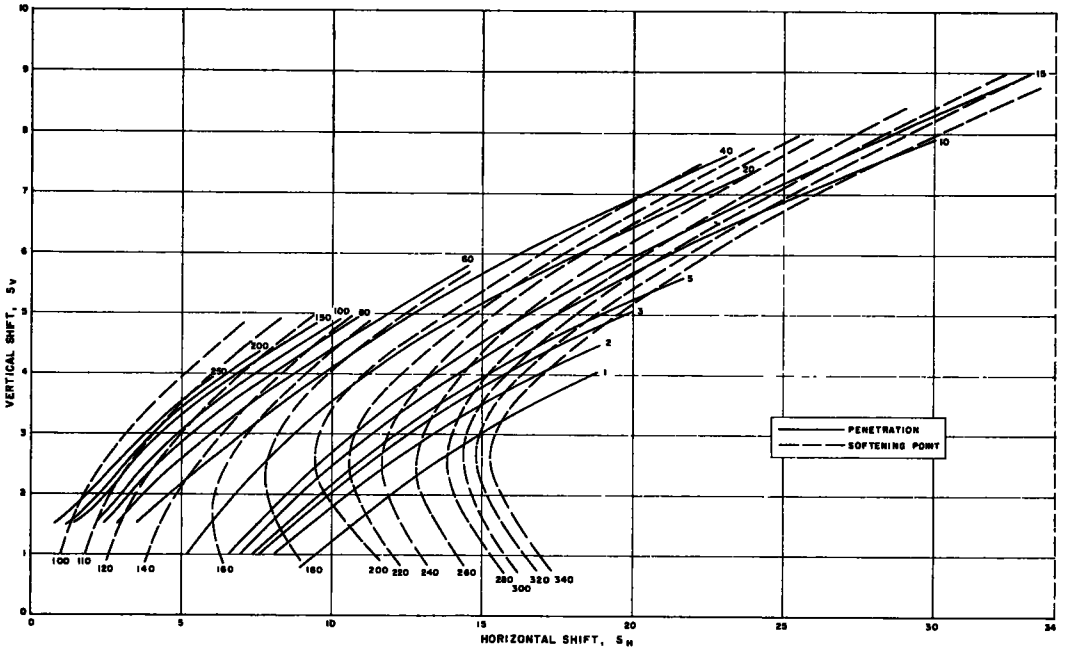Figure 9. Relation between complex modulus at f = 0.4 cps and penetration at 5 sec.

Figure 10. Relationship between horizontal and vertical shifts for given softening point and penetration (basis: 10 asphalts).

The transverse velocity of the liquid at the distance x from the oscillating surface is:

$$v_1 = v_0 e^{-\Gamma x} e^{i\omega t}$$

where Γ is the complex propagation constant, $\Gamma = (i\omega\rho/\eta*)^{\frac{1}{2}}$

$$i = \sqrt{-1}$$

ρ is the density, and

$\eta*$ is the complex viscosity defined as $\eta* = \eta' - i\eta''$

$$\eta' = \frac{G''}{\omega} \quad \text{and} \quad \eta'' = \frac{G'}{\omega}$$

Therefore if it is assumed that $\Gamma = \alpha + i\beta$, that is,

$$v_1 = v_0 e^{-\alpha x} e^{i(\omega t - \beta x)}$$

$$\Gamma^2 = \alpha^2 - \beta^2 + 2\alpha\beta i = \frac{i\omega\rho}{\eta' - i\eta''}$$

By suitable algebraic manipulation

$$\alpha = \frac{\omega\rho^{\frac{1}{2}} G''}{|G*| (G' + |G*|)^{\frac{1}{2}} (2)^{\frac{1}{2}}} \quad \text{and} \quad \beta = \frac{\omega\rho^{\frac{1}{2}} (G' + |G*|)^{\frac{1}{2}}}{|G*| (2)^{\frac{1}{2}}}$$

α is the attenuation constant and measures the rate at which the wave is damped or attenuated. It can be seen that at a given frequency the attenuation is essentially dependent on the ratio $G''/|G*|^{3/2}$. Therefore for rapid attenuation it is imperative to have a large value of G'' with respect to $|G*|$, that is, $G'' >> G'$. To transmit energy with little attenuation it would be necessary to have $G'' << G'$.

As an attenuation constant, α measures the rate at which energy is dissipated. Actually, vibration is not always caused by a shearing wave. For example the impact of an

object on the surface of an asphalt highway surface would send a compressional wave through the material but it would be attenuated in qualitatively the same manner as a shearing wave. Therefore it may not be possible to tell quantitatively the exact amount of attenuation of a wave, but asphalts can be compared and it is known that the one with the larger ratio of G'' to $|G*|^{3/2}$ will dissipate energy faster.

Use of Results of Classical Elastic Theory

Once the properties of a visco-elastic material have been described, there still remains the problem of the behavior of visco-elastic objects in which the stress and strain are functions of both position and time. The bending of a beam under a concentrated load at the center is taken as an example. The classical elastic law (18) gives

$$\frac{\partial^2 \xi}{\partial x^2} = \frac{-M_B}{EI} \tag{1}$$

where

ξ = deflection of the beam at a distance x from the support on one side,

M = moment causing the deflection,

E = Young's Modulus,

I = moment of inertia.

For a visco-elastic body, ξ , E and M are also functions of time;

$$E^*(t) I \frac{\partial^2 \xi(x,t)}{\partial x^2} = -M_B(x,t) \tag{2}$$

The differential equation can be solved using the well-known method of separation of variables. Therefore, $\xi(x,t) = X(x) T(t)$ is assumed and $-M_B(x,t) = g(x) f(t)$ and one obtains:

$$E^*(t) I \frac{d^2 X(x)}{dx^2} T(t) = g(x) f(t) \tag{3}$$

Collecting like terms on opposite sides of the equal sign and equating them to a constant $(1/k)$ one obtains:

$$I k \frac{d^2 X(x)}{dx^2} = g(x) \tag{4a}$$

$$E^*(\omega) T(t) = k f(t) \tag{4b}$$

Under these conditions it is seen that the visco-elastic problem leads to a space equation that is identical with that obtained in the pure elastic problem, with k acting as the modulus of elasticity. Consequently, its solution is known.

$$X(x) = \frac{PL^3}{kbh^3} \left(\frac{3x}{4L} - \frac{x^3}{L^3} \right) \tag{5}$$

and as $\xi(x,t) = X(x) T(t)$,

$$\xi(x,t) = \frac{L^3}{bh^3} \left(\frac{3x}{4L} - \frac{x^3}{L^3} \right) \frac{Pf(t)}{E^*(\omega)} \tag{6}$$

Here the classical Young's Modulus is replaced by the complex modulus and the term gives the time dependence of the stress. The maximum stress and deformation are given by the equations:

$$\sigma_{max}(t) = \frac{3}{2} \frac{L}{bh^2} Pf(t) \tag{7}$$

and

$$\xi_{max}(x,t) = \frac{L^2 \rho(t)}{6hE^*(\omega)} \quad \text{or} \quad \xi_{max}(x,t) = \frac{L^2}{6h} Y(t) \tag{8}$$

If the application of stress is sinusoidal, then $\sigma(t) = \sigma_0 \sin \omega t$, or

$$\xi_{max}(x, t) = \frac{L^2 \sigma_0 \sin \omega t}{6hE^*(\omega)} \qquad (9)$$

However, if a constant stress is applied, then σ_{max} is not a function of time, that is,

$$\sigma_{max} = \frac{3L}{2bh^2} P$$

In this problem it may be desired to know the deformation after a given time. The strain will be determined by the equation (20)

$$Y = \left[\epsilon_\infty + t/\eta + \psi(t) \right] \sigma \qquad (10)$$

$\sigma \epsilon_\infty$ is the instantaneous component of strain and, being quite small, may be neglected; η is taken to be the initial viscosity if σ is less than 3,000 dynes/cm^2 and $\psi(t)$ is the creep function with $\psi(0) = 0$. In this particular case,

$$\xi_{max}(x, t) = \frac{L^2}{6h} Y(t)$$

thus

$$\xi_{max}(x, t) = \frac{L^2}{6h} \left[t/\eta + \psi(t) \right] \sigma$$

governs the flow or deformation of a beam at the point of concentrated load. To determine $\psi(t) \sigma$ from the basic data of G' and G'' vs f is a matter of graphical evaluation.

First to be determined is what is known as the relaxation distribution function, Φ, as a function of relaxation time, τ. If it is assumed that $\tau = 1/\omega$ where $\omega = 2\pi f$ for each evaluation, Φ is given approximately by the following equations (9):

$$\Phi(-\ln \omega) = G' \frac{d \log G'}{d \log \omega} \qquad (11a)$$

$$\Phi(-\ln \omega) = G'' \left(1 - \frac{d \log G''}{d \log \omega} \right) \qquad (11b)$$

This function then can be determined from the family curves. The Φ vs τ curves for the NARC asphalts are given in Figure 11. Ferry et al have shown that the course of stress relaxation after cessation of steady flow, the author's $\psi(t) \sigma$, is given approximately by

$$\dot{Y} \int_{\ln t}^{\infty} \tau \Phi \, d \ln \tau$$

where $\dot{Y}$ is the rate of shear strain and it may be approximated by σ/η.

If $\tau \Phi$ vs $\log \tau$ is plotted and if one evaluates graphically from $\log t$ to infinity, $\psi(t) \sigma$ can be obtained; therefore, the deformation under a constant concentrated load, such as the wheel of a parked car can be obtained.

In this example several noteworthy features of general nature are seen. The complete space and time dependent problem splits neatly into one spatial problem and one temporal problem. The spatial problem is identical with that for a purely elastic problem and the temporal one may be solved with the knowledge of the time behavior of the elastic moduli.

This method of attack may be used on many problems, such as the deflection of an asphalt road bed under passing cars, rutting, shoving, etc.

Thermal Stresses

When the temperature of an unrestrained body is increased by ΔT, dilation of an amount proportional to ΔT can be produced without any corresponding change of pressure. This implies extension of all linear elements by $\alpha \Delta T$, where α is a constant, the coefficient of linear expansion. If forces are applied to the body, the strain at a point consists of such extension superposed upon a strain connected with the stress by the usual stress-strain equations.

According to these assumptions the stress, (σ) and strain in a body strained by change of temperature do not obey Hooke's Law, but are connected by the equation:

$$\gamma \text{ (tensile strain)} = \alpha \, \Delta T - \frac{\sigma \text{ (tensile)}}{E}.$$

If the asphalt is constrained so that it cannot move, that is, $\gamma = 0$ then a compressive stress is created which is equal and opposite to $\alpha \, \Delta T E$.

As $\alpha = 2.0 \times 10^{-4}$ (24) and $E \sim 3G'$ if incompressibility is assumed a relationship between the change in temperature and a compressive stress is obtained.

Therefore $\sigma = 6.0 \times 10^{-4} G'\Delta T$ and this stress must be below the breaking stress if a crack-free continuum is to exist. As the temperature change must be measured in a finite time and both G' and the breaking stresses are dependent on time, the rate at which the temperature changes is very important. For slow changes, except at very low temperatures, the stresses are low and should be able to relax with the loss mechanisms coming into play. However with rapid changes of temperature G' will be of the order of 10^9 to 10^{10} dynes/cm^2 and $\sigma = 6.0 \times 10^5 \Delta T$ to $6.0 \times 10^6 \Delta T$. In the section on breaking strength it was shown that the breaking stresses vary from 0.7×10^7 to 2.4×10^7 dynes/cm^2 at high rates. Therefore one must have $(6.0 \times 10^5$ to $6.0 \times 10^6) \Delta T < 0.7 - 2.4 \times 10^7$. This means that it might be possible to have a change of 100 C without any cracks.

The results depend upon the equation

$$6.0 \times 10^{-4} \Delta T < \frac{\sigma}{G'} \text{ Breaking}$$

where ΔT is the temperature change which takes place during the time of the experiment. This shows that the change in temperature a material can take depends upon the ratio of the breaking stress to the storage modulus. Therefore materials must be sought which have high breaking strengths and comparatively low moduli.

Figure 11. Distribution of relaxation times (all NARC asphalts).

CONCLUSIONS

All the foregoing information, the dependence of the moduli, G' and G'', on frequency, the temperature dependence of the asphalts, ets., show that asphalts behave very much like concentrated solutions of high polymers, that is, typical visco-elastic bodies. Therefore it has been possible to incorporate much of the work, both theoretical and experimental, in the high polymer field into the framework of an asphalt technology. It has then been possible to condense all the experimental information into a few
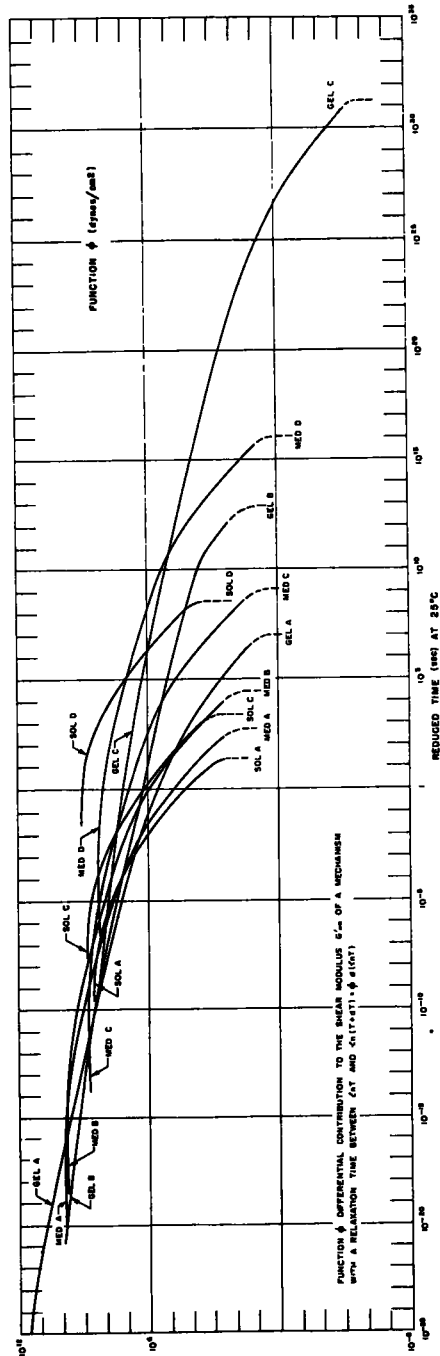
curves and tables: the family curves of moduli vs frequency, the curves showing the dependence of log a_T on $T - T_s'$ the dependence of initial viscosity on temperature, etc. These are essentially convenient methods for representing a great number of experimental results. If more data become available, changes may be required but major changes are unlikely as such a wide variety of types have been investigated.

With the calculation of the parameters involved in the two typical asphalt tests, softening point and penetration, it is possible now to decide in which family a particular asphalt belongs, its temperature dependence and its moduli dependence on frequency, and finally the dependence of its initial viscosity on temperature. Therefore from these two simple tests it is possible to find the whole rheological behavior of an asphalt, provided the generalized asphalt curves are available.

In the work just described the macroscopic behavior of asphalt has been investigated. No correlations with molecular structure are indicated but this is the ultimate aim of the physicist or chemist. Some work, not reported here, has been done in an attempt to relate empirically various portions of the relaxation spectra (Φ vs log τ) to various components of asphalt. Although partially successful more information is needed to extend the method. Possibly the new technique of Nuclear Magnetic Resonance might be helpful. An attempt, by the author, also not reported here, was made to estimate the molecular weights of the large particles involved in the flow of asphalt from the dynamic behavior of asphalt and present-day theories on the dynamic behavior of high polymers. The results indicated very large molecular weights for the flow particles. These are only initial attacks on the molecular basis of asphalt behavior and have yet to be followed up in detail.

The test on which the experimental results are based were made on freshly-poured asphalts. Therefore not much can be said about the change of the rheological behavior with aging. These aging properties are tied up with molecular motions and orientations which occur during application and service. Here again the new technique of Nuclear Magnetic Resonance may be able to show what changes take place.

It is hoped that this paper, which gives details on how asphalts react in flow, stimulates further work to answer why asphalts react the way they do.

ACKNOWLEDGMENTS

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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 fun -
damental nature, but duplicate film thicknesses encountered in the
pavement. This necessity of matching geometry of testing to geom-
etry 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 ap-
proach 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 dupli-
cate 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 specifi-
cations. 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 un-
answerable by empirical tests, does not seem to help here.

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

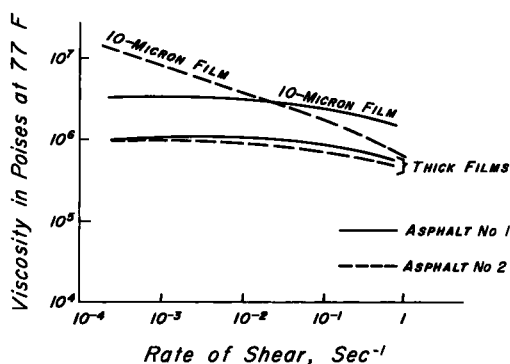In going from thick to thin films, the viscosity of asphalt No. 1 has increased and

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

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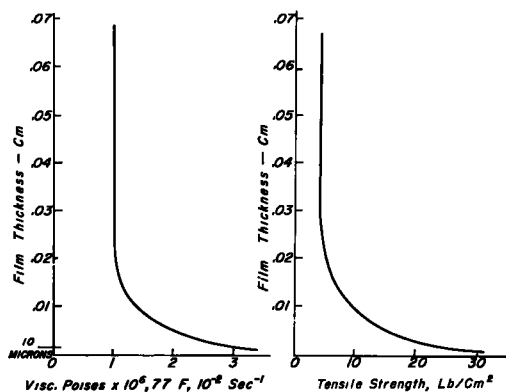
Even though these two Venezuelan asphalts are from the same source, there must be enough difference in molecular composition to account for the difference in behavior in thin films.

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 1½ 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 ½ 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.

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[a] |
	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

[a] Blocks on end; 2,500-g loading at 140 F; time to sag $\frac{1}{8}$ in.

[b] 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-
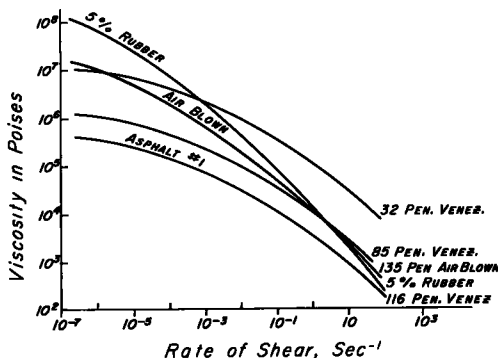

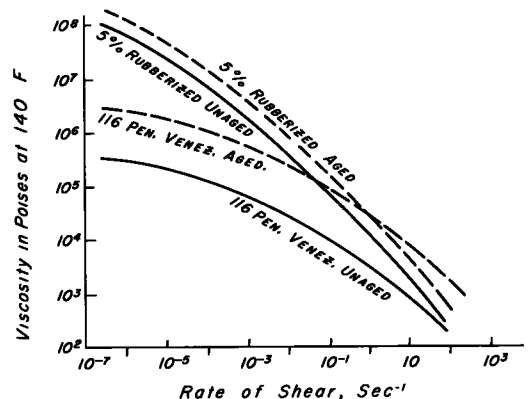Figure 3. Steady-state viscosity at 140 F.

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

[a] 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 (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 ½-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.

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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).
5. Rostler, F.S. , and Sternberg, H.W. , Ind. Eng. Chem. , 41:589-608 (1949).
6. Van Oort, W. P. , Ind. Eng. Chem. , 48: 1196-1201 (1956).

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[1] is quoted to illustrate this point:

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[1] "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 $^{-1}$
69.4	1.55×10^6
50.8	1.50×10^6
29.3	1.50×10^6
10.2	1.40×10^6

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[2], which are quoted from the paper "Sliding Plate Microviscometer for Rapid Measurement of Asphalt Viscosity in Absolute Units." Another slightly non-Newtonian $85/100$ penetration grade asphalt was used in this case.

Viscometer Type	Film Thickness, microns	Viscosity, Poises at 77 F, Shear Rate 0.05 sec $^{-1}$
Covette conicylindrical	5,000	7.9×10^5
Open end ring viscometer	2,000	7.8×10^5
Sliding plate, air bath model	109	7.6×10^5
Sliding plate, water bath model	11	7.8×10^5

In the case of a third $85/100$ 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
Microns	Inches	Shear Rate 0.05 sec $^{-1}$
9.25	0.000364	1.28×10^6
6.60	0.000260	1.37×10^6
4.85	0.000191	1.23×10^6

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.

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[2] "Road and Paving Materials," Spec. Tech. Pub. No. 212, ASTM (1957) (See Table III).

Progress with Adhesion-Improving Bitumen Additives

ANDREJS ZVEJNIEKS, Chemical Division, General Mills, Inc., Kankakee, Ill.

Some theoretical aspects of adhesion are discussed and the test methods for testing adhesiveness of bituminous binders are reviewed. An attempt is also made to summarize and compare the current practices with bitumen additives in the United States and in Europe. A coordinated large-scale road test program is suggested in order to keep up with the recent European development.

Where bituminous binders are used, many problems and failures are caused by water. It has been demonstrated experimentally that the tensile strength of a hot-mix pavement can be lowered to one-fourth of its original value by soaking in water for four days. Adhesion-improving bitumen additives are used to avoid and overcome these failures. Generally these additives consist of polar molecules, which tend to concentrate in the interfaces, adhere to the aggregate surfaces, and strongly improve the bond between the binder and the aggregate. For cold-mixed pavements and seal coats, an active adhesion is required; that is, the additive-improved bitumen must have the ability to adhere to wet aggregates and to replace water on wet surfaces.

Reliable test methods are of prime importance for evaluation and classifying of adhesion-improving additives. The test methods used can be described as measurement of fundamental physio-chemical properties, and simulation of road conditions.

Usage of adhesion-improving bitumen additives in some European countries seems to be far ahead of the corresponding usage in the United States. In Western Europe additives are used much more frequently and at higher levels. Extensive tests in Sweden and England have resulted in acceptance of amine-type additives. The latest trend is essentially toward new applications for improved bituminous materials.

The limited heat stability of additives known to be really efficient and economical does not allow heating of "doped" bitumens for prolonged periods. European practice is to mix additives and cut-back asphalt directly in the distributors. Additives in solid form are often preferred, owing to easier and safer handling.

