SURFACE PRESSURE STUDIES OF CERTAIN BITUMENS
ON VARIOUS AQUEOUS SUBSTRATA

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1944

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1949

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INTRODUCTION

An investigation of the literature reveals a voluminous amount of work on asphalt and its related bituminous substances; its physical and chemical properties have been the subject of a tremendous amount of research over a period of many years. Only in the past few years, however, has the problem of stabilization of bitumen-soil systems been investigated actively. Bitumen-soil adhesion leaves much to be desired, in fact, large stretches of bituminous highways must be repaired or relayed each year because water stripping and poor bitumen-soil adhesion cause disentegration of the highway surface. This problem is of utmost importance because a large share of all bituminous substances produced goes into highway construction. Although this problem has been approached from many angles, too little has been done with respect to the surface properties of bitumens. The purpose of this research has been to help find some substances that might possibly be used to increase the work of adhesion between bitumen and soil. This problem has been studied with the aid of the surface pressure balance in which the spreading tendencies of asphalts and coal tars on various aqueous substrates have been examined. A substrate that causes a marked increase in spreading might possibly be used as a roadbed treatment or admixed with the bitumen before it is applied, to promote better "wetting" of the aggregate by the bitumen, thereby increasing the work of adhesion. A stabilized asphalt or coal tar-soil system should thus result.

SURVEY OF THE LITERATURE

Asphalts

History. Asphalt is one of the oldest and most used con-
struction materials. As early as 3800 BC, the Sumerians, inhab-
itants of the Euphrates Valley in Babylonia, were using natural
asphalts for water-proofing, ornaments, and as an adhesive. A
few centuries later it was being used in building construction
and floor surfacings.

However, at the beginning of the Christian era the material
fell into disuse and it was not until 1852 that the first modern
asphalt highway was constructed (in France). Since that time,
it has come into wide use throughout the world in many types of
construction (Abraham, 1).

Types of Asphalt. There are two types of asphalt, natural
and petroleum. Natural asphalt was first used in highway con-
struction and came chiefly from the large deposit on the island
of Trinidad. Another important deposit is that found in the
State of Utah, U. S. A., and is known commercially as Gilsonite.
Gilsonite is employed principally as a protective coating and
serves as an ingredient in certain black paints and varnishes.
Chemically (18) the natural asphalts are complex hydrocarbons
consisting of open-chain paraffins, olefines, acetylene, etc.;
closed-chain cyclo-paraffins, napthenes, polycyclic benzenes,
etc.; also oxygenated, nitrogenous and sulfurated bodies. There
is no generally accepted theory of the origin of asphalts, al-

though it is conceded that the mother substance is petroleum. The discussion centers around the origin of the petroleum from which the asphalts are supposed to have been formed by a process of metamorphosis, under the influence of time, heat, and pressure. Several chemical processes are involved, e.g., oxidation, sulfurization, polymerization (i.e., the combination of like molecules), and condensation (i.e., the combination of unlike molecules). Some natural asphalts are derived from the slow evaporation of lower boiling-point fractions from the original petroleum; others indicate conversion by heat and pressure; still others show evidence of slow oxidation. It is likely that a combination of all three processes occurs simultaneously. Geologically, the natural asphalts are found throughout all the different formations. Trinidad asphalt occurs as a lake, and Gilsonite occurs in veins and is mined like coal except that more care and expense are involved.

The first oil wells in the United States produced paraffin-type oils which yielded practically no liquid asphaltic residue. However, the western oil fields discovered late in the nineteenth century made available a crude oil from which semi-solid and solid residual asphalts could be obtained. According to Kastens (10), petroleum asphalts can be divided into three classes; cracked, blown, and straight run.

Cracked asphalts are the residue from thermal cracking operations. They have lower average molecular weights than other commercial asphalts, and are believed to have a larger percentage of aromatic constituents. Cracked asphalts exhibit extreme

changes in viscosity with temperature and low oxidation resistance. Because of the latter property, cracked asphalts deteriorate relatively rapidly, and are not particularly good for road surfacing.

Blown asphalt is made by passing air (400° to 600°F.) through a liquid residuum obtained from either straight run distillation or thermal cracking for periods of from 3 to 24 hours. This produces a material used for roofing material, pipe covering, etc., which has high weather resistance, a high softening point, and plasticity at low temperatures.

Straight run asphalt is produced by distilling off the lighter fractions of a petroleum oil to produce a residue containing the heaviest compounds present in the charge. The charge to the distillation towers may be topped crude - crude from which the lightest fractions have already been removed - or high asphalt crude. This is the most important type of asphalt, produced primarily for use in road surfacing where it may be used unaltered.

Structure of Asphalt. Many of the properties of asphalts indicate that they are colloids. Nellensteijn (20) found that their solutions even at 1-30,000 dilution show the Tyndall effect. He also noted with ultramicroscopic examination perceptible Brownian movement in the solution (19). Nellensteijn has developed a theory for the colloidal structure of asphaltic bitumens based on his research. He proposes the existence of three components. They are (1) the fluid medium or dispersing phase, (2) the protective bodies which are lyophilic, and (3) a lyophobe

part. The micelles of the dispersed phase are composed of the last two groups, and the stability of the system is dependent upon the interfacial tension existing between the fluid medium and the micelles. When an asphalt solution is flocculated by the addition of some organic solvent, a new phase is not formed; the dispersed particles merely come together because of the change in interfacial tension which has taken place between them, and the surrounding liquid. The theory assumes that elementary carbon is at the center of the micelle, and Waterman and Nellensteijn (31) claimed to have obtained carbon from artificial and natural asphalts by successive extractions with gasoline, carbon tetrachloride, and benzene. The dark color of asphalt suggests the presence of free carbon inasmuch as most hydrocarbons are only slightly colored. Katz and Beu (11) examined thin films of asphalt and oil in the electron microscope in a search for colloidal asphaltene particles. These films appeared to be free from particles; but numerous particles appear when suspensions of asphalt in benzene and petroleum ether are examined. Micrographs at 156,000 diameters indicate asphaltene particles if present in undiluted oil and asphalt are less than 65 A^o in diameter.

Composition. The chemistry of bituminous substances is complicated by the fact that commercial specimens of any given material are rarely alike in composition. Even when emanating from the same source, asphalts - both natural and petroleum - vary considerably in composition. In the case of petroleum asphalts, the composition and physical properties depend upon the source of the raw material and the exact conditions to which they have

been subjected in their manufacture, including the temperature and length of treatment. Natural asphalts are in a constant state of transition, as the result of their age and environment, thus their composition will vary depending upon the degree of exposure and extent of metamorphosis (Traxler, 28).

Very little is known concerning the chemical composition of the numerous complex hydrocarbons present in asphaltic bitumen. Richardson (26) believes the series of polymethylenes make up part of petroleum asphalt. These compounds are unaffected by sulfuric acid even though less stable than paraffinic hydrocarbons. Substituting various hydrocarbon radicals for hydrogen makes the polymethylenes very complex. Small amounts of substituted hydrocarbons of the aromatic series may be found in the more volatile fractions of asphalt-base petroleums.

Molecular Weights. According to Traxler (28), Strieter determined the molecular weights of dissolved asphaltic bitumen in benzene by the lowering of the freezing point. The values he obtained ranged from 620 to 4252, depending upon the source of the asphalt. Katz (12) determined the weights to be in the range from 750 to 2200. The molecular weights of some air-blown asphalts gave values up to almost 4700, probably due to condensation and polymerization caused by the air.

Solvents. The most effective solvents for asphalt are carbon disulfide, carbon tetrachloride, benzene, and light petroleum naphtha.

Surface Tension. Obviously the measurement of the surface tension of asphalts is very difficult because of their high vis-

cosity. Only by making the measurements at elevated temperatures
has it been possible to obtain estimates of the interfacial ten-
sion between air and asphalts. Nellensteijn and Roodenburg (21)
measured the surface tensions of several asphalts at temperatures
ranging from 100° to 225°C. by means of the Du Nouy ring method.
The values obtained ranged from 20.7 to 37.4 dynes per centimeter
depending upon the particular type of asphalt used. Also all of
the temperature-surface tension curves showed a break at about
150°C. Nellensteijn and Roodenburg discussed the theoretical and
practical significance of this break and attributed it to sudden
changes in the internal structure of the bitumen.

