

Spreading Behavior of Bituminous Materials upon Aqueous Substrates

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SPREADING characteristics of the various bituminous materials is of utmost fundamental importance in the incorporation of such substances into and upon materials used in construction. The surface pressure balance was used in this work to measure the spreading behavior of such materials through the force exerted by films upon a floating pressure indicator. Bituminous films were spread upon various aqueous substrates at 25 C. and their surface pressures measured.

The bituminous substances used, which included asphalts, reclaimed asphalts, Gilsonite, coal tar, and cutback solvent, spread poorly upon pure water. The spread films were undoubtedly polymolecular in thickness. Upon acid water or upon aniline hydrochloride solutions the spreading areas were about three times the areas on pure water. Common salt and basic solutions had little effect upon the areas. Aluminum sulfate, which hydrolyzes acid, was but slightly superior to water. Coal tar showed poorer spreading tendencies upon salts than did the various asphalts.

When oxidizing agents were used in dilute solution, spreading efficiencies increased remarkably. Solutions of potassium permanganate were especially effective in causing increased spreading, giving surface areas up to 20 times the areas obtained on pure water. The curves so produced showed an unexpected horizontal bench. Here the areas occupied per surface molecule changed by as much as $10(\text{\AA})^2$ with no change in surface pressure. When asphalt was refluxed with KMnO_4 and spread on water a similar bench occurring at higher pressures was evident. Some reclaimed city pavement asphalt that had been in use about 20 years showed a similar bench at medium pressures with areas per molecule five to eight times the usual water value. These pressure benches seem to be associated with oxidation of bituminous materials or hysteresis effects in the spread surface film.

● THE tremendous present-day use of bitumens depends almost entirely upon their being used in some type of construction material. A large amount of asphaltic materials goes into highway construction where it is mixed with and spread upon various types of aggregate, such as rock, sand, soil. The success of such spreading and mixing processes depends upon a great many variables. Such factors as the weather, substrate type, materials pretreatment, engineering practice, and the physical and chemical condition of the bitumen and aggregate are of utmost importance and significance. Still more important to the permanent successful adhesion of such materials are the surface chemical forces at play at the multitude of phase interfaces in such systems. The physical and chemical forces bind the various phases together and cause the

bituminous material to spread upon, encapsulate, and anchor itself to the aggregate. These forces resist efforts towards eventual separation and stripping. A careful evaluation of these forces and a knowledge of their kinds and variations would be of extreme value in the design and construction of new structures.

It is therefore the purpose of this investigation to begin a study of the spreading pressures and forces, areas occupied by spread bitumens, and some factors that might influence such properties when various bituminous films are placed upon the surface of aqueous solutions. Such types of information might eventually help answer some of the many problems current in bituminous construction.

The problem of final stability and waterproofing of bituminous structures has been successfully solved in many cases. In other

cases, difficulties of many types have arisen and have been poorly understood. The field of additives is a rapidly expanding one and the use of such materials is common. Just what part such additive materials play, the best type to use, and the reason why some are good and some not is but incompletely understood. Studies of the basic surface chemistry of such systems may eventually help in the production of truly successful additive bonding agents and a more-complete understanding of the systems before, during, and after construction.

It was shown by Andrews and Noble (1) that the chemical nature of many added stabilizing agents had a pronounced effect on the ease and success of bituminous-mix formulations. It still remains for much work to be done to elucidate the mechanism by which such materials spread and orient upon, adhere to, and affect the physical properties of, the finished system.

PROPERTIES OF SURFACES

Spreading

Whenever a small quantity of an insoluble and nonvolatile substance is placed on water, it will remain either as a compact drop, leaving the rest of the surface clean, or it will spread out over the entire water surface. According to Harkins and Feldman (2) there are four general criteria for spreading: (1) All liquids spread on a pure surface. (2) A liquid *b* will spread on liquid *a* if $\gamma_a > \gamma_b + \gamma_{ab}$, where γ_{ab} represents the interfacial tension between the two liquids, and γ_a and γ_b the respective surface tensions. The condition for nonspreading is $\gamma_a < \gamma_b + \gamma_{ab}$. (3) Liquids whose molecules are polar, or whose molecules contain polar groups, spread on water. (4) A liquid will spread if its work of surface cohesion, W_c , is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion, W_a with respect to the surface of the substrate upon which the spreading is to occur. These relations of W_a and W_c give rise to the quantity, *S*, called the spreading coefficient and defined as: $S = W_a - W_c$.

The spreading coefficient, *S*, thus appears to establish the necessary condition for any substance to spread on a substrate by requiring the spreading molecules to attract the substrate molecules more than they attract themselves. During the spreading process, as many molecules as possible will move into

direct contact with the substrate, forming a film one molecule thick. If space on the water surface permits, the whole of the spreading substance will spread into a monomolecular film. The term "film" is used here in the sense that a film will exist whenever a layer having a different composition from the body of the liquid or solid is present at the boundary surface, provided the area and form of this layer are independent of all gravitational effects. Whenever the film area and film form depend on gravitational effects, as well as surface forces, a lens exists. A surface film is considered to exist whenever the gravitational forces tending to change the form or area are inappreciable in comparison to the surface forces acting on the spreading material.

