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ADHESION BETWEEN BITUMENS AND AGGREGATES

by

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INTRODUCTION

The problem of the adhesion of bituminous coatings to mineral aggregates is of great importance to the service life of a bituminous pavement. In recent years, asphalt paving technologists are much concerned with the problems of stripping and durability of such a pavement. Some aggregates have a greater adhesion tension for water than bitumen, as a result, large percentage of failure occurring in bituminous pavements is caused by water displacement of the bitumen films from the aggregate surface. At the same time, poor adhesion between bitumen and dry aggregate exists if conditions of application such as temperature or consistency are not carefully controlled. Good spreading or wetting will not occur with certain viscosities and surface tensions of the bitumen. Conversely, the grade of bitumen should be such that its viscosity under such shearing forces may be expected to withstand the load imposed and will not cause the bitumen film to be separated from the surface of the aggregate.

Adhesion between two different materials is a surface phenomenon and is dependent upon their intimacy of contact and the mutual affinity of the surfaces of the two materials.

The adhesion may be due to either specific or mechanical adhesion. According to the A.S.T.M. Committee D-14 on Adhesives (5) (1), the specific adhesion formed between surfaces are held together by valence forces of the same type as those which give rise to cohesion, and are also associated with adsorption phenomenon. Mechanical adhesion, on the other hand, is the interlocking action between the two adjoining materials. It is formed by any liquid which penetrates through porous surfaces and then changes into solid, tenacious materials as the liquid viscosity increases.

Before the best possible adhesion between two substances can be obtained, it is necessary that their surfaces be brought into the most intimate contact. Such contact, as in the case of viscous bitumen binder and aggregate could be possible only when one is temporarily liquefied at the time of contact. The ability of the liquefied bitumen binder to make intimate contact with the mineral aggregate is its wetting power. When a liquid wets a solid, the liquid surface energy may increase, decrease or remain constant. These changes are the principle problems of wetting and adhesion. The extent of the changes are limited by the surface tension of the liquid and by the contact angle formed between the liquid and solid phases.

Besides these two major factors, the problem of adhesion and wetting is also affected by many other factors of equal or lesser degree of importance. The viscosity, adsorption, surface textures and chemical composition either directly or indirectly influence the complexity of the problem.

Since the phenomena of adhesion or wetting are correlated properties, a quantitative measurement of these properties is extremely complex. It is even more complicated in the case between bitumen and aggregate. The chemical composition of the bitumen binder itself is still a mystery and much has to be learnt and explored by the organic chemists. Furthermore, the complicated rheological properties of the bitumen at atmospheric temperature make the investigation even more difficult, if not impossible, with the general techniques adopted for other organic liquids and solids.

It seems more important for the engineers to know the extent of the adhesiveness between bitumen and aggregates under various changes of the rheological conditions, than to learn why and how the adhesion is created. For this reason, the present research was conducted.

The prime purpose and scopes covered by this investigation were as follows:

1. To study the relationship between the viscosity and temperature of various grades of bitumens.

2. To measure the surface tensions of these materials

at different elevated temperatures so as to study the interrelationship between the surface tension and viscosity at the same temperature.

3. To evaluate the adhesion tension between bitumen and solid materials at various temperatures by the measurement of their contact angles.

4. To establish a relationship between spreading and viscosity of the bitumen.

5. To find the mathematical expression which would represent the data so obtained in this investigation.

REVIEW OF LITERATURE

Rheological Properties of Bitumen Binders

The scientific study of the mechanical properties, such as flow, ductility, and plasticity of concentrated colloidal systems has been termed rheology by the colloid scientists.[2] Nellensteyn (45) indicated that paving bitumen is a protected lyophobe sol or an extremely stable carbon-oleosole in the form of a colloidal system, in which the asphaltenes are dispersed in the oily constituents, and the solution is stabilized by the resin fraction, which acts as a protective colloid.

The more important rheological properties of the paving bitumen are the character of the colloidal system[2] and its consistency. The main difference in the character of the system concerns its deviations from Newtonian flow,[2] while the differences in consistency can be indicated by the values of its viscosity.[2]

Pittman and Traxler (53) indicated that majority of petroleum products behaved as a Newtonian liquid in which the viscosity is independent of the rate of shear at the time of measurement. Bitumen as the residue from the petroleum crude distillation sometimes deviated appreciably from Newtonian flow at normal atmospheric temperatures.

Traxler and Coombs (64), Lee, Warren and Waters (36), Hughes and Hardman (31), Mack (38), and Saal and Labout (59) all seem to agree that common types of flow exhibited by bitumen at low temperature is of non-Newtonian or complex flow properties, and that their viscosity depends on the rate of shear, which decreases in value as the rate of shear increases.