● THE PRINCIPLE of improving the properties of a cheap basic material with additives is successfully used throughout industry. For instance, modern lubricating oils are "built" to such an extent that some authorities regard the base oil as being only a carrier for different types of additives.

For the road building industry where bituminous binders are used, many problems and failures are caused by water. Special bitumen additives are used to overcome these problems and failures.

At present stage of development, the usage of asphalt adhesion-improving additives in some European countries, particularly in Sweden, England, France and West-Germany, is far ahead of the usage in the U.S. For instance, asphalt consumption for road building in Sweden was about 0.7 percent of the asphalt consumption in the U.S. (45,000 vs 6,000,000 tons in 1955). For this same period, the usage of additives in Sweden was approximately equal to the total usage of additives in the U.S.

The aggregate has a greater affinity for wager than for bitumen, therefore, a wet aggregate cannot be successfully mixed with an unimproved binder. Thermodynamic considerations show that energy is gained when water replaces bitumen on the aggregate surface, and stripping is likely to occur in areas exposed to water. Nevertheless, apparent stripping is only part of the problem. It has been demonstrated experimentally,

using a test method similar to U.S. Public Roads Administration immersion compression test, that the tensile strength of a "hot mix" type pavement can be lowered to one-forth of it's original value by soaking in water for four days, even if no visible stripping occurs. Figures 1a and 1b present tensile strength curves of two mixes—one with and the other one without additive. The relative tensile strength t, defined as:

$$t = \frac{\text{tensile strength of wet slabs at 2.5 mm extension} \cdot 100}{\text{tensile strength of dry slabs at 2.5 mm extension}}$$

is 26 percent without additives compared with 81 percent with additives. This, as well as many other observations, illustrates that the static immersion-stripping tests and the nomenclature anti-stripping agents are inadequate. The term adhesion-improving additives is proposed and used in this paper.

BASIC THEORIES

The author considers the adhesion between aggregate and bitumen to be constituted as shown in Figure 2a. Polar molecules present are adsorbed by the aggregate and by the colloidal asphaltene particles. The lipophilic parts of these adsorbed molecules are solubilized by the non-polar part of the bitumen. As mentioned, water has a greater affinity for the aggregate surfaces, and the polar molecules found in natural bitumens are not adsorbed strongly enough to withstand water. After soaking in water these organic molecules are replaced by the water as shown in Figure 2b.

Adhesion-improving additives are chemicals which are especially well adapted to assist and improve the action of compounds already found in natural bitumen. The primary requirements for an adhesion-improving additive are:

1. To be efficient when present in small amounts;
2. To be economical;
3. To give an adhesion which is able to withstand the aggresion of water (passive adhesion); and
4. To have no undesirable side effects on the binder.

Moreover, for all types of cold mixed pavements and seal coats, an active adhesion is required; that is, the additive—improved bitumen must have the ability to adhere to wet aggregate and to replace water on wet aggregate and on wet road surfaces.

There are two basic interpretations of the function of adhesion-improving additives in the road building industry. The opinion which was predominant until the late forties, regarded the additives as an insurance against failures caused by unforeseen circumstances. The more recent opinion realizes that, with adhesion-improving additives, the properties of the bitumen can be changed to such an extent, that a material with principally new properties and new potential uses is obtained. This improved bitumen often enables the use of cheaper construction and can be used in fields where a conventional bitumen fails.

METHODS OF TESTING

The full benefits of bitumen additives can not be utilized without satisfactory test methods and without intelligent specifications. Particularly due to the great cost of road construction work, reliable test results are required to decide why, where, which and how much of the adhesion-improving additives are to be used. In practice, there are too many variations in the test methods and in the test results as well.

Having no possibilities to determine which additive is the most efficient and the most economical one, contractors are forced to use the cheapest one.

In order to check the adhesion, an old contractor in the author's old country used to chew a piece of asphalt. The one which stuck to his teeth was a good one. More modern test methods which are used for testing of bituminous binders on aggregate surfaces for adhesiveness and for resistance against water can be divided in two main classes, as follows:

1. Measuring of fundamental physio-chemical properties.
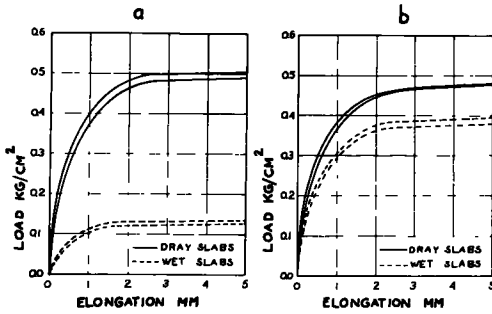2. Methods simulating road conditions.

Figure 1. Tensile strength curves for (a) test slabs made of binder without additives, (b) test slabs made of binder containing 1 percent octadecyle amine.
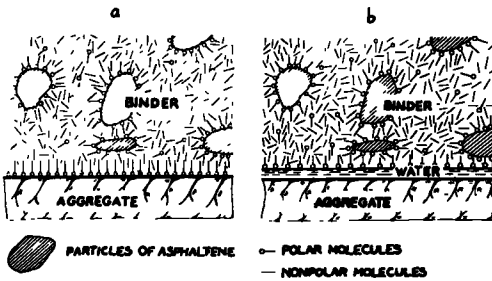

Figure 2. Adsorption of polar oil molecules to the particles of asphaltene and aggregate, (b) the same binder and aggregate after soaking in water.
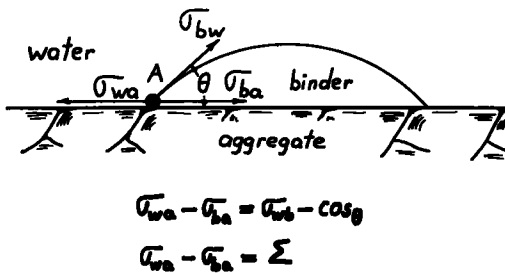

$$\sigma_{wa} - \sigma_{ba} = \sigma_{wb} - cos_\theta$$

$$\sigma_{wa} - \sigma_{ba} = \Sigma$$

Figure 3. A droplet of liquid binder on the aggregate immersed in water.

MEASURING OF PHYSIO-CHEMICAL PROPERTIES

Of the simple physio-chemical properties connected with adhesion in the presence of water, the interfacial tension between binder and water (which is numerically equal to the interfacial energy) and the adhesion tension are very important. These two properties have been measured and used successfully as an indication of the type and strength of adhesion. The conception of adhesion tension, Σ, is explained in Figure 3, representing a droplet of liquid binder on the aggregate immersed in water.

Any point A on the solid surface which lies on the dividing line between the two liquids is a junction for three forces—interfacial tensions. By an unbalance of these three forces, point A has to move along the surface of the aggregate, the aggregate being a solid. The condition for A being in balance is:

$$\sigma_{wa} \qquad \sigma_{ba} \quad = \quad \sigma_{wb} \quad \cos \theta$$

where:

σ_{wa} = the interfacial tension between water and aggregate,

σ_{ba} = the interfacial tension between binder and aggregate,

σ_{wb} = the interfacial tension between water and binder,

θ = the contact angle.

The expression σ_{wa} and σ_{ba} is symbolized by Σ and is called the adhesion tension. At present, it is not possible to determine σ_{wa} and σ_{ba} separately, whereas Σ can be measured according to Bartell (2) in his cell, or according to Hallberg (3) in his adhesion meters.

Some complications are caused by hysteresis. The hysteresis known for the contact angles is observed also for adhesion tension. Hallberg solves this problem by measuring two limit values,

$$\Sigma_b = \Sigma_{binder} \text{ and } \Sigma_w = \Sigma_{water},$$

as follows:

1. $\Sigma_b = \Sigma_{binder}$ = the adhesion tension of the binder on an aggregate is the maximum resistance in dynes per cm which the binder is capable of withstanding when exposed to water under pressure. This value of adhesion tension corresponds to the receding contact angle for the binder:

$$\Sigma_b = \sigma_{wb} \quad \cos \theta_{receding}$$

ERRATA

BULLETIN 192

In Bulletin 192, the formula on page 28
should read:

$$\sigma_{wa} - \sigma_{ba} = \sigma_{wb} \cos \theta$$

and the first line of the following
paragraph should read:

The expression $\sigma_{wa} - \sigma_{ba}$ ....

2. Σ_W = Σ_{water} = the adhesion tension of the water on an aggregate is the maximum resistance in dynes per cm which the water is capable of withstanding when exposed to binder under pressure. This value of adhesion tension corresponds to advancing contact angle for the binder (receding for water):

$$\Sigma_W = \sigma_{wb} \quad \cos \theta \quad \text{advancing}$$

Typical Σ_b and Σ_W curves as functions of concentration of the additive (octadecyl amine) are shown in Figure 4.

Both Σ_b and $-\Sigma_W$ are negative for unimproved binder, which means that binder can be displaced by water without the aid of exterior forces. At an amine concentration of about 0.05 percent, Σ_b becomes positive, which means that water cannot replace binder without the help of exterior force. This condition is called passive adhesion.

At an amine concentration of about 1.0 percent, the Σ_b is 12 cyn/cm, which means an exterior force of 12 dyn/cm is necessary to displace binder with water. At this concentration, $-\Sigma_W$ also becomes positive, which means that the binder is able to adhere to wet aggregate and to displace water spontaneously from the aggregate surface. This condition is called active adhesion.

METHODS SIMULATING ROAD CONDITIONS

The methods in this category start from the static immersion-stripping tests and stretch through more elaborate stability tests, to "road machines" and full scale road tests. Immersion-stripping tests have the advantage of being simple and fast. Nevertheless, these tests are inadequate for the more thorough investigations because of the poor reproducibility of results and also because the trends obtained often are not in agreement with the actual performance of the material on the road.

For definite answers to all of the questions connected with the economical usage of adhesion-improving additives, advanced tests in road laboratories as well as full scale tests are necessary.

Figure 5 shows a photograph of the "road machine" built and used at the Swedish State Road Institute, Stockholm.

In this apparatus (4), the traffic speed and load on the test pavement which was laid on a circular track could be varied within ranges to duplicate the speeds and loads of commercial vehicles. The test pavement could also be exposed to artificial rain and the temperature in the test room could be lowered below the freezing point. Among the numerous test results obtained with this apparatus, the one concerning seal coats and reported by Hallberg at the 9th Road Congress, Lisbon, 1951, could be of particular interest. Hallberg states (5); "A surface treatment with M_C-5 without additives was quite free of chippings after 800 wheel passages when subjected to heavy traffic in rain immediately after laying, whereas a surface treatment tested in the same way, but with

Figure 4. Adhesion tension—concentration curves for octadecyl amine in cut-back (MC - 0).

1.5 percent amine in the cut-back, was still, after 50,000 wheel passages, practically without defects."

Figure 6 (7), is a reproduction of a photo taken of a maintenance seal coated Swedish highway showing a rather sharp dividing line between a section using cut-back containing 1.5 percent amine (in foreground) and a section using the same cut-back but without addi-
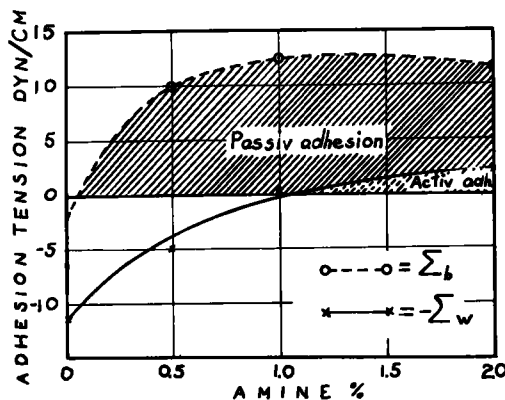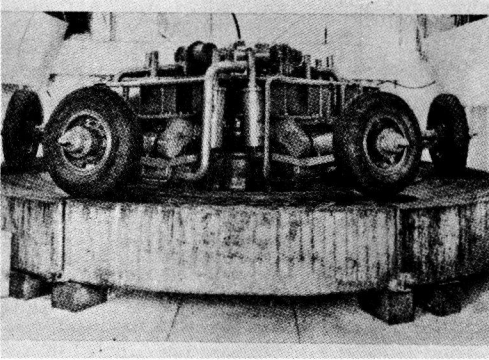
Figure 5. Road machine of Swedish State
Road Institute.

tive (in background). These seal coatings
were made in good weather. Heavy rain-
fall occurred 3 days after laying.

CHEMICALS USED

The number of chemicals proposed for
use as adhesion-improving additives to bi-
tumen or for treating of aggregate is very
large. These are often marketed under
imaginative synonyms and trade names.
For an intelligent evaluation, it would be
desirable, or perhaps even necessary, if
the chemical composition or equivalent in-
formation concerning the additives were
made known and stated along with the pub-
lication of the test results. Classes of
compounds which, to the author's knowledge,
are most widely used as adhesion-improv-
ing additives in commercial road construction are: primary fatty amines, fatty amino
amides and imidazolines, fatty diamines, fatty acids, fatty acid-amine mixtures, and
metal soaps. Also, alkynolamine fatty esters, secondary and tertiary fatty amines,
rosin amines, quarternary ammonium compounds, fatty alcohols, and silicones have
been proposed and used.

The heat stability of additives is often considered to be critical. Unfortunately, all
of the additives known to be really efficient cannot withstand heating for prolonged peri-
ods. As a rule, for best results the chemicals have to be added to the bitumen the same
day as it is to be used. Some progress has been made in development of more heat-
stable adhesion-improving additives which can be added to the asphalt at the manufactur-
ing stage. Nevertheless, the original efficiency of the heat-stable additives seems to be
much lower.

PROGRESS IN THE UNITED STATES

The present U. S. road building program is at an all-time high and demands tremen-
dous quantities of materials, labor and equipment. However, it seems that the adhe-
sion-improving bitumen additives have not yet found their proper place in this program.
Some states and also some private companies and contractors are using addivites en-
thusiastically, while the others are more
or less indifferent toward the use of addi-
tives.

One of the reasons why the use of addi-
tives is still a questionable matter is that,
in too many cases, insufficient amount of
active ingredient is used. The adhesion
at low concentrations of additive is only
"passive" and, therefore, is often inade-
quate for severe conditions. A concentra-
tion in excess of 0. 5 percent, and often
even in excess of 1. 0 percent of the active
chemical is required to obtain "active ad-
hesion." Some failures could also origi-
nate in the numerous and different types
of aggregate. There are additives which
are efficient only on some particular types
of aggregate.

Many types of adhesion-improving
chemicals are used in this country, none
being especially predominate.

Figure 6. A maintenance seal coat on a
Swedish road with cut-back (MC - 5) con-
taining 1.5 percent amine (in foreground)
and the same seal coat but without amine
(in background). Seal coating was made in
good weather—heavy rainfall three days
later.

The major consumption is in cheaper types of pavements for secondary roads. The trend is to incorporate additives in the asphalt at the manufacturing stage, therefore, it has been suggested that the heat stability is of critical importance. Some promising work has been done in developing heat-stable adhesion-improving additives, nevertheless, heat stability requirements which are too hard, eliminate all the classes of compounds currently known to be really efficient and economical. For this reason, some compromise has to be made between the heat stability requirements and the other desirable properties. Particularly owing to the simplicity with which the additives can be added to the cut-back directly into the distributors, the same day the cut-back is used, the requests for absolute heat stability could be given some new considerations.

Rapidly increasing interest in the amine type additives for asphalt emulsions is occuring.

PROGRESS IN EUROPE

In Sweden the use of primary fatty amines as adhesion-improving additives to bitumen broke its way through dur ng the years 1951-1953. This caused revolutionary changes in paving technology and during these years consumption of cut-back asphalt in Sweden increased 15 fold. Seal coatings, then on decline, made a strong come back and are now used not only on secondary roads, but also on heavily traveled highways.

The development in England has been a very similar one. The English authorities Lee and Nicollas stated in a paper presented at a conference held in London in 1952 (6): "Surface dressing carried out in the unsettled weather often experienced in Great Britain can be a hazardous technique, and in the wetter areas of the country much money has been lost in poor seasons. This has been the position until recently; now a reliable solution of these troubles has been found."

In England, amine type additives are also used successfully in tar surfacings and with limestone chippings.

In general, the European practice is to purchase asphalt or cut-back and the additive separately, making the mixing in the distributor tanks and shortly before the use. Additives in solid form are often preferred owing to easier and safer handling.

A new promising line of development in Sweden, made possible through the use of efficient adhesion-improving additives, is low cost secondary roads of gravel and residue oils. These roads require very little maintenance and can be regraded after about one year's service without addition of new material. Additives are also used to some extent in "hot mixes," particularly for thin carpets and for open textured asphaltic concrete.

SUMMARY

For the road building industry, where bituminous binders are used, many problems and failures are caused by water. It has been demonstrated experimentally that the tensile strength of a "hot mix" type pavement can be lowered to one-fourth of its original value by soaking in water for four days. Adhesion-improving bitumen additives are used to avoid and overcome the failures.

For cold mixed pavements and seal coats, an active adhesion is required; i. e., the additive-improved bitumen must have the ability to adhere to wet aggregate and to replace water on wet surfaces.

Usage of asphalt adhesion-improving additives in some European countries seems to be far ahead of the corresponding usage in the United States. Extensive tests under varying, and sometimes very hard service conditions, have been run in Sweden and in England. The result of these tests was that during the years 1951 to 1953 amine type additives broke their way through definitely.

The limited heat stability of additives which are known as being really efficient and economical does not allow heating of prepared asphalts for prolonged periods. European practice is to mix additives and cut-back asphalt directly in the distributors. Additives in solid form are often preferred owing to easier and safer handling.

The author feels that adhesion-improving additives are here to stay and that European practice could be of some value also in the United States.

DISCUSSION

Being at an early stage of development bitumen adhesion improving additives could solve many problems and have a great future. The fields to be conquered first are seal coats and all other types of "cold mix" and "road mix." Grouting techniques using improved bituminous materials could be of particular interest for highway base course stabilization.

More test data is badly needed before the right chemicals and the right methods can be prescribed and sanctioned for each individual case. For the best results, laboratory investigations will have to be coordinated with full scale road tests and certain correlations between laboratory results and actual performance will have to be established.

The author feels that the facts accumulated justify a large scale U.S. road test program, planned and carried out by the cooperative efforts of the road authorities and industries involved. This program should have mutual advantages and be of nationwide value.

Last but not least, essentially new applications for improved bituminous materials might be possible or even probable.

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Asphalt Composition and Properties

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The technical material consists of an abbreviated discussion of certain techniques in solvent extraction and adsorption separation procedures for asphalt. It is shown that sharp fractionation is obtained by selective adsorption of methyl cyclohexane solutions on silica gel. These separations produce fractions similar to those from solvent fractionation based on ultraviolet absorption measurements. Additional information is also indicated by infrared absorption studies but the implications at these latter energy levels are not clear at this time. This information provides a basis for evaluating the differences in chemical composition of asphalts which can be valuable in classifying bituminous materials into separate categories.

Based on a gross classification into naphthenic, intermediate or aromatic type asphalts, the paper then discusses the range of physical properties to be expected for each type as a function of processing. The physical properties considered are penetration, softening point, ductility and consistency in absolute units. Generalized charts relating consistency and complex flow and the common physical tests used by asphalt technologists are presented. Comments are made concerning the durability of asphalts as a function of their composition.

● ACCEPTANCE of the statement that "knowledge in a field is measured by the brevity with which the concepts can be presented" makes the asphalt technologist pause when the voluminous literature on asphalt is considered. The novice in the field is at first intrigued and finally confused in attempting to deduce simple generalizations regarding asphalt behavior from the numerous empirical relations, incomplete data and conflicting viewpoints found in the art of production and utilization of bituminous materials. To put this art on a scientific basis will require the use of new fundamental concepts to replace obsolete empirical tests and relationships. It is the purpose of this paper to suggest possible improvements in present concepts and to illustrate their application.

Stated briefly the properties and behavior of asphalts are a priori a function of the chemical composition of the material. However, some variation in properties may be expected for a given chemical composition depending upon the history of the material as is the case with metallic alloys where the properties may be altered (for a given chemical composition) by suitable metallurgical treatment. The asphalt technologist's problem therefore reduces to the apparently simple problem of determining the composition of the material, and, considering its history, correlating this composition with the properties and behavior of the material. Unfortunately, such a simple approach is blocked by a lack of suitable methods for determining the composition as pointed out by Csyani and Fong (4) and the recourse is to develop empirical correlations for those properties in which the investigator is interested. These empirical correlations eventually are discarded because further investigations by others prove them invalid as a greater variety of materials is considered.

In general, the properties of asphalt which make it an article of commerce or which control its use can be reduced to one or more of the following: water resistance, resistance to corrosive agents, adhesiveness, stability (or resistance to oxidation or change in physical properties), viscosity, change in viscosity with temperature, emulsifiability, electrical properties, solubility in solvents and a few other special properties, all of which certainly are a function of chemical composition. However, because the physical properties are the most important from the viewpoint of the major commercial uses for asphalt, the principal emphasis has usually been on attempts to correlate them alone. Since most of the physical tests (e.g., penetration, softening point, adhesiveness, etc.) themselves are empirical tests, there result empirical relations among empirical tests for whatever value such relations may have. Fundamental relations be-

tween composition and the individual properties would appear to be more likely to yield valid correlations if a simple logical method for delineating composition could be developed.

The most generally accepted theory regarding the composition of asphaltic materials is that they are composed of a group of hydrocarbons of the general formula $C_nH_{2n+b}X_d$ where n and b vary (b may be negative) and X may be other elements such as sulfur, nitrogen, oxygen and metals (traces of vanadium and other metals are found in many petroleum residuals) (32). O'Donnell (19) presented evidence for empirical formulas of $C_{62}H_{97}N_{0.2}S_{0.5}$ for an asphalt fraction obtained by molecular distillation. The amount present of any individual hydrocarbon may be very small and the value of d is also usually small. Accordingly, the mixtures of these materials, known as asphalt, varies over a range of composition from low molecular weight to very high values with isomers, ring structures, combination of rings, straight chain hydrocarbons, and bridge structures containing other elements as summarized by Gruse and Stevens (10). At the higher molecular weight ranges, polymers and condensation products formed during the processing are also present, but it is doubtful that colloidal carbon exists except as a result of decomposition in certain processing operations as concluded by Katz and Beu (12) from electron microscope studies. Other data refuting the concept of dispersed carbon particles has been presented by Mack (16) based on dialysis. A similar conclusion is presented by Eilers (7) based on X-ray analysis.

