

# Surface Energy and Adhesion Properties In Asphalt-Aggregate Systems

EDMUND THELEN, Chief, Colloids Section, Franklin Institute Laboratories, Philadelphia, Pa.

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  $2\frac{1}{2}$  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.

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<sup>2</sup>, which compares closely with 72 ergs/cm<sup>2</sup> 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,

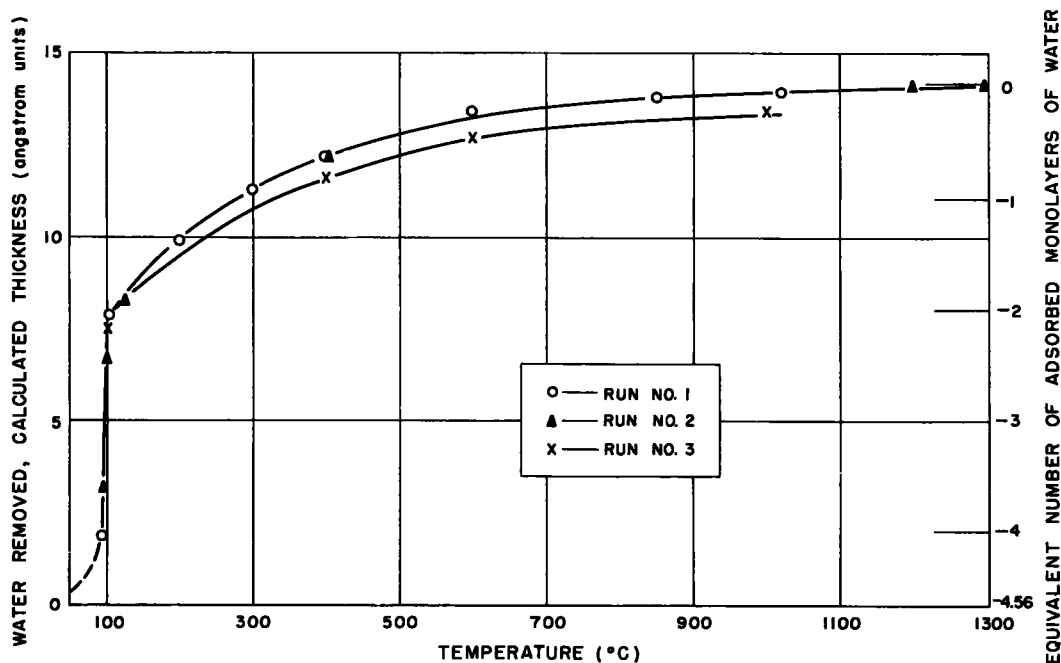


Figure 1. Removal of adsorbed water molecules by heat.

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

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

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

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

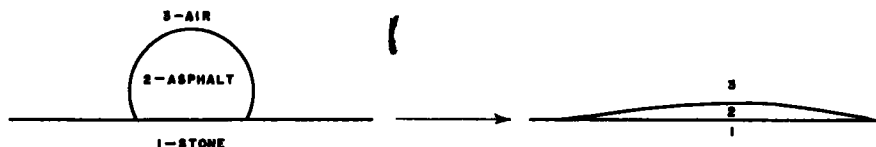


Figure 2. Spreading in air.

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

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

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

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<sup>2</sup>:

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

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

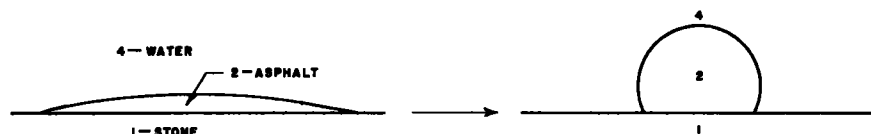


Figure 3. Normal stripping.

### 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  $\gamma_{12}$  = interfacial tension, stone-asphalt =  $17 \pm 3$  ergs/cm<sup>2</sup>

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

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

( $\gamma_{14}$  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

$$\Delta F = \gamma_{12} + \gamma_{24} - \gamma_{14} \quad (2)$$

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

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 magnitude of the free energy evolved ( $\Delta F$ ), but in practice probably is controlled chiefly by the viscosity of the asphalt.