Positive and Negative Asphalts. Petroleum asphalts have
further been classified as positive and negative. The basis of
the classification is a test worked out by Oliensis (22). The
standard test consists of adding 10.2 cc of naphtha to 2 cc of
asphalt. After the asphalt is dissolved under controlled condi-
tions, 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 bi-
tumen 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 a test or measure of the stability of the colloid, and high temperatures are generally thought to reduce this colloid stability. In certain borderline cases, Oliensis modified his test by using other solvents and changing the dilutions. Winterkorn and Eckert (32) have used the Oliensis test on a number of different asphalts, and their results support the claims made for the standard spot test; however, in certain borderline cases their results do not distinguish between positive and negative asphalt following the method of oliensis.

Coal Tar

Coal tar is a general term that applies to all varieties of tar obtained from coal. When bituminous coal is destructively distilled or carbonized, coke, gas, tar, phenol, and other products may be recovered.

Low temperature tars are produced by carbonization equipment which operates at relatively low temperatures, approximately 950 to 1300°F. These tars have low binding capacity or small cohesion. They have been produced only in small quantities in this country, and have been used to a very limited extent in road materials.

High temperature coal tars are produced at temperatures of approximately 1800 to 2100°F. In general they have higher binding capacities than low temperature coal tars. The principal varieties of high temperature tar produced in the United States

are coke oven tar, horizontal retort tar and vertical retort tar. Of these three, coke oven tar is produced in the greatest amount, and is used most extensively in road tars. Horizontal retort and vertical retort tars are produced in smaller quantities and, when used in road tars, usually are blended with coke oven tars. The physical and chemical characteristics and high binding capacities of high temperature coal tars make them especially suitable for road tar purposes.

The quality of the tars derived from different carbonizing equipment varies according to those characteristics of each type of apparatus which influence the temperature and the time of contact of the tar vapors with the heated surfaces. Horizontal retort tars usually have a high percentage of so-called free carbon, a low concentration of tar acids, and a high specific gravity. Vertical retort tars are low in "free carbon", have a high concentration of tar acids, and a low specific gravity. Intermediate between the two are the by-product coke oven tars.

Constitution of Coal Tars. Coal tars are complex mixtures of a great number of organic compounds, principally of aromatic structure. They contain also small amounts of inorganic matter.

According to Spielman (27), several hundred constituents so far have been identified in coal tars. Some of those occurring in higher concentrations are: naphthalene, monomethyl and dimethyl naphthalenes, acenaphthene, phenanthrene, phenol, cresols, xynols, napthols, and pyridene.

One of the components of coal tar is the so-called "free carbon". This term was originally used to describe the solid

material which is removed from tar by solvent extraction. It probably was chosen in the belief that the solid residue consisted of elementary carbon. The term has been retained in industry to describe the amount of benzene - or carbon disulfide - insoluble matter, although it is almost certain that it is not pure carbon.

With regards to its physical structure, coal tar is a complex dispersoid. As such it contains:

(1) The dispersing medium consisting of tar oils

(2) The dispersed phase

Within the dispersed phase Klinkmann (13) distinguishes between a colloidal part and the coarsely dispersed solid material which can be observed under the microscope. The colloidal part consists of high molecular polymers which are partly true liquids and partly also crystalline. Nellensteijn (20), differing from these views, contends that the dispersed phase is made up solely of solid materials consisting of elementary carbon surrounded by a layer of protective bodies. In general, Klinkmann's polymers or resinous materials are similar to Nellensteijn's protective bodies. By resinous materials are meant those organic substances of high molecular weight which upon isolation appear to have an essentially amorphous structure. Very little is known of the chemical structure of these compounds.

Nellensteijn has done much work on the stability of the colloidal system. The chief factor which determines the stability of colloidal dispersions he considers to be the interfacial tension between the solid and liquid phases and the solvation effect

of the protective layers. He bases his opinion on the well-known
fact that flocculation occurs if tar is brought into contact with
a solvent miscible with the oily medium as well as the protective
bodies provided the surface tension of the solvent reduces ma-
terially that of the liquid phase. Two such solvents are aniline
and pyridine, and the amount insoluble is probably the same ma-
terial which is visible under the microscope and removable by fil-
tration.

Surface Tension. Surface tension determinations on coal tars
have been carried out by Nellensteijn and Roodenburg (21), Klink-
mann (13), Fricke and Meyering (5), and Volkmann et al. (30).
The best values obtained seem to be those of Nellensteijn deter-
mined by the maximum bubble pressure method between the tempera-
tures of 120° and 40°C., and those obtained by Volkmann by the
Du Nouy tensiometer method at 37°C. Their results show values
ranging from 32.0 and 38.7 dynes/cm. at 80°C. by the maximum bub-
ble pressure method and values from 36.3 to 48.6 dynes/cm. by the
Du Nouy tensiometer method.

A comparison of the three types of tars shows that the ver-
tical retort tars have surface tensions lower than those of the
other two groups. The values for the coke oven tars and hori-
zontal retort tars fall within the same range.

The Properties of Surfaces

Spreading. Whenever a small quantity of an insoluble and
non-volatile substance is placed on water (which has a high sur-
face tension), it will either remain as a compact drop, leaving

the rest of the surface clean, or it will spread out over the surface. According to Harkins and Feldman (9) there are four general views of the criterion 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 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 under the conditions hereafter specified gives a measure of the tendency to spread, is defined as

$$S = W_a - W_c$$

It therefore appears that the necessary condition for any substance to spread on water is that its molecules must attract the water more than they attract each other. If the substance spreads, as many of the molecules of the spreading substance as possible move into direct contact with the water, forming a film one molecule thick. If space on the water surface permits, the whole of the substance spreads into such a mono-molecular film. Harkins and Feldman (9) define the term film by saying that a film exists whenever a layer, which has 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 the gravitational forces acting. Whenever the area and the forms of the layer depend both upon the surface and gravitational forces, a lens exists. So the layer of liquid at a phase boundary may be considered to constitute a film whenever the gravitational forces which tend to change its form or area are inappreciable in comparison with the surface forces which are active.

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

Three forces are in operation when a drop of oil b forms a globule on the surface of liquid a. These forces represented by γ_b, γ_a, and γ_{ab} respectively are the surface tension of the liquids b and a, and the interfacial tension between these liquids. If the globule is to remain stable, the sum 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 stability

$$\gamma_b + \gamma_{ab} > \gamma_a$$

On the other hand, if γ_a is greater than the sum of γ_b and γ_{ab}, the globule will not be stable, but the large value of γ_a will cause the liquid oil b to spread over the surface of a. The difference $\gamma_a - \gamma_b - \gamma_{ab}$ has been called the spreading

coefficient (S) by Harkins et al. (8).

$$S = \gamma_a - \gamma_b - \gamma_{ab} \qquad (I)$$

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 surfaces of a and b 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 interface between the liquids a and b, since no other energy changes are involved in the process under consideration. Hence it is possible to write

$$\gamma_a + \gamma_b - \gamma_{ab} = W_a \qquad (II)$$

where W_a is the adhesional work between a and b; this relationship is known as Dupre's equation, and was first deduced in 1869. If a single liquid, for example b, is imagined to be in the form of a column of 1 sq. cm. cross section, and the two ends of the column are pulled so that the liquid is divided into two parts without any lateral contraction, then two new surfaces each of 1 sq. cm. area will be formed. The work required to form these two surfaces is

$$W_c = 2\gamma_b \qquad (III)$$

A combination of equations (I), (II), and (II) gives

$$S = W_a - W_c$$

which states the simple relation that spreading occurs if the

adhesion between the two liquids is greater than the cohesion in
the liquid which is in the position for spreading, while spread-
ing does not occur if the cohesion is greater than the adhesion.
It is obvious that a positive value of the spreading coefficient
corresponds to spreading, a negative to non-spreading. It is all
evident that because the liquid b spreads upon a, it is not at
all a necessary conclusion that a spreads on b. Thus the spread-
ing coefficient is given above for the case where a is the liquid
whose surface is already formed. The coefficient for a to spread
upon b is

$$S = \gamma_b - (\gamma_a + \gamma_{ab})$$

so a high surface energy for the liquid a acts in favor of spread-
ing when a is the lower liquid, and against spreading when b is
the lower liquid. Corresponding with this it is found that al-
most all organic liquids spread upon water, while water spreads
upon very few organic liquids. Harkins and Feldman (9) showed
that hexane, decane, ethyl benzene, and other pure hydrocarbons
with no polar groups have a positive spreading coefficient and do
spread upon water. Therefore, contrary to the views of many sur-
face chemists, the polar group is not essential to spreading.