Spreading Coefficient

When liquid *b* is placed upon the surface of liquid *a* and spreading occurs, the original surface of liquid *a* disappears and its place is taken by substantially an equal area of the surface *b*, plus an equal area of interface *ab*, provided the surface of *b* and the interface *ab* do not lose their identity. If they do, then only a composite surface *c* takes the place of surface *a*.

Three forces are in operation when a drop of oil, *b*, forms a lens or globule on the surface of liquid *a*. These forces, represented by γ_a , γ_b , γ_{ab} are respectively the surface tensions of the liquids *a* and *b*, and the interfacial tension between these two liquids. If the globule is to remain as a stable one, the sums of the tensions holding it together, that is of γ_b and γ_{ab} must exceed the tension γ_a tending to cause the drop to be pulled apart. It follows, therefore, that for the stability of such a lens $\gamma_b + \gamma_{ab} > \gamma_a$.

On the other hand, if γ_a is greater than the sum of $\gamma_b + \gamma_{ab}$, the globule will not be stable. The large value of γ_a will cause the liquid *b* to spread over the surface of *a*. The difference $\gamma_a - \gamma_b - \gamma_{ab}$ has been called the spreading coefficient, *S*, (Harkins, et. al., 3) as

$$S = \gamma_a - \gamma_b - \gamma_{ab}. \quad (1)$$

If the area of contact between a layer of liquid *b* on the surface of another liquid *a* is reduced by 1 sq. cm., the individual areas of *a* and *b* must be increased by 1 sq. cm. Since the work done in producing any surface is equal to the surface tension multiplied by the area of

the surface formed, the work done in increasing the surface of a and b by 1 sq. cm. is $\gamma_a + \gamma_b$, and the work resulting from the diminution of the ab interface is γ_{ab} . The net work done is thus $\gamma_a + \gamma_b - \gamma_{ab}$ ergs, and this must equal the work done against the forces of adhesion acting across the common interface between liquids a and b . There are assumed to be no other energy changes involved in this process. Hence it is possible to write:

$$\gamma_a + \gamma_b - \gamma_{ab} = W_a \quad (2)$$

where W_a is the adhesional work between a and b . This relation is known as Dupre's equation (17), and was first deduced in 1869. If a single liquid, (for example liquid b) is imagined to be in the form of a column 1 sq. cm. in cross-section, and the two ends of the liquid column are so pulled as to divide the liquid into two parts without any lateral contraction, then two new surfaces, each 1 sq. cm. in area, will be formed. The work required to form these two surfaces is called the work of cohesion, W_c , defined as:

$$W_c = 2 \gamma_b \quad (3)$$

Combining Equations 1, 2, and 3 gives $S = W_a - W_c$, which states that spreading occurs if the adhesion between the two liquids is greater than the cohesion within the liquid which is in position to spread. Spreading would not occur if the cohesion is greater than the adhesion. Thus a positive value for the spreading coefficient corresponds to spreading, a negative value to nonspreading. It can also be seen that because the liquid b spreads upon a , it is not necessary that a will spread on b . The coefficient for a to spread upon b is $S = \gamma_b - (\gamma_a + \gamma_{ab})$. Therefore a high surface energy for liquid a acts in favor of spreading when a is the lower liquid, and against spreading when b is the lower liquid. Corresponding to this, it is found that nearly all organic liquids spread upon water, while water spreads upon few organic liquids. Such compounds as hexane, decane, ethyl benzene, and other pure hydrocarbons with no polar groups have a positive spreading coefficient and do spread upon water. Thus polar groups are not essential to spreading (2).

One of the principal effects of the presence of polar groups within a molecule, as has been shown by Harkins and his co-workers (4, 5) is

to increase the work of adhesion, W_a . It is well known that the presence of a polar group, e.g., $-\text{OH}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{CN}$, $-\text{CONH}_2$, generally confer solubility in water on the molecule to which it is attached. As the length of the hydrocarbon chain is increased, however, the solubility of the molecule decreases markedly. This decrease in solubility is probably not due to any diminution in the attraction between the water and the polar group, which is probably the primary cause of the solubility, but rather to the increased length of the insoluble hydrocarbon chain. If a very polar group is present, then W_a is very high, and the term W_c in the equation: $S = W_a - W_c$ is never large enough to give a negative value to the spreading coefficient. Nevertheless, when the work of adhesion towards water is small, the liquid may still spread provided W_c remains smaller. The extremely great effect of the presence of polar groups in producing spreading is due to the fact that, in general, polar groups increase the work of adhesion toward water much more than they increase the work of cohesion.

If the surface of water is impure, the surface tension of the water (which occurs as a positive term in the spreading coefficient equation) is lowered, thus decreasing the value of the spreading coefficient. Therefore, it often has been found that a liquid with a positive spreading coefficient will not spread, due to the presence of this slight impurity in the water surface. Langmuir (6) found that the presence of multiple bonds in the hydrocarbon chains causes the films to expand more easily than films of saturated chains of similar length. Langmuir attributed this to the multiple bonds attracting the water more than a saturated linkage. Therefore, it appears probable that double or triple bonds will increase the work of adhesion, W_a , between the unsaturated film and water.