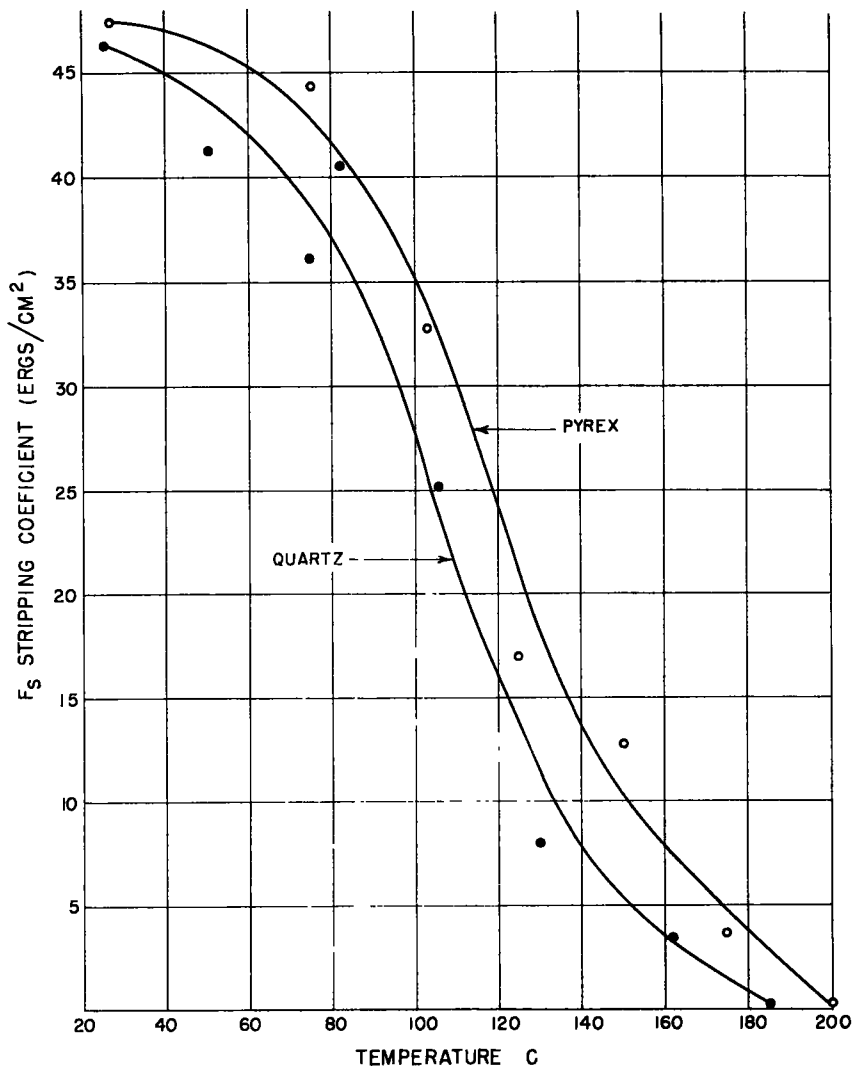


Figure 4. Stripping coefficient of preheated rock.

### 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,  $\Delta F$  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  $1\frac{1}{2}$  to  $1\frac{3}{4}$  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-