Classical methods for determining the composition of asphalt using hydrocarbon solvents such as pentane or propane have never been of any great value for explaining the behavior of asphalts in service although such methods are useful in determining the uniformity of the product. A review of the available data from classical procedures including bibliographies (17, 18) has been given by Neppe. The classical methods fail because they separate on the basis of molecular weight rather than on the basis of chemical composition. It is believed that the proposed Traxler-Schweyer (38) method overcomes some of these difficulties. This method utilized a two step solvent extraction procedure summarized as follows:

	Butanol Extraction	Acetone Extraction
Asphalt Sample 5 grams.	{ Extract Asphaltics (Raffinate)	{ Saturates (Raffinate) Cyclics (Extract)

The n-butanol is employed to extract the low molecular weight oils leaving a residual raffinate of high molecular material called asphaltics. The butanol free extract is subsequently extracted with acetone to yield a cyclic (extract) fraction and a saturates (raffinate) fraction. Typical results for this method of analysis are shown in Figure 1, and experience with over 2,000 analyses has indicated that this procedure is of considerable value. It is not to be inferred that the procedure is a cure-all or a utopian method, but its simplicity and usefulness in explaining asphalt behavior in the experience of the author has shown it to be of merit. (Note: since the acetone raffinate is probably composed of a variety of types of saturated hydrocarbons, the term "paraffinics fraction" used in the earlier paper (38) is somewhat restrictive and hence, in this paper is replaced by the term "saturates" fraction.)

Asphalts exhibit colloidal properties in a variety of ways as has been discussed by Traxler and Romberg (37). It has been recognized that asphalts may exhibit the properties of a gel — examples are highly blown asphalts showing age-hardening characteristics (37), a great propensity to stain paper because of oil exudation or synersis (13), high elasticity and other complex flow characteristics where deformation is not linear with the applied stress (24). Conversely other asphalts exhibit the properties of sols and show low stain propensity, little change with age and essentially truly viscous flow. Other ashpalts may exhibit any of the properties intermediate between those of a true gel and those of a true sol. The term sol as used in this paper indicates a highly solvated material having properties similar to those of a true solution regardless of whether the material is or is not a true solution.

Attempts to explain differences in asphalts by use of hydrocarbon selective solvents

alone is not fruitful because the quantity of "asphaltenes" or high molecular weight material alone is not controlling (37). It is the kind of low molecular weight material associated with the high molecular weight material that is important. This is particularly true where the amount of high molecular weight material separated is critical with the amount of solvent and the conditions employed as is the case for "asphaltenes" and so called "resins."

As an example, two 55 penetration asphalts from different Texas crude oils might have properties somewhat as given in Table 1, where each shows about 24 per cent asphaltenes.

The data illustrate that at some given empirical consistency (55 penetration) the asphaltene content is of no value in distinguishing between the two materials. Furthermore, "homogeneity" as deduced from a negative spot test is also a meaningless term, since Asphalt A is definitely more nearly a mixture of heterogeneous phases having the properties of a gel as evidenced by its higher stain, lower ductility, and greater degree of complex flow.

Figure 1. Generalized composition ranges for various bituminous residuals.

It is obvious that these variations must be the result of differences in chemical composition. The application of component analysis to these asphalts provides some information concerning these chemical variations as indicated by the data in Table 2.

The higher refractive indices for the components from Asphalt B together with the greater amount of cyclic fraction (acetone solubles at -10 F) are indicative of a higher degree of unsaturation. This unsaturation may be from aromatics or some other configuration and for Asphalt B would be expected to produce a stronger solubilizing action for the high molecular weight asphaltic materials present with less tendency to form a gel. The oils in Asphalt A are, relatively, more naphthenic or more saturated in nature and although the amount of high molecular weight material (asphaltics) is less, this asphalt has a higher viscosity at a given power input. This higher viscosity and the higher degree of complex flow (smaller values of "c") are manifestations of the gel-like nature of the asphalt which is also indicated by the high stain index resulting from syneresis or exudation of the oily components. Such colloidal phenomena point to partial solvation of the high molecular weight asphaltics by the saturated oils rather than the formation of highly solvated mixtures with aromatic oils of higher refractive index as in Asphalt B.

In order to confirm the relative degree of saturation in the oil fractions obtained by component analysis, ultraviolet absorption analyses have been made on numerous asphaltic materials. Typical results are given in Figure 2 which are for a Gulf Coast petroleum residual. The analyses were made using a Beckman spectrophotometer Model DU with a 15 percent normal butanol—85 percent spectral grade iso-octane as the solvent, using a technique by Schweyer (26) reported elsewhere. The butanol was employed to assist in effecting complete solution of the oils in the solvent since the butanol extract as obtained by component analysis at 122 F apparently contains some colloidal material. The absorption solvent mixture used produced solutions with no apparent turbidity in ordinary light, but a definite Tyndal effect was observed when some of the solutions were exposed in a Tyndallometer. These effects would tend to reduce the sensitivity of the spectral analysis.

The results in Figure 2 may be considered to indicate the following: (a) The component analysis method is partially effective in separating the components consisting of CH = bonds as indicated by the lower optical densities of the saturate fractions for wave
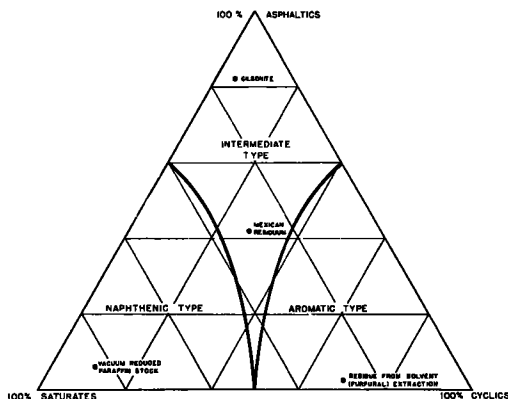
TABLE 1
PROPERTIES OF TWO 55 PENETRATION ASPHALTS

	Asphalt A	Asphalt B
% Asphaltenes	24	24
Sp. Gr. at 77 F	0.980	1.035
Pen. 32 F, 200 g/60 sec	27	16
77 F, 100 g/5 sec	55	55
115 F, 50 g/5 sec	135	290
R and B softening point, F	149	125
Ductility, 77 F, 5 cm/sec	6	200
Viscosity at 77 F, megapoises[a]	24	3.0
Complex flow, "c"[a]	0.5	0.9
Stain Index[b]	10	5
Spot Test	N	N

a See reference 24.
b See reference 13.

lengths above 220 millimicrons. If the separation had been complete, the saturate
fraction would show no appreciable absorption in this range. (b) The peaks shown in
the range from 220-240 millimicrons indicate the presence of conjugated acyclic dienes
which are separated (partially) in the acetone extraction. (c) The shoulder at 250 to
270 millimicrons indicates the presence of monocyclic aromatics and/or conjugated
acyclic trienes which also are partially separated and concentrated in the cyclic frac-
tion. (d) The absorption in the range from 270 to 350 millimicrons indicates a gener-
alized absorption attributable to a variety of compounds such as polycyclics, unsatu-
rated heterocyclics and oxygenated compounds, etc., which are present in relatively
small amounts. In general the ultraviolet absorptions confirm the relative naphthencity
and aromaticity based on the refractive indices of the fractions separated by component
analysis. The average deviation in spectral absorption of the fractions for combined
component analysis and spectral analysis is of the order of plus or minus 2 percent.
Thus, in comparing different materials a minimum variation of about 4 percent in ab-
sorptivity might be considered the minimum for significant differences in composition.
    Certain selective adsorption studies (27) using a chromatographic procedure with
silica gel have been made on the asphalt shown in Figure 2. The ultraviolet spectral

TABLE 2
COMPONENT ANALYSIS FOR TWO 55 PENETRATION ASPHALTS

	Asphalt A	Asphalt B
Asphaltic content—%	36	44
Saturates—%	54	38
RI at 158 F	1.5000	1.5300
Cyclics—%	10	18
RI at 158 F	1.5500	1.5700

absorptions for two separated fractions are similar to those separated by solvent extraction as illustrated. However, it should be noted that the asphaltic component is present in the chromatographed samples whereas it has been separated out by solvent fractionation prior to the ultraviolet analyses. At this stage of the study no advantage of either method for delineating composition is indicated. In addition to the ultraviolet absorption, infrared absorption data have been reported by Schweyer (26), but here also the data are of a preliminary nature. They appear to confirm information from the ultraviolet studies as shown in Figure 3 for the saturate fraction from a naphthenic asphalt similar to the one shown in Figure 2 and for the cyclic fraction from a so-called aromatic asphalt. To date both asphalts and their components show significant absorption at 3.41, 3.49, 5.85, 6.20, 6.85, 7.28, 9.7, 10.3, 11.5, 12.3, 13.45 and 13.9 microns which indicate the presence of various functional groups. Straight chain hydrocarbons on aromatic nuclei are shown by absorption at the lower wave lengths. At the two higher wave lengths the absorption at 13.45 microns is considered to represent short chain CH_2 groups whereas at 13.9 microns the absorption is attributed to long CH_2 chains. The relative absorption at the intermediate wave lengths and in the ultraviolet region may eventually provide a means for quantitative characterization of asphalts by such techniques. However, the variation for different fractions obtained from the same or different sources are small and at the present time there is some question as to the value of such measurements on these gross mixtures of hydrocarbons and their mixtures with other oxygen, sulfur and metallic complexes. Additional research in this field is indicated.
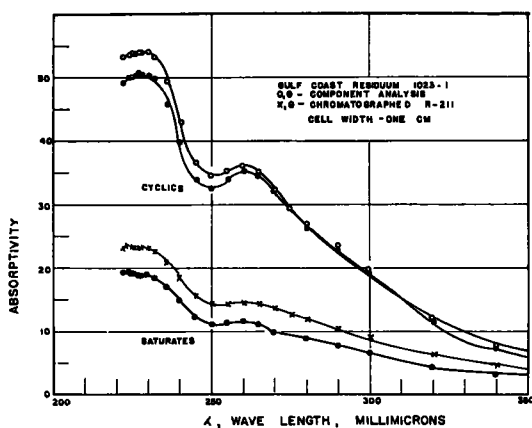

Figure 2. Ultraviolet spectrograms for certain residual asphalt components.

COMPOSITION OF ASPHALTS

Little information is available in the literature on the chemical composition of asphalts since it is expected that any one chemical compound is present in only minute quantities making the separation and identification of individual compounds tedious and difficult. Gruse and Stevens (10) have considered the available data as has also Sachanen (25). Some comments on the chemical composition were presented previously (38) in which it was pointed out that asphaltic residues might be expected to contain higher molecular weight homologues of the materials found in lubricating oils. The problem is more complicated, however, since the high temperatures employed in producing asphalts may result in decomposition with the subsequent loss of hydrogen, sulfur and oxygen originally present in the crude oil and particularly when any of these elements tend to concentrate in the asphaltic fraction as is usually the case for sulfur.

In studying the complex compositions present in asphalt it appears that, as a first step, the most expedient procedure is to consider the types of compounds present and how their presence affects the properties. Following a delineation as to type, subsequent study can be pointed toward further subdivisions of each type. Based on available data and the literature the following appear to be reasonable statements regarding the materials to be found in asphalts.

1. Naphthenic and aromatic ring compounds (with or without side chains) constitute the major chemical types with the probability that the aromatic condensed rings pre-
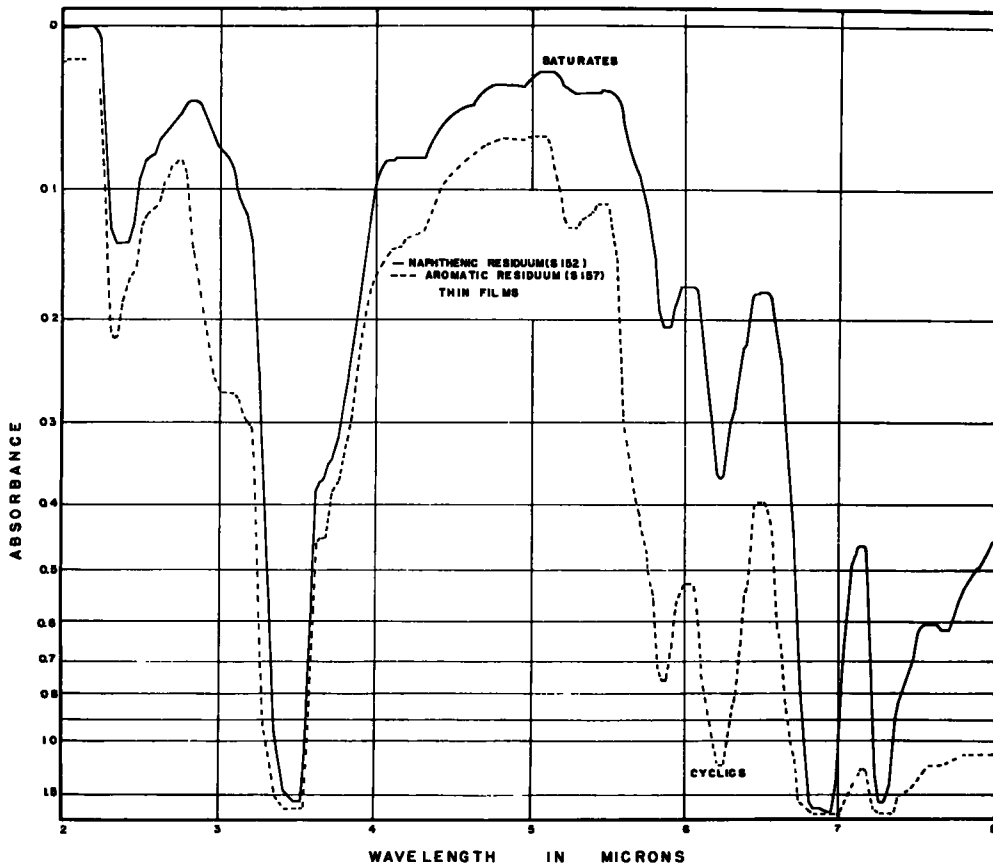
Figure 3. Infrared spectrograms for certain residual asphalt components.

dominate in the cyclic fraction as obtained by the Traxler-Schweyer method.

2. The ring compounds may be condensed aromatic nuclei, or five and six member rings connected by side chains with or without sulfur, nitrogen or oxygen bridges, although these elements also may be present as part of the ring structure. The saturated ring compounds with long paraffin chains are found in the saturates fraction by component analysis. The efficiency of separation will influence the shape of such plots as shown in Figures 2 and 3.

3. Pure aliphatic compounds (paraffin or isoparaffin hydrocarbons) are present only in small quantities with paraffinicity being imparted to the asphalt by the presence of long side chains on the ring compounds, with the cyclic fractions having the shorter chains. Waxes representing solid hydrocarbons, either amorphous or crystalline in nature, are found in the saturates fraction with the waxes being predominately naphthenic in character. Waxes that are insoluble in n-butanol are found in the asphaltic fraction.

4. Unsaturated straight chain compounds are present in minor quantities except where the material has undergone considerable thermal treatment such as cracking.

5. The range of molecular weights encountered for the components for the mixture is wide and varies upward from about 200 for the lighter oils present (8, 11) It is this wide range of materials and the mutual solubility effect of their presence which permits the solution of high molecular weight material in solvents which otherwise would not dissolve the pure high molecular weight material. Partial or selective solvents destroy these mutual solubility effects permitting the separation of the asphalts into components of a general type, that is, high molecular weight, high degree of saturation or high degree of aromaticity.
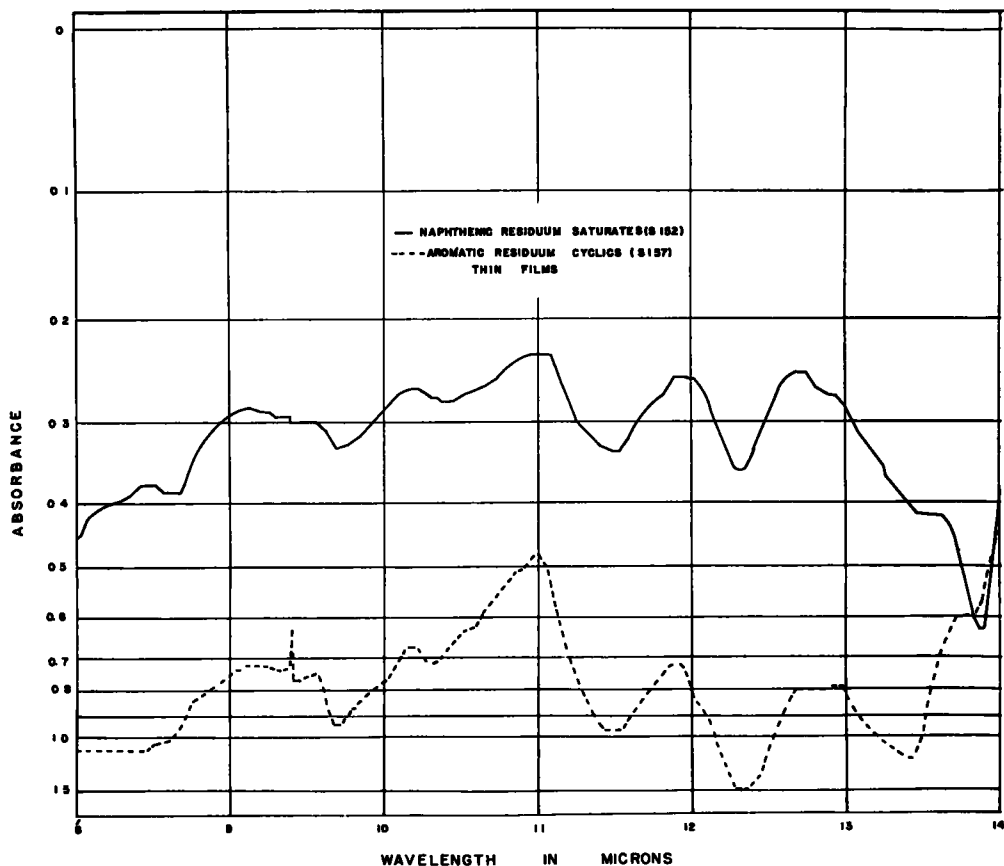
Figure 3. (Continued)

6. The properties of the asphaltic material are controlled by the relative amounts of these types of compounds present with a high preponderance of aromatic rings tending to produce "sol" or aromatic type asphalts where the high molecular weight material is more or less completely dissolved. If the naphthenic rings containing long side chains predominate for the lower molecular weight material, the high molecular weight material is not dissolved but is partially solvated to produce a "gel" or naphthenic type asphalt. The possible presence of organic complexes (33) or metallic chelates (31, 32) introduces additional complications in influencing these mutual solubility effects.

The component analysis method (38) appears to be a logical and simple procedure as the first step in determining the general types of materials present in asphalts. This conclusion is based upon the general application of the results that have been obtained as shown in Figure 1, which is based on a previous article (38) and other confirming data. If gilsonite is considered as a highly asphaltic material, a residual from a naphthenic crude is considered as containing a high content of paraffinic naphthenes and a furfural free residue from furfural refining of a lube oil which extracts the aromatic materials is considered as representing materials of relatively high aromaticity, then these materials should, by analysis, appear near the apices of a ternary diagram such as given by Figure 1. Component analysis shows this to be true and on a purely arbitrary basis it is possible to divide the diagram into segments as shown for the purpose of classifying materials that fall within the defined areas. Starting at the lower right, the area may be considered as that into which will fall the residues from crude residues containing a high proportion of aromatic ring compounds. Similarly residues from thermal and catalytic cracking will show component analysis that fall in this region.
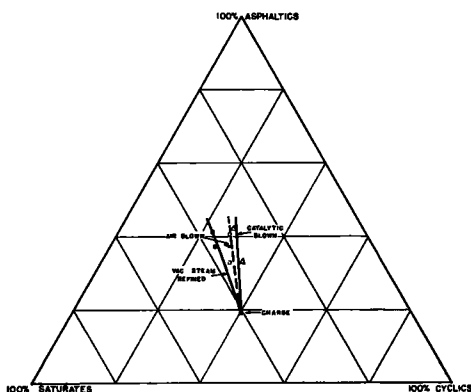
Figure 4. Changes in composition when processing Florida (Sunniland) residuum.

Such materials would be expected to show a preponderance of ring structures with only short side chains and with the aromatic type of ring compound predominating.

The refractive index at 158 F for the cyclic components from asphalts range from about 1.520 to 1.600 regardless of source material even over a wide range of consistencies. From some special petroleum residues from cracking operations considerable higher values have been obtained, but these would normally not be considered as asphalts. The refractive index increases linearly with the density of the cyclic fraction(38). Since the variations to be found are primarily a matter of degree, the residuals in this area have been labeled "aromatic" with the c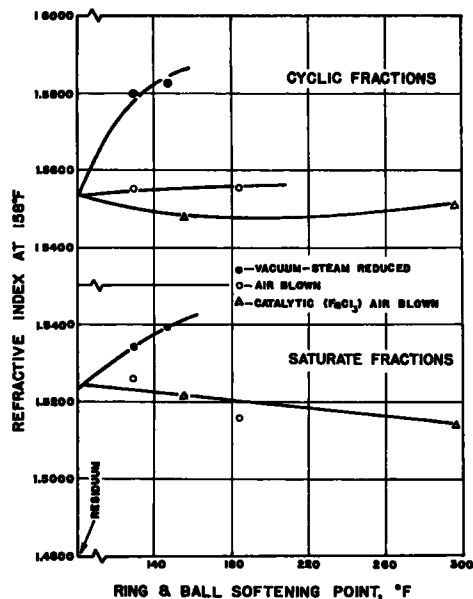onnotation that they contain a relatively large proportion of compounds with conjugated double bonds either aromatic or acyclic with a minimum of side chains. This is confirmed qualitatively by ultraviolet absorption analysis, chromatography and infrared analyses indications.