According to Pfeiffer (52, p. 10), the different rheological characteristics of bitumen in relation to rate of shear, shearing stress and time can be shown in the following (Figure 1).

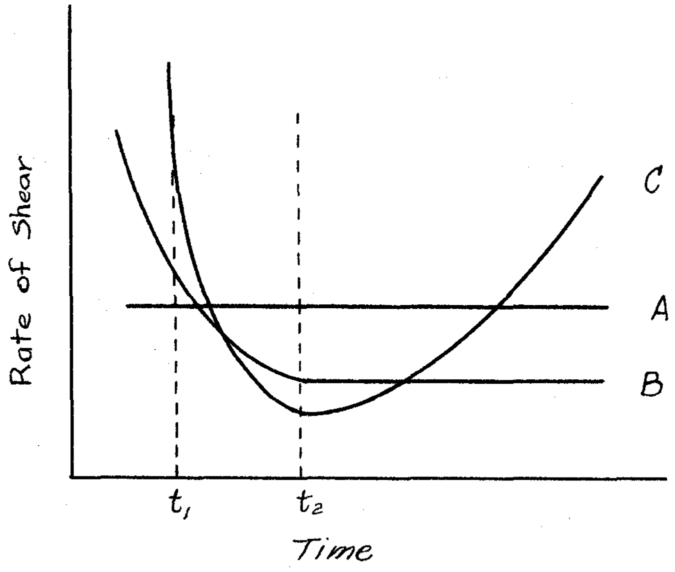

Fig. 1. Rate of shear of bitumen under a constant shearing stress as a function of time (after Pfeiffer)

The rheological behavior of some bitumens (Curve A) is of simple nature, wherein it behaves entirely in accordance with Newtonian flow, and the rate of shear is constant and proportional to shearing stress applied. This type may be a viscous, non-colloidal liquid or a sol with slightly or non-elastic particles. In other bitumens (Curve B), the behavior is more complex where the rate of shear decreases at the beginning of the deformation. After reaching the time t_2, the rate of shear becomes constant and proportional to the shearing stress applied. In still others, the rate of shear (Curve C) drops at the beginning, then passes a minimum value and subsequently rises. After the release of the shearing stress, the elastic recovery may be complete or be partial within certain limits. Type C bitumens are often thixotropic, wherein the viscosity under flow diminishes at first owing to the alteration of internal structure, and increases after an interval of rest.

Saal (56) observed a marked thixotropy in the case of paving bitumen. His experiments consisted of forcing a bitumen through two capillaries of exactly the same diameter but of different lengths. The pressure necessary in each case was proportional to the length of the tube, but one tube was inclined to permit equal quantities of bitumen to be forced through the tubes per unit of time. As a result of its internal movement, the bitumen became less viscous in the longer tube and various viscosity values were obtained with repeated determinations. The original viscosity did not seem to recover after a rest period of many hours.

The Physical Meaning of Viscosity

Maxwell (42) defined viscosity as the measure of internal resistance or deformation of a fluid. There is a certain measurable resistance when one layer of a fluid is made to move in relation to another layer. The viscosity measurement is perhaps the most valuable means of studying the inner nature of bituminous substances.

Phenomena involving the deformation of the matter are the stress and motion, or the stress and strain. Shear as described by Markwood (41) is one kind of stress occurring in the sliding areas that produces strain without being accompanied by changes in volume. The ratio of the velocity with which one of these areas slides past another for a certain distance is called, by him, the rate of shear.

Newton (20, 16) assumed the shearing forces between two parallel planes in a liquid in relative motion to be proportional to the area of the planes and to the velocity gradient between them. His well known equation:

$$\mathcal{T} = \eta \frac{dv}{dl} A$$

where $\frac{dv}{dl}$ is the velocity gradient perpendicular to the planes, A is the area of the planes, η the coefficient of viscosity, and τ the shearing forces. In another form, the viscosity $\eta = \frac{\text{shearing stress } (\tau)}{\text{rate of shear } (s)}$. The value η is not a dimensionless unit but is expressed in the three dimensional units of mass (M), distance (L) and time (T). Since rate of shear

$$S = \frac{\text{velocity}}{\text{distance}} = \frac{(L/T)}{L} = 1/T$$

Shearing stress

$$\tau = \frac{\text{force}}{\text{area}} = \frac{(ML/T^2)}{L^2} = M/LT^2 = ML^{-1}T^{-2}.$$

Therefore the viscosity $\eta = \tau/S$ will have the dimension of $\frac{(M/LT^2)}{(1/T)} = ML^{-1}T^{-1}$ unit.

The usual mode of expressing viscosity has been referred to as absolute viscosity with the unit of poise (15) (or centipoise = 0.01 poise).