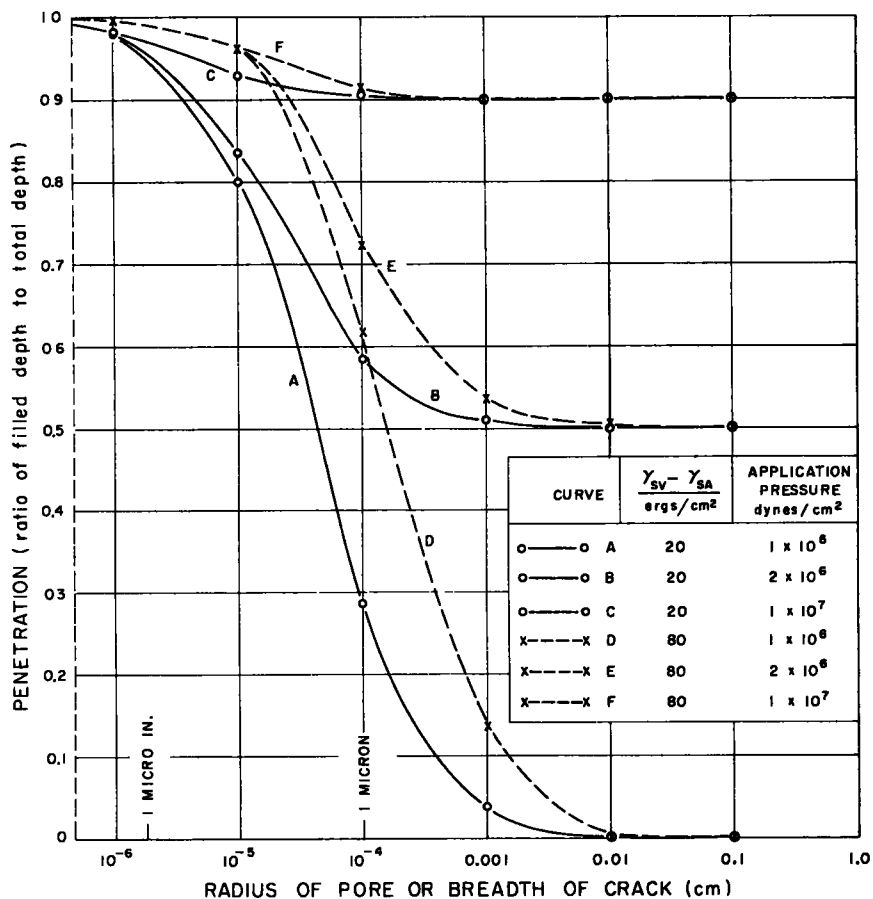


Figure 5. Penetration into closed pores.

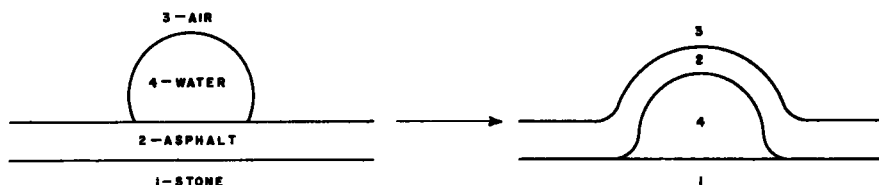


Figure 6. Blister formation.

tween the rates of penetration of two different asphalts, or of one asphalt at two temperatures, 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. Deep or Open Pores. If the pores are open, or if the depth of penetration is small compared with the depth of pore:

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

where

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

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

2. Two-Step Penetration. 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:

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

$t_2$  and  $\eta_2$  are the times and viscosities during the second stage of penetration.

3. Closed Pores. 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:

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

where

$P_0$  is initial pressure on the system, and

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<sup>2</sup>. If the pores in the rock have radii of 0.1 micron ( $10^{-5}$  cm), then from Eq. 3:

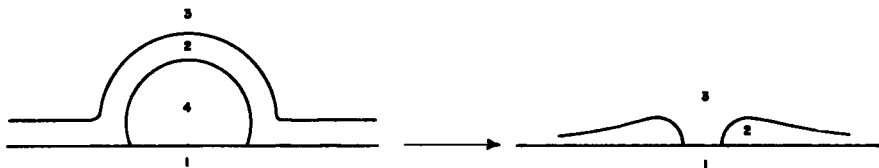


Figure 7. Pitting.

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

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 "drier" 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.

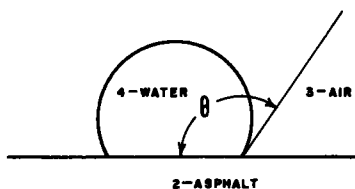


Figure 8. Interfacial tension of water on asphalt.

### 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 intimate 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:

$$\Delta F = \gamma_{34} - (\gamma_{24} + \gamma_{23}) \quad (6)$$

$$72 - (17 + 30) = 25 \text{ ergs/cm}^2$$

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

$$\Delta F = \gamma_{24} + \gamma_{23} \quad (7)$$

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

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

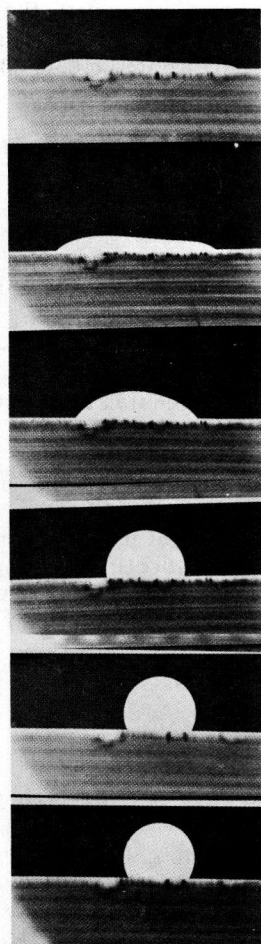


Figure 9. Stripping of Med A asphalt from Pyrex by water at 148 C.

### 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  $25.8 \pm 0.6$  ergs/cm<sup>2</sup> at 77 F, and decreasing by 3 ergs/cm<sup>2</sup> 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<sup>2</sup>, 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 molecular 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:

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

$\gamma_{24}$  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  $\gamma_{24}$ . 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  $\gamma_{24}$  is calculated by Eq. 8.

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