One of the principal effects of the presence of a polar
group, as has been shown by Harkins and his co-workers (6, 7),
is to increase the work of adhesion (W_a). It is well known that
the presence of a polar group such as $-OH$, $-COOH$, $-CHO$, $-CN$,
$-CONH_2$, etc. generally confers solubility in water on the mole-
cules to which it is attached. As the length of the hydrocarbon
chain is increased, however, the solubility of the molecule de-

creases very markedly. This decrease is probably not due to the diminution in the attraction between the water and the polar group, which is the primary cause of the solubility, but to the increased length of the 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 toward water is small, the liquid may still spread if W_c is still smaller. Thus hexane, for which the value of W_a is very small (40.23 ergs), spreads since W_c is extremely small (36.86 ergs), and the value of S is 3.37. The extremely great effect of the presence of a polar group in producing spreading is due to the fact that, in general, it increases the work of adhesion toward water very much more than it increases the work of cohesion. If the surface of the water is impure, then the surface tension of the water (which occurs as a positive term in the spreading coefficient equation) is lowered, thus lowering 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 a slightly impure water surface. This probably accounts for the nonspreading tendencies of certain organic compounds reported by some investigators but which later were found to spread. Langmuir (15) found that the presence of double linkages in the middle of some hydrocarbon chains causes the films to expand much more easily than films with saturated chains of similar length. Langmuir attributed this to the double bonds attracting the water more than a sat-

urated linkage. Therefore, it appears probable that double bonds will increase the work of adhesion (W_a) between the unsaturated film and water.

If a very small quantity of a long chain spreading oil with a polar group is put on water so as to form a film one molecule in thickness, it is supposed that the molecules of oil arrange themselves with their polar groups all attached to the water surface, and the hydrocarbon chains are arranged parallel to one another, more or less vertically above the polar groups. Being a long chain hydrocarbon, it will be insoluble due to the fact that the long chain is difficult to pull into the water. If further oil is now added to the surface, there is no tendency for these additional molecules to become anchored to the water surface, as the latter is entirely covered by an oil film; hence there will be no influence tending to encourage the formation of a second molecular layer. In fact, the polar groups of the molecules will tend to associate together, and this can occur more readily if the oil forms globules or lenses rather than if it is spread out in a film.

Surface Films. Interest in monomolecular films on the surface of water was first aroused by the work of Rayleigh (24) and Pockels (23) about 1890. It was discovered by Pockels that the area covered by a spreading oil on the surface of water could be varied at will by confining the film between movable barriers; these were made of strips of glass placed across a tray filled with water on which the oil was spread. Rayleigh repeated and extended the experiments of Pockels, and confirmed the observa-

tion 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, when the tension dropped sud-
denly to about one-half the original value for water. From the
volume of oil placed on the surface and the area it occupies, the
thickness of the film at any stage may be calculated. Rayleigh
(26) concluded that the fall in surface tension occurred when the
surface was just covered with a complete film one molecule in
thickness. Further observations of oil films on water were made
by Devaux (4) and by Marcelin (17), and these confirmed the view
that the films were unimolecular.

In 1917 a considerable advance in experimental technique
was made by Langmuir (16), and this opened a new era in the study
of surface films. In the course of his preliminary investiga-
tions, Langmuir noted that the forces exerted by the oil films
on the paper barriers which enclosed them were quite consider-
able, and so he conceived the idea of measuring these forces by
means of a balance. A shallow trough was filled with water, and
near one end was floated a paper strip which 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 sides
of the trough. Vertical glass rods attached to the paper strip
were fixed to the knife edge of a balance, so that any movement
of the strip caused by a force acting in the liquid surface caused
a displacement of the equilibrium of the balance. The weight re-

quired to be added to the balance pan to bring the paper float back to the original position is a measure of the force acting on the latter. A definite amount of an oil, insoluble in water, was placed on the surface of the water in the trough by dropping a suitable volume of a solution of the oil 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 which could not float, was placed at the other end of the trough; by moving this barrier towards the float the area covered by the oil could be varied at will, and the force exerted for different areas could be determined by means of the balance. The results of these experiments were plotted on a graph with the values of the surface force in dynes per cm as ordinates and of the area occupied per single molecule as abscissae; the latter were calculated from the measurement of the total area of the film and a knowledge of the weight of the oil on the surface, its molecular weight, and the Avogadro number. By extrapolation of the curve to zero pressure, a value was obtained giving the area per molecule at zero pressure.

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 close-ly, and very steeply oriented to the surface, as with the acids and alcohols investigated by Langmuir;

(2) liquid-expanded film, which are still coherent, but oc-cupy 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;

(3) 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, be-
tween coherent and gaseous or vapor film on the surface, and;

(4) gaseous or vapor films, in which the molecules are sep-
arate, moving independently, the surface pressure being exerted
on the barriers by a series of collisions.

EXPERIMENTAL PROCEDURE

Description and Use of the Cenco Hydrophil Balance

The balance manufactured by the Central Scientific Company
of Chicago closely resembles that used by Langmuir (16) and later
modified 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, to one end of which a bridge casting, car-
rying a torsional device for measuring forces against a mica
float, is mounted. The tray is accurately machined at the work-
ing edges to permit making accurate measurements of area. Other
portions of the tray are not machined, thus providing 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 mov-
able 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 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 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 length of the respective lever arms between the weight and torsion wire and the torsion wire and the float.

Before use, the inside of the tray and the working edges were thoroughly scoured with a stiff brush and scouring powder. The tray was thoroughly rinsed, dried, and then carefully cleaned with benzene. All parts of the apparatus which come in contact with the oil film during measurement were coated with paraffin. The tray and barrier were coated with molten paraffin applied with a camel's hair brush. The platinum ribbons and mica float were coated with paraffin applied as a solution in a volatile solvent (benzene).

Physical Determinations

The paraffined tray was leveled by means of the leveling screws after being placed in a water bath at 25° C. The tray was filled with the desired substrate until the meniscus rose above the edges of the tray. The surface of the liquid on both sides of the paraffined float was swept free of contaminants by scraping the excess liquid away from the float by means of a paraf-

fined straight edge. It was found impossible to remove all traces of contaminants by this method, so a small bore glass tube connected to suction was touched lightly to the surface. This was found effective in removing the last traces of contamination. The surface was then tested for impurities by moving the barrier the length of the tray towards the float. If no deflection of the pointer arm was produced, the surface was then clean. Leaks past the barriers or float were tested by sprinkling talc or powdered sulfur on the surface; this traveled with the film leaking past, and could be seen at once.

A film was formed between the movable barrier (initially placed near the far end of the tray) and the float by dropping a definite weight of asphalt-benzene solution upon the liquid surface. The asphalt was weighed into a clean volumetric flask and diluted with a weighed, dried, and redistilled amount of benzene. This permitted an accurate knowledge of the asphalt concentration in the solution. The benzene itself must not form a stable film, but serve the dual purpose of diluting the asphalt so that small quantities may be dispensed as relatively large volumes of solution and of diminishing the viscosity of the asphalt to the point where films form almost instantaneously and measurements may be begun as soon as the solvent evaporates. The purity of the solvent benzene was tested previously by placing some on the surface of the liquid and then by moving the barrier towards the float to see that no deflection on the pointer arm was indicated. The asphalt-benzene solution was dropped on the substrate surface by means of a standard 2 cc medical hypodermic syringe, with a

fine needle. A small cork stopper was kept on the needle except during the dropping to prevent evaporation losses. By weighing the syringe before and after dropping, the weight of the solution added was accurately determined.

After waiting approximately one 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 exerted a pressure against the float. The force was measured in degrees torsion necessary to bring the pointer back to the hair-line on the mirror surface (zero position). A record was taken of the positions of the movable barrier as it was moved intermittently toward the float and the corresponding forces exerted.