According to Einstein (22) work done in overcoming frictional resistance is transformed into heat, and a connection exists between the viscosity coefficient and the kinetic energy transformed into heat. Thus the useful alternative definition of the viscosity coefficient is

$$q = \eta\left(\frac{dv}{dl}\right)^2$$

where q is the kinetic energy transformed into heat in unit time for unit volume. This view of viscosity coefficient as a measure of the energy dissipated is sometimes more fruitful than one in which a physical picture of the processes affecting viscosity is involved.

Influence of Temperature on Viscosity

In work reported by Andrade (8) and Sheppard (60), the rate of change of viscosity of a fluid with temperature is affected on both degree of solvation and molecular shape. Increased temperature usually involves decreases in relative viscosity. However, increased temperature also causes more vigorous internal Brownian motion, which may result in flexible macromolecules in increased or decreased asymmetry according to whether the molecules at the lower temperature were respectively in a compact or extended form.

The molecular orientation as reported by Burgess (17) is also affected by the change of the temperature. The increasing effectiveness of Brownian motion at higher temperatures leads to decreased orientation and, therefore, to an increased relative viscosity.

Robinson (55) showed that at low velocity gradients, where orientation was not complete, an increasing temperature will cause an increase in relative viscosity, and simultaneously, decreased double refraction. Thus the increasing effectiveness of Brownian motion at higher temperatures leads to decreased orientation and increased relative viscosity.

Paving bitumen, as generally assumed by the chemists (30, p. 165; 46), is a colloidal system in which the solubility of the dispersed phase asphaltene in the oily continuous phase of the maltenes is influenced by the change of temperature.

According to Traxler and Coombs (65),

> the solubility of asphalt at high temperature is increased, except for free carbon if it is present. As the temperature is progressively lowered, the two phases, dispersed and continuous, became more distinct and the colloided properties of the system became more exaggerated. However, even at low temperatures, the system usually is stable, the asphaltenes remaining dispersed owing to the protective action of the asphaltic resins. Various investigators are divided in their opinions as to whether this system has the form of a suspensoid or of an emulsoid. The opinion has been expressed that the temperature-viscosity curves for asphaltic bitumen should have two marked points of transition, one where the system passes from the liquid to the semi-liquid, and then to the solid state.
>
> From the rheological standpoint, the latter statement is ill-defined. For as far as flow properties are concerned, a transition from the true liquid state to anything approximating the solid state means a change from purely viscous properties to definitely plastic behavior involving yield values and mobilities rather than viscosities.

The rate of change of the viscosity of the paving bitumen with temperature cannot be solved by simple formula. For ordinary homogenous fluid, Andrade (8) and

Sheppard (60) have derived the relationship between the viscosity and the temperature. They denoted the potential energy of the adjacent molecules as ϵ (numerically negative), then the probability that two molecules will combine is proportional to $e^{-\frac{\epsilon}{KT_R}}$, where k is the Boltzmann constant. From this, the viscosity in the first approximation should be proportional to $e^{-\frac{\epsilon}{KT_R}}$, and so

$$= Ae^{-\frac{\epsilon}{k\, T_R}}$$

or

$$\log \eta = \log A + \frac{\epsilon}{k\, T_R} \log e$$

where A is a constant and T_R the temperature in terms of absolute unit. According to Andrade, a straight line in general should be obtained when log η is plotted against the reciprocal of corresponding absolute temperature.

The change of viscosity of bitumen with temperature has been represented by various authors (48) in as many as six main different graphical ways with the sole purpose to obtain some straight-line relationship. These are:

(1) Log viscosity vs. ordinary temperature (in either Fahrenheit or Centigrade).

$$\log \eta = k - mt$$

where η is the absolute viscosity in poises,

t is the temperature of ° F. or ° C.

k and m are constants.

The straight line relationship has been illustrated by Saal (57), Neppe (48), Traxler and others (66) to be fairly linear within a limited temperature range. This indicates that there is no sudden change in the physical properties, but a gradual transition from a condition approximating true solution to a distinctly colloidal state. The asphaltenes gradually separate from solution in the maltenes and become associated when the bitumen is cooled. This gives rise to a stable system, the colloidal properties of which become more pronounced as the temperature is lowered farther and farther. As a result, their straight line relationship only holds in narrow range of temperature.

(1) log viscosity vs. log ordinary temperature

$\log \eta = k - n \log t$

where n, k are constants.

This temperature-viscosity relationship has been used by Evans and Pickard (24), Lewis and Hillman (39), Lee and associates (35), and Mitchell and Lee (43). Resultant plot from this relationship has a slight curvature, but only over really wide ranges of temperature and the equation is reasonably applicable for narrow ranges.

(3) log viscosity vs. log absolute temperature

$\log \eta = k - n \log T_{abs}$.