When a very small quantity of a long-chain spreading oil with a polar group is placed on the surface of water, it will form a film upon the water one molecule in thickness. It is supposed that the molecules of oil arrange themselves with their polar groups all attached to and buried in the surface of the water. The hydrocarbon chains are arranged parallel to one another, more or less vertically above the polar groups. If the hydrocarbon chain is long enough, it will impart insolubility to the whole

molecule, because of the extreme difficulty experienced in pulling such hydrocarbon groups into the liquid. Thus, the entire water surface is covered with exposed hydrocarbon groups, and if further oil is now added to the surface, there is little or no further tendency for more molecules to become anchored to the water. The surface of the water is saturated with oil molecules, and there will be little success in forming a second layer. In fact, the polar groups of the additional added oil and those of the oriented films will tend to associate together. When such polar group association occurs, globules or lenses tend to form rather than spread out into a second film.

Surface Films

Interest in monomolecular films on the surface of water was first shown in the work of Rayleigh (7) and Pockels (8) about 1890. Pockels found that the area covered by a spreading oil on the surface of water could be varied as desired by confining the film between movable barriers. These barriers were made of strips of glass placed across a tray filled with water upon which the oil was spread. Rayleigh repeated and extended the work of Pockels, and confirmed the observation that as the area occupied by a given amount of olive oil on the surface of water was diminished by bringing the barriers closer together, the surface tension remained almost unchanged until a certain area was reached. The surface tension then suddenly dropped to about half the original value for water. From the volume of oil placed on the surface and the area it occupied, the thickness of the film at any stage was calculated. Rayleigh (9) concluded that the fall in surface tension occurred when the surface was just covered with a complete film one molecule in thickness. Further observations on water of such oil films were made by Devaux (10) and Marcelin (11), who confirmed the view that the films were monomolecular.

In 1917 a considerable advance in experimental technique was made by Langmuir (12), and opened a new period of intensive study of surface films. In the course of his preliminary investigations, Langmuir noted that the forces exerted by the oil films on the paper barriers which enclosed them were quite considerable, and he devised a means of measuring these forces by use of a balance. This

balance consisted of a shallow trough filled with water, near one end of which floated a paper strip whose length was just less than the width of the trough. This strip acted as one of the barriers to the oil film. Jets of air were used to prevent leakage of oil through the narrow spaces between the ends of the strip and the sides of the trough. Vertical glass rods made connection between the paper strip and knife edge of a balance and actuated the balance beam when any force upon the liquid surface tended to displace the paper float out of its equilibrium position. The weight required to be added to the balance pan to restore the paper float to its original equilibrium position was then a measure of the force acting on the float through the surface film. A definite amount of an oil, insoluble in water was then placed on the surface of the water in the trough by dropping a suitable volume of oil dissolved in benzene at a known concentration. The benzene soon evaporated, leaving a clean oil film. Another paper barrier, extending across the width of the trough but not floating, was placed at the other end of the trough. By moving this barrier progressively towards the float, the area covered by the oil could be varied as desired, and the force transmitted through the film to the float could be measured at each particular area. The area each surface molecule occupied was plotted against the corresponding pressure and a reversed S-shaped curve obtained. Extrapolation of the nearly vertical portion of the curve to zero pressure gave the area of each molecule at zero pressure.

EXPERIMENTAL PROCEDURE

Description and Use of the Hydrophil Balance

The surface pressure balance used in this work was a Hydrophil Balance as manufactured by Central Scientific Company of Chicago and briefly explained by Andrews and Noble (1). This balance closely resembles that used by Langmuir (6) and later modified by Adam (13). It consists of an aluminum tray, 27 inches long and 6 inches wide, provided with leveling screws, drain cock, and a movable barrier, to one end of which is fastened a bridge casting, carrying a torsional-wire device for measuring forces against a mica float. The tray is accurately machined at the upper working edge to permit making measurements of the area. Other parts of the

tray are not machined, thus providing a rough surface to which a paraffin film will adhere. A metric scale is attached along one edge of the tray to indicate the distance of the movable barrier from the mica float. The torsional device consists of a suspension for a torsion wire which is attached to a vernier pointer moving around a circular vernier. The vernier records the torsional force applied to the mica float by compression of the surface film. The mica float extends to within 0.5 cm. of either side of the tray, and is joined to the sides by thin pieces of platinum foil. The vernier scale is calibrated by suspending weights from a hook at the end of the lever arm and noting the number of degrees of torque necessary to restore the pointer to the zero point.

Before use, the inside of the tray and the working edges were thoroughly scoured with a stiff brush and cleansing powder, thoroughly rinsed and dried, and then carefully cleaned with benzene. Then all parts of the dried apparatus that could come into contact with the solution or film were coated with paraffin. The platinum ribbons and the mica float were coated with paraffin applied as a solution in benzene, all the remainder of the coated apparatus was painted with molten paraffin.