Computations

The data thus obtained are converted to dynes of force per centimeter (total force divided by the number of centimeters active length of float, which includes the length of the mica float plus one half the width of the gaps occupied by the platinum ribbons) and areas in square centimeters. 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 involved in a measurement can be calculated from the weight of solution used. The approximate molecular weight of the asphalt is known, and by employing Avogadro's number, 6.023×10^{23}, the total number of molecules can be determined. By dividing the total film area in square Ang-

strom units by the total number of molecules, the area per molecule in square Angstrom units can be determined.

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

Comparing this area obtained on distilled water with that obtained on other substrates should then give the relative spreading tendency of asphalt on various substrates with respect to water.

Molecular Weight Determinations

An attempt was made to determine the molecular weights of asphalts and coal tars used in this problem by the method of lowering the freezing point of benzene.

The experiment was carried out with a salt and ice-water bath, a Beckman thermometer, and a glass jar into which was suspended a freezing tube. The freezing tube, containing the Beckman 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 in order to prevent supercooling. The air jacket provided for a slow rate of cooling, thereby minimizing the possibility of supercooling.

For benzene, the freezing point is 5.4° C. and the molal freezing point constant is 5.12° C. In other words, a mole of a soluble substance will lower the freezing point of benzene 5.12°C. so that the mixture will freeze at 0.28° C. The molecular weights are then calculated by the use of the following equation

$$M_b = \frac{1000\ m_b\ K}{m_a\ \Delta T}$$

where M_b is the molecular weight of the solute, m_b the weight of
the solute used, m_a the weight of solvent used, ΔT the freezing
point lowering, and K the molal freezing-point constant.

RESULTS AND DISCUSSION

Molecular Weights

The molecular weights of the bitumens used in this work were
determined by the lowering of the freezing point method, using
benzene as the solvent. This method was discussed above under
the section on experimental procedure. The values obtained were:
MC-2 negative asphalt 494.46, MC-2 positive asphalt 364.65, and
RT-4 coal tar 230.72. These results are in poor agreement with
those obtained by other workers who found the molecular weights
to range from 620 to 4250. Producers of petroleum asphalt com-
monly "cut back" their product with kerosene or other light sol-
vents so as to reduce the viscosity. It is probable that the
bitumens used in this work had been "cut back", which would tend
to give low values such as those obtained above, since the mole-
cular weights of the solvents are lower than those of the bitu-
mens. The other workers did not specify what methods they used
to remove the "cut back" solvents before making a molecular weight
determination. This difficulty would not be encountered for nat-
ural asphalts which gave the higher values of around 4000.

In an effort to gain some idea as to the percentage of vola-
tile substances present in these bitumens, they were heated in

open beakers at 50° C. for 40 days. It was found that they lost weight as follows: MC-2 negative asphalt 20.6 per cent, MC-2 positive asphalt 15.7 per cent, and RT-4 coal tar 22.0 per cent. However, these values do not give accurate information on the amounts of "cut back" solvent present since bitumens themselves contain a certain amount of volatile products which would be lost at the same time. A certain amount of oxidation of the bitumens probably occurred at the same time which would, of course, cause an increase in weight.

It is interesting to note that the molecular weight of the negative asphalt is about 33 per cent larger than that of the positive. In the course of their preparation, positive asphalts are subjected to higher temperatures than negative asphalts. On the basis of the molecular weights obtained, it would appear that the positive asphalts undergo considerable "cracking" at the higher temperatures, thereby producing smaller molecules.

Surface Pressure Measurements

General Considerations. The data for the surface pressure-area per molecule measurements are given in Table 1. The data for each curve given represent an average taken from 5 to 7 curves, all measurements made with the substrate at 25° C. Close agreement was obtained for all curves of one type of bitumen on a particular substrate, although occasionally at very low pressures, some deviations were encountered. However, these deviations have no effect on the results obtained, since it is the upper part of the curve (at high pressures) that is extrapolated to

Table 1. Effect of substrates upon areas per molecule (sq. A°) of certain bitumens at varying pressures.

Surface pressure in dynes/cm.	Area per molecule (sq. A°)					
	Water substrate			0.1N KOH substrate		
	Asphalt		:Coal tar	Asphalt		:Coal tar
	Neg.	Pos.	RT-4	Neg.	Pos.	RT-4
1	6.79	8.00	-	9.54	8.43	-
3	6.08	5.73	4.43	7.86	6.65	-
5	5.68	5.12	2.78	7.13	5.36	9.76
7	5.35	4.81	1.80	6.73	4.47	8.49
9	5.08	4.63	1.18	6.42	3.95	7.30
11	4.92	4.48	0.87	6.17	3.69	6.26
13	4.82	4.39	0.69	5.98	3.51	5.36
15	4.73	4.27	0.59	5.80	3.37	4.65
17	4.65	4.21	0.53	5.65	3.26	4.16
19	4.53	4.12	0.49	5.52	3.17	3.74
21	4.43	4.00	0.46	5.38	3.10	3.45
23	4.33	3.90	0.45	5.25	3.05	3.25
	0.1N AlCl₃ substrate			0.3N NaCl substrate		
1	13.48	10.02	4.67	11.11	10.21	-
3	10.90	7.70	3.53	9.53	8.09	7.91
5	8.46	6.30	2.58	8.75	7.00	5.88
7	7.03	5.50	1.96	8.29	6.37	4.16
9	6.32	5.06	1.65	7.95	6.05	3.06
11	5.98	4.80	1.52	7.67	5.84	2.43
13	5.66	4.48	1.43	7.44	5.68	1.85
15	5.38	4.20	1.35	7.25	5.57	1.66
17	5.06	3.90	1.27	7.08	5.46	1.55
19	4.80	3.58	1.17	6.92	5.38	1.46
21	4.52	3.26	1.11	6.76	5.28	1.40
23	4.22	2.98	1.02	6.59	5.22	1.32
	0.1 N HCl substrate			0.3N HCl substrate		
1	30.60	-	-	28.00	23.88	-
3	26.56	21.38	-	22.37	17.50	-
5	24.58	17.42	22.06	19.51	14.55	-
7	22.66	14.86	19.24	18.00	13.23	25.40
9	20.92	13.58	16.38	17.20	12.42	22.32
11	19.78	12.81	13.52	16.62	11.78	19.25
13	18.74	12.15	10.78	16.08	11.25	17.05
15	18.06	11.63	8.52	15.62	10.85	15.39
17	17.47	11.10	7.74	15.20	10.54	14.14
19	16.88	10.64	7.24	14.78	10.30	13.22
21	16.27	10.14	6.80	14.32	10.10	12.45
23	15.77	9.69	6.34	13.90	9.90	11.80

Table 1. (concl.).

Surface pressure in dynes/cm.	Area per molecule (sq. A°)					
	0.1N H₂SO₄ substrate			0.3N H₂SO₄ substrate		
	Asphalt		:Coal tar:	Asphalt		:Coal tar
	Neg.	Pos.	RT-4	Neg.	Pos.	RT-4
1	-	-	43.85	-	-	-
3	28.56	21.60	36.40	25.12	20.72	-
5	25.48	19.40	31.82	22.40	18.10	-
7	23.72	17.72	28.46	20.45	15.81	22.02
9	22.44	16.54	25.28	19.64	13.80	19.42
11	21.38	15.64	22.36	18.73	12.41	16.83
13	20.50	14.96	19.66	17.94	11.50	14.10
15	19.70	14.48	17.10	17.36	10.90	11.63
17	18.92	14.05	15.10	16.84	10.54	9.77
19	18.06	13.68	13.48	16.42	10.26	8.20
21	17.29	13.27	12.32	16.02	10.06	7.16
23	16.48	12.84	11.31	15.64	9.86	6.49
	0.1N Aniline hydrochloride			0.1N Aniline hydrochloride		
1	29.86	-	28.14	28.00	21.20	-
3	26.28	28.16	24.36	24.50	17.68	29.68
5	23.40	24.84	20.62	21.40	14.72	26.72
7	21.40	21.56	16.90	19.35	12.92	23.72
9	20.19	19.04	13.24	17.35	12.04	20.66
11	19.34	17.58	10.02	15.87	11.62	18.12
13	18.79	16.72	8.08	15.03	11.28	16.46
15	18.26	16.14	7.16	14.52	10.94	15.44
17	17.87	15.68	6.48	14.13	10.57	14.70
19	17.43	15.28	5.98	13.80	10.22	14.04
21	17.02	14.92	5.50	13.45	9.96	13.44
23	16.60	14.54	5.06	13.17	9.60	12.96
	0.1N KMnO₄ substrate					
1	-	98.60	67.18			
3	68.70	95.22	64.62			
5	65.84	91.69	63.50			
6	-	89.55	-			
7	63.42	85.68	62.74			
8	-	83.04	-			
9	61.19	82.04	62.04			
11	59.11	80.12	61.32			
13	56.77	78.12	60.65			
15	53.72	76.18	59.89			
16	50.50	-	-			
17	46.24	74.14	59.04			
18	43.60	-	-			
19	41.12	71.54	57.74			
21	35.94	68.18	56.32			
23	32.41	64.66	54.92			

obtain the areas per molecule at zero pressure.