This method as used by Lang and Thomas (32) differed from the preceding ones in that the log of the absolute temperature is used. From a scientific point of view, it is decidedly more rational, as it gives a relation which is absolute in basis.

(4) log viscosity vs. reciprocal of absolute temperature

$$\log \eta = \log A - B/T_{abs.} \log e$$

where A and B are constants.

This is based on Andrade's (8) fundamental equation for pure liquid.

(5) log viscosity vs. reciprocal of square of absolute temperature

$$\log \eta = k - m/T^2_{abs.}$$

Umstatter (68) used this formula and obtained a straight line relationship at the low temperature range and checked fairly well on the high temperatures, except that the slopes m varied at both the low and high temperature ranges. This clearly indicated that the structural system of the bitumens are affected by temperature.

(6) log log viscosity vs. log absolute temperature

$$\log \log \eta = k - m \log T_{abs.}$$

According to Ubbelohde and his co-workers (67), the most satisfactory graphical representation for the relationship between temperature and viscosity of liquid petroleum products was the log-log expression similar to the Nevitt's fundamental equation (48):

$$\log \log A\ (\mu + c) = k - m \log T_{abs}.$$

where c is a small correction factor which is equal to 0.8,

μ is the kinematic viscosity at absolute temperature, which can be converted to absolute viscosity by dividing the kinematic viscosity with the specific gravity of the material.

Works by Fair and Volkmann (25), and Saal (56) on tars all agreed the validity of this equation but they suggested that the correction factor for the kinematic viscosity be changed to 0.95 in order to establish a better straight line relationship.

Ordinarily, the kinematic viscosity of the viscous petroleum products are very high. Since the correction factor in the equation is extremely small, it can therefore be neglected without materially affecting the accuracy of the plotting or the viscosity value obtained by using the equation. Consequently, if the double logarithm of viscosity is plotted against the logarithm of the absolute temperature, a straight line relationship can also be obtained.

Methods of Viscosity Measurement

Methods of viscosity measurement involve a number of principles of motion. They all serve to describe, in one way or another, the resistance of fluids to flow when acted upon by external forces. A great number of these instruments have been devised for the measurement of viscosity in the relative values only. There are however, several distinct methods which are susceptible to mathematical treatment so that absolute viscosities may be obtained. The possible methods for measuring viscosity may be classified under three distinct groups.

Group I -- the measurement of the resistance offered to a moving body (usually a solid) in contact with the viscous fluid. The various methods of measuring viscosity under this group generally maintain the fluid in a nearly fixed position.

Group II -- the measurement of the rate of flow of a viscous fluid by the time efflux through the calibrated horizontal or vertical tubes or orifice.

Group III -- methods in which neither the flow nor the resistances to flow are measured. The decay of oscillations of a liquid, the decay of waves upon a free surface of the vibrations in a viscous substance and the rate of crystallization are the general means of obtaining the viscosities under this group of methods.

The more important classes of instruments as generally used in conjunction with the measurement of the viscosity of paving bitumen are grouped as follows (48):

1. Flow from an orifice
2. Capillary tube viscometers
3. Coaxial cylinder viscometers
4. Falling sphere viscometers
5. Rotating cylinder viscometers
6. Torsion type viscometers
7. Flow along inclined plane
8. Miscellaneous, such as vibrational viscometers and torsional cyrstal viscometers.

Each type of apparatus has its own special characteristics of limited applicability, sensitivity, advantages and disadvantages. Formulae converting measurements empirically and directly into absolute unit of viscosity have been derived for most of the instruments on the basis of the relevant theoretical principles involved.

In the torsion viscometers group, the drag of the liquid on a spindle rotating at a constant speed is transmitted in tension through a calibrated spiral spring and recorded on a dial rotated at the same speed. Rotating speed of the dial and the spindle can be changed so as to enable the behavior of bitumen to be studied at definite pre-determined rates of shear. Such facilities are particularly valuable in the study of identifying non-Newtonian bitumens and of establishing the presence and extent of thixotropic, dilatant and other rheological properties.

In efflux-type viscometers, the rate of shear is very low and cannot be varied.

Capillary tube viscometers based on the volume of flow per unit time are directly proportional to the pressure drop through the tube and the fourth power of the capillary diameter, and inversely proportional to its length. Viscometers of this type such as the Koppers Capillary Rise Viscometer (54) are particularly adaptable to high-viscosity and highly colored liquids. Deviations from purely viscous flow can be indicated and investigated by use of different applied vacua.

The conicylindrical viscometers are so designed that the shearing stresses can be controlled as desired.