The residuals that fall in the lower left area of Figure 1 have been called "naphthenic" and may also be considered to consist of ring structures with naphthenic rings predominating, but with relatively long side chains on the rings which distinguish the saturate fraction from the cyclic fraction as obtained by component analysis and chromatography. Evidence for this distinction lies in the lower refractive indices for the saturates fraction. Other confirmation is found in the fact that the separated saturates fraction will polymerize faster (as measured by the increase in viscosity) than the cyclic fraction when processed with air or catalysts. This is in accordance with published results that long chain paraffin hydrocarbons on ring structures are quite susceptible to oxidation. The boundary for this region is shown concave looking from the left because certain asphalts containing a high wax content fall in the concave area. The waxy hydrocarbons may appear in either the asphaltic or the saturates fraction depending upon their molecular weight or solubility in n-butanol. The presence of wax as a separate component is not considered important. What is important is that wax, if found, indicates the presence of certain types of chemical compound (solid saturated hydrocarbons probably naphthenic in nature) and the properties of the containing asphalt may be expected to be affected accordingly.

Refractive indices for the saturate fractions vary from about 1.4800 to 1.5600. The higher values for the saturate fraction are found in the "aromatic" type asphalts which show a correspondingly higher refractive index for their respective cyclic fraction. This emphasizes that variations in composition are matters of degree rather than absolute differences. The lower limit of refractive index for the saturates fraction may ex-

Figure 5. Changes in refractive index of components when processing Florida (Sunniland) residuum.

ABSORPTIVITY
0
10
20
30
40
50
60
200
250
300
350
λ , WAVE LENGTH, MILLIMICRONS
CYCLIC FRACTIONS
SATURATE FRACTIONS
102-C
101-B
151-C
112-D
102-C
112-D
101-B AND 151-C
CELL WIDTH — ONE CM
FLORIDA ASPHALTS FROM 101-B
101-B — RESIDUUM
102-C — STEAM REFINED (130°F R&B)
112-D — AIR BLOWN (130°F R&B)
151-C — CATALYTIC BLOWN (166°F R&B)

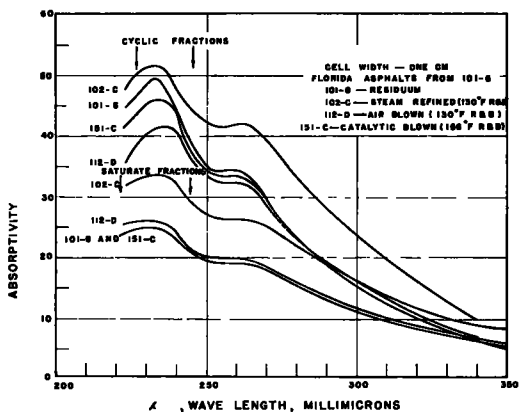

Figure 6. Ultraviolet spectrograms for processed asphalt components.

tend below 1.4800 for some very fluid residuals. (Paraffin wax shows a value of about 1.43 at 158 F.)

Highly asphaltic materials are represented in Figure 1 by the area at the top of the diagram. Materials containing over 50 percent asphaltics usually have a high consistency (of the order of 15 penetration). Certain softer materials may show high asphaltics contents where the peculiarities of composition affect the solubility relationships. Road tars and propane solvent treating residues are examples. In certain cases the asphaltene contents will exceed the asphaltic content whereas normally the reverse is true. This occurs where the solvent has disturbed the bituminous system to such an extent that excessive precipitation occurs at the solvent ratios for pentane employed in the test.

The asphaltic fraction as determined by component analysis is reproducible and when fluxed with the combined saturate and cyclic fractions (in proportion to production) will yield asphalts similar to vacuum reduced products made from the mother stock. Similarly air blowing of the combined saturate and cyclic fractions will produce products similar to air blown asphalts from the mother stock. These results would indicate that the asphaltic fractions as derived from the oily components present are related chemically with differences being account-

STEAM REFINED ASPHALTS
PENETRATION
0
20
40
60
80
100
120
140
160
180
200
80
100
120
140
160
180
200
RING AND BALL SOFTENING POINT °F
AROMATIC (KERN RIVER, CALIFORNIA)
INTERMEDIATE (TAMPICO, MEXICO)
AROMATIC
INTERMEDIATE
AROMATIC
INTERMEDIATE
PEN AT 115° F (50 G/5 SEC)
PEN AT 77° F (100 G/5 SEC)
PEN AT 32° F (200 G/60 SEC)

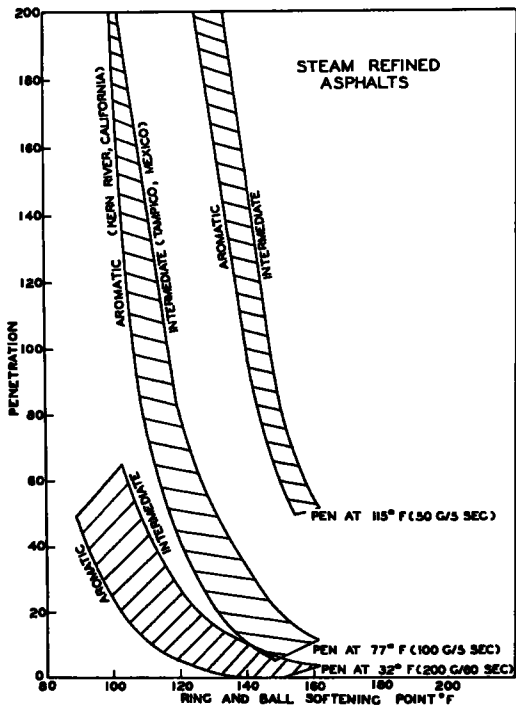

Figure 7. Effect of composition of properties of steam-refined asphalts.

ASPHALTS FROM MENE GRANDE VENEZUELA RESIDUUM
PENETRATION
20
40
60
80
100
120
140
160
180
200
80
100
120
140
160
180
200
220
RING & BALL SOFTENING POINT °F
STEAM REFINED
HIGHLY BLOWN
STEAM REFINED
HIGHLY BLOWN
SEMIBLOWN
STEAM REFINED
HIGHLY BLOWN
SEMIBLOWN
PEN AT 115° F (50 G/5 SEC)
PEN AT 77° F (100 G/5 SEC)
PEN AT 32° F (200 G/60 SEC)

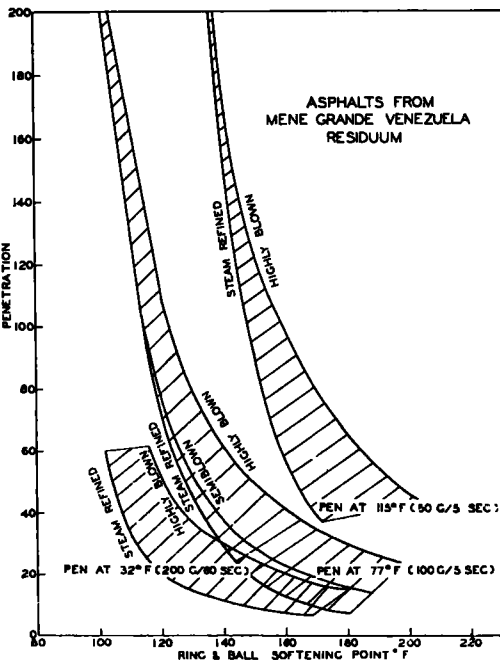

Figure 8. Influence of charge consistency on properties of resulting air-blown asphalts.

able primarily to a higher molecular weight.

An upper center area is shown in Figure 1 which is labeled "intermediate." This section represents a less rigorously defined area of composition where no one general type of component predominates. Many asphaltic materials will fall in this area. Panuco (Mexican) asphalts show analyses which place them in the intermediate region as do many other types that have proven satisfactory for paving purposes. As might be expected the asphaltic materials whose analysis places them in the "intermediate" area will show, in general, smaller variations in refractive index for the cyclic and saturate components. The ranges are intermediate between those for the asphalts found in the lower left area and those that fall in the lower right areas of Figure 1 with some overlapping of the values occurring. Grader (9) found that Mexican asphalts showed relatively fewer paraffinic side chains on the rings.

One other factor in the chemical composition of asphalt that appears significant is the sulfur content. Practically all pub-

Figure 9. Influence of charge consistency on penetration of air-blown asphalts of an intermediate type.

lications on the subject include consideration of sulfur. O'Donnell (19) has commented on mecuric chloride-sulfur complexes from asphalt and indicated that the sulfur is concentrated in the aromatic fractions and the higher molecular weight material. This is also confirmed by sulfur analyses on fractions separated by the Traxler-Schweyer method. Apparently, the importance of sulfur lies in its ability to form both rings and bridge structures. In the latter form it would permit the combining of long side chains to produce more complex molecules of higher molecular weight (thus increasing the asphaltics content). It is known that the densities of asphaltic materials of similar consistency ranges will increase almost linearly with sulfur content. Similarly as was shown, (38) the density increases with the increased C/H ratios generally expected for the higher molecular weight materials in the asphaltic fraction. This results in the high sulfur content asphalts appearing in the upper intermediate region of Figure 1. The high sulfur contents of Mexican asphalts is well known and their appearance in the intermediate area is an illustration. Certain Californian and South American asphalts are similar in this respect.

The effect of nitrogen and oxygen (32) even though present in only small amounts eventually may be found to affect the composition of asphalts considerably in the high molecular weight ranges. Like sulfur, if they form bridge linkages, the small weight percents present may permit the formation of long side chain polymers which otherwise might not be produced. Ball and co-workers (2) have shown that nitrogen (like sulfur) tends to concentrate in the high molecular weight portions of asphalt. Richter and others (23 a) have also studied the distribution of nitrogen.

A consideration of the relations between true chemical compositions and general types of compounds present as indicated by component analysis permits a general classification of asphalts as "naphthenic," "intermediate" or "aromatic" according to the respective areas in Figure 1. Such a classification should not be construed as rigorous since the boundary lines in Figure 1 have been drawn arbitrarily to form a symmetrical diagram and apply relatively for straight run residuals of viscosities of the order of 200 seconds Saybolt Furol viscosity at 210 F. Furthermore, borderline cases obviously will occur and asphalts of different consistencies made from the same
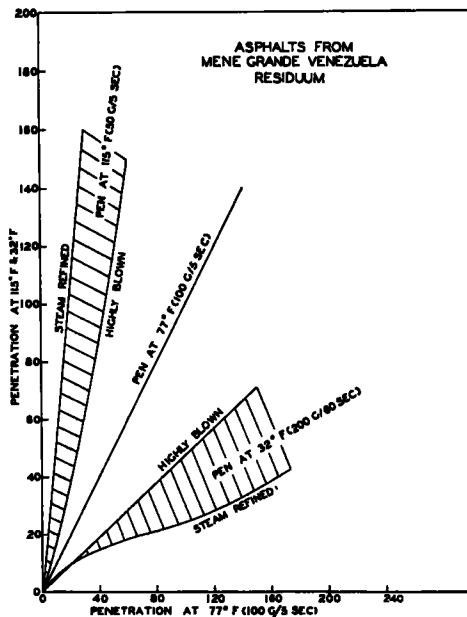
stock may appear on different sides of a boundary line. The areas shown have been drawn to represent normal asphalts likely to be encountered in commercial practice. The use of this simple system with the connotations regarding chemical composition as previously stated will facilitate the following discussion of the influence of composition on the properties of asphalts. That these concepts are in accord qualitatively with experimental facts regarding asphalts will be demonstrated in the next sections.

COMPOSITION AND COLLOIDAL PROPERTIES

The wide range of chemical compositions found for asphalts would be expected to produce a variety of properties for them and the practice of describing these variations on the basis of colloidal behavior is gaining favor. The concept of "sol" or "gel" type asphalts is not new, and Traxler and Romberg (37) have summarized certain pertinent data useful for classifying asphalts as to colloidal types. Oliensis (20) has discussed the analogous colloidal behavior of asphalts with that for aqueous gelatin mixtures to explain syneresis and compatibility of asphalts. The "solvation potentials" discussed by this author appear to be an attempt to evaluate chemical composition on the basis of physical effects. Reiner (23) has proposed a mathematical analysis as a means of differentiating between a sol and a gel structure based on the relative elastic and non-elastic deformation of asphalts under stress.

In general, any given asphalt produced as a residual in refining operations at high temperatures consists of high molecular weight material which may be considered as being more or less associated as its temperature is decreased according to Krenkler and Wagner (15) and Krenkler. (14) These authors also suggest the build up of a spherical type micelle in contradistinction to long chain polymers because the asphalts do not exhibit the highly elastic properties of chain type elastomers. Pfeiffer and co-workers (21) have considered the asphalt micelle to be built up first with the aromatic portions followed by gradation to the more paraffinic materials, but Krenkler et al. suggest that the association potential rather than progressive chemical differentiation is the controlling factor.

The presence of lower molecular weight materials as the oily portions of the asphalt appears to be the critical factor in controlling the colloidal nature. Whatever the nature or structure of the high molecular weight portions (asphaltics) it is reasonable to assume that they will imbibe the oils and become solvated to a greater or lesser extent. The degree of this solvation will determine the properties. If the oils are powerful solvents a complete solution of the high molecular weight material results in producing a "sol" type asphalt. An imbibing of the oils with incomplete solution where the oil is the discontinuous phase or the production of a suspension of the "asphaltics" in the oil will yield a "gel" type asphalt. In this connection it is interesting to note that Oliensis (20) has suggested that the intermediate hydrocarbons (or so called resins) may be considered as solvents or peptizers while contrawise the lighter oils act as desolvents. Chemical type would appear to be more important than molecular weight as a criterion for the solvent ability of the oils. It will be found that those asphalts falling in the "naphthenic" region of Figure 1 will usually exhibit the properties of gels whereas those in the "aromatic" region usually are sols. Asphalts having intermediate compositions on Figure 1 will show some properties of both the sol and gel type with no distinct demarcation indicated. This might be expected since the degree of solvation is a relative rather than a quantitative term and requires that any comparisons be made for asphalts of about the same viscosity.

Where the gel type asphalt persists, the partial solvation (rather than solution) of the high molecular weight material apparently is the result of insufficient solvent power (high interfacial tension, etc.) or the absence of an intermediate mutual solvent as sometimes occurs in blending of two dissimilar asphaltic materials. The relatively weak solvent power of the paraffin hydrocarbons compared to aromatic hydrocarbons would explain why asphalts in the lower left region of Figure 1 are of the gel type. Conversely, the high solvent power of aromatics would explain why sol type asphalts usually show a relatively high cyclic content. In connection with solvation it should be pointed out that the viscosity of the mixture is not a function of the amount of high
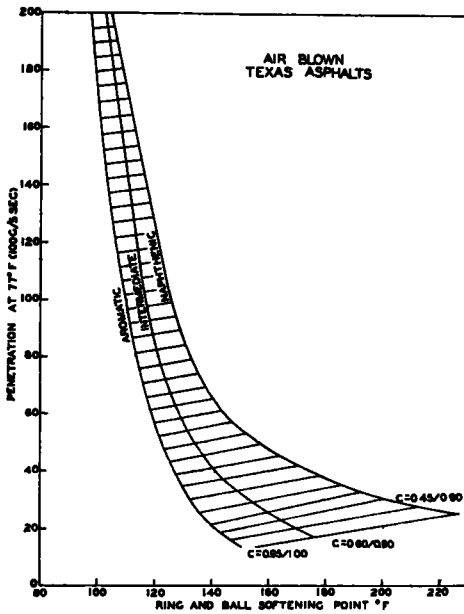
Figure 10. Effect of composition of pro-
perties of air-blown asphalts (starting
material of 100 to 200 Saybolt Furol vis-
cosity at 210 F).

molecular weight material present as has
been demonstrated in Tables 1 and 2 and
by Traxler and Rombers (37) and others.
The degree of solvation is the controlling
factor since a sol type asphalt may have a
considerably higher asphaltic content than
some other gel type.

In studying the influence of composition
in producing a gel or sol type asphalt, the
amounts of the respective components to-
gether with their refractive indices both
may be considered. It is interesting to
note that the "intermediate" type asphalts
with high asphaltics contents show smaller
differences in the refractive indices for
the saturate and cyclic fractions than do
other asphalts. This would indicate a con-
tinuous phase of less variable composition
for intermediate type asphalts. The varia-
tions, however, are a function of both the
degree of processing as well as the method
(i. e., vacuum reduction, air blowing, or
catalytic polymerization).

Many of the peculiar effects of blending
can be rationalized on the basis of com-
position of the materials used for the mix-
ture. For example, the use of high con-
sistency naphthenic asphalts usually will
not produce satisfactory sol type asphalts
because of the low degree of solvation even before blending; the latter operation ac-
centuates the effect. Conversely, highly asphaltic materials from solvent refining
operations are good blending materials because: first, the relatively high cyclic con-
tent acts as a solvent, and second, the high asphaltic content presupposes high mole-
cular weight material of a wide gradation which would exercise a mutual solubility
effect on the high molecular weight material in the other asphalt or asphalts making up
the mixture. This mutual solubility effect is perhaps the most important factor in mak-
ing sol type asphalts. A common reverse procedure is the production of gel type as-
phalts by fluxing a hard asphalt with a light oil. The lack of mutually soluble com-
ponents produces a mixture showing a high degree of complex flow, staining and other
properties of a highly colloidal material. The degree of colloidality will be affected
by the molecular weight of the fluxing oil and its relative naphthenicity with the more
naphthenic oils producing the gels. Sludging or incompatibility in blending asphaltic
materials of low viscosity will be recognized as another manifestation of incomplete
solvation of the high-molecular weight material present. The exudation and insudation
reactions (20) of asphaltic materials in contact with each other is also a colloidal phe-
nomenon which should be more readily rationalized on the basis of chemical composition
than by complicated empirical test procedures.

It is this degree of colloidality together with certain chemical properties (resistance
to oxidation, resistance to corrosion, etc.) which in the final analysis determine the
suitability of the asphalt for commercial use.

ASPHALT COMPOSITION AS AFFECTED BY PROCESSING

Asphalts are produced commercially by a variety of methods and the composition of
the product is affected accordingly. Among the major methods used are:
1. Vacuum reduction by volatilization of the lighter fractions.
2. Air blowing of residues at elevated temperatures (500 F).
3. Catalytic polymerization in the absence or presence of air at elevated temperatures.

4. Air blowing and concomitant refluxing with low volatility oils or fluxing with fresh feed stock.

5. Blending of products from the preceding operations.

Corbett (3) has presented data showing how the "asphaltene" contents and refractive indices of the pentane soluble portions of asphalt vary with source and process. This author also suggested the possible use of specific refraction evaluations for characterization purposes.

The production of asphalts by vacuum processing in general results in a gradual hardening of the asphalt through loss of volatile vapors. The composition of the asphalt changes primarily as a result of concentration of the asphaltics fraction with the composition varying in several ways in Figure 4 and with progressive increases in density of the asphalt and in the refractive indices of the components of a residue from the Sunniland, Florida field as illustrated in Figure 5. A vertical line in Figure 4 is significant because on a ternary diagram it represents an equal conversion in amounts of both the cyclic and saturate fraction with a corresponding increase in asphaltics. However, a removal of equal amounts of cyclics and saturates without an increase in asphaltics results in a line sloping to the right or left since the percent asphaltics must increase (the line rises vertically if the saturates and cycles are present in the original charge stock in equal proportions). Obviously, combination of changes in any of the components caused by vaporization or chemical changes will produce other configurations on the chart which are not necessarily straight lines. Since the oils present regardless of chemical nature may be considered as having similar vapor pressures (otherwise they would be volatilized and appear in the distillates during the refining operation), it is probable that vaporization of both aromatic and saturated hydrocarbons should occur in essentially equal amounts. In addition polymerization may also occur during the processing to increase the asphaltics content. In Figure 4 the vacuum refining produced a relatively larger loss in cyclic fraction than for the saturate fraction. The resulting residual oils of high molecular weight apparently are good peptizers and solvents for the asphaltic materials since steam or vacuum refined asphalts generally show less tendency to form gels than other products from the same stock. The exception to this are the products from vacuum reduction of highly paraffinic stocks which are difficult to process. In this case the removal of a portion of the aromatic oils from a source material already deficient in them accentuates the deficiency and produces a gel type product. The excess of saturates is difficult to remove by volatilization because of the low (relatively) vapor pressure of saturated hydrocarbons compared to aromatics of the same viscosity.

In the air blowing process a different result is obtained (38) because the refractive indices of the components show a tendency to remain constant or to increase or decrease slightly (Fig. 5) depending upon the extent of the blowing. Volatilization occurs to a limited degree, and the asphalt density is increased considerably less than in vacuum reduction, even though the percent of asphaltics increases appreciably as shown in Figure 4. A reasonable explanation is that the higher molecular weight saturate and aromatic oils are dehydrogenated and polymerized to higher molecular weight asphaltics. This causes a depletion of intermediate molecular weight solvent material and tends to produce gel type asphalts because of the deficiency of intermediate solvent oils. If the remaining light oils are resistant to dehydrogenation the refractive indices of the fractions containing them will decrease progressively. However, sufficient polymerization may occur in the lighter oils also to raise their refractive indices to the original values but the quantity of these materials will now be less than in the original charge. The locus of the composition line tends to move upward on the ternary diagram. When the saturates to cyclics ratio remains constant the line moves toward the asphaltics apex. This would mean that the relative amounts of saturates and aromatics converted to asphaltics depend upon the charge stock composition and that air blowing converts proportionate quantities of each to the higher molecular weight asphaltics. It is known that the naphthenic residues from petroleum crude oils are more amenable to alteration of their properties by air blowing which implies that a higher proportion of the saturate fraction relative to the cyclics is converted (38) to asphaltics.

This is true where the lines on Figure 4 slope upward to the right. Such results also are in accord with the concept that ring compounds with long side chains are readily broken, and are confirmed by the fact that saturate fractions separated from a given stock will process faster than cyclic fractions when subjected to the same operating conditions. However, highly aromatic materials must show a relatively higher loss of the cyclic fraction if the composition line moves upward to the left toward the 100 percent asphaltics apex. This phenomenon usually occurs when the charge stock composition lies to the right of a line projected downward vertically from the asphaltics apex.

Air blown asphaltics exhibit the properties of gels and will have lower asphaltic contents than vacuum reduced products of the same ring and ball softening point in accord with the theory that the degree of solvation rather than quantity of high molecular weight is the critical factor in controlling consistency.