For the purpose of this work, the molecular weights of the asphalts and road tars were all assumed to be 2000, which is about the mean of the values obtained by Strieter (Traxler, 28) and Katz (12). The exact values are not necessary here since the measure of spreading is taken from the apparent cross sectional area of the molecule on a particular substrate with relation to its area on water taken as the standard. In other words, only the relative apparent molecular cross sectional areas are necessary to determine the degree of spreading. If the exact molecular weights could be obtained and substituted in the equation given previously under the section on experimental procedure to determine the area per molecule, each curve would be offset an amount such that the relative areas are unaffected.

Spreading on Water. Figure 1 illustrates the spreading of positive and negative asphalts and coal tar on a pure distilled water substrate. The extrapolated values for the areas per molecule of positive (5.05 sq. A°) and negative (5.50 sq. A°) asphalt are in close agreement but probably too low if it can be safely assumed that 2000 is close to the true molecular weight of the asphalts. The cross sectional area of a straight chain hydrocarbon is 20.5 sq. A°, and because of the complexity of asphalts they should have even larger areas. Coal tars are complex aromatic compounds, so that their molecular cross sectional areas should be at least 24.0 sq. A° which is the area of cross section of the benzene ring. However, the extremely small value of 0.95 sq. A° was obtained. The overall low values obtained here would
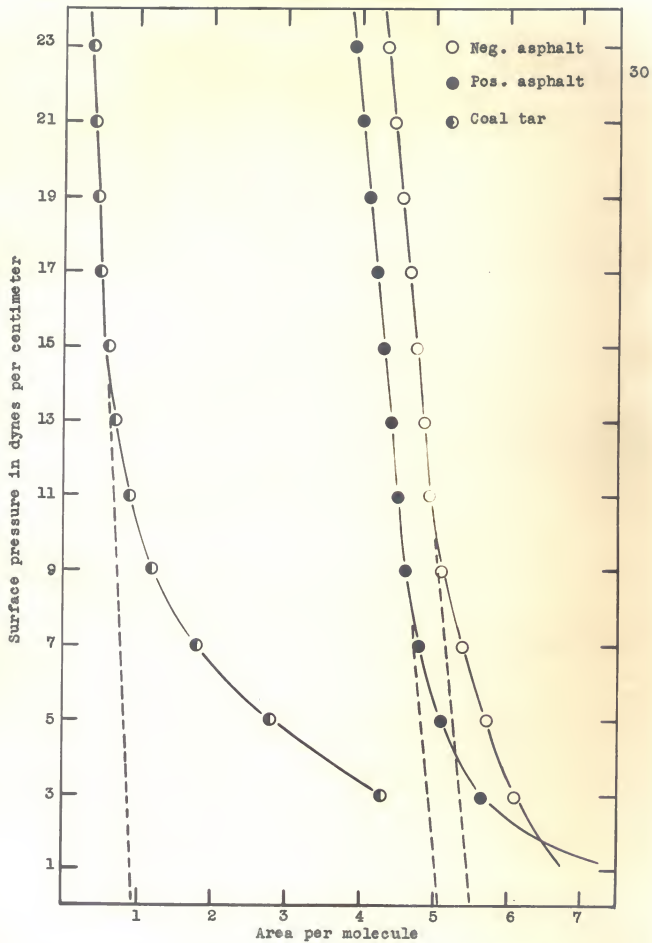
Fig. 1. Bitumen spreading on a water substrate.

seem to indicate that asphalts and tars do not form monolayer films, but, instead, multi-layer films.

Interference colors due to the interference of light waves reflected at the top and bottom surfaces of the film made it visible. The observed films seemed to be "patchy" in that certain small areas of the substrate surface were not covered by film. This would make it appear that bitumens do not spread completely on water. When a piece of cotton batting, saturated with benzene, was placed near the voids in the surface, these void areas soon filled and a coherent film resulted. As stated previously, the conditions for spreading are that the work of adhesion (W_a) between film and substrate must be greater than the work of cohesion (W_c) in the film itself. A polar group or a double bond tends to increase the work of adhesion more than that of cohesion, and therefore causes spreading. Although not too much is known of the actual composition of asphalts and coal tars, there is little evidence of any great number of polar molecules present. Since a certain amount of spreading was visibly observed, the best possible explanation is that double bonds and certain oxidized groups in the molecule increase the work of adhesion between bitumen and water. Incomplete spreading was due, then, to certain molecules being saturated and unoxidized; thus their work of adhesion for water is less than the work of cohesion of the bituminous molecules for themselves.

Hysteresis was noted in the films of the bitumens on water as well as on all other substrates, in that they reacted somewhat sluggishly to pressure changes. A lapse of a few seconds was

necessary after compressing the film by moving the barrier towards the float before taking the pressure reading. The full pressure was not transmitted to the float instantaneously but required from four to five seconds to reach a maximum. When the compression on the film was reduced by moving the barrier away from the float, the pressure fell off slowly. Sometimes 10 minutes was required for equilibrium to be established. Even so, the film did not expand along the original compression curve, since the pressures always were lower.

Spreading on 0.1N KOH. (Fig. 2) The 0.1N KOH substrate had an unusual influence on the positive asphalt in that it reduced the cross sectional area to 3.85 sq. A^o while it caused a slight increase in the cross section of the negative asphalt to 6.85 sq. A^o. No plausible explanation seems to fit this phenomena. The KOH caused an increase in the spreading of the coal tar to 6.20 sq. A^o.

Spreading on 0.1N AlCl₃ and 0.3N NaCl. (Figs. 3 and 4) A substrate of 0.1N AlCl₃ caused all three bitumens to spread slightly better than on pure water. A 0.3N NaCl substrate had practically the same effect as the AlCl₃.