Surface Tension and Surface Energy

The information of surface tension of paving bitumens is just as important as the viscosity to the asphalt paving technologists. The extent of adhesion, penetration and spreading of the bitumen on a mineral aggregate is greatly dependent on the relative relations between the surface tension of the liquid and of the solid.

The surface tension of a material as described by Adams (1, p. 2) is due to the attraction of the surface molecules for one another which acts simultaneously sidewise and inward, and as a result, it causes the surface to diminish to the smallest surface area possible. Against the inward molecular attractive forces is the work done or energy of each molecule to extend to the surface. This additional energy due to their superficial position may be regarded as surface energy which is numerically equal to the surface tension.

Saal (58) attempted to measure the surface tension of various bitumens by means of the apparatus developed by Du Nouy (in a hydrogen atmosphere); at high temperatures the bitumen was sufficiently liquid to permit the determination. With this apparatus, the force necessary to draw a metal ring of known diameter from the bitumen is determined. Correction must be applied for the peculiar shape of the liquid film which the ring formed.

Surface tension at or below the room temperature cannot be measured directly with the apparatus and had to be calculated by extrapolation from the data at higher temperatures. The total surface energy E_s was calculated by Saal from the following equation:

$$E_s = \sigma - T \frac{d\sigma}{dT}$$

where E_s = total surface energy in ergs/sq. cm.

σ = surface tension in dyne/cm.

T = absolute temperature.

The difference between the values obtained by linear extrapolation and the true values is very slight.

The correction factor for the ring method surface tension measurement depends upon the density of the liquid, the maximum pull on the ring and the dimension of the ring.

According to Zuidema and Waters (73), this correction can be calculated by the following formula:

$$(F - a)^2 = \left(\frac{4b}{\pi^2} \times \frac{1}{R^2}\right) \times \frac{P}{D-d} + C$$

where $F = \frac{S}{P}$ = correction factor

S = interfacial or surface tension, dynes per cm.

P = maximum pull on ring, dynes per cm.

D and d = densities of the lower and upper phases respectively (liquid-air, water-oil)

R = a constant, which depends upon the ratio r/R

r = radius of the wire of the ring, in the following manner

$$C = 0.04534 - 1.679 \frac{r}{R}$$

and $a = 0.7250$ and

$b = 0.0009075$ standard universal constants for all rings.

They found that the dependence of F upon the quantity $\frac{P}{(D-d)}$ obeys a parabolic law for any given ring.

Mack (39) devised another method for the measurement of surface tensions of bitumens at low temperatures without the influence of high viscosity. The method was based on the fact that a thread of bitumen suspended vertically is exposed to two different forces -- viz, gravitation and surface tension. If the thread is very short and gravitation is exceeded by surface tension, the latter tends to reduce the surface of the thread by reduction of its length. In the reverse case the gravitational force tends to elongate the thread. At a definite length of the thread, the gravitational and surface tension are in equilibrium, and the thread will retain its original length. This length corresponds to the height to which the bitumen would rise in a capillary tube of the same diameter as the thread. Thus the surface tension can be obtained at lower temperature without any correction by using the formula

$$S = \frac{1}{2} lrdg,$$

where S = surface tension in dyne/cm.

l and r = length and radius of the thread in cm.

d = specific gravity

g = gravitational constant.

The variation of surface tension of bitumen with temperature is of great importance to the question of wetting and spreading when the variable viscosity is held constant, their relationship in many instances being inversely proportional.

Investigation by Nellensteyn and Roodenburg (47) revealed that an abrupt transition point generally occurred in the surface-tension-temperature curve of the paving bitumen. Below a certain temperature the values obtained for the surface tension increase rapidly with decreasing temperature. Above this transition temperature the bitumen behaves like an ordinary oil. The surface tension in both cases varies as a straight line with the relative temperature change. The transition point is probably due to sudden decrease in the cohesion of the colloidal liquid as temperature increased.

Measurement of the surface tension of the solid to which the bitumen adhered is of considerable difficulty, and the progress has been very slow. Works by Zwikker and Loman (74) has been based on a simplified Antonow Theorem that the resulting interfacial tension at a surface of contact of a liquid and a solid is the difference of the surface tensions of the two materials. If the surface tension of the solid is much greater than that of the liquid, the latter spreads and measurement is not possible, but if the surface tension of the liquid is greater, the liquid assumes the shape of a drop and the angle of contact with the solid can be measured.

