

SURFACE PRESSURE STUDIES OF CERTAIN BITUMENS  
ON VARIOUS OXIDIZING SUBSTRATA

by

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## INTRODUCTION

The problem of the effect of oxidizing substrata on the spreading of asphalt and the theoretical explanation of the pressure-area curves on such substrates was an outgrowth of work previously done at this institution by Duane Sawhill. (24) In this previous investigation a rather interesting surface pressure-area curve was obtained using 0.1 M  $\text{KMnO}_4$  as the substrate. In this previous work no attempt was made to extend the work on oxidizing substrata nor to really give a satisfactory explanation of the nature of the curves obtained. The purpose of this investigation is to find the effect of oxidizing substrates on the spreading of asphalts and to postulate an explanation of the surface pressure-area curves obtained.

Recent investigation (3) has again brought the subject of bituminous-soil stabilization to the fore. The great amount of bitumenous substances that go into highway construction make this stabilization problem a very important one. It is hoped that these surface pressure studies may aid in the solution of the problem of better bitumen-soil adhesion. A substance that increases the spreading of a bitumen, that is, gives better wetting, increases the work of adhesion, and this should aid in stabilizing the bitumen-soil system. This investigation was carried out with the aid of a Genco Surface Pressure Balance by which the surface pressure-area curves were obtained.

## SURVEY OF THE LITERATURE

An investigation of the literature revealed a voluminous amount of work on the physical and chemical properties of asphalts and related bituminous substances. There has also been much research in the past few years particularly concerned with the problem of stabilization of bitumen-soil systems. However, the literature survey proved fruitless regarding the specific problem of this investigation, that is, the effect of oxidizing substrates on the spreading and surface pressure-area curves on such substrates.

## Asphalts

History. Asphalt is one of the oldest and most widely used of construction materials. The Sumerians, inhabitants of the Euphrates Valley in Mesopotamia, were using natural asphalts as early as 3800 B. C. for such purposes as waterproofing, adhesives, and in the making of ornaments. A few centuries later it was being used in building construction and for floor surfacing.

Asphalt fell into disuse about the beginning of the Christian era, not reappearing extensively until the 18th and 19th centuries. The first modern asphalt road was constructed in France in 1852 (1). At the present time asphalts are widely used throughout the world for various purposes, primarily road building. The use of natural asphalts has been replaced in this country, almost exclusively, by

petroleum asphalts.

Constitution of Petroleum Asphalts. Early attempts to describe the chemical constitution of petroleum asphalts have been based upon solubility of the different fractions (16). It has been found possible to separate such material into three categories: the asphaltenes, the resins, and the oily constituents.

The asphaltenes are insoluble in hexane. They are solid, hard, dark in color, and of high molecular weight. The resins are dark in color and are liquid at temperatures above 60° C. The oily constituents are liquid at room temperature and are very similar in appearance to heavy lubricating oil.

This classification is now widely used. It is assumed that the resin fraction includes all the intermediate products formed in the transformation of oily constituents into asphaltenes, both by air oxidation and by reaction with sulfur or sulfur-containing compounds occurring in the crude petroleum. The physical properties of the individual molecular kinetic units comprising the resin fraction appear to represent a continuous variation between those of the oily constituents and those of the asphaltenes. The three constituents are believed to be combined as a colloidal system in the complete asphalt. The asphaltenes are dispersed in the oily constituents and the sol is stabilized by the presence of the resin fraction, which serves as a protective colloid.

The structure of such a colloid micelle can be postulated.

The bulk of the substances with the greatest molecular weight and with the most pronounced aromatic nature are arranged the most closely to the center. These again are surrounded by the lighter constituents of less aromatic nature and so on, until a gradual and nearly continuous transition to the intercellular phase is formed. In other words, there is no distinct interface. Neither at the outside of the micelle, nor around the nucleus, is there a contact of substances with distinct differences, for instance, in surface tension. Thus it is impossible to make a sharp and rigid distinction between fractions such as the so-called resins and the oily constituents. When the entire system contains sufficient constituents for the formation of the outer regions of the micelles, the asphaltenes are fully peptized and able to move through the bitumen as freely as the viscosity of the intermicellar phase permits. Such a system will show almost pure viscous flow, except for a marked intramicellar elasticity.

Theories concerning the chemical constitution of the component parts of the asphaltic bitumens have centered mostly on the asphaltene fraction. Nellensteyn (18), in an early paper, states that this material is essentially graphitic carbon and consequently must be assumed to be nonpolar in character. In a later article (19), this viewpoint is reiterated and confirmatory evidence obtained from x-ray studies is cited. Swanson (26), from dielectric constant

data, has demonstrated that the asphaltene and resin fractions are polar while the oily fraction is nonpolar in character. Hillman and Barnett (11) tentatively postulate a structure for the asphaltenes and resins based upon the proximate analysis of the materials. It is shown that for carbon-to-hydrogen ratios between ten and twelve the basic unit could be the naphthalene group. For ratios between twelve and fourteen, polymerized anthracene groups give a reasonable picture. Bonding between the groups may consist either of one or two single bonds, or else one single bond and an oxygen or sulfur linkage.

There has been a considerable amount of speculation regarding the requirements of a good solvent for the asphaltenes. Nellensteyn (18), in 1928, stipulated a minimum surface tension in the range of 25 dynes per centimeter as a requisite. Other investigators, in furthering this idea, have adopted internal pressure as a criterion, and have set up corresponding solvent series. The behavior of the asphaltenes as reported from such studies, as well as their high adsorbtivity on surfaces such as glass, suggest the presence of a specific, and reasonably strong inter-molecular attraction, such as dipole-dipole interaction. The constitution of asphaltic bitumens has been investigated by numerous workers (4, 6, 8-9, 11-14, 16-19, 21-23, 25-27). It must be admitted, however, that the exact nature of asphalt make up still remains a



matter of reasonable doubt.