The apparatus when ready was placed in a water bath at 25 C., filled with the desired solution, and allowed to temperature equilibrate. The surface of the solution was then swept clean of any surface contamination by suction and by pushing barriers over the surface. Leaks around the ends of the float were detected and stopped. A film of the desired bitumen was formed upon the liquid surface between the movable barrier (initially placed near the far end of the tray) and the float by dropping a definite weight of bitumen in benzene solution upon the surface. The solution dropped upon the surface was made by weighing into a volumetric flask the desired amount of bitumen, diluting to the mark with purified, dried, and distilled benzene, and weighing again. In this way the exact concentration of the bitumen-benzene solution was known. The concentration was so adjusted that less than 1 ml. would give a film covering at least half of the liquid surface. It was found that a 1 cc. B. D. hypodermic syringe, with the needle point filed blunt, made the best weighing pipette. The benzene itself will not form a film, but serves the dual purpose of diluting

the bitumen and of diminishing the viscosity to the point where films form almost instantly. Measurements were begun as soon as the solvent evaporated.

After waiting approximately a minute to permit the benzene to evaporate, the movable barrier was carefully moved toward the float until a point was reached at which the film began to exert a pressure against the float. The force exerted, measured in degrees of torsion, was determined for various positions of the movable barrier as it was moved progressively toward the float.

Computations

The data so obtained were converted to dynes of force per centimeter of float length and surface areas in square centimeters. The float length is considered to be the active length of the float plus half the width of the gaps occupied by platinum ribbons. By plotting the forces as ordinates and the areas as abscissas, a curve may be obtained which can be extrapolated to zero pressure to give the total film area under zero compression.

The weight of the asphalt involved in a measurement can be obtained from the weight of solution dropped on the liquid surface. Assuming an approximate molecular weight for the asphalt, and by employing Avogadro's number (6.023×10^{23}), the total number of molecules added to the surface can be determined. By dividing the total film area, expressed in Angstrom units, by the total number of molecules in the film, the area per molecule in square Angstrom units can be calculated from:

$$\frac{\text{Area}}{\text{Molecule}} = \frac{\text{Total area in cm.}^2 \times 10^{15}}{\left[\frac{\text{wgt. of bitumen} \times 6.023 \times 10^{23}}{\text{molecular wgt. of bitumen}} \right]}$$

Comparing this area obtained on distilled water with that obtained on other substrates, should give the relative spreading tendency of the bitumen on various substrates compared to water. The work reported here is concerned with such comparisons of various bituminous materials on several types of aqueous substrates.

Molecular Weight Determinations

An attempt was made to determine the molecular weights of certain of the asphalts

and coal tars used in this work. The method of freezing-point lowering using benzene as solvent was used.

The apparatus used consisted of a salt-and-ice-water bath, a Beckman thermometer, and a glass container into which was suspended a freezing tube. The freezing tube, containing the thermometer and a stirrer, was prevented from touching the sides of the glass jar by the use of wooden collars. An air jacket was thus provided between the freezing mixture and the freezing tube. Vigorous stirring of the solution was required to prevent supercooling. The air jacket served to slow down the rate of cooling; thereby helping to minimize the possibility of supercooling.

For benzene, the freezing point is 5.4 C. and the molal freezing-point-lowering constant is 5.12 C. Thus, a mole of solute dissolved in 1,000 grains of benzene will lower the freezing point of the benzene 5.12 C, so that the mixture will freeze at 0.28 C. The molecular weights are then calculated by use of the following formula:

$$M_b = 1000 m_b K / m_a \Delta T.$$

Where M_b is the molecular weight of the solute (the bitumen in this work), m_b , the weight of bitumen used, m_a , the weight of solvent used, ΔT the freezing point lowering produced, and K is the molal freezing-point constant.

RESULTS AND DISCUSSION

Molecular Weights

The molecular weights of the bitumens and cutback solvent used in this work gave values by the freezing-point-lowering method, using benzene as a solvent of: MC-2 negative asphalt, 494.5, MC-2 positive asphalt, 364.6, and RT-4 coal tar of 230.7. The value obtained with a sample of cut-back (Socony-Vacuum) solvent was 175.5. These results were in poor agreement with those obtained by other workers who found the molecular weights to range from 620 to 4,250. It is probable that the low values obtained in this work were due, at least in part, to the presence of cut-back solvent with its low molecular weight. The other investigators did not specify the methods used to remove the cut-back solvent if any was present. This difficulty was not encountered for natural asphalts which gave higher values around 4,000.

In an effort to gain some information as to the percentage of the more volatile low molecular weight substances present in these bitumens, they were heated in open beakers at 50 C. for 40 days. It was found that the weight lost was as follows: MC-2 negative, 20.6 percent; MC-2 positive, 15.7 percent; and RT-4 coal tar 22.0 percent. However these values do not give accurate information on the amounts of cut-back solvent present, because the bitumens themselves contain a certain amount of volatile substances which would be lost at the same time. Also a certain amount of oxidation and thermal destruction of the bitumen probably occurred. Such products of heating might also be volatilized causing an error in the weight lost.

It is interesting to note that the molecular weight of the negative asphalt is about 33 percent larger than that of the positive. In the course of their preparation, positive asphalts are often subjected to higher temperatures than negatives (18, 19). On the basis of the molecular weights obtained, it would appear that the positive asphalt undergoes considerable thermal cracking at the higher temperatures, and thereby producing smaller molecules.