Theoretical Significance of Interfacial Tension and Contact Angle

Energy relations at the interface between bitumen and aggregate have been used by many workers (29) as the scientific approach to measure the durability of bituminous pavements in the presence of water. The stability of the mixture depends on the energy of the interfacial tension between solid and liquid. Although no method has yet been found of determining this interfacial tension directly (1, p. 178), yet the work of adhesion W_a of a liquid to solid can be easily measured indirectly. Dupré (21~~, p.~~ 2 44) was the first to indicate the relationship between work of adhesion per unit area of solid and their surface and interfacial tensions.

$$W_a = \gamma_{SA} + \gamma_{LA} - \gamma_{SL}$$

where γ_{SA} and γ_{LA} are the surface tensions of solid and liquid, γ_{SL} the interfacial tension between solid and liquid. This expression was suggested by Bartell ~~(9, p.~~ 9 3 44) as the adhesional wetting. While the work of spreading W_s was considered as the different free surface energy changes which occur during the process of spreading, he equated this free surface energy change as

$$W_s = \gamma_{SA} - (\gamma_{LA} + \gamma_{SL})$$

$$= \gamma_{SA} - \gamma_{LA} - \gamma_{SL}.$$

The two equations involve the difference between the two unknown solid surface tensions, and their differences can be found as the liquid frequently rests on the solid at a definite angle of contact, θ, measured in the liquid. Young (72) derived an expression for the equilibrium condition existing in this solid-liquid system in terms of this contact angle and the different interfacial tension as

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos\theta .$$

From this equation, Freundlich (26, p. 157) suggested that the difference between the surface tension of the solid γ_{SA} and the interfacial tension γ_{SL} be designated as the adhesion tension.

By combining Young's equation with the equation of adhesional wetting, the unknown solid surface tension was eliminated and the equation

$$W_a = \gamma_{LA}(1 + \cos\theta)$$

was generally used in the calculation of the adhesional wetting of the bitumen to aggregate.

Stillwaag (61, p. 11) and English (23) used the angle of contact made by a liquid with the solid on which it rests as an indication of wetting ability in the measurement of adhesional phenomenon.

Bartell and co-worker (10) introduced a new constant to Young's expression for use where liquids possess zero angle of contact. They developed the Bartell cell technique for the measurement of adhesion tension between liquid and solid. This method was used by Nicholson (49) in the early attempt to determine the adhesion tension in bituminous paving mixtures.

Hallberg (27) used Bartell's displacement cell together with his own adhesion meter and was able to measure directly the interfacial tensions of bitumen-aggregate and bitumen-water. Together with the corresponding angle of contact, he successfully calculated the degree of adhesion in the bituminous mixtures under the effect of water with amazingly good results.

Mack (39), however, analyzed the energy relations at the interface between bitumen and aggregate with different methods. He measured the interfacial tension between solids and liquid by allowing the powdered solids to settle freely in liquid. The volume to which a lyophilic powder settles in a pure bitumen solution is proportional to the interfacial tension between the two phases. The validity of the extrapolation of the diluted bitumen solution to the full concentration is doubtful as the concentration-interfacial tension curve might not hold a straight line variation to the hundred per cent concentration. This physico-chemistry approach is, however, quite valuable for the basic investigation of the adhesion problem between bitumen and aggregate.

The Phenomenon of Wetting

The phenomenon of wetting has been recognized by many experimenters as an important step in the coating of bitumen binder to aggregate, in the performance of the contact insecticide, process of detergency in laundering and the problem of flotation of valuable mineral.

Nuttall and Cooper (50) regarded the wetting of a solid by a liquid as analogous to the spreading of a liquid on another liquid. They assumed that liquid on solid would follow the equation of spreading of liquid to liquid. The surface tension of the lower liquid must be greater than the surface tension of the upper liquid plus the interfacial tension, if spread is to take place. They reasoned that wetting will occur if the former value is greater than the latter.

Moore (44) considered wetting as slight chemical affinity exhibited between liquid and solid, and stated that a given liquid will spread on a given solid when its adhesion to the solid is greater than the cohesion of the liquid.

Woodman (71) differentiated spreading as indicating the area covered by a drop of given liquid, and wetting as the amount of the liquid adhering to a glass slide after drainage. Such adherence is influenced by the viscosity of the liquid studied.

Methods of Angle of Contact Measurement

The study and use of contact angles in connection with bitumen and aggregate has always been complicated by the prevalence of hysteretic effects of the measured angles and the viscosity of the bitumen. There are various methods available for measuring contact angles of organic compounds on solids, however only a few may be of practical use with bituminous materials.

Among these methods only four can be used to measure contact angles formed by bitumen on aggregates. They are:

(1) Direct measurement.

Langmuir and Schaefer (33) and others have used this method by placing a drop of the liquid in question on a flat solid surface or an air bubble trapped purposely under a solid. A magnified image of the drop or the bubble is thrown on a screen, and the angle of contact is marked and measured by means of a protractor. Or the image is photographed and the angle then measured from the enlargement. This method is very simple but cannot be utilized when the lower part of the drop cannot be seen distinctly if the edge of the solid is not flat. Measurements obtained by this method will only be a single point on the surface. Such a procedure is rather unsatisfactory for working with naturally occurring objects having variable surface properties such as in the case of aggregate surface. However, for uniform homogenous surfaces, this point measurement generally yields a fairly reliable result.