Molecular Weight. The molecular weights for asphalts as found in the literature vary widely ranging from 500 to 10,000 (12, 22, 27). The molecular weights of the asphalts used were not determined as this previously had been done by Lawhill (24) with little success, primarily because of the existence of the cut-back solvent. As in this previous investigation, the molecular weights were taken as 2000 for all the asphalts used.

Solvents. The solvents found to be most effective for these petroleum asphalts were, benzene, carbon tetrachloride, carbon disulfide, and light petroleum naphtha.

Positive and Negative Asphalts. Petroleum asphalts have been classified as positive and negative on the basis of a test worked out by Oliensis (20). The standard test consists of adding 10.2 cc of naphtha to 2 cc of asphalt. After the asphalt is dissolved under controlled conditions, a spot is made by applying a drop to a No. 50 Whatman filter paper. Spots which have a dark nucleus or center due to a small amount of material precipitated from the bitumen by the naphtha are called "positive", and bitumens giving this type of spot are designated as heterogeneous. Spots which are uniform throughout are called "negative", and the bitumens giving them are designated as homogeneous. Materials that have been cracked or subjected to abnormally high temperatures give positive spots, and it is believed by some that such asphalts are poor materials for highway construction.



It has been found that failure of a bitumen to function properly in a pavement usually is associated with excessive hardening. This hardening is often due to a change in the colloidal structure of the bitumen. The Oliensis test is then assumed to be a measure of stability of the colloid. High temperatures are generally thought to reduce this colloid stability.

### The Properties of Surfaces

Spreading. When a drop of a liquid is placed on the surface, either of another immiscible liquid, or on a solid, it may remain as a drop without spreading, or it may spread to form a film. The surface tensions of the two liquids, and the interfacial tension between them, determine whether or not the liquid will spread, this also is true if the lower phase is a solid.

There are four general views of the criterion for spreading according to Harkins and Feldman (10).

1. All liquids spread on a pure surface.
2. A liquid b will spread on liquid <sup>a</sup> if  $\gamma_a > \gamma_b + \gamma_{ab}$ , where  $\gamma_{ab}$  and  $\gamma_b$ , the respective surface tensions. The condition for non-spreading is  $\gamma_a < \gamma_b + \gamma_{ab}$ .
3. Liquids whose molecules are polar or 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 liquid or solid upon which the spreading is to occur. The spreading coefficient which gives a measure of the tendency to spread is defined as

$$S = W_a - W_c$$

The condition of spreading is simply that the upper liquid must adhere to the lower more strongly than it adheres to itself.

Spreading liquids often spread first as a film of visible thickness, sometimes showing interference colors, but are often too thick for this. As soon as the whole surface is covered, however, this thick film breaks up and, after passing through a variety of stages, settles down as a monomolecular film in equilibrium with visible drops of liquid. The final stage is a film in equilibrium with one drop if sufficient time is allowed. These changes have been described by Hardy (7), and Peachem and Rideal (5).

Monomolecular Films on Water. When a pure saturated liquid hydrocarbon such as pentane,  $C_5H_{12}$ , is placed on the surface of pure water, it forms a globule resembling a circular lens. The surface tension of the water surrounding this lens is not altered. If one of the hydrogen atoms from the number one carbon of this molecule is replaced by a hydroxyl group to give primary amyl alcohol,  $C_5H_{11}OH$ , it is found that the alcohol is relatively very soluble in the water. This increase in solubility is a result of the strong attractive forces that the hydroxyl groups of the alcohol exert on the hydroxyl groups of the water molecules.

When a higher hydrocarbon, such as  $C_{18}H_{38}$ , is placed on water, it, too, will form a lens globule. If, however, the methyl group,  $-CH_3$ , at one end of the molecule is replaced by a carboxyl group,  $-COOH$ , there will be an instantaneous spreading of these molecules over the surface of the water. The carboxyl group in this case renders the end of the molecule to which it is attached relatively soluble in water, whereas the remainder of the molecule remains insoluble. The spreading of the molecules occurs as a result of the solution of the carboxyl groups in the water. The other ends of the molecules, however, are not soluble in the water and, therefore, they spread out as a film over the water surface. If the entire molecule were soluble, they would be dissolved and distributed homogeneously throughout the water.

The Main Types of Films. The different types of insoluble films can best be classified according to the lateral adhesion between the molecules. Adam (2) classifies them as follows:

1. Condensed film, in which the molecules are packed closely, and very steeply oriented to the surface, as with the acids and alcohols investigated by Langmuir.

2. Gaseous or vapor films, in which the molecules are separate, moving independently, the surface pressure being exerted on the barrier by a series of collisions.

3. Liquid-expanded film, which are still coherent, but occupy a much larger area than the gaseous films. These can

form on the surface a separate phase from a vapor film with which they are in equilibrium.

4. Vapor-expanded films, which are rather similar to liquid-expanded films but have less cohesion and do not show a region of constant surface pressure, with two distinct types of film, between coherent and gaseous or vapor film on the surface.

#### EXPERIMENTAL PROCEDURE

##### Description and Use of the Cenco Hydrophil Balance

The balance manufactured by the Central Scientific Company of Chicago is similar to one developed by Langmuir (15) and later improved by Adam (2). It consists of an aluminum tray, 27 inches long by 6 inches wide, provided with leveling screws, drain cock, and a movable barrier. At one end a bridge casting, carrying a torsional device for measuring forces against a mica float, is mounted. The tray is accurately machined at the working edges to permit making accurate measurements of the area. Other portions of the tray are not machined to provide a 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, to one end of which a vernier pointer is attached for indicating the torsional force applied to the

mica float on the circular graduated scale over which the vernier travels.

The scale is calibrated by suspending weights from a hook at the end of the lever arm and noting the number of degrees of counter torque necessary to restore the pointer to the zero point. The relationship between the counter torque caused by gravity acting on the weight used and the torque caused by film pressure is calculated from the respective lever arms between the weight and torsion wire and the torsion wire and the float. In this instrument both lever arms are made the same length and therefore film torque would be the same as torque applied by weights.