Spreading on 0.1N and 0.3N HCl. (Figs. 5 and 6) A very marked improvement in the spreading qualities of all three bitumens was produced by a HCl substrate. A 0.1N HCl solution increased the apparent molecular areas of negative asphalt about 4 times, positive asphalt 3 times, and coal tar about 12 times over that observed on water. However, the more concentrated 0.3N HCl substrate reduced the spreading tendencies of the as-
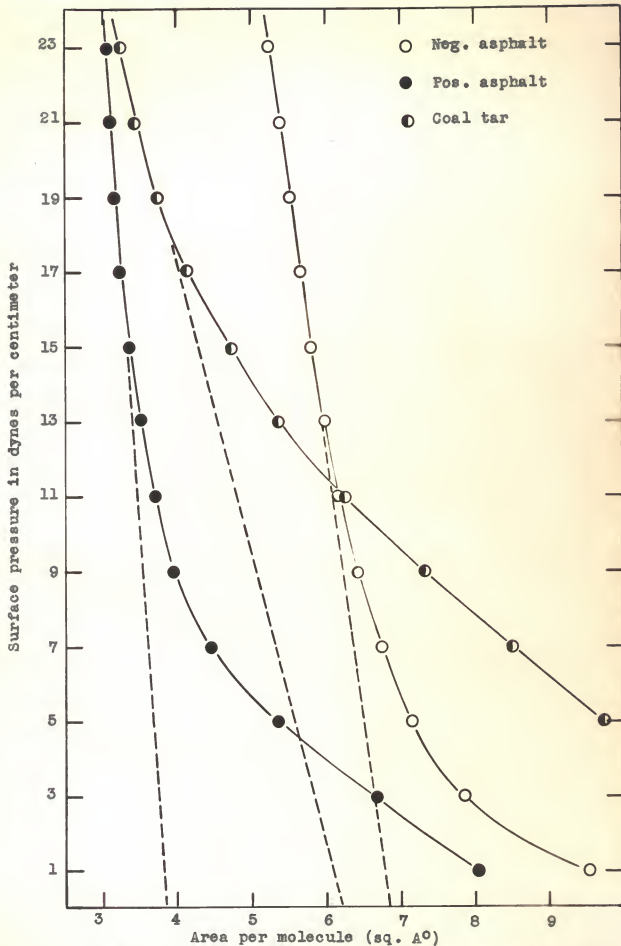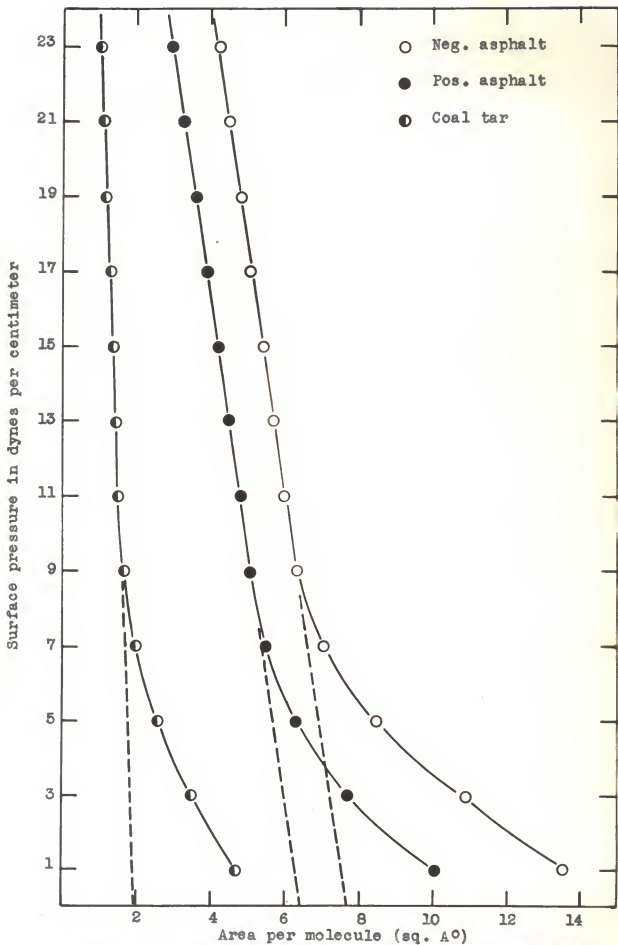
Fig. 2. Bitumen spreading on a 0.1N KOH substrate.

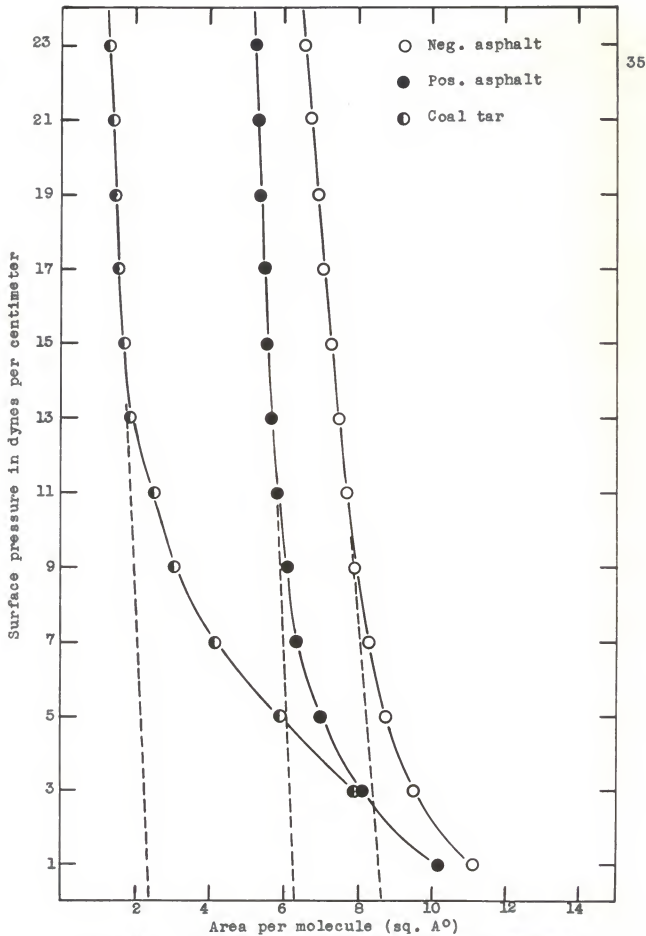Fig. 3. Bitumen spreading on a 0.1N AlCl₃ substrate.

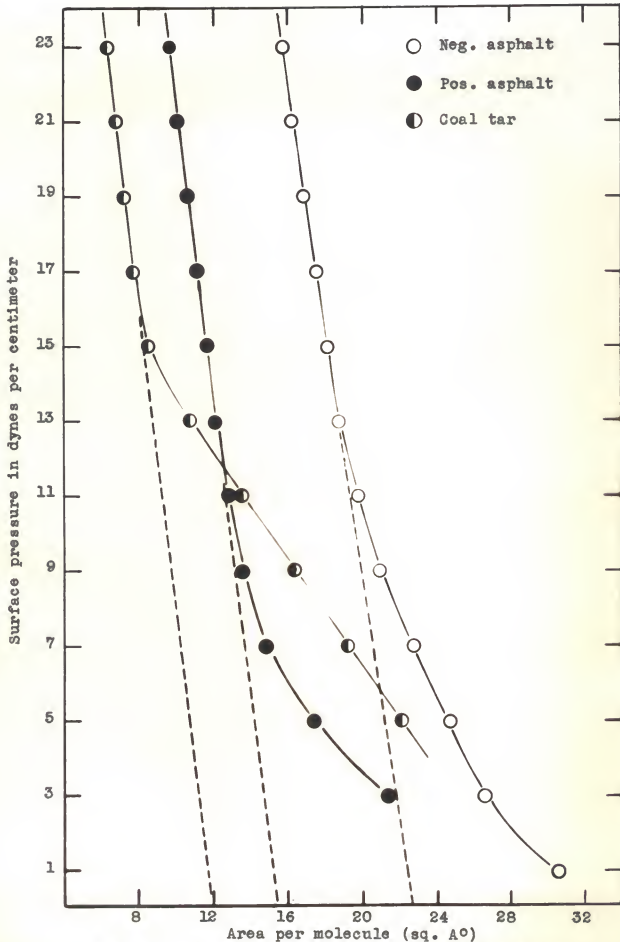Fig. 4. Bitumen spreading on a 0.3N NaCl substrate.

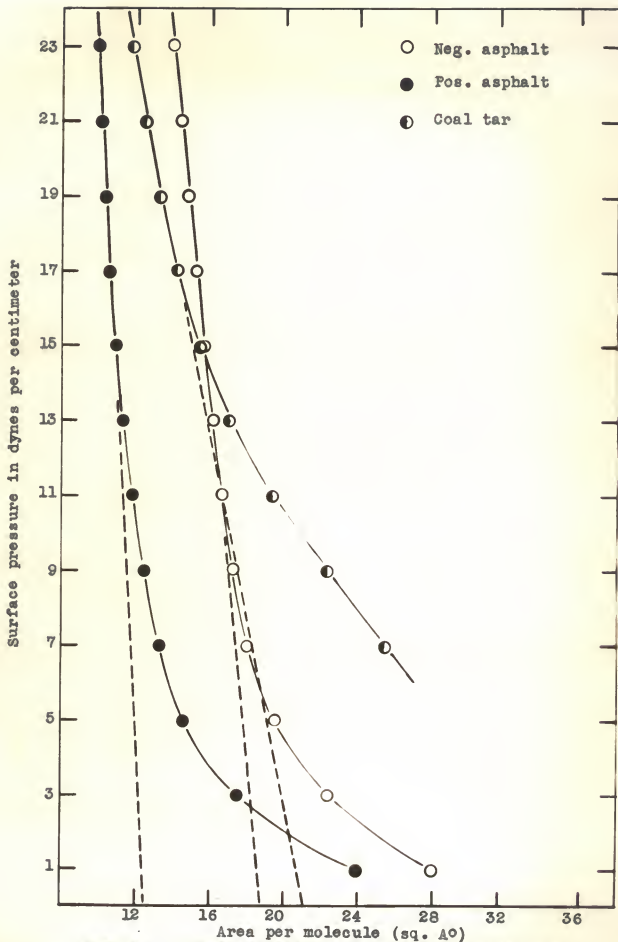Fig. 5. Bitumen spreading on a 0.1N HCl substrate.