Catalytic polymerization where the petroleum residual is treated with a catalyst in the presence or absence of air must be considered as a separate case where the mechanism is specific with the charge stock and catalyst employed. The catalyst may selectively accelerate the polymerization of either the naphthenes or the aromatics which will alter the slope, accordingly, of the line in Figure 4 indicating composition changes. In some cases the catalyst tends to produce a vertical line, but the refractive indices of the components may be either higher or lower than those of the corresponding fraction for air blown asphalts from a given source stock. The specific results for one residuum are illustrated in Figure 5 and Table 3. In general, the refractive indices usually are higher for the saturates and lower for the cyclics than the indices of the corresponding fractions of air blown asphalts of the same softening points. These differences are less pronounced at higher consistencies. A peculiar result occurs sometimes where an increase in the cyclics content with catalytic processing has been noted with certain residuals. An indicated possibility here is that some low molecular weight saturates are converted (catalytic cracking) to cyclic compounds which would also account for the decrease in refractive index of the composite cyclic fraction and the increase for the residual saturates. These specific results will vary with the charge stock, catalyst employed and extent of processing. The catalyzed product also exhibits more colloidal properties than the straight air blown asphalt of the same softening point although the former may contain fewer asphaltics than the air blown one. These differences indicate a variation in the nature of the high molecular weight material produced by the catalyst which tends to result in reduced solvation by the oils present. The naphthenic and intermediate type asphalts are more amenable to catalytic blowing than the aromatic asphalts with the latter showing some tendency for an increase in refractive indices for both oily components (saturates and cyclics) but not to the extent that results from vacuum reduction.

Certain of the above processed asphalts when subjected to component analysis and the fractions studied for ultraviolet absorption characteristics gave results as shown in Figure 6. The data indicate that the saturate fraction remaining after air or catalytic blowing are but little different from the original saturates of the mother stock but the amounts change.

This is somewhat in accord with the results shown in Figure 5. In steam refining the remaining saturates show a higher unsaturation as do the cyclic fraction confirming the results in Figure 5. Since steam reduction removes oil primarily by vaporization these data indicate that the higher molecular weight materials present in steam refined asphalts may have relatively greater C=C groups.

The different results for air blowing and catalytic blowing indicate that the catalyst tends to control the dehydrogenation or polymerization in such a manner as to produce a residual cyclic fraction less changed than in air blowing but yet producing a more gel-like product. The difference appears to a matter of degree, but the mechanism is not clear. Apparently the remaining cyclic fractions after air blowing are less saturated because the ones of higher molecular weight have been used in making asphaltics or some saturates may be converted to cyclic material. Perhaps the catalyst accentuates the polymerization to produce some type of condensation effect that is different from that obtained with air alone. Thus, the catalytic blown asphalt is more colloidal at a given

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TABLE 3

PROPERTIES OF ASPHALTS FROM FLORIDA (SUNNILAND) RESIDUUM[a]

	Steam Refined	Air Blown	Catalytic Blown	
R and soft point — F	150	150	150	- -
Penetration, 77F, 100g/5sec	19	43	98	- -
Asphaltics—%	43.0	37.0	32.0	- -
Saturates—%	36.0	34.5	34.0	- -
RI/158F	1.5400	1.5210	1.5210	- -
Cyclics—%	21.0	28.5	34.0	- -
RI/158F	1.5850	1.5555	1.5495	- -
R and B soft point — F	- -	200	200	296
Penetration, 77F, 100g/5sec	- -	19	33	17
Asphaltics — %	- -	43.0	38.0	42.5
Saturates — %	- -	32.0	32.0	31.0
RI/158F	- -	1.5200	1.5195	1.5140
Cyclics — %	- -	25.0	30.0	26.7
RI/158F	- -	1.5550	1.5480	1.5518

[a]Data by interpolation and extrapolation from curves for experimental points necessary in order to show properties for comparable softening points.

softening point but the compositions are quite similar (Table 3). A study of the properties of the asphaltic fractions from comparative air blown and catalytic blown asphalts might prove very informative on this point but data are not available. From the foregoing it should be apparent that it is possible to obtain from a given source two asphalts having quite different properties but which show the same composition on a weight basis. Determinations of the refractive indices or ultraviolet absorptiongrams of the saturate and cyclic fractions may be helpful in explaining the variation in properties.

The other commercial methods of producing asphalts require special consideration of the composition of the individual stocks and the specific process employed. As a generalization, the components of blends may be considered additive on a basis of weight percent with the physical properties of the resulting mixture being a function of its colloidal properties. Any subsequent processing of the blend will affect the composition (and properties) in a variable amount depending upon the proportion and susceptibility of the components to the particular processing method used. In connection with blending it is interesting to note that Dengler et al. (5) blended a Mexican asphalt with a cracked residue and through mutual solubility effects were able to increase appreciably the solubility of cracked residue in carbon tetrachloride. This improvement usually is greater the more viscous and/ or the more aromatic the blending agent. Other peculiar phenomena (21) of binary mixtures such as blends having softer penetrations or lower softening points than either material making up the blend can be explained readily by the colloidal nature of the blend as a function of the composition of original materials used.

COMPOSITION AND FLOW PROPERTIES

One of the most striking examples of the lack of scientific approach in asphalt technology is the continual use of empirical tests such as penetration, ductility and others. The data from such tests with few exceptions are difficult to correlate quantitatively with the performance of asphalt in service. It is true that such tests have been valuable tools to the technologist in the past, and it is true that they are simple and rapid tests, but as more useful procedures for evaluating the flow properties become available the use of the old methods should be discouraged. A similar attitude should be taken regarding any new empirical tests for evaluating hardness, consistency, etc., which will only add more confusion and result in uneconomic investigations. The position taken by this author is based on experience and the opinion of others. For example, Reiner (22) states "It is

doubtful whether either asphalts or bitumens show plastic deformation, — except perhaps in blown bitumens — this being a deformation connected with the existence of a yield value." The present author would not except blown bitumens since with proper techniques no yield values have ever been shown conclusively for asphalts, although Thelen (34) has proposed such analyses. The discussion of Thelen's paper also raised this question. The study of deformation requires a consideration of time as well as stress and strain and it is believed that most asphalts of commercial use will show deformation at very small stresses if sufficient time elapses. There are two reasons for empirical flow tests being unattractive. First, it is difficult to get two investigators to agree to the same word definition as to what the test measures. Second, and by far the most important, all deformation characteristics of asphalts when subjected to an applied stress are amenable to rigorous mathematical analysis. That such analysis may not have been made does not mean that it cannot be done. The application of sound rheological techniques such as those being studied by Reiner (23) will eventually replace the empirical tests as has been done in the rubber industry and is being done in the plastics industry.

It is apparent from the literature that more and more emphasis is being placed on rheological phenomena where the data are measured in scientific units. In the final analysis the flow properties of an asphalt are a function of its composition, the stress-strain relations, temperature, time and the history of the sample. These variables affect the behavior of the asphalt under stress and by their control and measurement the behavior may be predicted. In general, the major flow tests required are viscosity, the degree of complex flow (the gel-sol evaluation), and the change in consistency with temperature and elasticity. In the following sections the influence of composition on these properties will be illustrated. Data for the commonly used empirical tests are included as a matter of interest along with the more fundamental rheological relations.

The influence of composition on asphalts from the standpoint of standard penetration and softening point tests is illustrated in Figure 7 using various data.(29)

In general, the range as shown may be considered to cover all asphaltic materials obtained by steam reduction of crude petroleums. The range extends from the low values for aromatic types of residues, of which those from Kern River (California) crude oil are an example, to the high values shown for those from Tampico (Mexico) crude oil, which is an example of an intermediate type source of residual. It is possible that there might be found some exceptions to the range shown, but it is not likely, since the two examples may be considered more or less as extremes of their respective types. It should be noted that no steam refined naphthenic residuals are shown. This is because it is difficult to steam reduce residues from paraffinic crude oils to make satisfactory commercial asphalts. The steam refining of asphalts consists primarily of the removal of the more volatile fractions, and it is generally not possible to process paraffinic residuals without causing cracking since the more oily fractions in paraffinic crude oil residues have extremely low volatilities and thus very high temperatures would be necessary to remove any material by steam refining.

The curves indicate that the more aromatic residuals produce asphalts for a given softening point having lower penetrations at all three of the standard temperatures used in asphaltic testing. The characteristic difference between the aromatic type residues and the intermediate type residues are believed to be due to a relatively greater number of aromatic and naphthene rings with short paraffinic chains present in the intermediate type. If steam refined naphthenic residues were plotted on this same chart, the curves would lie upward to the right above the respective curves for the intermediate materials.

The curves in Figure 7 can be considered generally applicable for all straight reduced residuals, since in general the processing of asphaltic residues either by steam alone, or combined steam and vacuum, produces about the same results.

The effects of air blowing upon the flow properties of asphalts made from different consistencies of an intermediate type of source material are illustrated in Figure 8 with the steam refined asphalts from the same source being shown for comparison since it represents the least amount (none at all) of blowing. The curve for the highly blown asphalts made from this particular crude oil source illustrates the properties when a
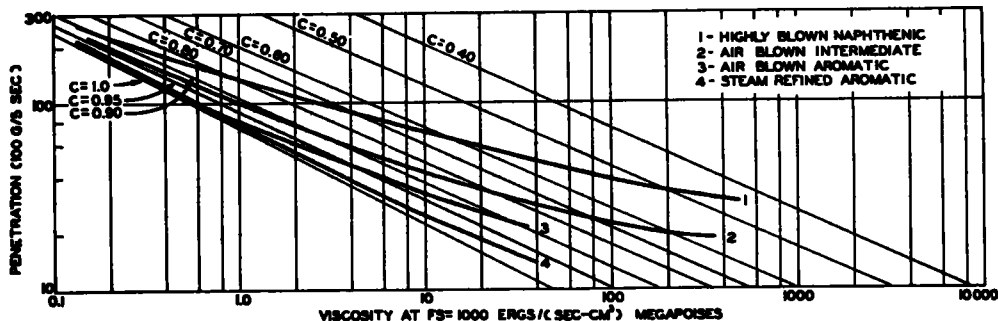
Figure 11. Generalized rheology—penetration curves for asphalts.

residue of about 300 sec Saybolt Furol viscosity at 210F is air blown. The curve for the semi-blown asphalts was derived by air blowing a residue of 100 penetration. As shown, the asphalts made from the softer starting material have a higher penetration for a given ring and ball softening point than the ones made from the 100 penetration starting material. These relative effects are characteristic of air blown asphalts made from different starting consistencies and the relative effects for penetration are shown to be similar for all three standard temperatures at which penetration is measured.

The curve for the highly blown asphalts from this particular source should not be considered as representing the most highly blown asphalts that could be made, since by the use of a still lower viscosity starting material (lower than 300 sec Saybolt Furol at 210 F), very highly blown asphalts could be made and the position of such curves on Figure 8 would be above and to the right of those shown for the highly blown asphalts. Furthermore, the curves for a given starting consistency for all intermediate type residuals will not necessarily superimpose on the curves in Figure 8. This is illustrated elsewhere (28) for Sunniland (Florida) residues, which may be considered a borderline naphthenic-intermediate residual, but which require a starting viscosity considerably below 300 sec Saybolt Furol at 210 F in order to produce highly blown asphalts similar to those shown in Figure 8.

The explanation for these differences in the properties of the asphalts produced by various degrees of blowing lies in the fact that the softer starting materials contain a larger quantity of the less viscous oils. The oils of intermediate molecular weight that are present are converted in the air blowing process to compounds of higher molecular weight through a process of dehydrogenation and polymerization, and it is the combination of these polymers and the low molecular weight oils that yields the peculiar properties of air blown asphalts. The more highly blown asphalts have the properties of gels indicating a partial solvation of the high molecular weight material rather than a solution. A hard semi-blown asphalt when fluxed back with the softer mother stock shows a tendency to have the properties of the highly blown asphalt confirming the partial solvation concept. The tendency is greatest with naphthenic type asphalts. In the case of the semi-blown asphalts, the quantities of the low viscosity oils are less and the air blowing process results in a smaller amount of polymerization with the result that the properties of semi-refined asphalt tend to approach those of the steam refined residues. The refractive indices of the components therefore are intermediate between those of the highly blown and steam refined products.

The penetration data in Figure 8 have been replotted in Figure 9 to illustrate the influence of the degree of blowing upon the tests results. Certain relationships (such as the vertical distance between the penetration at 32 F and 115 F) from these empirical tests are often used to evaluate the susceptibility of asphalts to temperature change. The fallacies of such methods become apparent when the penetration at 32 F is higher than at 115 F. This is not a rare occurrence and results for materials having a high degree of complex flow where the deformation is greater at the lower temperature in a given time with a given load than at the higher temperature in a shorter time with a smaller load.
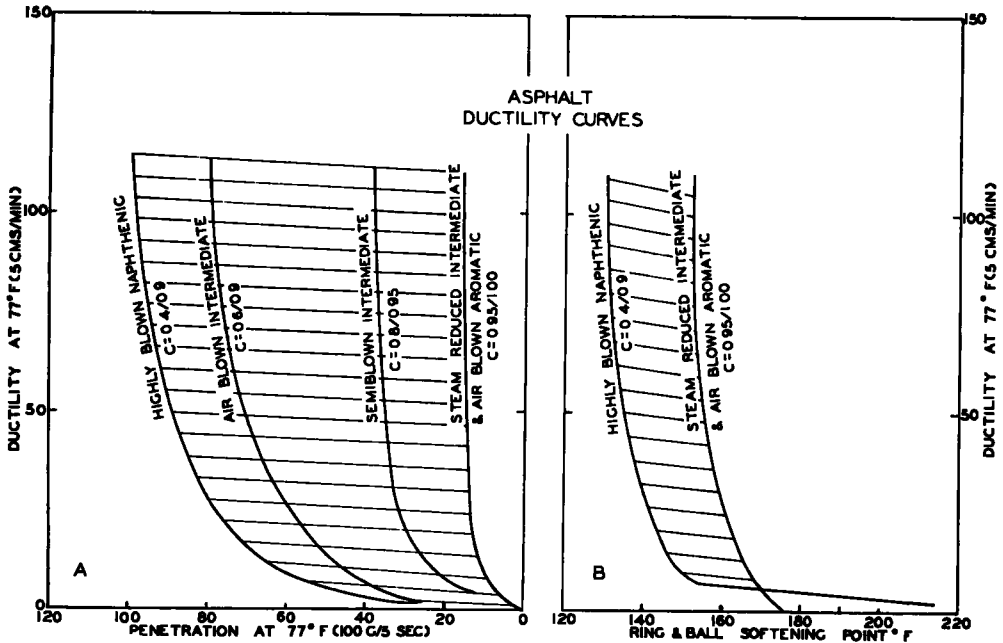
Figure 12. Effect of composition ductilities of asphalts.

Composition exerts a considerable influence on the flow properties of asphalts as might be expected and the remaining illustrations are an attempt to correlate the available information. The wide variations in composition encountered for petroleum residues preclude quantitative relationships at the present state of knowledge, but certain generalizations can be made.

It was shown in Figures 4, 5 and 8 that a given mother stock will yield asphalts of varying composition and properties depending upon the type of processing. The effect of composition on the properties of steam refined asphalts was shown in Figure 7; in Figure 10 the effect of composition on the properties of certain air-blown asphalts is plotted from published data. (39) The variable of charge consistency has been eliminated by comparing the products made from stocks of a similar viscosity. The naphthenic type residues yield asphalts with higher penetrations for a given softening point than the other types. These same relative effects as shown in Figure 10 will apply regardless of the starting consistency used for air blowing, but the range shown does not necessarily encompass the range of penetrations that may be obtained, since certain specific residuals of the same viscosity as used in Figure 10 when air blown, may have still higher pe penetrations for a given softening point. That 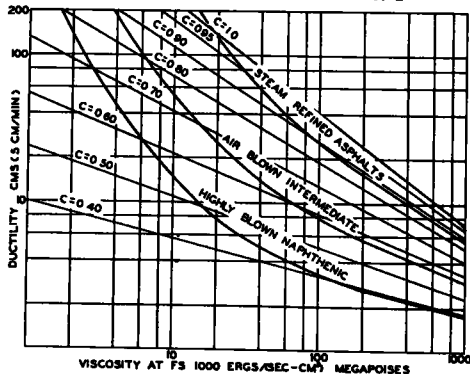is, the curve might be displaced upward and to the right above the naphthenic type curve shown. It is also possible to displace all of these curves upward and to the right when using the same starting viscosity for air blowing by varying the process conditions such as to retard the removal of oils by volatilization. Such processing might be accomplished by air blowing at low temperatures (not commercially feasible because of the extended time required), by air blowing under high pressure (not generally used because of the hazard due to possible explosion), or by refluxing during the blowing operation which has been done commercially. Catalytic blow-

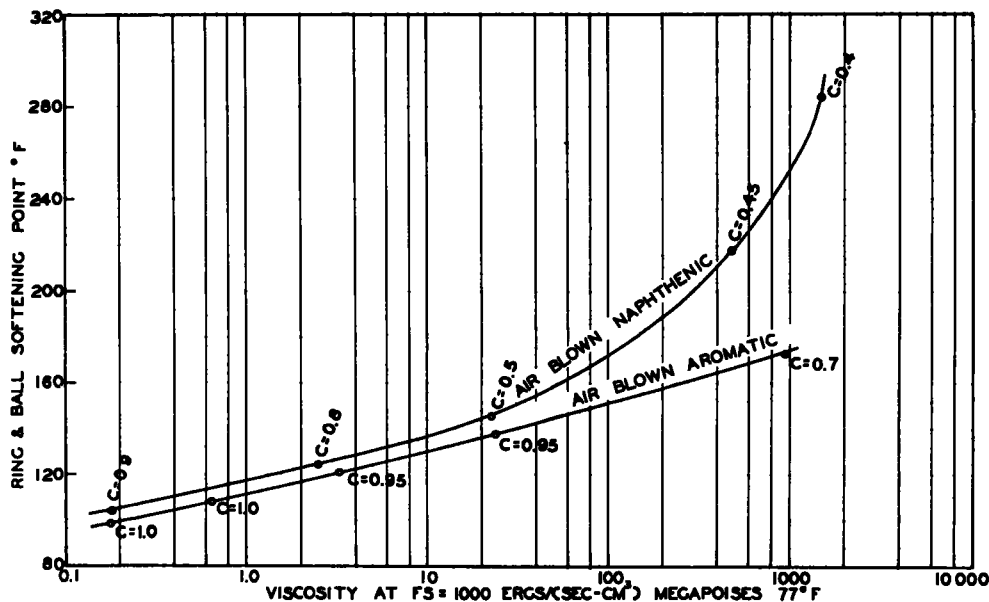Figure 13. Generalized rheology—ductility curves for asphalts.

Figure 14. Generalized rheology—softening point curves for asphalts.

ing of a given feed stock will also shift the curves upward to the right.

The data in Figure 10 are typical for penetrations at 77 F and the relative effects will be similar at other standard temperatures for penetration measurements. The ranges to be expected can be estimated from the data in Figures 8 and 9.

The differences in the curves in Figure 10 are attributed to the differences in composition of the residuals with the naphthenic residues being considered to contain a greater amount of side chain paraffinic hydrocarbons on more or less saturated ring compounds. At the other extreme are the aromatic types containing a relatively large proportion of single and condensed aromatic rings with fewer side chains, with the intermediate residuals being intermediate in composition. At the present state of knowledge it is impossible to state that the naphthenic asphalts contain only single naphthenic rings since undoubtedly their high molecular weight indicates condensed rings. Similarly the aromatic asphalts are made up of condensed rings with a larger proportion of C=C bonds or CH groups whereas the naphthenic asphalts have higher proportions of C—C and CH₂ groups with all differences being relative. Such theories are confirmed qualitatively by spectral absorptions but quantitatively an evaluation is difficult.

In order to explain the difference in behavior of the asphalts on a more scientific basis than the relationship of penetration and softening point, it has been found that measurement of the rheological properties such as viscosity, elasticity and departure from true Newtonian flow are quite informative. (24) Some evidence of this is illustrated in Figure 10, where the range of complex flow has been evaluated quantitatively for the three different series of asphalts. This evaluation appears as the value of "c" shown on the plot. The value of "c" is a measure of the departure from true Newtonian flow and indicates whether a material is behaving as a true liquid (c=1), or whether it possesses considerable anomalous flow characteristics (c=0.5). Thus, for a given softening point the anomalous flow exhibited by the naphthenic type airblown asphalts is considerably greater than that shown for the air blown aromatic types. It is these differences in complex flow characteristics that account for the higher penetration at a given softening point obtained for the air blown naphthenic types. The subject of rheological properties as related to standard asphaltic tests will be discussed more completely with respect to the curves that follow.
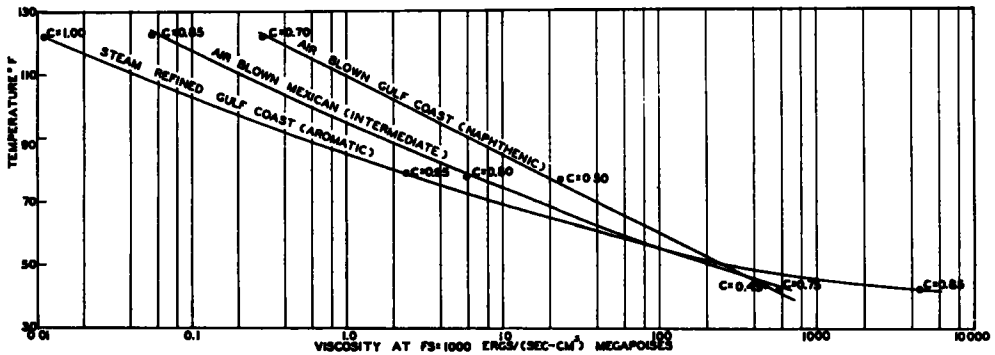
Figure 15. Generalized temperature susceptibility curves for asphalts (50 to 60 penetration at 77 F).

A generalized correlation developed from published rheologic data (39) with the A.S.T.M. penetration is shown in Figure 11 to illustrate the influence of complex flow at a given viscosity on the standard penetration test. The curves show that most low viscosity asphalts (at approximately 100,000 poises) show relatively small amounts of complex flow, whereas the higher consistency asphalts resulting from processing show greater differences in amount of anomalous flow. In all cases the degree of complex flow increases with increase in consistency for any series of asphalts from a given charge stock. The curves should apply generally where the penetration (100 g/5 sec) and viscosity are measured at the same temperature.

The consumer of asphalts who uses the standard ASTM tests (penetration, ductility, softening point) as controlling specifications is in reality attempting to evaluate the rheological properties in a crude, arbitrary manner. It is possible to replace these unscientific tests with fundamental rheological measurements which, after the initial period of confusion because of lack of familiarity with the meaning of the test results, will ultimately prove their value. The methods of measurement are available (36); it is merely a matter of all concerned agreeing on the procedures to be followed.