All parts of the apparatus which come in contact with the film during measurement must be coated with paraffin. "Parawax" has been found to be quite satisfactory. The tray and barrier may be coated with molten paraffin which is smoothed out after hardening by gentle surface heating. The movable float and platinum ribbons are coated with paraffin by applying as a solution in a volatile solvent such as benzene.

#### Physical Determinations

The paraffined tray should be filled with the solution to be used as substrata until the meniscus rises above the edges of the tray. The surface of the solution on both sides of the

paraffined float is swept free of contaminants by running a paraffined straight edge over the surface of the solution.

A film is formed between the movable barrier (initially placed near the far end of the tray) and the float by dropping a definite weight of the substance under investigation upon the surface of the solution. In most cases this substance is diluted with a volatile solvent such as benzene. Concentration of this solution is so adjusted that a quantity less than 1 ml dropped from a weighing pipette will give a film covering at least one half the area of the solution surface. It was found that a 1 cc B. D. tuberculin hypodermic syringe, with the needle filed blunt, made the best weighing pipette. The solvent itself must not form a stable film. It serves the dual purpose of diluting the substance under investigation so that small quantities may be dispersed as relatively large volumes of solution and of diminishing the viscosity of this substance to the point where films form almost instantaneously. Measurements may be begun as soon as the solvent evaporates.

The movable barrier is next carefully moved toward the float until a point is reached at which the film begins to exert a pressure against the float. The force is measured in degrees torsion necessary to bring the pointer back to the zero position. A record is taken of the positions of the movable barrier as it is progressively moved toward the float and corresponding forces exerted.



### Computations

The data thus obtained are converted to dynes of force per centimeter and areas in square centimeters. Dynes of force per centimeter are total forces divided by the number of centimeters active length of the float. This includes the length of the mica plus one-half the width of the gaps occupied by the platinum attaching strips. By plotting the forces as ordinates and areas as abscissae, a curve results which may be extrapolated to give the total film area under zero compression at the prevailing temperature.

The weight of the asphalt in these measurements can be determined from the weight of solution used. From the assumed approximate molecular weight of the asphalt the total number of molecules added can be determined by employing Avogadro's number,  $6.023 \times 10^{23}$ . By dividing the total film area in square Angstrom units by the total number of molecules, the area per molecule in square Angstrom units can be determined.

$$\text{Area/Molec.} = \frac{\text{Total Area} \times 10^{16}}{\frac{\text{Wt. of Asphalt} \times 6.023 \times 10^{23}}{\text{Molec. Wt. of Asphalt}}}$$

By comparing the area obtained on distilled water with that obtained on other substrates the relative spreading tendency of asphalt on various substrates with respect to water is obtained.



## RESULTS AND DISCUSSION

Determination of the Molecular Weight of  
Cut-back Solvent

In order to obtain area-pressure curves for the cut-back solvent it was first necessary to determine the approximate molecular weight of this solvent. Such a determination was made by the method of lowering the freezing point of benzene. The freezing point constant for benzene was taken as 5.12 and the apparatus for this determination was set up in the usual manner. The molecular weight of Socony-Vacuum laboratory sample No. 9510 was determined and found to be 175.5. This was the value to be expected.

## Surface Pressure Measurements

General Considerations. The curves in this thesis are average ones, and 5 to 10 curves were used to obtain these average values. All measurements were made at 25° C. The curves obtained for one type of bitumen on a particular substrate were in good agreement with only occasional deviations being encountered at very low pressures. The results were not affected by these deviations as the higher pressure regions were extrapolated to find the area per molecule at zero pressure.

In these investigations the molecular weights of all the asphalts were assumed to be 2000. This value is about the mean of the values obtained by Strieter (Traxler 27) and Katz (12).

and is also about the average of the various reports found in the literature. As far as this work is concerned, the exact values are not necessary since the measure of spreading is taken from the apparent cross sectional area of the molecule on a given substrate relative to its area on water taken as a standard. Even if the exact molecular weights were known and were used in determining the areas per molecule the relative areas would be unaffected.

Spreading on Water. Figure 1 illustrates the spreading of positive, negative, and air-blown asphalts on distilled water substrate. The areas per molecule obtained by extrapolation for positive (5.04 sq. Å), negative (5.49 sq. Å), and air-blown (7.20 sq. Å) asphalts are too low considering the complex structure of the asphalts. These low values for the cross sectional area can only be explained by assuming multi-layer films and not monolayer films.

Spreading on .001 M  $\text{KMnO}_4$ . Figure 2 illustrates the spreading of positive and negative asphalts on .001 M  $\text{KMnO}_4$  as a substrate. Although the general shape of the curves are little changed from those on water, the increase in spreading is considerable. The apparent cross sectional area has jumped to 49.6 sq. Å per molecule for the positive asphalt and to 46.7 sq. Å per molecule for negative asphalt.

Spreading on .005 M  $\text{KMnO}_4$ . Figure 3 illustrates the spreading of positive and negative asphalt on .005 M  $\text{KMnO}_4$  as a substrate.

The shape of the curve is the same as on .001 M  $\text{KMnO}_4$  but again the spreading has increased. On this substrate the positive asphalt has a cross sectional area of 59.0 sq. Å per molecule and the negative an area of 56.2 sq. Å per molecule.

Spreading on .01 M  $\text{KMnO}_4$ . Figure 4 illustrates the spreading of positive and negative asphalts on .01 M  $\text{KMnO}_4$  as a substrate. The apparent cross sectional area per molecule has again increased to 63.9 for positive and 65.1 for negative asphalt. The shape of both curves has changed, however, due to the appearance of a step or bench. Both these benches appear between 6.5 and 9 dynes per cm. These benches which represent a rather large change in area with a relatively small change in surface pressure are not too well defined on this substrate as can be seen from the fact that they are not flat occurring between 6.5 and 9 dynes per cm.