Fig. 6. Bitumen spreading on a 0.3N HCl substrate.

phalts from that of the 0.1N HCl, yet increased the coal tar spreading an additional 9 times. Other films have been observed to spread better on acids, and Adam (2) postulates that the polar ends are ionized by the change in acidity of the substrate. The ionization develops similar charges on the adjacent end groups, causing mutual repulsion, and hence a loss of lateral adhesion between molecules. The net result was an increase in the area occupied by a molecule of the film.

Spreading on 0.1N and 0.3N H_2SO_4. (Figs. 7 and 8) A 0.1N H_2SO_4 substrate produced a marked increase in the spreading qualities of bitumen; more so than an equivalent concentration of HCl. This might be attributed both to the ionization of polar groups and also to an anion valence effect. A very slight oxidation may have occurred, but this seems unlikely because of the low H_2SO_4 concentration. A 0.3N H_2SO_4 solution caused a reduction in spreading of both asphalts and coal tars from that noted at the more dilute concentration, yet still caused better spreading than that detected for pure water.

Spreading on 0.1N and 0.3N Aniline Hydrochloride. (Figs. 9 and 10) A 0.1N aniline hydrochloride substrate caused a large increase in the spreading of both asphalts and tar. The magnitudes of the increases were similar to those produced by 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 lower concentration, yet increased the spreading of the coal tar; in fact, almost doubled it. Aniline hydrochloride hydrolyzes acid, thus causing ionization of the end groups, so
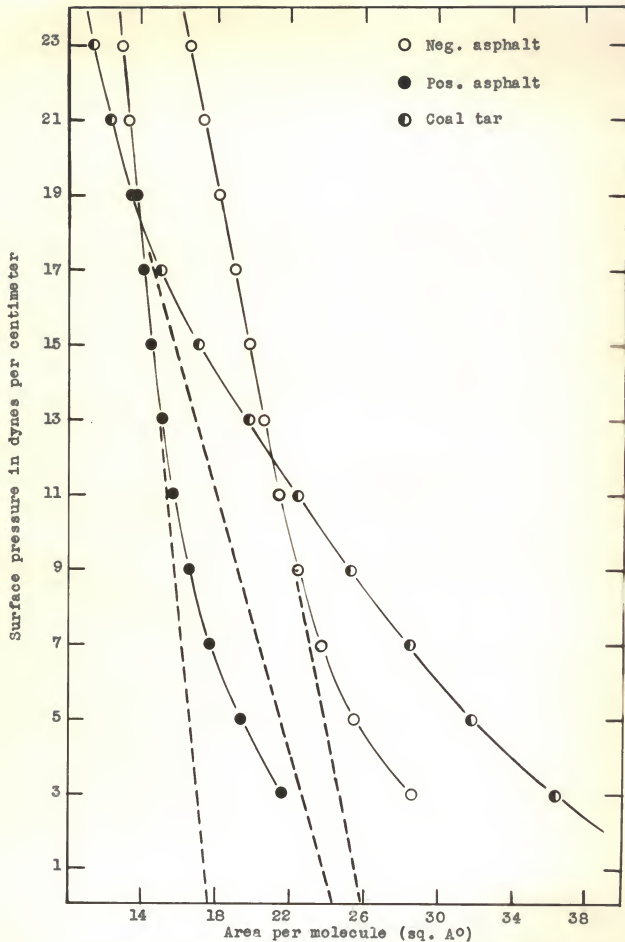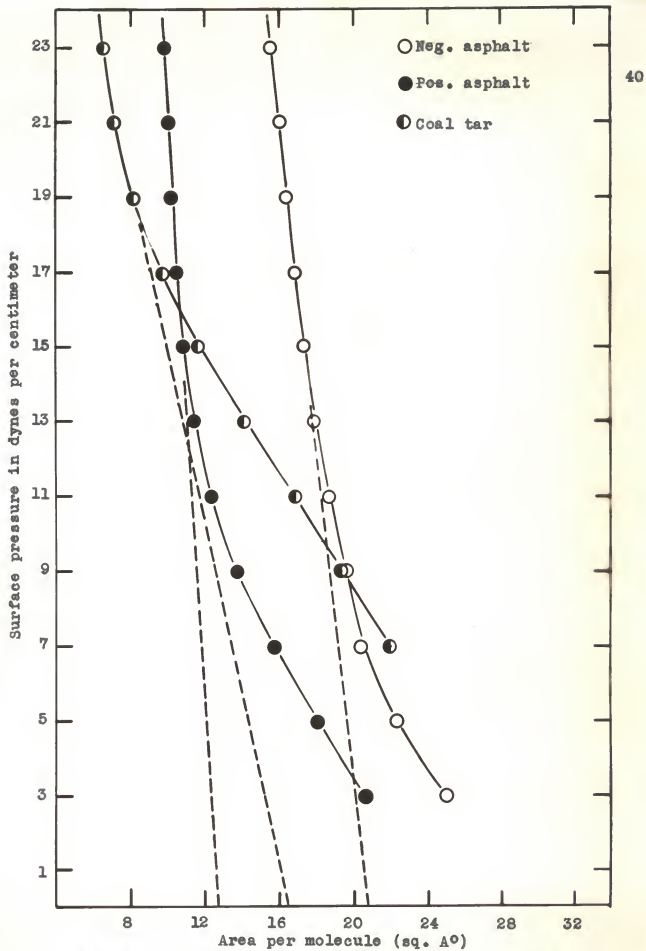
Fig. 7. Bitumen spreading on a 0.1N H_2SO_4 substrate.

Fig. 8. Bitumen spreading on a 0.3N H_2SO_4 substrate.
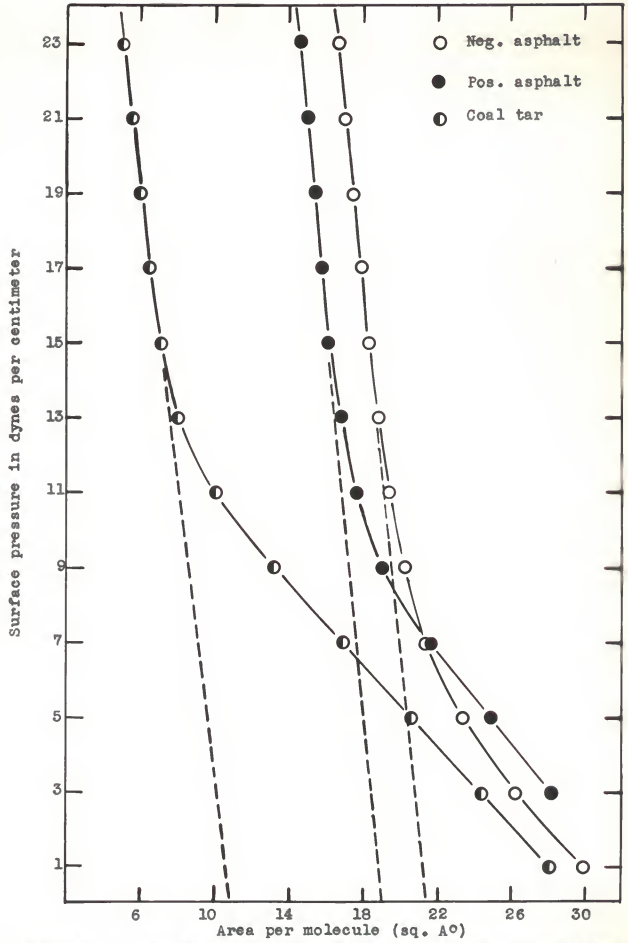
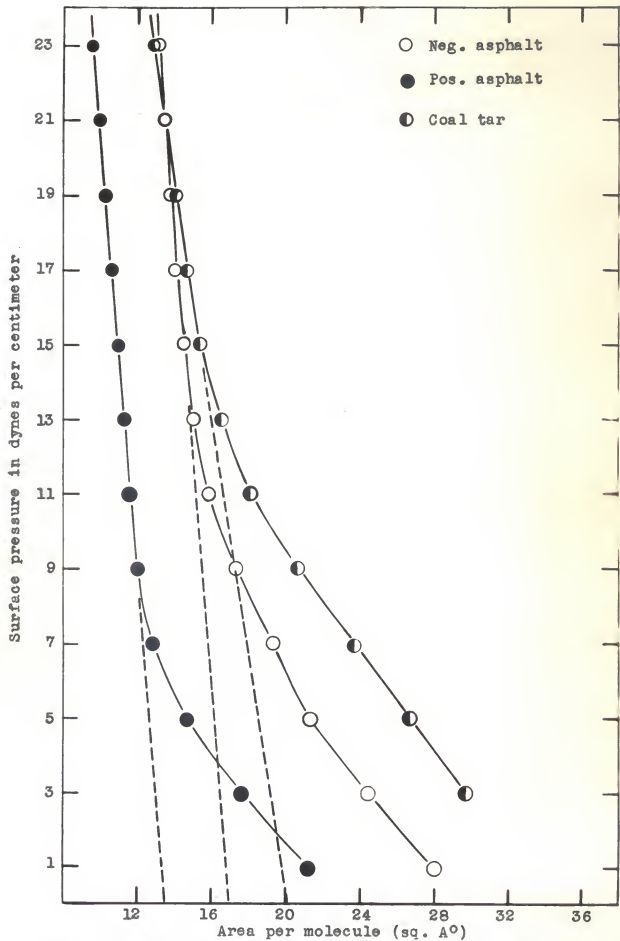Fig. 9. Bitumen spreading on a 0.1N aniline hydrochloride sub-
strate.