A basic rheological relationship was proposed by Romberg and Traxler (24) as follows:

$$M = F/S^c \qquad (1)$$

where F is shearing stress, dynes/cm^2; S is rate of shear, sec^{-1}; M is the value of F when S equals one; and c is the slope of a log F versus log S plot. When c equals one (Newtonian flow), M is the viscosity in poises since for this case Eq. 1 is the integration of the differential equation defining viscosity. For comparing asphalts showing complex flow where c is not equal to one, the "viscosity" in poises is taken as equal to the ratio of F/S arbitrarily at a work input of 1000 ergs/(sec-cm^3) or when FS=1000 (24). The value of c decreases as the magnitude of complex flow increases where the rate of shear is higher (the usual case) at a given applied stress than prescribed for true Newtonian flow. For the unusual case where the rate of shear is less than prescribed by Newtonian flow the value of c is greater than 1.

The use of Figure 11 in evaluating the penetration from rheological data is satisfactory so long as a given series of asphalts is considered, but when different types of asphalts having the same viscosity and degree of complex flow are compared, they may not have the same penetration, although the chart indicates that they should. Such results raise pseudo objections that the rheological method is not as sensitive as the penetration method (see discussion of Figure 13). This is exactly the point, the penetration test measures a combination of so many properties (including elastic fore-effect and adhesion of asphalt to a steel needle) that it cannot be used for measuring consistency as pointed out by Traxler. (35) The inadequacy of such arbitrary tests is quickly recognized by the consumer when he learns that asphalts showing the same ASTM tests do not behave in the same way when put into service.

Many of the problems concerning the uses of asphalts will be rectified, it is believed, when rheological measurements are used in conjunction with the newer analytical

procedures to explain differences in the behavior of the asphaltic material. Techniques will be developed which will provide means for determining both quality specifications and behavior specifications in order to obtain reasonable duplication of material and "in service" performance.

The influence of composition on the standard ductility tests is illustrated in Figures 12A and 12B. The sharp break in ductility as a function of the penetration and complex flow has been discussed previously (39) where it was shown that the stress in the ductility test increases with deformation, and accordingly materials showing high complex flow yield lower ductilities because of "necking" effects. For Newtonian asphalts high ductility values result even for materials of very high viscosity because these materials flow readily. Photographs of the differences in behavior of asphalt types are given in the reference. These curves illustrate the necessity for interlocking specifications since a ductility specified for a given Ring and Ball softening point range is considerably less restrictive than for the same number of units range in penetration test results. The cross-over of the curves in Figure 12B explains the peculiar fact that high melting point gel type asphalts will show ductilities greater than the sol types in the 0.5 range for test results. The sol types usually are of such a high viscosity that they will fracture rather than flow an appreciable amount as is the case for the gel type products in this viscosity range.

Figure 13 is a generalized curve and more valuable than Figure 12 for studying ductility since the curves apply generally regardless of the temperature of test. The fundamental rheological data predict the ductility result in a semi-quantitative manner and illustrate the influence of complex flow upon the ductility result. Furthermore, Figure 13 covers a range of ductility of 1 to 100 for a 1000-fold variation in viscosity whereas the sensitivity ranges in Figure 12 are much less (about 100-fold for penetration and Ring and Ball softening point).

One factor that limits the rigorous application of Figure 13 is the influence of elasticity on the initial stages of the ductility test (or at low ductilities). This is particularly important for hard materials (usually less than 50 penetration at 77 F). A complete rheological evaluation of asphalts therefore requires consideration of elasticity as well as viscosity and degree of complex flow.

The measurement of elasticity in quantitative terms is difficult, but a method has been proposed (24) for evaluating them in terms of relaxation time after an initial stressing. If a truly elastic material is deformed and then the stress measured to maintain that deformation, the measured stress will remain the same as the initial stress for infinite time, if the body exhibits only a small elasticity, the measured stress will decrease rapidly from the value of the initial stress because of creep. The relation between residual stress and time approximates an exponential relation (Maxwell). For asphalts the measurement of the time required for the measured stress to fall to one-half the initial stress provides a relative measure of elasticity, although this "relaxation one-half time" is a function of sample size, magnitude of initial stress and temperature. The relaxation one-half times (24) of asphalts of different compositions as measured in a rotary viscometer at a power input of 1000 ergs/(sec-cm^3) are given in Talbe 4 for comparative purposes which illustrates that elasticity is associated with a high degree of complex flow.

That the relations among ductility, complex flow and consistency are quite complex is illustrated by these data since high elasticity (relatively) does not necessarily indicate high ductility. Considerably more study of the elastic deformation of asphalts is necessary because of the many service applications of asphalt wherein a knowledge of the elastic behavior would be valuable. Reiner (23) has indicated methods of attack that may aid in this problem.

Figure 14 is a re-plot of data (23) which shows the influence of composition and complex flow on the Ring and Ball softening point for a given viscosity at 77 F. A high degree of complex flow causes a divergence of curves at high consistencies. A study of Figures 11 and 14 explains why air blown asphalts have higher softening points than steam refined ones of the same penetration. The air blown asphalt has a higher viscosity at 77 F from Figure 11 and accordingly the softening point must be higher from Figure 14. Thus, the common evaluation of the susceptibility to tempera-

TABLE 4

COMPARISON OF ELASTICITY AND DUCTILITY DATA

Asphalt	Type	Pen at 77 F (100 g/5 sec)	Rheology at 77 F			Ductility 77 F (5cms/sec)
			Viscosity Megapoises	Complex Flow c	Relaxation one-half time-sec	
A	Air Blown Naphthenic	102	2.5	0.80	3.5	105
B	Air Blown Aromatic	100	0.62	1.0	1	179
C	Steam Refined Aromatic	100	0.55	1.0	1	200
D	Highly Blown Naphthenic	48	94	0.35	66	2
E	Air Blown Naphthenic	53	22	0.5	20	8
F	Air Blown Intermediate	55	5.8	0.80	4.5	114
G	Air Blown Aromatic	50	3.2	0.95	1.6	200
H	Steam Refined Aromatic	52	2.4	0.95	1	200

ture change of asphalts based on penetration — Ring and Ball relations are erroneous because the asphalts may not be of comparable viscosity at 77 F although they show the same penetration at 77 F.

A better comparison of temperature susceptibility can be obtained by plotting the rheology data in the form shown in Figure 15. The degree of complex flow increases as the viscosity is increased by lowering the temperature, which is analogous to the increase in complex flow with increase in viscosity at 77 F for any given series of asphalts as mentioned in the discussion of Figure 11. Asphalts of lower viscosity (higher penetration) than those show in Figure 15 would be expected to show tempera-ture-viscosity curves closer together and vice versa.

COMPOSITION AND OTHER PROPERTIES

The foregoing considered the influence of composition on flow properties which are perhaps the most important group properties of asphalts. However, another property of importance is durability or resistance to change which is definitely influenced by composition. Failure of asphalts is usually measured by changes in physical properties, but outside of age-hardening (37), changes in physical properties are usually a result of composition changes. The oxidation or polymerization of asphalts is catalyzed by ultraviolet and infrared as well as visible energy, and different asphalts are expected to react to the deteriorating agents in different ways. The use of accelerated weather-ing tests for roofing and paving asphalts has never been found infallible. Other oxidation tests (1,6) have been proposed but their efficacy has not been fully established. The difficulty with accelerated tests is that it is usually impossible to duplicate the service conditions by controlling all the variables in the same way that they apply in actual serv-ice. Until a satisfactory durability test is developed it will be necessary to rely on experience in selecting asphaltic materials to give the best performance.

In general, the naphthenic type asphalts are most suitable for roofing purposes. This is true even though the saturate fractions under process conditions at high temperature
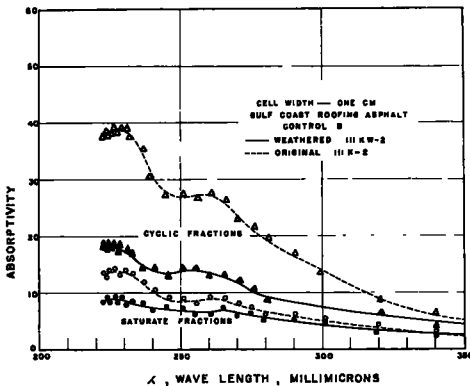
Figure 16. Ultraviolet spectrogram for fractions from a Gulf Coast roofing as-phalt.
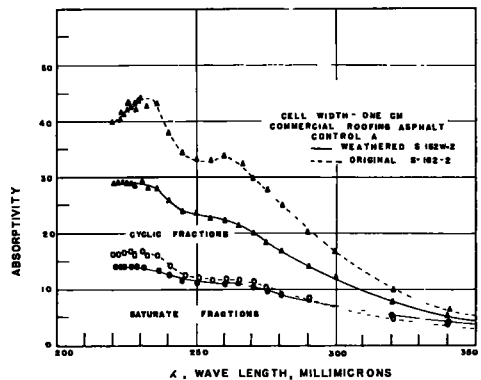
Figure 17. Ultraviolet spectrogram for fractions from a commercial roofing as-phalt.

may be more readily polymerized. However, the free energy of the aromatics decreases with lower temperature to a relatively lesser extent than for saturates and paraffinics which may account for the relatively higher stability of the saturates fraction at low temperature service conditions. The suitability of naphthenic asphalts for services requiring a high degree of durability varies considerably and no limits for composition can be firmly established. Data are given in Table 5 on changes in composition with atmospheric weathering as a matter of interest. Recently Hewett and Faid (10a) have proposed a correlation between durability and saturates content where the durability of roofing asphalts was shown to be greater for asphalts with higher saturates content, other things being similar.

Outside of noting the appreciable drop in refractive index on the cyclic fractions after weathering, the data in Table 5 do not appear significant regarding changes in composition and durability. The more stable Gulf Coast asphalt shows a saturates to cyclics ratio of about 4 whereas the ratio for the commercial product is about 2. The available data are insufficient to determine if such ratios are important. However, the relatively higher energy absorption for cyclics would indicate that a low cyclic content is desirable. In Figure 16 certain ultraviolet absorption data are shown for the commercial asphalt and in Figure 17 results for the Gulf Coast coating are given. These data confirm this theory in a qualitative way.

TABLE 5

COMPONENT ANALYSIS OF ASPHALT COATINGS BEFORE AND AFTER WEATHERING[a]

	Commercial		Sunniland (Florida)		Gulf Coast	
	Before	After[b]	Before	After[b]	Before	After[b]
Sample No. S	162	162-W	112-I	112-IW	111-K	111-KW
R and B Soft Pt, F	220	- -	216	- -	221	- -
Pen. 77 F, 100g/5 sec	18	- -	17	- -	20	- -
Asphaltics —%	46.6	55.4	44.0	54.2	39.7	50.1
Saturates — %	36.3	32.2	31.0	28.2	49.1	40.6
RI/158 F	1.5045	1.5015	1.5180	1.5208	1.4976	1.4935
Cyclics — %	17.2	12.5	25.0	17.6	11.2	9.2
RI/158 F	1.5520	1.5230	1.5560	1.5450	1.5496	1.5148
Appearance after weathering 3 years	Large number of cracks extending through coating layer. Failure imminent.		Some cracks extending through coating layer. Fair condition.		No indications of cracks extending through coating layer. Condition good.	
Appearance after weathering 4.5 years	50% of metal surface uncovered.		Large number of cracks. Failed.		Few surface cracks. Good condition.	

[a] Atmospheric exposure, 0.025 inch layer on aluminum panel.
[b] Analysis based on 4.5 years exposure.

Adhesiveness (for stone, paper, etc.) is another property of asphalts that would be expected to vary with composition, but its evaluation at present requires empirical tests for the specific materials. In general, the naphthenic asphalts lack adhesive properties and are often described as "cheezy." The aromatic and intermediate asphalts usually have good adhesive properties, and are utilized in paving and paper plying applications. However, adhesiveness is not an inclusive term since some asphalts will adhere to stone but not to the steel penetrometer needle. Interfacial tension and the nature of the second substance obviously are important factors with naphthenic asphalts exhibiting a better suitability in some instances.

Emulsifiability appears to be related to the chemical nature, since aromatic and intermediate asphalts usually are readily emulsified whereas the naphthenic ones, with some exceptions, do so with difficulty. The ability of Mexican asphalts to emulsify readily is well known and numerous other intermediate asphalts exhibit a similar property. Saponification number or neutralization number apparently will not correlate rigorously with emulsifiability.

Asphaltic materials are used in a variety of applications where their electrical properties (21) are important. These properties are certainly influenced by the composition but few data are available for consideration. Swenson (30) concluded that the asphaltenes and resins were polar compounds whereas the oils showed little activity. The presence of polar compounds probably would have an effect on the electrical properties, and since the naphthenic asphalts would be more likely to contain polar

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compounds, they might be expected to show lower electrical resistivities. This has been confirmed in a general way.

Summarizing this paper briefly, it appears that an increasingly greater emphasis in asphalt research is being placed on the application of scientific methods. In the final analysis, the chemical composition will be the criterion in selecting an asphalt for a particular purpose. Improved methods will undoubtedly be developed, but at present the component analysis method is of considerable utility in separating the types of chemical compounds present. This in itself is an improvement in asphalt technology because it helps to explain variations in the colloidal nature of asphlats. The composition together with the colloidal properties will provide for a better understanding of the behavior of asphalt in commercial applications.

ACKNOWLEDGMENT

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Appendix

The belief that a reasonably simple analytical procedure for characterizing asphalts can be found has been a strong influence in motivating the writer's research. This has been influenced further by the feeling that such a development is necessary if progress in asphalt technology is ever to get beyond the Edisonian technique of "try
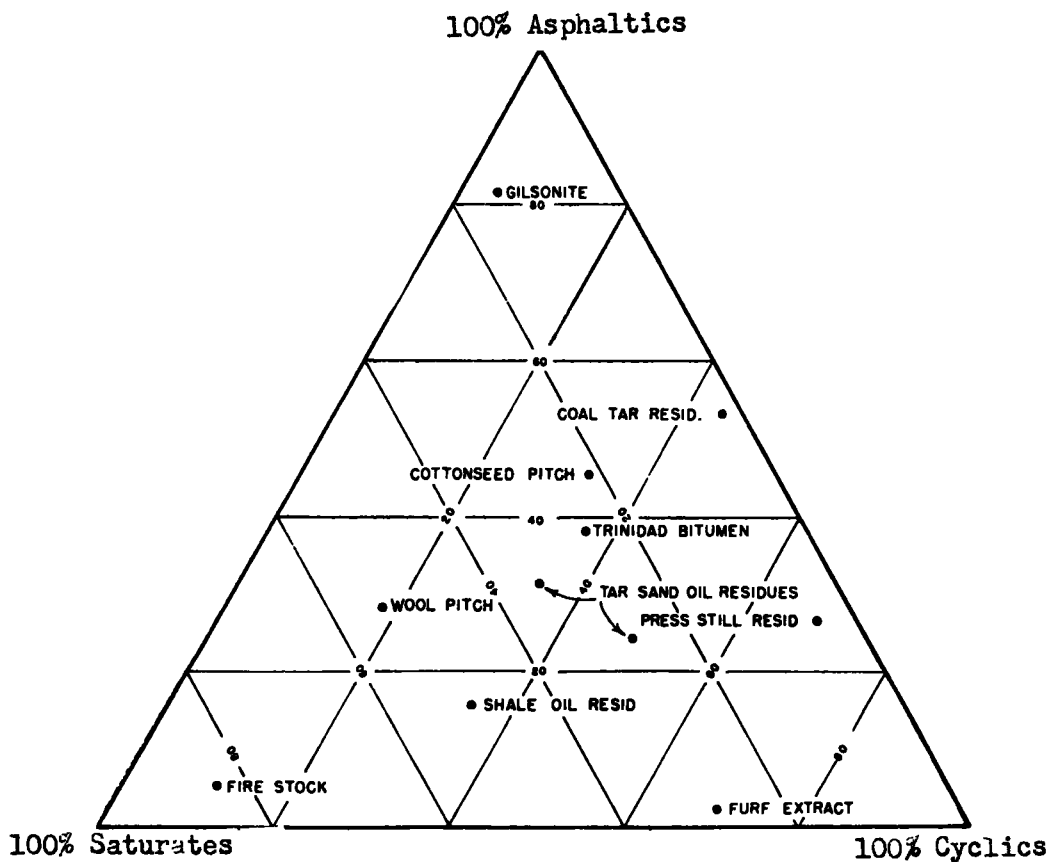
Figure 18. Component analysis of various materials.

this" or "try that." The results summarized in this bulletin are an attempt to apply a scientific approach to composition and to problems in asphalt technology.

A number of years ago the author borrowed a technique used in studying lubricating oils and asphalts, modified it somewhat and applied it to a variety of bituminous materials. The results are shown in Figure 18 taken from a previous article (38). The figure clearly indicated a definite separation of materials of known composition into certain areas on the chart. It showed further that a large group of materials clustered in the center of the chart although it was expected that many of these materials might vary considerably in composition. (The left side apex reads 100 percent "saturates" which is now considered by this author to be more appropriate than 100 percent "paraffinics" as used in earlier diagrams of this type.) These preliminary data served as a motive for an extensive study of a variety of petroleum residues leading to the development of the Traxler-Schweyer solvent extraction method (38) for separating asphalts into three components as mentioned in the bulletin proper and leading to Figure 1 in the bulletin. This latter figure shows a classification system discussed more fully in the bulletin based on the fractions obtained by the solvent extraction technique.

When the acetone-separated fractions of the butanol soluble part of the asphalt were studied by an ultraviolet light absorption technique (26) it was obvious that a separation had taken place but the rejection of pure saturated material by acetone is not rigorous. This is demonstrated by the lower line of Figure 2 which theoretically should be essentially a horizontal line of very low absorptivity. However, there must be something different in the fractions to produce the separation. The question of this difference provided a motivation to keep working on it.

(Note: the following may assist those who are interested in the quantitative values on

the absorption curves as illustrated. The basic absorption relation is:

$$A = \log(I_0/I) = abc,$$

where A is absorbance - sometimes called optical density.

I_0 is transmittance of blank solution.

I is transmittance of the unknown in solution.

a is the absorptivity defined as $A/(bc)$; if the product bc has a numerical value of one, then a and A are equal and the value of a is sometimes called the absorption coefficient, K.

b is the cell thickness, cms.

c is the experimental concentration, gms/L.

Certain of these variations in terminology appear in the literature but the terms and forms of plotting used in the bulletin proper are preferred and vary for ultraviolet and infrared presentations.)

In Figure 2 it will be noted that there is included the results for a chromatographic separation of the asphalt (by adsorption on silica gel from a methylcyclohexane solution) (27) into two parts each of which show ultraviolet analyses to be similar to those for solvent fractionation. This agreement certainly must be more than fortuitous. Actually in the process of separation by adsorption a very sharp break occurs in the refractive index of the solvent free effluent as shown in Figure 19 at 84 percent. This break is apparent to the eye during the processing and definitely indicates a difference in effluents before and after desorption of the adsorbant. Once again the question arises as to what is present to cause the differences in the fractions.

In an effort to establish the magnitude of the range of differences to be expected for bituminous materials, a solvent free furfural extract of a lubricating oil fraction and a pressure still residue (thermally cracked petroleum residue) were subjected to adsorption and the fractions analyzed. The results are shown in Figure 20 compared with the asphaltic residue of Figure 2 in the bulletin proper. The high values for
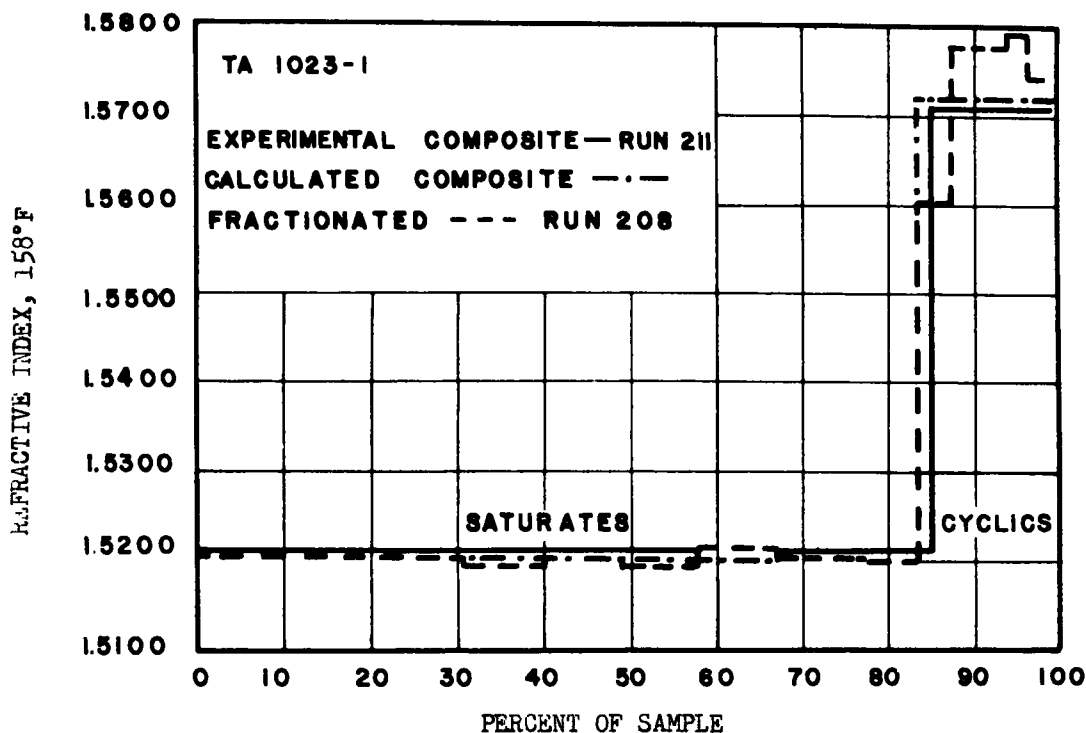

Figure 19. Adsorptogram for TA 1023-1.

absorption in the 230 and 260 millimicron ranges indicate the influence of greater quantities of conjugated acyclic polyenes and aromatics for the cyclic fractions of the furfural extract and pressure still residue. Variations in the saturate fraction are less pronounced and appear to be more a matter of efficiency of separation than real differences.