Because the molecular weight values obtained here were so low, especially when compared with literature values, the molecular weights of all the bituminous materials used in this work was taken as 2,000. This value seems to be about the mean of the values obtained by Traxler (14) and Katz (15, 16), and to be about an average of various reported values in the literature. As far as this work is concerned, the exact values are not necessary although highly desirable. The measure of spreading as used here is taken from the apparent cross-sectional area of the molecule on a given substrate compared to its corresponding area on water taken as a standard. Even if the exact molecular weights were known and used in calculating the areas occupied per molecule, the relative areas would be unaffected.

If however, it is ever possible to use correct values for the molecular weight which would differ from 2,000, the formula previously given for calculation of surface areas should be modified by the introduction of a factor n defined as the ratio of the correct molecular weight to 2,000 as a multiplicative factor as

$$\frac{\text{Area}}{\text{Molecule}}$$

$$= \frac{\text{Total area in cm.}^2 \times 10^{16} \times n}{\left[\frac{\text{wgt. of bitumen} \times 6.023 \times 10^{23}}{\text{molecular wgt. of bitumen}} \right]}$$

Obviously the ratio of the above equation for a particular substrate to the corresponding value on water, would cancel out the factor n .

General Considerations

The results of the surface-pressure-area studies of bituminous materials spread upon aqueous substrates are summarized in Table 1. Experimental curves for all the substances studied, with their various substrates, are included in Figures 1 to 9. The data which plotted each curve represents an average of all determinations of multiple runs. As many repeated determinations were made as seemed necessary to produce reliable data. In general the results were highly reproducible and close agreement was obtained on repeated attempts for any one type of bitumen on a particular substrate. Occasionally however some deviations were encountered at low surface pressures. These particular deviations in reproducibility have negligible effect on the final interpreted values because the upper portion of the curve (at higher pressures) is essentially all that is used for the extrapolation to zero pressure in obtaining molecular areas.

Spreading on Water

Figure 1 illustrates the spreading of Oliensis positive and negative asphalts and coal tar on a pure distilled water substrate. The extrapolated values for the areas per molecule of the positive asphalt are 5.05 sq. Å and of the negative asphalt are 5.50 sq. Å. These are in close agreement, but probably too small for the actual molecule if it is assumed that these molecules are comparatively large with molecular weight approximating the 2,000 value used. The cross-sectional area of a straight-chain hydrocarbon, as in stearic acid, is 20.5 sq. Å. Because of their complexity asphalts probably should have even larger areas. Coal tars are predominately complex aromatic compounds and their molecular cross sectional areas should be at least 24.0 sq. Å which is the area of the cross-section determined for the

TABLE I
APPARENT MOLECULAR CROSS SECTIONAL
AREAS, (SQ. Å)
(Extrapolated to Zero Surface Pressure)

Substrate	MC-2 Neg. Asphalt	MC-2 Pos. Asphalt	Coal Tar RT-4	Cut-Back Solvent	Air Blown Asphalt	Reclaimed City Pavement	MC-2 Refluxed KMnO ₄
H ₂ O	5.50	5.05	0.95	0.21	7.20	40.0	10.1
KOH							
0.1N	6.85	3.85	6.20				
AlCl ₃							
0.075N	12.0						
0.1N	7.65	6.40	1.95				
0.17N	7.0	7.0					
NaCl							
0.3N	8.60	6.30	2.40				
Aniline Hydro- chloride							
0.1N	21.40	19.00	10.80				
0.3N	17.00	13.60	20.10				
HCl							
0.1N	22.70	15.40	12.00				
0.3N	18.80	12.50	21.00				
H ₂ SO ₄							
0.1N	25.90	17.70	24.40				
0.3N	20.80	12.80	16.50				
KMnO ₄							
0.001M	46.70	49.60					
0.005M	56.20	59.00					
0.01M	65.10	65.90					
0.05M	66.80	68.70					
0.1M	71.80	76.00	65.30	0.36	78.00	77.72	
	88.00	91.00					
	71.00	100.30					
K ₂ Cr ₂ O ₇							
0.1M		11.00		0.87			
Sat. soln.		14.50					

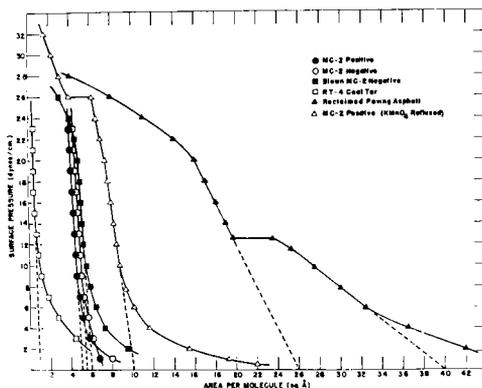


Figure 1. Bitumens spread upon pure water.

benzene ring. However, the extremely small value of 0.95 sq. Å was obtained. The overall low values so obtained would seem to indicate that asphalts and tars do not spread perfectly enough on pure water to form monolayer films, but instead form imperfectly spread multilayer films.

Interference colors due to the interference of light waves reflected at the top and bottom

surfaces of the film, made the film visible. The film appeared patchy as if certain small areas of the substrate were not completely covered by the film. This can well be expected from difficult-spreading substances. If a piece of absorbent cotton, saturated with benzene, was placed near these surface voids, the void areas soon filled and a coherent film resulted.