Spreading on .05 M  $\text{KMnO}_4$ . Figure 5 illustrates the spreading of positive and negative asphalts on .05 M  $\text{KMnO}_4$  as a substrate. The cross sectional area per molecule is still increasing slightly and has reached the values of 68.7 for positive and 66.8 for negative asphalt. The bench has now become quite pronounced, that for positive asphalt occurring at 9.5 dynes per cm and that for the negative at 12 dynes per cm.

Spreading on 0.1 M  $\text{KMnO}_4$ . Figure 6 illustrates the spreading of positive, negative, and air blown asphalts on 0.1 M  $\text{KMnO}_4$ . The positive asphalt now occupies an area of 76.0 sq. Å per

molecule while the negative asphalt has an area of 71.8 sq. Å per molecule. The air-blown asphalt has an apparent cross sectional area of 77.7 sq Å per molecule. The bench in the curves for positive and negative asphalts appears to be a little wider on both curves and now occurs at a greater pressure for both. The bench now develops at 12 dynes per cm. for the positive asphalt and at 15.6 dynes for the negative asphalt. The bench also appears on the curve for the air-blown asphalt showing up at a pressure of 20.6 dynes per cm.

Spreading on 0.1 M  $K_2Cr_2O_7$ . Figure 7 illustrates the spreading of positive asphalt on 0.1 M  $K_2Cr_2O_7$ . This oxidizing agent was used in an attempt to determine whether or not the bench found in the curve on certain concentrations of  $KMnO_4$  was peculiar to that oxidizing agent or if other oxidizing agents would give a like bench. A bench did appear, but it was quite broad and occurred over a range of two dynes per cm., between 4 and 6 dynes per cm. Because of the fact that this bench appeared at quite low pressures where discrepancies in surface pressure-area curves are most prevalent, too much faith could not be put in the results. Area per molecule from the straight portion above the bench was 11 sq. Å.

Spreading on Saturated  $K_2Cr_2O_7$ . Figure 8 illustrates the spreading of positive asphalt on saturated  $K_2Cr_2O_7$ . On this substrate a double bench appears, the first being rather ill defined between pressures of 17 to 18 dynes per cm. The

second bench is quite well defined and appears at 21.7 dynes per cm. The area per molecule from the longest straight portion of the curve is 14.5 sq. Å.

Spreading of Cut-Back Solvent on 0.1 M  $\text{KMnO}_4$ . Figure 9 illustrates the spreading of cut-back solvent, of the type used in MC asphalts, on 0.1 M  $\text{KMnO}_4$  as a substrate. This curve demonstrates that the substrate has little effect on the spreading and is certainly not responsible for the bench observed when asphalt is spread on this substrate. The trivial value of .05 sq. Å per molecule for the area is indicative of the poor spreading of this cut-back solvent. The absence of a bench is taken to mean that no oxidation of this cut-back solvent takes place.

Spreading of  $\text{KMnO}_4$  Refluxed Asphalt on Water. Figure 10 illustrates the spreading of positive asphalt, which has been refluxed with 0.1 M  $\text{KMnO}_4$ , on water as a substrate. The refluxing with  $\text{KMnO}_4$  has a marked influence on the spreading, the apparent cross sectional area having a value of 10.1 sq. Å per molecule. It is believed that this low value for the area per molecule is due to the precipitation of the asphaltene fraction during the refluxing process. The bench is present and well defined appearing at a pressure of 25.4 dynes per cm.

Spreading of City Park Asphalt on Water. Figure 11 illustrates the spreading of asphalt extracted from aged Manhattan City paving on water as a substrate. The paving was crushed and extraction made with benzene. The solution was set aside

for a day and allowed to settle. The supernatant solution was evaporated and the asphalt was again dissolved in benzene. This procedure was repeated until a pure solution was obtained. Since paving asphalt is often air blown and since oxidation almost certainly accompanies ageing this phase of the experimentation was carried out to see if the bench, which is best explained by an oxidation mechanism, would be present. The bench appeared at 12.6 dynes per cm of pressure. The spreading was unusually high for asphalt on a water substrate, 25.7 sq. Å per molecule extrapolating the portion of the curve above the bench and 40.0 sq. Å per molecule from the lower portion. This high spreading may be partially due to the loss of the cut-back solvent by evaporation and absorption during the ageing process.

Spreading of City Paving Asphalt on 0.1 M  $\text{KMnO}_4$ . Figure 12 illustrates the spreading of asphalt extracted from aged Manhattan city paving on 0.1 M  $\text{KMnO}_4$  as a substrate. The expected bench appears at 27.0 dynes per cm. of pressure. Extrapolation of the longer lower portion of the curve gives a value for the area of 92.0 sq. Å per molecule.

The extrapolated values for the apparent areas of the molecules at zero pressure, taken from Figs. 1 to 12 are summarized in Table 1.



Table 1. Extrapolated apparent molecular cross sectional areas at zero pressure in sq. Å.

Substrate :	Films			
	MC-2 Neg :	MC-2 Pos :	Air Blown :	City Park :
	Asphalt :	Asphalt :	Asphalt :	Asphalt :
H <sub>2</sub> O	5.49	5.04	7.20	25.7
0.001 M KMnO <sub>4</sub>	46.70	49.60		40.0*
0.005 M KMnO <sub>4</sub>	56.20	59.00		
0.01 M KMnO <sub>4</sub>	65.10	65.90		
0.05 M KMnO <sub>4</sub>	66.80	68.70		
0.1 M KMnO <sub>4</sub>	71.30	76.00		77.7
0.1 M K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		11.00		
Sat. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		14.50		

\*Extrapolation of lower portion of curve

Cut-back solvent on 0.1 M KMnO<sub>4</sub> gave an area of .05 sq. Å.  
MC-2 Pos. refluxed with 0.1 M KMnO<sub>4</sub> gave an area of 10.1 sq. Å on water.