For further exploration of the composition problem consideration was given (26) to the possibilities of infrared absorption being useful with the results as shown in Figure 3
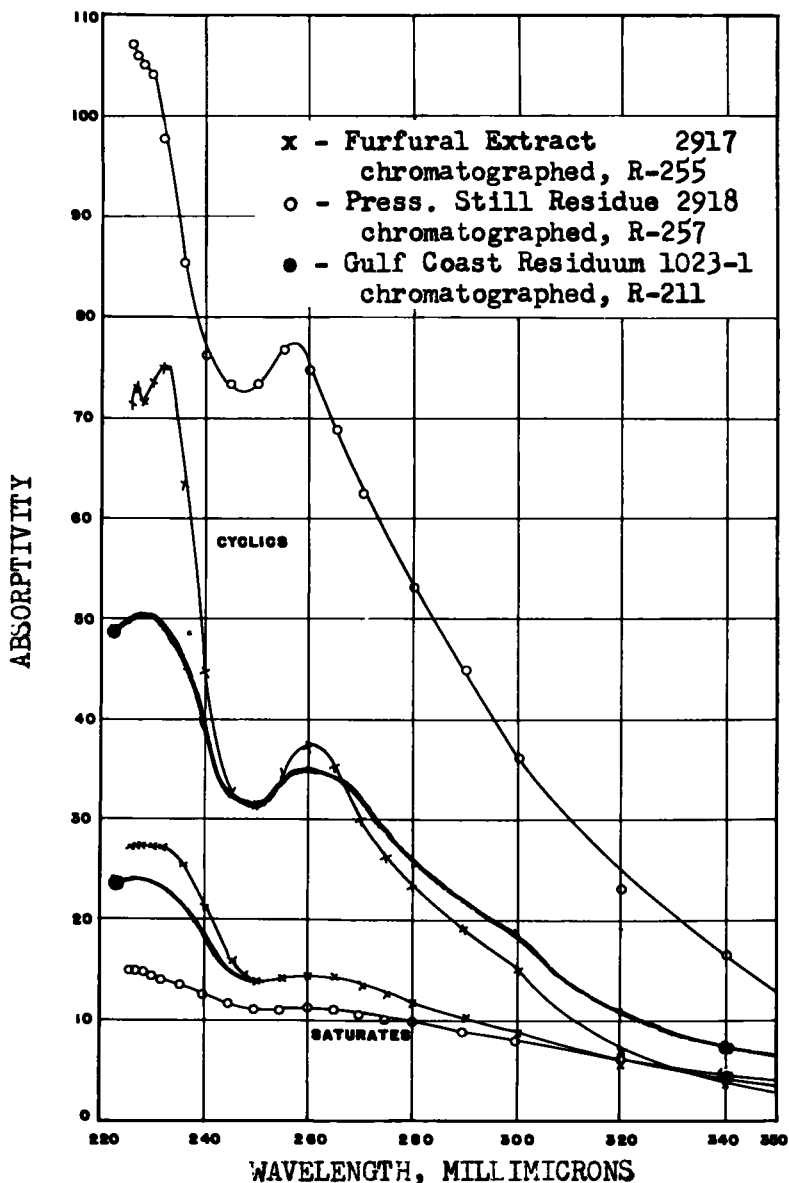
Figure 20. Ultraviolet spectrogram for certain materials.

of the bulletin proper. The spectrograms emphasize differences in absorbance which appear significant. For example, in Figure 3 the aromatic materials have a higher absorbance (lower line in the figures) at 5.85, 6.20, 9.7, 11.5, 12.3 and 13.45 microns; but these relative positions are reversed at 13.9 microns. The writer is not prepared to explain these differences at the present time but they are in qualitative agreement with certain known information concerning the relative saturation of certain hydrocarbons.

These data plus other inferences form the basis for the qualitative assignment of the descriptive terms "naphthenic," "intermediate," and "aromatic" to asphaltic residua as shown in Figure 1 of the bulletin which then provides a means of discussing the asphalts by types. It must be agreed as noted in the bulletin that the symmetrical diagram of Figure 1 is purely arbitrary. Because of overlapping of areas depending upon the consistency of the residuum it would be more realistic for the meeting point of the three areas on the base line to be moved 10 to 15 percentage points to the left to give a skewed diagram.

If the descriptive terminology proposed is accepted, at least for purposes of this discussion it then becomes possible to consider in a general way how the type of asphalt affects the properties of the material. For example, in Figure 7 of the bulletin the properties of steam refined asphalts are shown. These may be expected to cover the range normally expected since processing of naphthenic asphalts is not generally practiced by refiners except for borderline intermediate-naphthenic types which have properties of the intermediate type shown. The point here is that the range of properties available falls within a limited area. However, these areas vary in a specific way as the method of processing or source of the asphalt is changed as shown by Figures 8 and 10.

It is interesting to speculate on what happens during processing and some information is given by Figure 5 where the removal of volatile oils by steam refining is shown by the increase in the refractive indices of oils remaining in the asphalt. Note that this is a different effect from the one found for air blowing. In the latter case the refractive indices do not change much (but the amounts decrease). A reasonable deduction here is that the intermediate molecular weight oils are polymerized to higher molecular weight asphaltic materials producing complex mixtures of high molecular weight material with low molecular weight oils (but void of intermediate oils which might act as mutual solvents) having a variety of colloidal properties as shown by air blown and catalytic blown asphalts.

It is these colloidal properties which are measured by the asphalt technologist's empirical flow tests of penetration, softening point and ductility. A more scientific approach for measuring flow properties is required and is being used in many laboratories as evidenced by recent literature on microviscometers and thin film measurements. The purpose of these new rheological methods is to minimize or evaluate the influence of complex flow on the measurement of consistency. They will certainly lead to more and better information than the empirical methods have yielded in the past fifty years. In Figures 11, 13, and 14 of the original bulletin there are shown generalized correlations of penetration, softening point, and ductility as functions of the absolute viscosity and degree of complex flow shown by the asphalt. The purpose of these charts is to demonstrate the quantitative relations for known measurements which may be used for first approximations when certain data are missing. These charts also illustrate in a general way the range of properties to be expected as the composition of the asphalt changes.

One final property to be mentioned is durability which is definitely of interest to the highway engineer. Unfortunately no test in use at present offers much hope for reliable predictions. Here again, the problem certainly is one of composition. If one ever can determine what types of compounds resist deterioration in service and then find methods for analyzing for those compounds perhaps it will be possible to make some progress on the durability problem. In Figure 16 of the bulletin some data are given for a roofing asphalt with a lower cyclic content which gave better service and had lower ultraviolet absorption than another whose spectrogram is given in Figure 17. These data are much too limited to be conclusive, but others have noted similar results.

In conclusion the writer would like to emphasize that the value of the methods and deductions presented in the bulletin are but one opinion and serve to illustrate potential new fields of study. They are not considered infallible. When something new is shown to be better, the writer would not hesitate to discard any older methods provided it can be demonstrated that the replacement is really an improvement.

Too often a "good idea" is proposed which will not stand the tests of scientific analysis, reliability and logical deduction when applied to a variety of asphalts under different conditions.

A most important immediate goal is to develop the latent desire for scientific tools into a motivating demand for more intensive research in these areas. Such new techniques may become more complex but the highway engineer should be prepared to learn them and apply them if progress is to be made in asphalt technology for road improvement.

Surface Energy and Adhesion Properties In Asphalt-Aggregate Systems

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The various factors that determine the formation and permanence of joints between asphalt and mineral aggregates are discussed. These include the effects of adsorbed films, preheating the stone, weathering, pores and cracks, dust on the stone surface, asphalt surface energies and viscosity, and surface-active agents. Mechanisms for spreading, stripping, blistering, pitting, pore penetration, and diffusion are elucidated. New directions for research on the fundamental properties of asphalt-water-aggregate systems are suggested.

● THE OBJECT of this paper is to present the findings of the National Asphalt Research Center regarding the formation, stability, and permanence of asphalt—stone interfaces. These conclusions are based for the most part on concepts of the significant operating mechanisms, derived from study and experiment. They appear to explain logically many field observations regarding asphalt—stone systems, and to provide bases for predicting the effects of "stripping agents," type and treatment of stone, and other factors on the formation and stability of asphalt—stone interfaces.

BONDING ENERGIES AT STONE SURFACES—ADSORBED WATER FILMS

The nature of the stone surface to which the asphalt is to adhere is the first item to be considered.

Stones in general are atomic lattices, in which each atom is bound to the ones around it through coordination bonds of an electronic nature. If a stone is cleaved, the atoms at the new surfaces are bereft of some of their neighbors, and hence some of their coordination bonds are broken. These atoms then seek to form new bonds to replace the old, broken ones. New coordination bonds can be formed in two ways:

1. In some cases, the coordination forces that are originally directed outward from the surface tend to turn around and conjugate with internal atoms in the stone. This is accompanied by a distortion of the crystal lattice as the surface atoms are pulled closer to the internal atoms, or

2. Water, oil and other contaminants in the air are attracted to the fresh surface.

If all the coordination forces were directed inward, the stone would have no affinity for asphalt or other externally-applied materials. This, as far as is known, never happens, and all freshly cleaved stones do adsorb surface layers or films in varying degrees.

The most usual adsorbed film is water, since water vapor is always present when rocks are cleaved in air. At room temperature, it takes only a few minutes for a rock to adsorb the equivalent of several molecular layers of water.

Experience with quartz confirms the presence of several adsorbed layers of water molecules in usual ambient conditions. A powdered quartz, with a surface area of 22 sq meters per gm, was equilibrated in air at 25 C and 80 percent relative humidity. It was then transferred to a combustion furnace where it could be heated while dry nitrogen was sweeping out the liberated water vapor. The water was collected in an absorption cell which was weighed at intervals as heating proceeded. Thus it was found that on heating to 100 C, the equivalent of 2½ molecular layers of water was driven from the powder surface. Another layer had evaporated by the time the temperature reached 280 C; the last layer required a temperature of over 1000 C completely to remove it. Figure 1 shows the data from three such experiments. Some idea of the binding energies exerted by the quartz on the adsorbed water films can be gained from the temperatures to which the rock must be heated to drive off the water films.

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The possibility was considered that some of the adsorbed water on the quartz might have been contained in pores or fissures, and that it was held in by capillary forces. To check this hypothesis, the surface area of the quartz powder was considered after it had been heated to various temperatures up to 600 C. The B. E. T. liquid nitrogen absorption technique (1) was used, since by this method it is feasible to heat the powder in vacuo, cool, and measure the nitrogen adsorbed as a monolayer on the surface without danger of contaminating the sample. These experiments showed that the area of the powder did not change between 100 and 600 C, hence no pores were evacuated as the adsorbed water film was reduced from the equivalent thickness of 2 molecules of water to that of $\frac{1}{4}$ of a molecule. It was concluded that·in the powdered quartz, the adsorbed water was held on the surfaces and not by capillary forces in pores or fissures.

Fresh rocks normally have adsorbed water layers several molecules thick. The outermost layer of this film is in equilibrium with the water vapor in the ambient air, and hence has approximately the properties of free water at 25 C, in normally-humid air, the surface tension of the adsorbed film is found by experiment to be 74-78 ergs/cm^2, which compares closely with 72 ergs/cm^2 for free water at 25 C.

SPREADING AND STRIPPING

Asphalts and other organic compounds which are insoluble and non-reactive with water will spread over a water surface in air; the rate at which they spread depends largely upon their viscosity. The rapid spreading of oil on water is an example; this spreading continues until the oil film is so thin that it exhibits interference colors (50-200 molecules thick).

Spreading

Spreading occurs spontaneously, in accordance with the Second Law of Thermodynamics, when it decreases the free energy of the system. This is illustrated graphically in Figure 2.

Let 1, 2 and 3 stand respectively for substrate, spreading liquid, and enveloping atmosphere. If 1 is liquid water or an adsorbed film having the properties of free water,
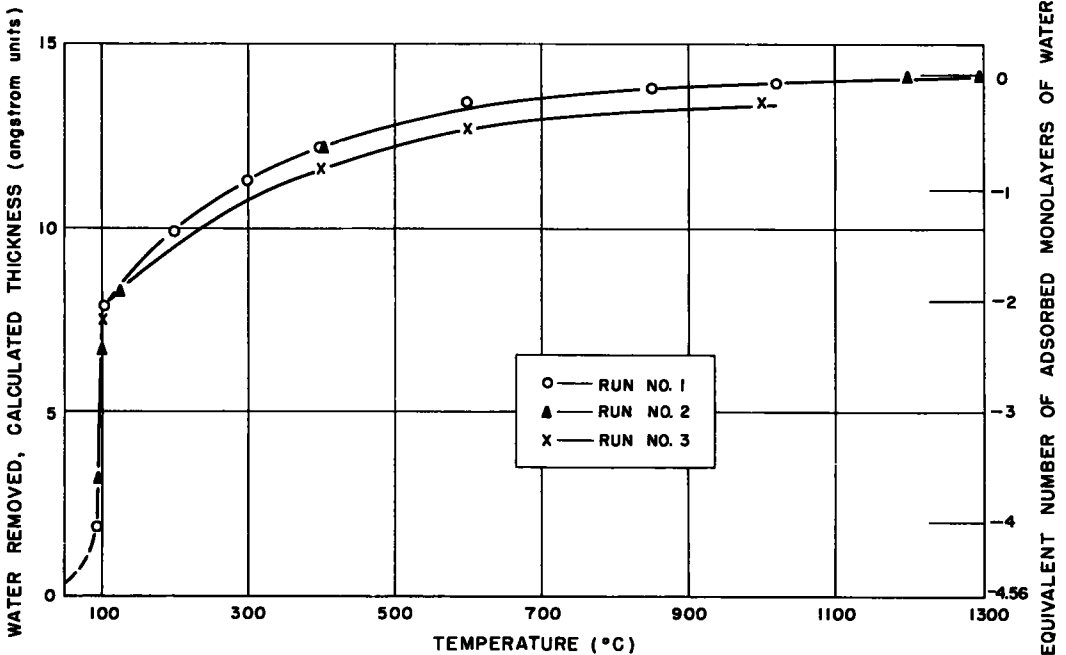

Figure 1. Removal of adsorbed water molecules by heat.

2 is asphalt, and 3 is air, the surface or interfacial tensions, γ, between these phases are approximately as follows:

$$\gamma_{13} \text{ (water-air interface)} = 72 \text{ ergs/cm}^2$$

$$\gamma_{23} \text{ (asphalt-air interface)} = 26 \text{ ergs/cm}^2$$

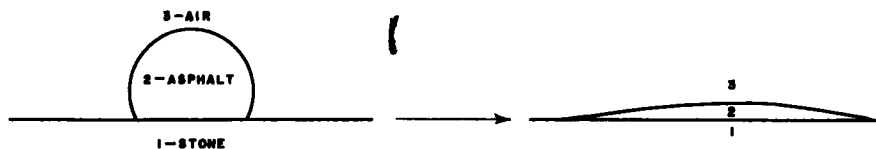$$\gamma_{12} \text{ (asphalt-water interface)} = 30 \pm 5 \text{ ergs/cm}^2$$

Figure 2. Spreading in air.

As Figure 2 shows, the process of spreading wipes out the water-air interface, γ_{13}, and greatly increases the area of the water-asphalt interface, γ_{12}, and of the asphalt-air interface, γ_{23}. Therefore the free energy change, ΔF, as asphalt spreads on water is

$$\Delta F = \gamma_{13} - (\gamma_{12} + \gamma_{23}) \tag{1}$$

$$= 72 - (26 + 30) = 16 \text{ ergs/cm}^2$$

The surface energy relations are similar for the spreading of asphalt over the water film adsorbed on rocks. The numerical values are slightly different:

$$\gamma_{13} \text{ (solid-air)} = 76 \text{ ergs/cm}^2$$

$$\gamma_{23} \text{ (asphalt-air)} = 26 \text{ ergs/cm}^2$$

$$\gamma_{12} \text{ (asphalt-solid)} = 17 \pm 3 \text{ ergs/cm}^2$$

Substituting these values into Equ. 1, the free energy change for the spreading of asphalt over stone at room temperature and humidity is approximately 33 ergs/cm^2:

$$\Delta F = 76 - (26 + 17) = 33 \text{ ergs/cm}^2$$

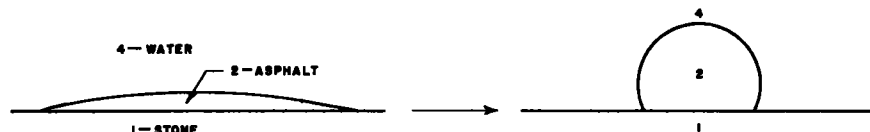Thus, asphalts tend to spread voluntarily over "clean" stones and other hydrophilic surfaces.

Figure 3. Normal stripping.

Stripping

While the destruction by water of asphalt films on stone can occur under various conditions by several mechanisms, the most likely one occurs when there is a discontinuity and, hence, a line of juncture where asphalt, free water and stone are all in contact. This is illustrated in Figure 3.

Let

$$\gamma_{12} = \text{interfacial tension, stone-asphalt} = 17 \pm 3 \text{ ergs/cm}^2$$

$$\gamma_{24} = \text{interfacial tension, water-asphalt} = 30 \pm 5 \text{ ergs/cm}^2$$

$$\gamma_{14} = \text{interfacial tension, stone-water} = 0 \text{ ergs/cm}^2$$

(γ_{14} is approximately zero since under usual ambient conditions the "stone" surface is approximately a free water surface.) Then, as illustrated in Figure 3, the energy potential to cause stripping is

$$\Delta F = \gamma_{12} + \gamma_{24} - \gamma_{14} \tag{2}$$

$$17 + 30 - 0 = 47 \text{ ergs/cm}^2.$$

Thus usual asphalts and normal organic materials will voluntarily spread over water films on stone, and will also tend to be stripped from these films by water. The rate at which these processes occur no doubt depends somewhat on the maginitude of the free energy evolved (ΔF), but in practice probably is controlled chiefly by the viscosity of the asphalt.
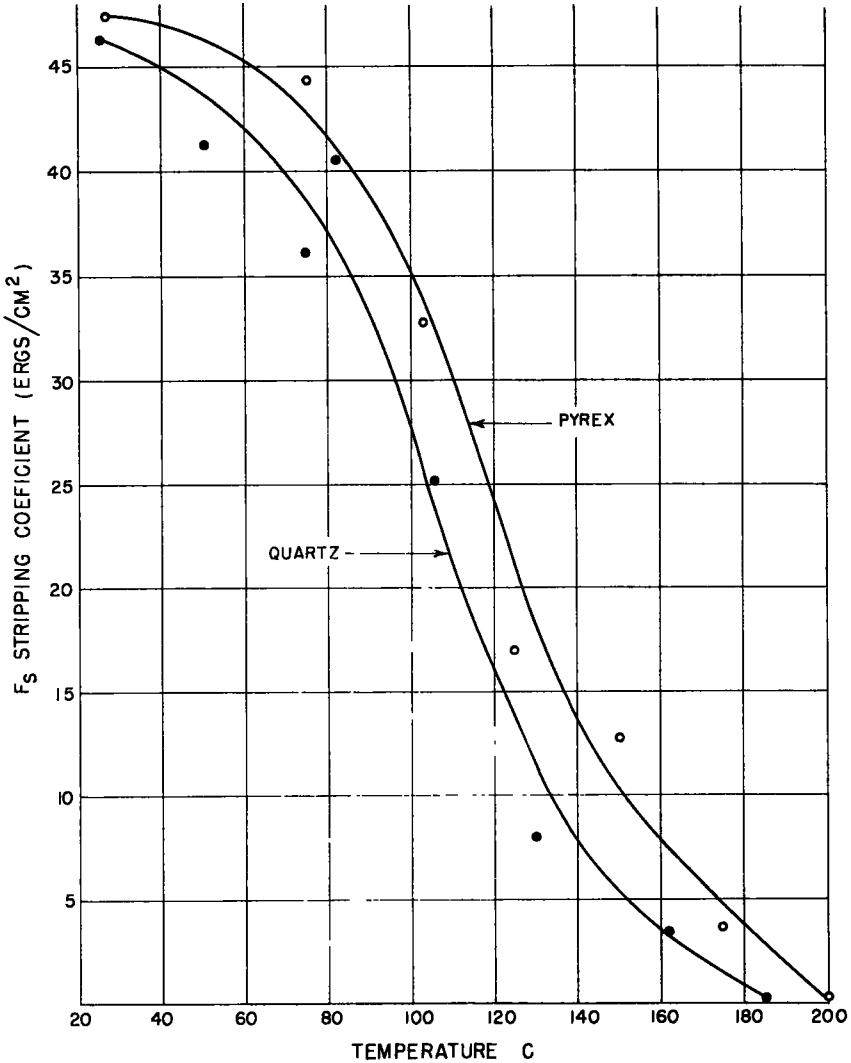

Figure 4. Stripping coefficient of preheated rock.

Preheating of the Stone

When stone with an adsorbed water film is heated under such conditions that water vapor can escape, it loses its outermost adsorbed water molecules. This causes its interfacial tension to asphalt to decrease; asphalt applied to the hot stone is bound much more strongly than when applied to cold stone. Figure 4 shows how the stripping coefficient, ΔF of Eq. 2, drops to zero when the stone is heated to 350 - 400 F (177 - 205 C). In this temperature range, according to Figure 1, quartz has an adsorbed water layer whose thickness is the equivalent of 1⅓ to 1½ molecules.

It appears that hot mix asphalt concrete, in which the asphalt is applied to the hot stone, will be satisfactorily resistant to stripping if the stone is preheated enough before the bitumen is applied, and the resulting water vapor is permitted to escape.

Weathering of Stone

At least one important effect of weathering on stone is predictable from surface energy considerations. As the stone ages and is exposed to cycles of varying temperature and humidity, its outermost adsorbed water molecules are partially replaced or covered by organic contamination-fatty acids and the like from the air. This reduces the spreading coefficient (Eq. 1) and also the stripping coefficient (Eq. 2).

The reduction of the stripping coefficient may be very significant, and is thought to be the reason why weathered stone is considered in practice to be superior to freshly-·cleaved stone in macadam and sheet paving.

Stone stored in a refinery laboratory was found (by one of the sponsors) to resist stripping better than freshly cleaved rock. The stored stone apparently had adsorbed oils from the laboratory atmosphere.