Surface-Film Hysteresis

Hysteresis was noted in the behavior of the films of the bitumens on water as well as on other substrates, in that the films reacted somewhat sluggishly to pressure changes. A lapse of time, maybe minutes, was necessary after compression of the film by movement of the barrier towards the float before the final pressure reading could be taken. Apparently the full pressure was not transmitted to the float instantaneously.

These hysteresis effects were especially noticeable in films spread upon oxidizing substrates. It was first supposed that a new, unexplainable surface behavior had been observed because often isobaric compressions of $10(\text{\AA})^2$ or more were observed whose appearance was highly reproducible. These isobaric compressions produced horizontal benches in the curves; some at high pressures but more often at moderate pressures. Upon further examination it was found that if sufficient time was allowed between successive compression changes the size of these horizontal benches decreased. After 20 to 30 minutes' wait, these isobaric-area changes were practically eliminated, and the curve would tend to become smooth. By varying the times between compressions, in such a manner that insufficient time was allowed for the film to equalize the surface forces, curves of a stair-step nature could be obtained over a good length of the entire curve. It thus became necessary for all determinations to be taken after sufficient time had elapsed to allow for surface equilibrium. As a consequence the intervals between compressions were carefully regulated with a stopwatch.

Spreading on 0.1N KOH

The 0.1N KOH substrate had an unusual influence on the positive asphalt in that it reduced the apparent cross-sectional area to 3.85 sq. \AA . No plausible explanation seems to

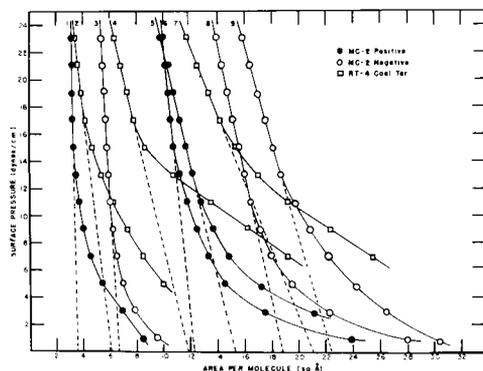


Figure 2. Bitumens spread upon aqueous acid and base. Curves 1, 2, 3 upon 0.1N KOH; 4, 5, 9 upon 0.1N HCl; 6, 7, 8 upon 0.3N HCl.

account for this phenomena. At the same time the KOH caused an increase in the spreading of the coal tar from the extremely small value 0.95 to $6.20 (\text{\AA})^2$. It also caused a slight increase in the areas occupied by the MC-2 negative asphalt.

Spreading on 0.1N and 0.3N HCl

A marked improvement in the spreading qualities of all three bitumens was produced by hydrochloric acid substrates. A 0.1 N HCl solution increased the apparent molecular areas of negative asphalts about four times, positive asphalts three times, and coal tar about twelve times over that observed on water. However, the more concentrated 0.3 N HCl substrate reduced the spreading tendencies of the asphalts from that of the 0.1 N HCl areas, causing at the same time the coal tar to extend its spreading area an additional nine times. Other substances have been reported whose films were observed to spread better on acid substrates, and Adam (13) postulates that the polar ends, if any, might be ionized by the change in acidity of the substrate. This ionization, developing similar charges on adjacent-end groups, would cause mutual repulsion, and hence a loss of lateral adhesion between molecules. The net result would be an increase in the area occupied by a molecule in the film while, at the same time, the overall spreading of the material would become more perfect, approaching more nearly a monolayer.

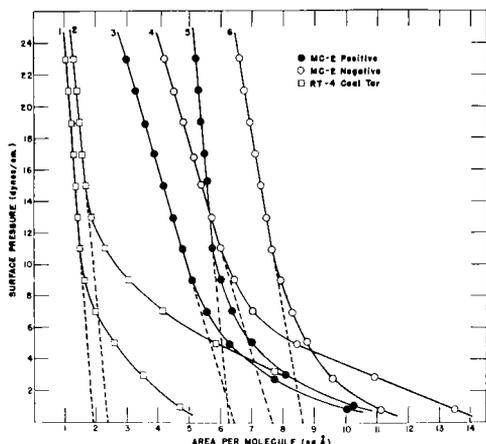


Figure 3. Bitumens spread upon salt solutions. Curves 1, 3, 4 upon 0.1N AlCl_3 ; 2, 5, 6 upon 0.3N NaCl .

Spreading on 0.1N AlCl_3 and 0.3N NaCl

A substrate of 0.1N AlCl_3 caused all three bitumens to spread slightly better than on pure water. A 0.3N NaCl substrate had practically the same effect as the AlCl_3 .

Spreading on 0.1N and 0.3N H_2SO_4

A 0.1N sulfuric acid substrate produced a marked increase in the spreading qualities of bitumen, more so than an equivalent concentration of hydrochloric acid. Again this might be attributed to ionization of possible polar groups causing an anion valence effect. It seems doubtful if this effect could be due to oxidation of the bitumen by the sulfuric acid, because acid of this extreme dilution is a poor oxidizing agent. If the acid concentration was increased to 0.3N, a reduction in spreading of both asphalts and coal tar was obtained compared to the spreading on the more dilute solutions, yet 0.3N acid caused better spreading than that obtained on pure water.