### General Discussion of Results

The following discussion is made considering the constitution of petroleum asphalts to be that given earlier in this thesis. They are to be considered as consisting of three fractions, the asphaltenes, the resins, and the oily constituents, which are all combined as a colloidal system. The asphaltenes are dispersed in the oily constituents and the sol is stabilized by the presence of the resin fraction, which serves as a protective colloid.

As a colloid system consisting of a goodly percentage of insoluble, non-spreading, nonpolar oily fraction, asphalt could be expected to spread, but very poorly on a water substrate. The only thing which makes these surface pressure measurements practicable is the use of weak benzene solutions of the asphalt.





Fig. 1. Spreading on water.

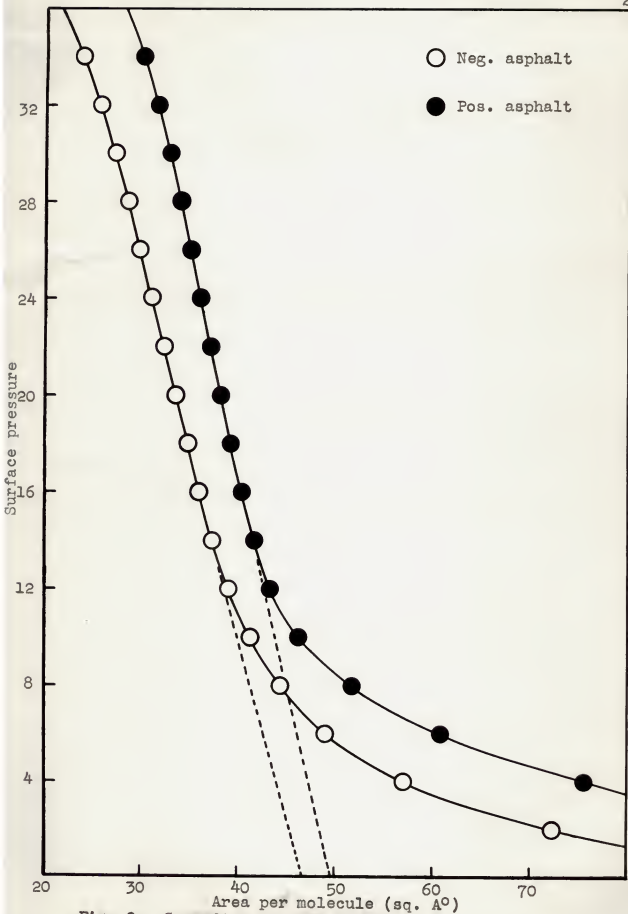


Fig. 2. Spreading on .001 M  $\text{KMnO}_4$ .

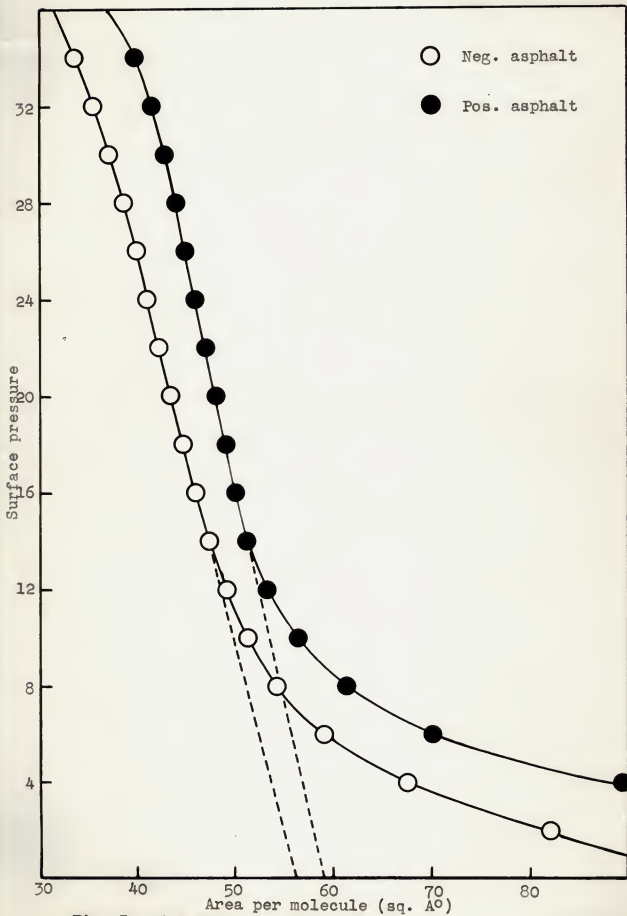


Fig. 3. Spreading on .005 M  $\text{KMnO}_4$ .

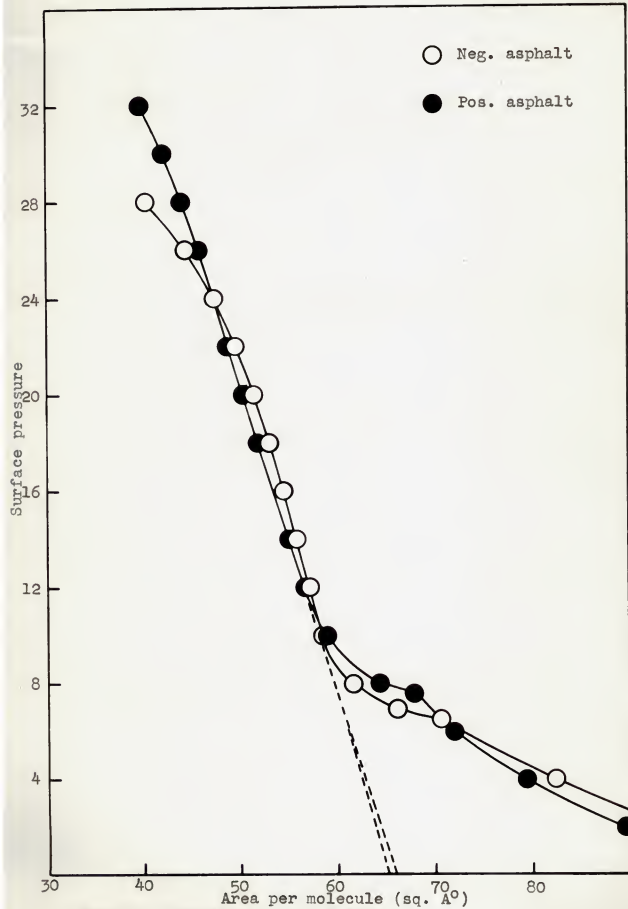


Fig. 4. Spreading on .01 M  $\text{KMnO}_4$ .