Role of Pores and Cracks in Stone

There is evidence that an asphalt, or the oils from it, normally will penetrate into tiny pores or cracks in a solid surface. The interlock of the asphalt with these pores should make its adhesive joint to the solid stronger and less readily stripped by water.

At ambient temperatures, where the asphalt is very viscous, the rate of penetration with aging may be a reason why joints tend to gain in strength during aging.

Certainly no rigorous assumptions can be made about shape, number, or size of the paths taken by asphalt as it penetrates into a solid surface. It therefore is difficult to arrive at any numerical comparisons between the rates of penetration of an asphalt into two different porous surfaces. Comparison can be made, at least in theory, be-
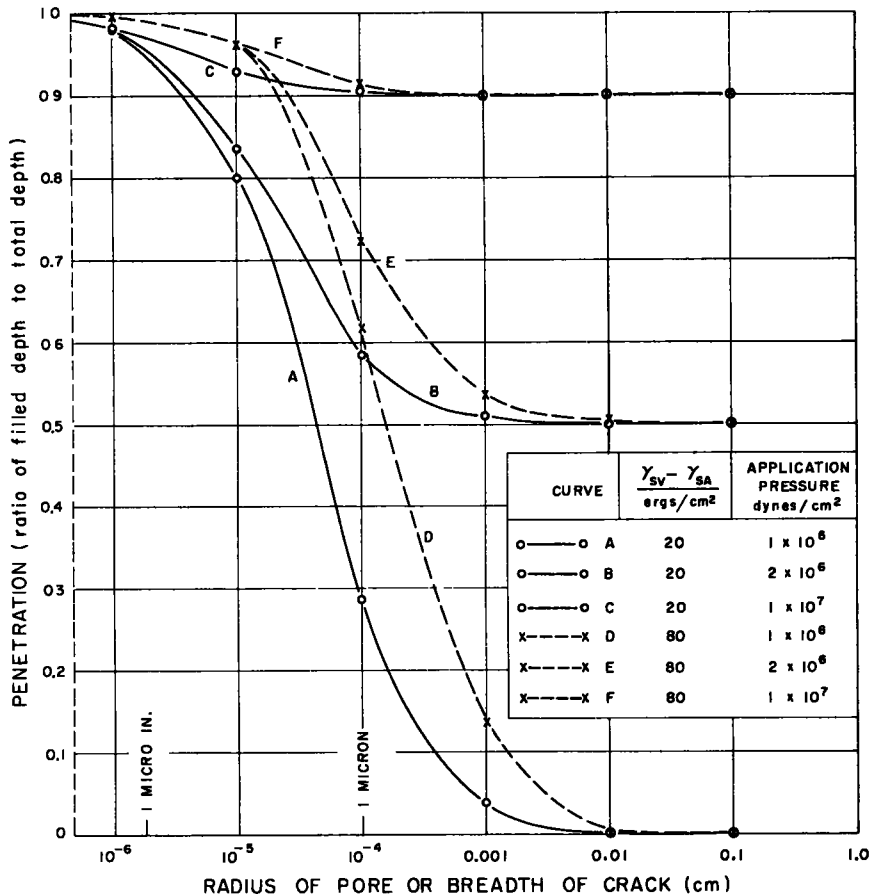

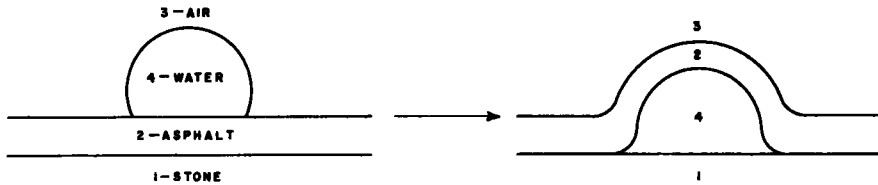Figure 5. Penetration into closed pores.

Figure 6. Blister formation.

tween the rates of penetration of two different asphalts, or of one asphalt at two temper-
atures, into identical solids. From a study of even an erroneous geometrical model
the way in which various physical factors probably influence penetration can be learned.
The following study is based on Poiseuille's equations for flow in cylindrical capillaries:

1. <u>Deep or Open Pores</u>. If the pores are open, or if the depth of penetration is
small compared with the depth of pore:

$$d = \sqrt{\frac{Art}{2\eta}} \qquad (3)$$

where

d =	depth of penetration	(cm)
A =	adhesion tension $= \gamma_S - \gamma_{SL} = \gamma_L \cos\theta$	(ergs/cm^2)
r =	radius of pore	(cm)
t =	time	(sec)
η =	viscosity	(poises)
γ_S =	surface tension of solid	(ergs/cm^2)
γ_{SL} =	interfacial tension, solid-liquid	(ergs/cm^2)
γ_L =	surface tension of liquid	(ergs/cm^2)
θ =	contact angle, liquid to solid	(deg)

In this case, it is assumed that no significant external pressure is assisting the flow.

2. <u>Two-Step Penetration</u>. If the asphalt penetrates a distance of d_1 while hot, it may
penetrate further, to d_2, on aging when the sun is warm:

$$d_2^2 - d_1^2 = \frac{Art_2}{2\eta_2} \qquad (4)$$

t_2 and η_2 are the times and viscosities during the second stage of penetration.

3. <u>Closed Pores</u>. If the pore is closed, rate of penetration decreases and finally
ceases when the air in the pore is compressed to a pressure equal to $\frac{2A}{r}$. Ultimate
depth of penetration in closed cylindrical pores, assuming that Poiseuille's Law holds,
would be:

$$d = 1 - \frac{P_0 1}{P_0 + \frac{2A}{r}} \qquad (5)$$

where $\qquad\qquad$ P_0 is initial pressure on the system, and

$\qquad\qquad\qquad\qquad$ 1 is the depth of pore.

To illustrate these equations by hypothetical examples, if rocks heated to 300 F are
mixed for 10 min with asphalt at the same temperature and the asphalt is an 85-pen
sol type, such as might be used in paving, its viscosity at this temperature would
be about 5 poised. If the rock is hydrophilic, at 300 F it would have lost part of its
adsorbed water film and its adhesion tension to asphalt would be about 75 ergs/cm^2.
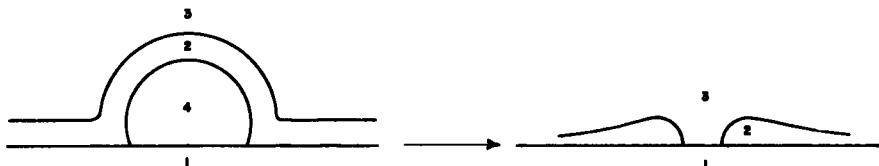If the pores in the rock have radii of 0.1 micron (10^{-5} cm), then from Eq. 3:

Figure 7. Pitting.

$$d = \sqrt{\frac{75\,(10^{-5})\,(600)}{2\times5}} = \sqrt{0.045}\ cm = 0.212\ cm$$
$$= 0.084\ inches$$

Now suppose the same aggregate is immediately spread and cooled. Assuming that for 8 hours a day (summer) the asphalt has a temperature of 95 F, and that only in this time will appreciable flow take place, it can be calculated from Eq. 4 how much the total penetration would be in a month. The viscosity is now about 800,000 poises. From Eq. 4, the increase in depth of penetration during this aging period would be 0.0063 cm = 0.025 in. This process, of course, slows down with time, particularly if the pores are closed and shallow.

The importance of this exercise is that it provides some conception of the effect of pore size, time, viscosity, and adhesion tension on the rate of creep of asphalts into solid surfaces. It may explain why rocks with relatively large pores, like limestone, appear to give better joints than those with fewer and/or smaller pores, like quartz.

There is some evidence that only the oil molecules of asphalt are small enough to enter pores in some rocks. These molecules thus are preferentially absorbed, leaving the asphalt "dryer" and harder. There is at present no quantitative approach to this behavior, but note only that it is a facet of the problem of pore penetration by asphalts.

The effect of adhesion tension and pore size upon the depth of penetration into closed pores is illustrated in Figure 5. This shows how the percent of length of a closed pore, which is penetrated by asphalt, varies with the size of pore, assuming it is circular in cross-section. It shows also that ultimate depth of penetration into large pores should be much greater for hydrophilic surfaces than for surfaces on which hydrophobic (oily) molecules have been adsorbed.
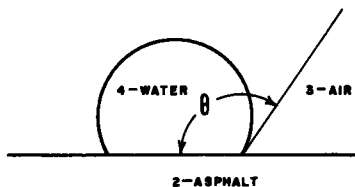

Figure 8. Interfacial tension of water on asphalt.

DUST ON STONE SURFACES

Dust on aggregate surfaces has a tendency to trap air when the road oils or cutbacks are applied. This weakens the joint by preventing initimate contact between the stone and bitumen. It also promotes stripping by providing channels at the interface, where water can penetrate. How important these effects are in practice is not known, but theoretically, at least, they could be significant. If this is the case, washing freshly crushed stone to remove dust particles should be beneficial.

PITTING AND BLISTERING

These are mechanisms by which bituminous coatings can be punctured, and sites created from which stripping and channeling could occur. Their practical importance probably depends upon climatic conditions.

When the sun comes out after a rain has covered a pavement with water drops, the warmed asphalt will tend to flow out from under the drop, and spread over it, as shown

in Figure 6. As the sun gets hotter, the water blister expands in volume, and eventually breaks, leaving a pit. The energy potential for blister formation (Fig. 6), using the previous interfacial values is:

$$\Delta F = \gamma_{34} - (\gamma_{24} + \gamma_{23}) \tag{6}$$
$$72 - (17 + 30) = 25 \text{ ergs/cm}^2$$

The surface energy potential for pitting (Fig. 7) when the blister breaks is:

$$\Delta F = \gamma_{24} + \gamma_{23} \tag{7}$$
$$= 17 + 30 = 47 \text{ ergs/cm}^2$$

Eq. 6 shows that low interfacial tension between asphalt and water, γ_{24} should tend to promote blister formation, but to retard pitting.
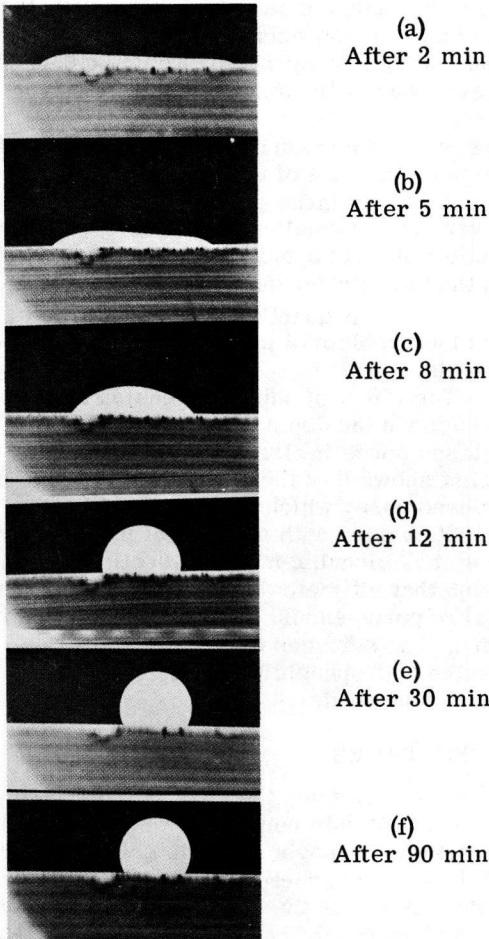

(a) After 2 min

(b) After 5 min

(c) After 8 min

(d) After 12 min

(e) After 30 min

(f) After 90 min

Figure 9. Stripping of Med A asphalt from Pyrex by water at 148 C.

DIFFUSION OF WATER MOLECULES THROUGH ASPHALT

Diffusion of water molecules through asphalt is a very slow process, hence is not expected to be so significant a cause of water damage as stripping and blistering. Beckman, Badger, Gullekson and Stevenson (2) report that discontinuities in the asphalt film, rather than diffusion, are the most likely means of ingress of water. Nevertheless certain observations regarding diffusion are of interest.

Asphalts, like resins and plastics, will absorb water molecules, and gain in weight thereby, until their moisture content is in equilibrium with that of the ambient. These absorbed water molecules will not escape from the asphalt unless the ambient conditions are altered, or an external pressure is applied. Among the several ways of applying external pressures are:

Thermal Gradients. Moisture will tend to migrate in most materials from a hot surface to a cold one. Solar energy applied at the surface of a pavement might drive the absorbed water inward to the aggregate.

Absorption by the Substrate. If the aggregate surface is dusty or has trapped air or dry voids, water will leave the asphalt to wet the aggregate surfaces.

Chemical Reaction. An exothermic reaction between the substrate and water (such as rusting of iron), can cause water molecules to leave the asphalt and enter into the reaction.

Osmosis. Salts or other materials at the substrate surface, which are soluble in water, tend to attract water molecules and form more dilute solutions.

It is apparent that absorption by the substrate, chemical reaction, and osmosis are dependent upon the condition of the aggregate.

Figure 10. Stripping test equipment.

SURFACE ENERGIES OF ASPHALTS

The usual methods for measuring surface tensions of liquids and interfacial tensions between immiscible liquids are not accurate when the liquid is as viscous as asphalt. Accordingly, the surface tensions of asphalt are measured by an adaptation of the Bashforth-Adams (3) method, and the interfacial tension with water is determined by measuring the contact angle of water on an asphalt surface. These measurements showed that the surface tensions of 11 asphalts in air are remarkably similar, being 25.8 ± 0.6 ergs/cm^2 at 77 F, and decreasing by 3 ergs/cm^2 per 100 F rise in temperature.

Interfacial tensions to water calculated from the asphalt-water contact angle as shown in Figure 8, ranged from 25 to 35 ergs/cm^2, being low for soft asphalts (130 pen) and high for hard asphalts (0 - 13 pen). The asphalts tested included vacuum distilled Santa Maria, airblown Venezuelan, and airblown MidContinent. No significant differences in surface energies were attributable to the source of the asphalts.

The adhesion tension of asphalt and stone was determined indirectly by the method of Bartell-Osterhof (4).

STRIPPING TESTS

From the foregoing, it is apparent that the rate and extent that water may strip asphalt from an aggregate will depend on the following:

1.   The preheating of the aggregate before asphalt is applied, and the application of the asphalt while the aggregate is still hot.
2.   Cleanliness of the aggregate (oil and dust on surface).
3.   Porosity of the aggregate.
4.   Perfection of the asphalt coating. (If the coating were free of discontinuities, it would not be stripped by water.) Normally the asphalt films in paving would not be expected to be free of discontinuities.

5. Viscosity (hence temperature) of the asphalt under conditions of test.

6. Interfacial tensions: asphalt-water, asphalt-stone, and water-stone.

7. Possible chemical reactions between asphalt and aggregate, resulting in a higher energy bond than that due to purely physical adsorption.

Items 1, 2, 4 and 5 must be controlled in a suitable test for stripping; items 3 and 6 are probably the material parameters that the test is supposed to evaluate.

In accordance with this thinking, a proper stripping test is believed to be one in which the aggregate is ground to produce a plane surface, preheated, and coated with asphalt while both the asphalt and the aggregate are at the temperatures to be used in the mixing plant, cooled and then stripped with hot water until equilibrium is reached. From the resulting contact angle, the stripping coefficient can be calculated (Eq. 2). A suitable method for such a test is described in the Appendix. Figure 9 illustrates the stripping of an asphalt (ASTM penetration, 77 F/100g/5 sec = 141 dmm ASTM softening point, R and B, 112 F) from pyrex by water at 148 F. In this case, the pyrex had not been preheated before the asphalt was applied.

USE OF ANTI-STRIPPING AGENTS

Since experience and knowledge of anti-stripping agents is based on theoretical calculations and laboratory experience only, dogmatic statements cannot be made. Nevertheless there may be some purpose in suggesting what this experience would indicate regarding the use of anti-stripping agents:

1. It has been shown that if the aggregate is preheated to a high enough temperature to drive off the equivalent of three or more molecular layers of adsorbed water, the asphalt should form an unstrippable bond to it. The use of anti-stripping agents in hot mix asphaltic concrete under these conditions appears to be unnecessary.

2. If the bituminous product must be applied to cold wet aggregate, anti-stripping agents may be beneficial. The calculations suggest that normal asphalt will spread about as readily over free water as over stone. Suitable anti-stripping agents cause the asphalt to displace water and stick to stone if they are brought into contact. It is noteworthy that the treated asphalt does not voluntarily spread over stone under water, but it does adhere to stone if it is, by mechanical means, brought into contact with stone.

3. If the asphalt is applied to cold, dry stone, the permanence of the joint is favored (a) if the stone is porous, free of dust, and weathered, (b) if the asphalt is quite fluid when applied (to promote perfect coating), and (c) if the asphalt becomes viscous on cooling. If these parameters are unfavorable, the use of anti-stripping agents should be considered: A non-porous stone like quartz may warrant an anti-stripping agent where a porous stone might not. Conservatively speaking the use of anti-stripping agents cannot be recommended except where they demonstrably are needed. They tend to lower interfacial tensions to water and hence promote blistering, and although there is no evidence, it is thought that they promote diffusion of water molecules.

The calculations (Eq. 2) show that a completely effective anti-stripping agent must be capable of chemisorption to the aggregate surface or to the innermost layers of the adsorbed water film. A "wetting agent" that is not chemisorbed, but merely acts to lower the interfacial tensions between asphalt and water and between asphalt and stone theoretically cannot confer complete immunity to stripping, although it may greatly reduce the stripping potential.

FUTURE RESEARCH

This paper has discussed some of the behaviors of asphalt-aggregate-water systems in terms of classical surface energy and viscosity properties.

Recently, new tools and concepts have come into being which should further the understanding of such systems, particularly in the direction of their aging and deterioration in service. Briefly, the following program is now considered worthy of exploration:

1. DeBruyne has shown that there is a high probability that air is trapped at the

interface between an adherend and a solid surface such as between asphalt and aggregate and has suggested ways to estimate its coverage. What happens to this air on aging, and how it affects the performance of the adhesive joint could be important.

2. The water content of asphalts and its fluctuations with environmental and aging factors can be studied by broad resolution nuclear magnetic resonance, and possibly by radioactive tracer techniques. The rate and mechanism of diffusion of water vapor through asphalt also can be investigated.

3. The sorption of asphalt molecules at the interface with mineral aggregate hinders their molecular and atomic motions, and alters the heats of activation of their molecular motions. There is at least a possibility that these effects can be analyzed by broad resolution nuclear magnetic resonance. A study of these effects would contribute evidence as to the nature and mechanisms of the bond between bituminous compositions and aggregates.

4. The selective adsorption or absorption of asphaltic components at interfaces and into minerals might be pinned down by the use of radioactive tracer techniques.

Any significant differences in any of these characteristics, between fresh and aged systems would be clues to the causes of their deterioration in service. It would appear to be a good research risk to determine the feasibility of making these measurements of air and water diffusion, asphalt bonding and moleqular diffusions in view of their probable importance in the asphalt paving system.

ACKNOWLEDGMENTS

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Appendix A

Measurement of the Stripping Coefficient

The equipment, Figure 10, consists essentially of an optical system with monochromatic light for projecting the silhouette of the test sample against photo-enlarging paper or polaroid film. This specimen is prepared as follows:

The aggregate, ground to have a smooth surface, is placed in the test cell. It is heated by a mantle surrounding the cell to the temperature at which it is to be mixed with the asphalt. During the heating process, dry nitrogen or air which has been dried through Drierite is passed through the cell, sweeping out any vapors which had been adsorbed by the aggregate. When the aggregate is up to operating temperatures, the molten asphalt is dropped through a glass stop-cock onto the solid surface. It spreads over this surface to form a flat film. Heating is now stopped and air is passed through the cell, until a temperature of around 80 C is reached. At this point distilled water is introduced into the cell until the cell is full. The temperature of 80 C is maintained for an hour, during which time the asphalt film will strip, if it is not stable in the presence of water. Stripping results in converting the asphalt film into a ball such as is illustrated in Figure 8. The silhouette of this ball is now projected on the sensitized

paper and its contact angle to the stone surface measured. The stripping coefficient is then calculated from the contact angle by the following equation:

$$\text{Stripping potential} = \gamma_{24} (1 - \cos \theta) \qquad (9)$$

γ_{24} is the interfacial tension between asphalt and water.

For asphalts, to which wetting or coupling agents have been added, it may be necessary to determine γ_{24}. This is done by forming a flat film of the asphalt on brass or other solid, and cooling until the film is rigid. This is now placed in the optical cell and a drop of water put on the film. The contact angle of a drop of water is now determined in the optical set-up, and from this γ_{24} is calculated by Eq. 8.

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THE NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL is a private, nonprofit organization of scientists, dedicated to the furtherance of science and to its use for the general welfare. The ACADEMY itself was established in 1863 under a congressional charter signed by President Lincoln. Empowered to provide for all activities appropriate to academies of science, it was also required by its charter to act as an adviser to the federal government in scientific matters. This provision accounts for the close ties that have always existed between the ACADEMY and the government, although the ACADEMY is not a governmental agency.

The NATIONAL RESEARCH COUNCIL was established by the ACADEMY in 1916, at the request of President Wilson, to enable scientists generally to associate their efforts with those of the limited membership of the ACADEMY in service to the nation, to society, and to science at home and abroad. Members of the NATIONAL RESEARCH COUNCIL receive their appointments from the president of the ACADEMY. They include representatives nominated by the major scientific and technical societies, representatives of the federal government, and a number of members at large. In addition, several thousand scientists and engineers take part in the activities of the research council through membership on its various boards and committees.

Receiving funds from both public and private sources, by contribution, grant, or contract, the ACADEMY and its RESEARCH COUNCIL thus work to stimulate research and its applications, to survey the broad possibilities of science, to promote effective utilization of the scientific and technical resources of the country, to serve the government, and to further the general interests of science.

The HIGHWAY RESEARCH BOARD was organized November 11, 1920, as an agency of the Division of Engineering and Industrial Research, one of the eight functional divisions of the NATIONAL RESEARCH COUNCIL. The BOARD is a cooperative organization of the highway technologists of America operating under the auspices of the ACADEMY–COUNCIL and with the support of the several highway departments, the Bureau of Public Roads, and many other organizations interested in the development of highway transportation. The purposes of the BOARD are to encourage research and to provide a national clearinghouse and correlation service for research activities and information on highway administration and technology.