Spreading on 0.1N and 0.3N Aniline Hydrochloride

A 0.1N aniline hydrochloride substrate caused a large increase in the spreading of both asphalts and of coal tar. The magnitudes of the increases were similar to those produced on 0.1N HCl . As in the case of the more-concentrated HCl , 0.3N aniline hydrochloride reduced the spreading tendencies of the asphalts relative to that on the lesser concen-

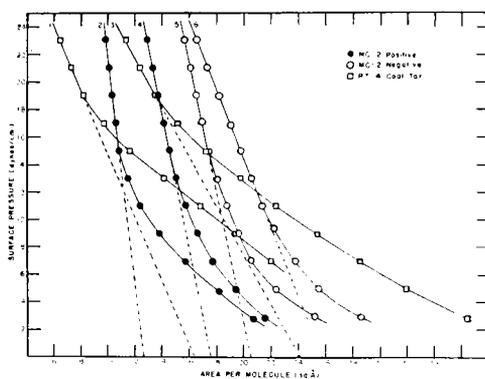


Figure 4. Bitumens spread upon aqueous sulfuric acid. Curves 1, 2, 5 upon 0.3N solution; 3, 4, 6 upon 0.1N solution.

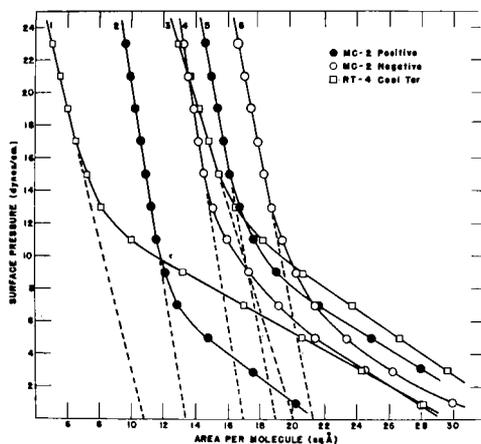


Figure 5. Bitumens spread upon aqueous aniline hydrochloride. Curves 1, 5, 6 upon 0.1N solution; Curves 2, 3, 4 upon 0.3N solution.

trated solutions; at the same time, however, it still further increased the spreading of the coal tar, in fact, almost doubled it. Aniline hydrochloride hydrolyzes acid, thus this substrate is also an acid medium and such films upon such acid media generally behave similarly. However, AlCl_3 , which also hydrolyzes acid, had but a negligible effect on bitumen spreading. An aniline hydrochloride molecule possesses polar and nonpolar ends, which could cause such molecules to orient themselves at the film-substrate interface with the nonpolar end dissolved in bitumen film and the amine hydrochloride polar end dissolved in the aqueous lower phase. In this manner

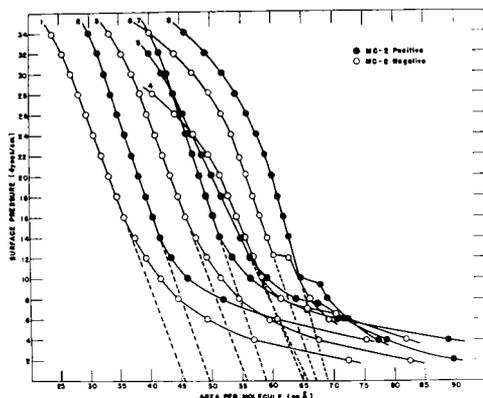


Figure 6. Bitumens spread upon aqueous KMnO_4 . Curves 1, 2 upon 0.001M; 3, 7 upon 0.005M; 4, 5 upon 0.01M; 6, 8 upon 0.05M solution.

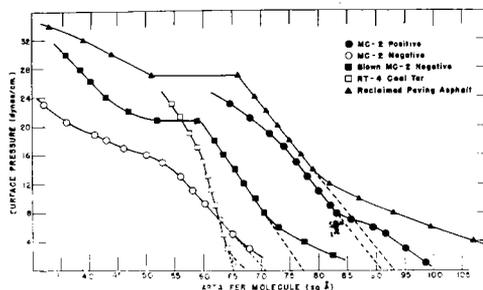


Figure 7. Bitumens spread upon 0.1N KMnO_4 .

the bituminous film would become a much more-perfect spreading substance. This difference in the spreading behavior of the asphalts and the coal tar could, in part, be due to the greater aromatic character of the coal tar, which would act as a better solvent for aniline hydrochloride than for the more hydrocarbon-like asphalts. This increased attraction of the solute in the substrate for the coal tar could cause further and better spreading of the tar film than of the asphalt film.