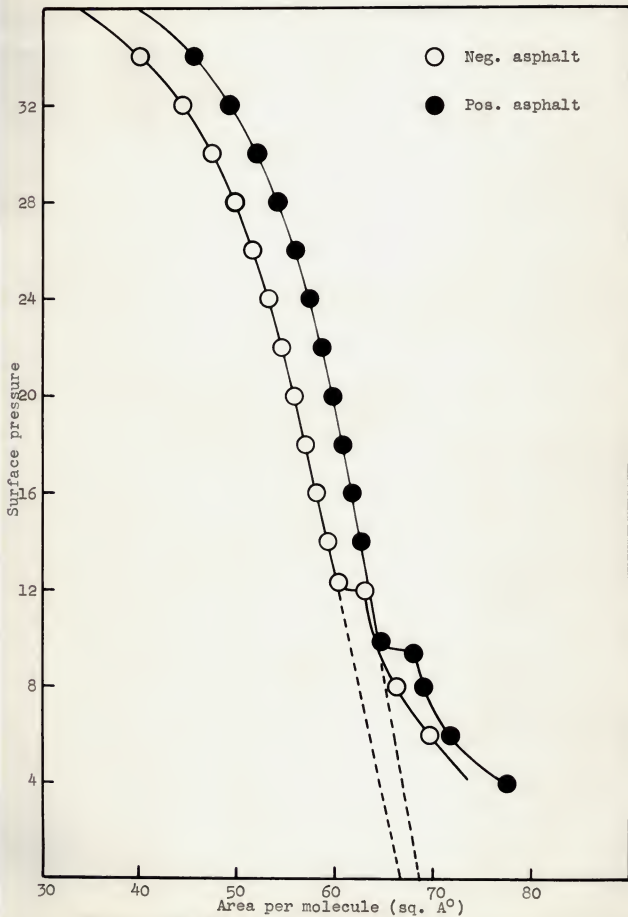


Fig. 5. Spreading on .05 M  $\text{KMnO}_4$ .

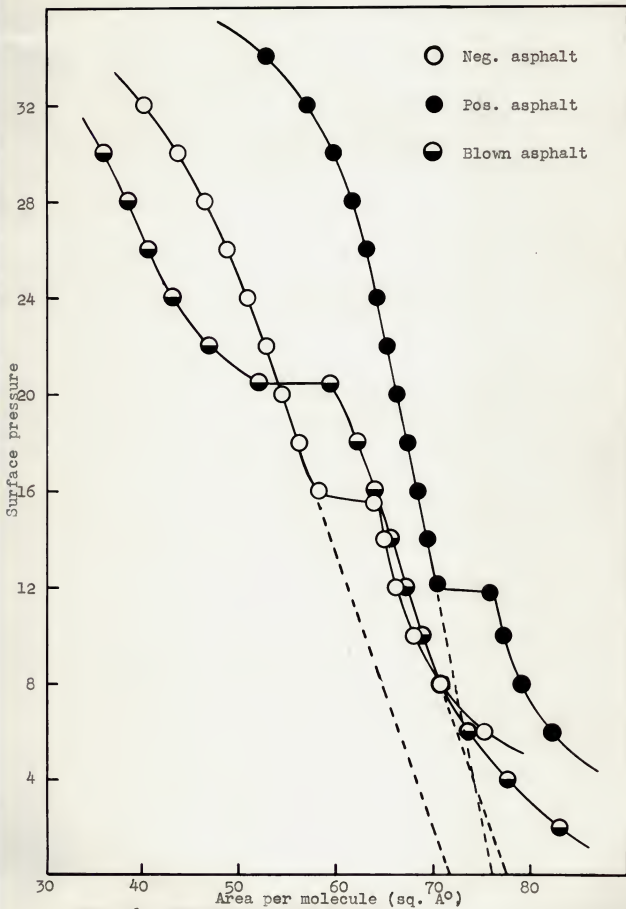
Fig. 6. Spreading on 0.1 M  $\text{KMnO}_4$ .



Fig. 7. Spreading on 0.1 M  $K_2Cr_2O_7$ .



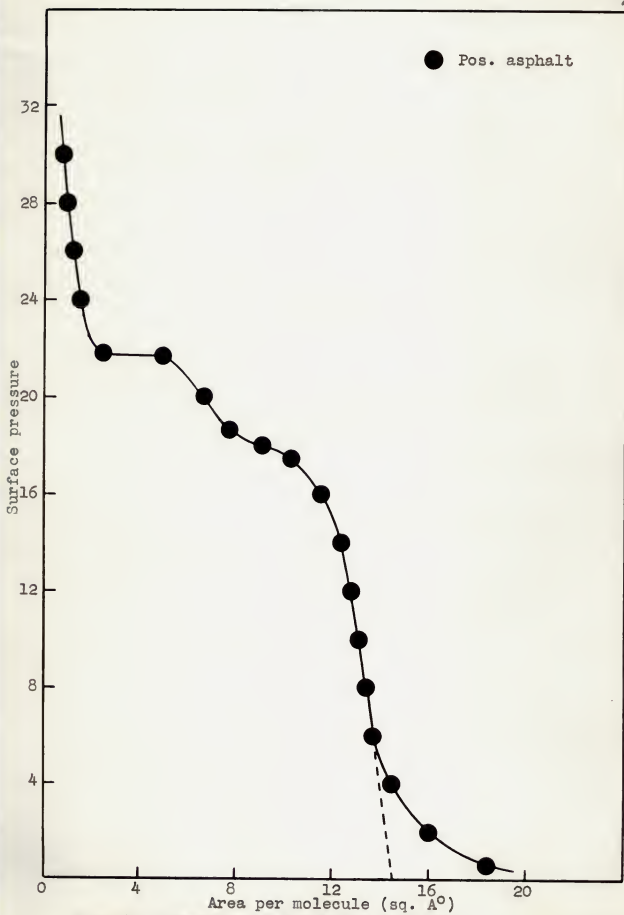


Fig. 8. Spreading on saturated  $K_2Cr_2O_7$ .