(2) Computation from the drop size.

The contact angle formed by a drop on a solid was computed from the dimensions of the drop. The computation is simple if the droplet is small and may be treated as a spherical segment. The gravity effect on a small droplet is so small that the assumption of the drop being a segment of a sphere is justified.

Bashworth and Adams (11), Mack (40), and Bikerman (12) indicated the angle between the horizontal plane through the base of the drop and the tangent to the spherical surface at the point of contact is

$$\theta = 2 \tan^{-1} \left(\frac{h}{x} \right)$$

where h is the greatest height of the drop and x, the radius of the base of segment. The distance x is measured by a micrometer eyepiece of a low power microscope, while h can only be measured with the high power travel microscope.

Often the determination of this height h of a small droplet is not convenient, especially in the case of small angles on a surface which is not perfectly plane. Mathematical relationship between volume of the sphere and its radius is related to the height of the sphere segment, so

$$\frac{V}{x^3} = \frac{\pi(2-3\cos\theta + \cos^3\theta)}{3\sin^3\theta}$$

where V is the volume of the sphere segment. Computation of the angle from the drop size yields an average value of all the contact angles occurring along the perimeter of the drop, and is independent of the form of the solid surface. For the measurement on aggregate surface this is the only method that has practical applicability.

(3) Level surface method.

Adam and Morrell (3) have used the quadrilateral plate immersed in the liquid and tilted until the liquid surface remains undistorted right up to the line of contact. The angle made by the plate with the horizontal and measured by means of a protractor is the angle of contact.

(4) Displacement pressure method.

Bartell and Osterhof (10) indicated the pressure P required to prevent a liquid of surface tension γ from entering a capillary of radius R as:

$$P \pi R^2 = 2 \pi R \gamma \cos\theta$$

and so

$$\theta = \cos^{-1} \frac{PR}{2\gamma} .$$

This method has been used by many workers in the study of adhesion between bitumen and aggregate with the presence of water. Aggregate used for such studies has to be pulverized into fine powder in order to pack into the displacement cell.

Contact angle between powdered aggregate and bitumen by this method may not be the same for the aggregate not pulverized.

Hysteresis of the Contact Angle

Hysteresis of contact angle is a complex phenomenon and the predominating factors contributing to it depend on both the chemical and physical nature of the solid surfaces. If a drop of liquid which is placedon the solid surface is tilted or a droplet is withdrawn or added to the first drop, the contact angle on the advancing edge is always greater than that on the receding edge. Sulman (62) called this effect the hysteresis of the contact angle.

Experiments of Ward and his collaborators (69) suggested that hysteresis is a result of frictional resistance to movement of the liquid over the surface of the solid.

Adam and Jessop (2) attempted to formulate hysteresis as an effect of a frictional force F, operating along the surface with equal intensity. When they are in equilibrium, the adhesion tension (A) for the advancing motion is

$$A = \gamma_{LA}\cos\theta_A + F$$

and for receding motion

$$A = \gamma_{LA}\cos\theta_R - F$$

θ_A and θ_R being the advancing and receding angles. Combining the two equations, the equilibrium contact angle which would be obtained in the absence of friction F will be (1, p. 181)

$$2\cos\theta = \cos\theta_R + \cos\theta_A .$$

Effect of Surface Roughness on the Contact Angle

The effect of roughened surface to the wetting or spreading problem of the liquid and solid is quite significant. It has been reported (13, p. 332) that the contact angles on rough solids are greater than on relatively smooth surfaces, and the hysteresis of wetting increases with the degree of roughness.

According to Bikerman (14), the roughen effect to wetting differed according to whether (a) the surface is grooved or ridged, (b) the drops expand or contract, and (c) the equilibrium contact angle is acute, right or obtuse.

Wenzel (70) indicated such effect is a direct function of the ratio between the actual surface to geometric surface, or the roughness factor r. The contact angle formed will be

$$\theta_r \text{ (rough surface contact angle)} = \cos^{-1} r \cos\theta .$$

Published data by Lee (34) on adhesion in relation to bituminous road materials indicated that the differences of contact angle made by tar on highly polished glass and stone surfaces under water were due to various degrees of roughness of the solid surface, and this variation is much greater than the nature of the materials. His results showed that the binder has much more difficulty in wetting a rough stone surface which is already in contact with water than in wetting a smooth surface. In addition to the frictional effect of the rough surface, water is presumably entrapped in the minute crevices of a rough surface and prevents the tar from wetting the solid. Of course, such changes as indicated in the adhesion tension equation will give a larger angle of contact.