Spreading on Aqueous KMnO_4 of Various Concentrations

The behavior of the various bitumens upon aqueous potassium permanganate substrates was particularly striking and unexpected. In all cases this substrate produced unexpectedly large areas per molecule. The increase in the spreading tendency, compared to water, in all

cases paralleled the increase in the concentration of the permanganate. All the bituminous materials tested gave areas on a particular permanganate solution of nearly the same value. The concentrations of permanganate solutions used were: 0.001M, 0.005M, 0.01M, 0.05M, and 0.1M. The areas per molecule for the negative and positive asphalts were respectively for the 0.001M solution: 46.70 and 49.60; and for the 0.005M solution: 56.20 and 59.00; for the 0.01M solutions 65.10 and 65.90; and for the 0.05M solution: 66.80 and 68.70 (\AA^2). The 0.1 N solutions gave somewhat erratic results yielding areas of 71.80, 88.00, and 71.00 for the negative asphalt and 76.00, 91.00, and 100.30 (\AA^2) for the positive asphalt. In comparison with the water values the spreading ability of the asphalts increased approximately 8.5 times on the most dilute permanganate to more than 13 times on the 0.1M solution.

Air-blown asphalt showed an area per molecule of 78.0 on 0.1 M permanganate and a sample of reclaimed city pavement asphalt showed 77.7 (\AA^2) on the same substrate. This would indicate that possibly some of the surface effects can be associated with oxidation, either induced through oxidizing agents or air, coupled with heat or long periods of exposure. The reclaimed asphalt came from a section of city pavement that had been down over 20 years and continuously subjected to exceedingly heavy city traffic.

Coal tar, an RT-4, when spread upon 0.1 M KMnO_4 , gave spreading surface areas per molecule of about 65.30 (\AA^2). This is significantly lower than shown by the asphalts and about comparable with areas obtained with asphalts upon 0.01M permanganate solutions. If oxidation by the potassium permanganate is, at least in part, responsible for the increase in spreading over the water values, then it would seem that the coal tar was less susceptible to surface oxidation than the more hydrocarbon-like asphalts.

When cut-back solvent was spread upon 0.1 M potassium permanganate, Figure 9, it produced poor films. The films seemed to slip off the surface and apparently formed an imperfect polymolecular layer. Its area per molecule calculated out to be 0.36 (\AA^2). This exceedingly low value is so slight that it has no relation to molecular dimensions; it seems to indicate that the cut-back solvent formed a

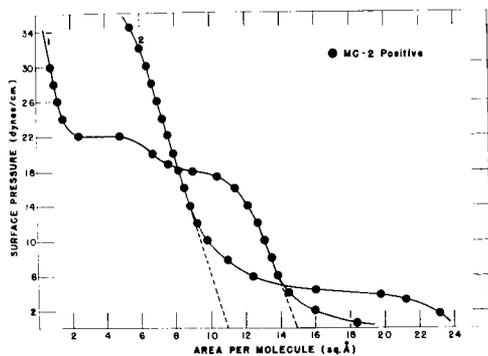


Figure 8. Positive asphalt spread upon aqueous $K_2Cr_2O_7$. Curve 1 upon saturated solutions; Curve 2 upon 0.1N solution.

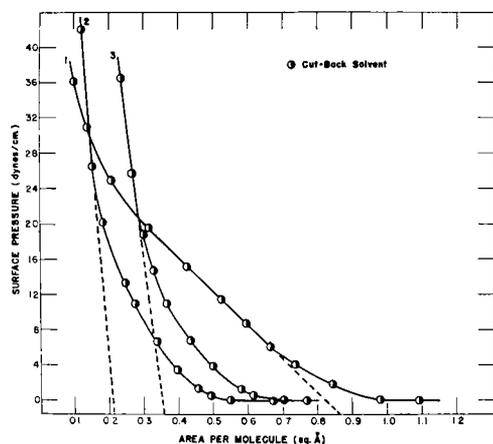


Figure 9. Cut-back solvent spreading. Curve 1 upon 0.1M $K_2Cr_2O_7$; Curve 2 upon pure water; Curve 3 upon 0.1M $KMnO_4$.

film many molecules deep. Apparently these films were resistant to any oxidative properties of the substrate.

A sample of MC-2 negative asphalt was refluxed slowly for several hours with $KMnO_4$ and then spread upon water (Fig. 1). The areas of these molecules in the film were about $10.1 (\text{\AA})^2$, or practically double the water values for the same untreated sample. Again evidence was obtained for a connection of possible oxidation of the bitumen with increased spreading.

Spreading on $K_2Cr_2O_7$

A sample of MC-2 positive asphalt was spread upon 0.1M $K_2Cr_2O_7$ and the film

showed an area of $11 (\text{\AA})^2$, double the value obtained by the same asphalt upon pure water. The same asphalt spread upon a saturated potassium dichromate substrate increased its surface area to $14.5 (\text{\AA})^2$. Again the effect of oxidizing substrates is shown by the larger area occupied by overlaying surface molecules, especially when compared to film areas on water substrates.

Spreading of Reclaimed Pavement Asphalt on Pure Water

When the sample of asphalt reclaimed from pavement, at least 20 years after it was laid down, was spread upon pure water, it gave surface films in which each molecule apparently occupied $40 (\text{\AA})^2$. This is nearly eight times the area occupied by fresh asphalt upon water. If air oxidation can take place in such materials with sufficient time, certainly this asphaltic material had available to it the time necessary for oxidation. Whatever happened to the molecular structure of the bitumen, the exposure apparently caused this asphalt to become similar to fresh asphalt films on permanganate. The areas occupied by this asphalt on pure water were close to those of the fresh asphalts on 0.001M potassium permanganate.

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