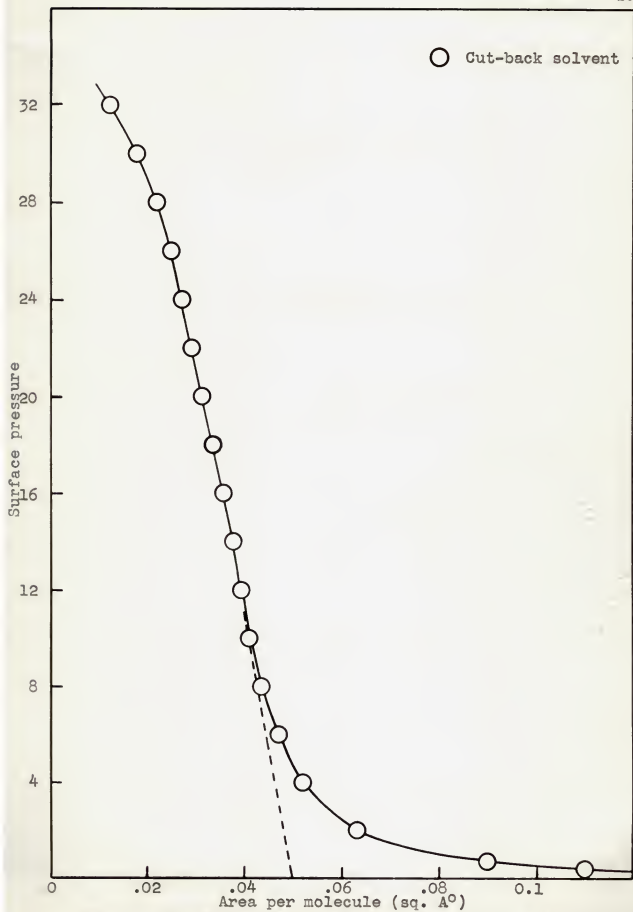


Fig. 9. Spreading of cut-back solvent on 0.1 M  $\text{KMnO}_4$ .

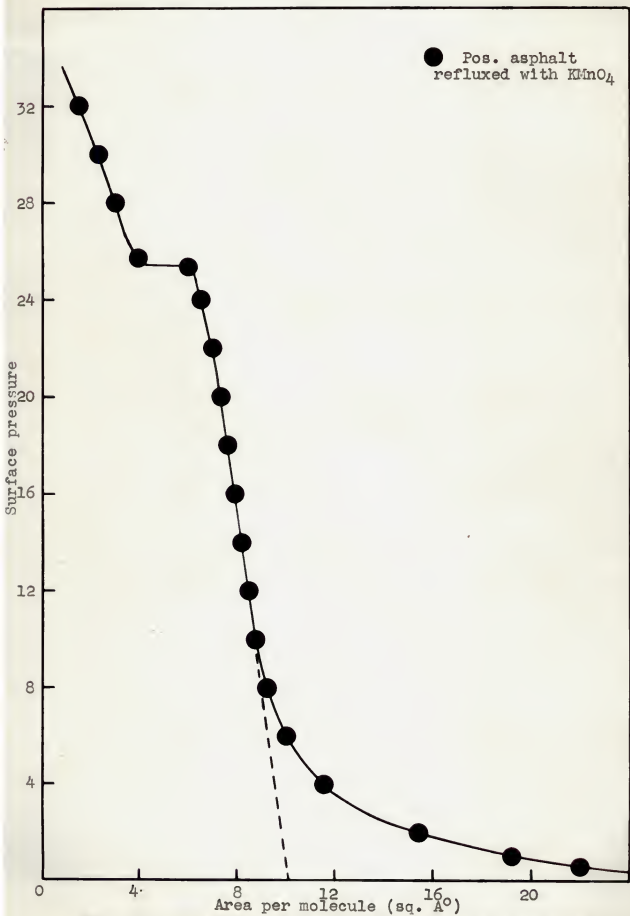


Fig. 10. Spreading of  $\text{KMnO}_4$  refluxed asphalt on water.