Fig. 10. Bitumen spreading on a 0.3N aniline hydrochloride
substrate.

this could be a possible explanation of the increased spreading. AlCl₃ should also hydrolyze acid, but it had only a negligible effect on spreading; therefore, it seems improbable that the aniline hydrochloride could hydrolyze sufficiently to produce the large increase in spreading noted. A molecule of aniline hydrochloride has a polar and a nonpolar end. Some of the molecules of the aniline hydrochloride probably orient themselves at the film-substrate interface with the nonpolar end dissolved in the bitumen film and the polar end dissolved in the substrate to produce an increase in spreading. This might account for the additional spreading on aniline hydrochloride over that on AlCl₃.

Spreading on 0.1N KMnO₄. (Fig. 11) The most startling results of all the films investigated were those on the 0.1N KMnO₄ substrate. A tremendous increase in spreading was observed for both asphalts and coal tar. Extrapolation of the upper portions of the respective curves gives an increase in area of 16 times for the negative asphalt and 18 times for positive asphalt over that on pure water, while extrapolation of the lower portion of the curves gives an increase of 13 times for negative asphalt and 20 times for positive asphalt. The cross sectional area of the coal tar increased in size 69 times over that on water.

Adam (2) found that when oleic acid was spread on permanganate, a large increase in spreading occurred, probably resulting from the oxidation of the double bond present into two hydroxyl groups. The oleic acid molecule then had several polar groups which tended to make it lie flat on the substrate and thus increase its cross sectional area. A similar mechanism
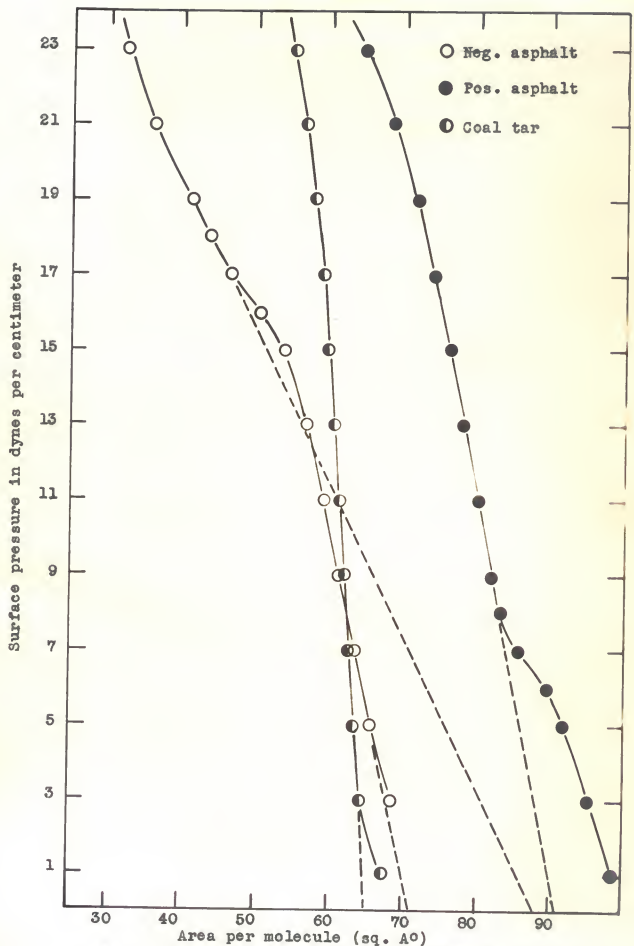
Fig. 11. Bitumen spreading on a 0.1N KMnO4 substrate.

could have occurred here with the double linkages in the bitumens oxidized to form hydroxyls. It is likely that simultaneous oxidation of certain other groups occurred with the formation of other polar groups. Both types of oxidation would contribute to the great increase in the apparent cross sectional area of the molecules. From the large increase in spreading noted for coal tar, it would appear that it is very susceptible to oxidation - much more so than either of the asphalts. Of the two asphalts, the positive spreads better on permanganate, which would seem to indicate that the high temperature it undergoes in preparation renders it more susceptible to oxidation.

The positive and negative asphalts gave unusual compression curves on the permanganate substrate, in that humps or shoulders appeared at definite pressures. The humps, which corresponded to a rapid diminution in cross sectional area per small increase in pressure, occurred in the region from 6 to 8 dynes for the positive asphalt and 15 to 18 dynes for the negative asphalt. This suggests that at those pressures there must be a rearrangement of the molecules in the film producing a sizeable diminution in the area per molecule. This might occur by a vertical rearrangement of some of the molecules such that their polar heads are tucked away into recesses in the chains of neighboring molecules. A study of crystal structure has proved that such chains are zigzag structures, not straight, so this would tend to support this theory. Apparently no rearrangement occurred in the coal tar for no humps appeared on the curve.

The extrapolated values for the apparent areas of the mole-

cules at zero pressure taken from Figs. 1 to 11 are summarized
in Table 2.

Table 2. Extrapolated apparent molecular cross sec-
tional areas at zero pressure in sq. A°.

Substrate		Films		
	:	MC-2 Neg. : Asphalt :	MC-2 Pos. : Asphalt :	RT-4 Coal Tar
H_2O	:	5.50	5.05	0.95
0.1N KOH	:	6.85	3.85	6.20
0.1N $AlCl_3$	:	7.65	6.40	1.95
0.3N NaCl	:	8.60	6.30	2.40
0.1N HCl	:	22.70	15.40	12.00
0.3N HCl	:	18.80	12.50	21.00
0.1N H_2SO_4	:	25.90	17.70	24.40
0.3N H_2SO_4	:	20.80	12.80	16.50
0.1N Aniline	:			
hydrochloride	:	21.40	19.00	10.80
0.3N Aniline	:			
hydrochloride	:	17.00	13.60	20.10
0.1N $KMnO_4$	:	88.00	91.00	65.30
"	:	71.00*	100.30*	

*Extrapolation of the lower portion of the curve

SUMMARY

1. The molecular weights of MC-2 negative asphalt, MC-2
positive asphalt, and RT-4 coal tar have been determined to be
494.46, 364.65, and 230.72, respectively.

2. Bitumens spread poorly on water.

3. Aqueous substrates of NaCl, $AlCl_3$, and KOH have only
small effects on the surface spreading of bitumens.

4. Aqueous solutions of H_2SO_4, HCl, and aniline hydrochlo-
ride produce marked increases in the surface spreading of bitu-
mens. In general, low concentrations of the above substances
promote better spreading than higher concentrations.

5. A solution of $KMnO_4$ produces a very large increase in bitumen surface spreading.

6. Plateaus appear at definite pressures on the surface pressure-area curves of the positive and negative asphalt films on permanganate which seems to indicate a molecular rearrangement in the films at those pressures.

7. An attempt has been made to suggest possible mechanisms which bring about bitumen spreading on various aqueous substrates.

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