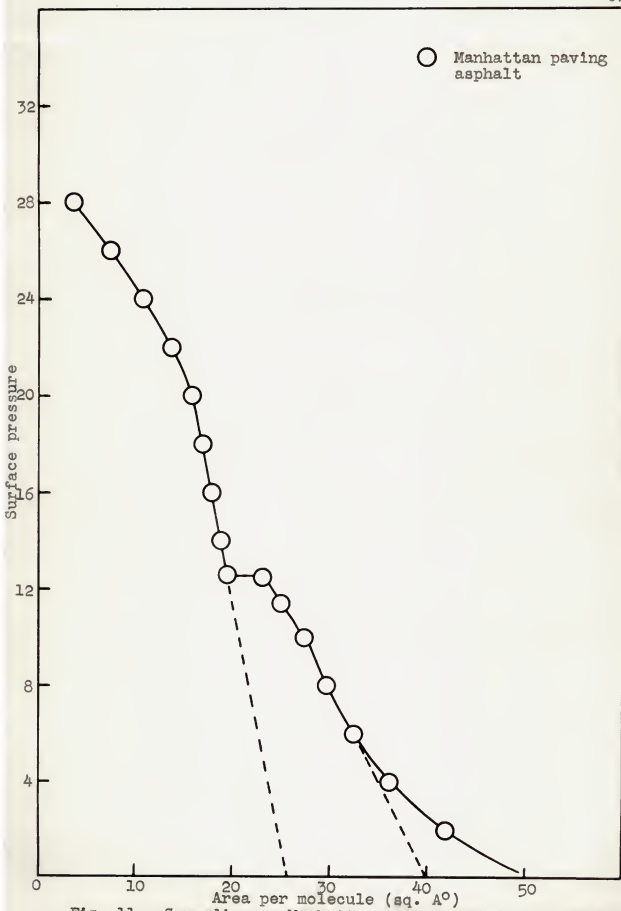


Fig. 11. Spreading on Manhattan paving asphalt on water.

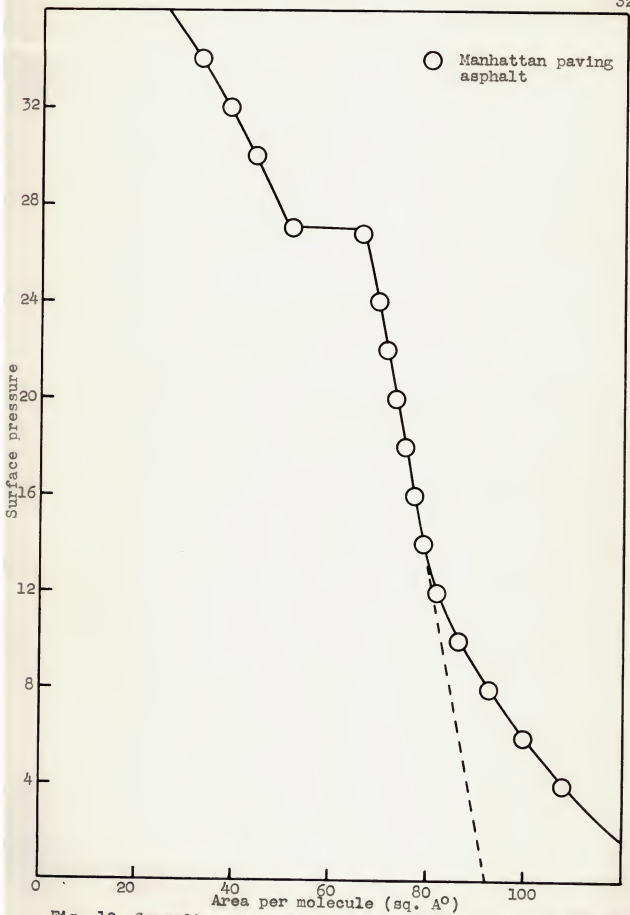


Fig. 12. Spreading of Manhattan paving asphalt on 0.1 M  $\text{KMnO}_4$ .

The benzene does not increase the spreading of the asphalt, but it serves as a dispersing medium. When the benzene has dissolved the asphalt is left as small colloidal aggregates (lenses) on the surface. Very low values are obtained for the cross-sectional area of asphalt on water because of the fact that a monolayer is not formed on this substrate.

Any agent which has the ability to destroy the stability of the colloid system could be expected to increase to a considerable degree the spreading of an asphalt. With the colloid system destroyed the asphaltene and resin fractions would no longer be required to remain in the oily fraction and since they are probably both polar they could be expected to occupy a considerable portion of the surface area over and above that occupied by the non-spreading oily fraction. This destruction of the stability of the colloid likely results from a possible oxidation of the resin fraction, which is the stabilizing fraction of the sol.

The results when MC-2 pos. was refluxed with .1 M  $\text{KMnO}_4$  lend support to the above view. The refluxing with  $\text{KMnO}_4$  apparently destroyed the stability of the colloid as the asphaltene fraction was deposited as a residue in the flask. This residue was similar to elementary carbon. If the resin fraction is considered to be an intermediate in the formation of the asphaltene fraction, as believed by some (22), it is possible that some of this fraction may have been converted to an asphaltene nature

and also left behind when the residue was extracted with benzene. The portion soluble in the benzene would then be primarily the oily fraction along with some of the resin fraction. In color this benzene solution was very similar to a heavy lubricating oil in that it was green and not at all like the normal asphalt-benzene solutions, which are dark brown. The spreading of this solution on water was only a little better than the non-refluxed on water. This is about the spreading to be expected.

The benches, which were found corresponding to a rapid diminution in cross-sectional area for a very slight increase in pressure, are most likely the result of a molecular rearrangement in the film. Polar groups of the asphaltene and resin fractions and perhaps polar groups formed by oxidation of double linkages in the oily fraction could slip into recesses in the chains of neighboring molecules at definite pressures, when these pressures are great enough to overcome the repulsion of like groups. The irregular outline of the molecules themselves would aid this slipping together and reduction of area.

#### SUMMARY

1. The molecular weight of cut-back solvent was determined and found to be 173.5.
2. Bitumens spread poorly on water except in the case where much of the oily fraction and cut-back solvent has been lost, as in aging.



3. Oxidizing substrate cause a marked increase in the spreading of bitumens,  $\text{KMnO}_4$  being much better than  $\text{K}_2\text{Cr}_2\text{O}_7$  in this respect.

4. The greater the concentration of the oxidizing agent the greater is the spreading.

5. The spreading of the cut-back solvent has little or no effect upon the increased spreading of bitumens on oxidizing substrates.

6. Benches appear at definite pressures on the surface pressure-area curves on strongly oxidizing substrates which are likely due to a molecular rearrangement at those pressures.

7. Air blown or oxidized bitumens also give a bench on the oxidizing substrata.

8. An attempt has been made to give a possible mechanism which brings about the increase in spreading on oxidizing substrata and the appearance of a definite bench in the surface pressure-area curves.

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