Experiments by Thiessen and Schoon (63), and Parker and Smoluchowski (51) on crystals and metal have demonstrated the significant effect on the contact angle due to various degrees of the roughness of the solid surface to be wetted, however the variation does not necessarily differ in direct proportion to the measurable degree of roughness.

INVESTIGATION

The experimental investigation of this problem was made on the bitumens most commonly used by the Mid-Western State Highway Departments for bituminous paving purposes. Selection of test procedures and equipments were based on the simplicity of operation and control. To minimize some of the variables involved, the preliminary study on contact angles between bitumens and solids were made on microscopic slides, then measurements were made on both polished and split aggregate surfaces.

Materials

Kinds of bitumens

Twenty-eight bitumen samples of different grades were included in this study. They were furnished through the courtesy of four major refineries located in the mid-western states.

Physical properties of these bitumens are given in Tables 1 through 4. Most of the informations tabulated were furnished by the refineries and have been checked with the standard tests (4, 7) described by the American Society for Testing Materials.

Table 1. Characteristics of bituminous materials

Sample no.	Tests									
	Penetration 77/100/5	Loss on heat % at 325° F.	Specific gravity 77° F.	Solubility in CCl_4, %	Solubility in CS_2, %	Flash point ° F.	Softening point, ° F.	Ductility 77° F., cm.	Asphaltene in 86° Be' Naphtha, %	Spot test
A-1	33	0.008	1.012	99.54	99.63	613	150	100^+	27.9	negative
A-2	59	0.018	1.014	99.60	99.73	587	140	84	23.7	negative
A-3	61	0.031	1.011	99.47	99.56	601	135	100^+	23.4	negative
A-4	73	0.017	1.015	99.62	99.84	598	135	100^+	22.8	negative
A-5	90	0.021	1.081	99.76	99.90	570	126	100^+	21.7	negative
A-6	108	0.014	1.020	99.64	99.92	576	129	100^+	21.5	negative
A-7	123	0.036	1.021	99.82	99.90	568	123	150^+	18.8	negative
A-8	161	0.014	1.012	99.84	99.92	549	120	150^+	18.6	negative
A-9	217	0.050	1.003	99.36	99.48	550	119	--	17.6	negative
Test method	ASTM D-5	ASTM D-6	ASTM D-70	ASTM D-165	ASTM D-4	ASTM D-92	ASTM D-36	ASTM D-113	*	AASHO T-102

*Csanyi and Fung Modified Method. Proc. Assoc. of Asphalt Paving Technologists. vol. 23, pp. 64-77, 1954.

Table 2. Characteristics of bituminous materials

Sample no.	Tests									
	Penetration 77/100/5	Loss on heat % at 325° F.	Specific gravity 77° F.	Solubility in CCl_4, %	Solubility in CS_2, %	Flash point ° F.	Softening point, ° F.	Ductility 77° F., cm.	Asphaltene in 86° Be' Naphtha, %	Spot test
B-1	45	0.026	1.007	99.50	99.72	654	142	--	4.9	negative
B-2	58	0.010	1.011	99.73	99.81	635	139	--	23.6	negative
B-3	67	0.006	1.004	99.54	99.62	644	138	100+	23.4	negative
B-4	82	0.008	1.008	99.61	99.72	630	130	100+	19.7	negative
B-5	86	0.002	1.021	99.67	99.80	620	126	100+	19.5	negative
B-6	117	0.008	1.001	99.70	99.82	598	123	100+	19.1	negative
B-7	141	0.001	1.008	99.42	99.84	612	120	100+	18.4	negative
B-8	190	0.010	1.019	99.56	99.82	596	115	100+	14.2	negative
B-9	216	0.013	1.042	99.64	99.80	598	114	--	9.8	negative
Test method	ASTM D-5	ASTM D-6	ASTM D-70	ASTM D-165	ASTM D-4	ASTM D-92	ASTM D-36	ASTM D-113	*	AASHO T-102

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*Csanyi and Fung Modified Method. Proc. Assoc. of Asphalt Paving Technologists. vol. 23, pp. 64-77, 1954.

Table 3. Characteristics of bituminous materials

Sample no.	Tests									
	Penetration 77/100/5	Loss on heat % at 325° F.	Specific gravity 77° F.	Solubility in CCl_4, %	Solubility in CS_2, %	Flash point ° F.	Softening point, ° F.	Ductility 77° F., cm.	Asphaltene in 86° Be'	Spot test
C-1	54	0.010	1.019	99.65	99.73	625	133	100$^+$	21.8	negative
C-2	61	0.040	1.001	99.74	99.90	610	126	100$^+$	20.5	negative
C-3	76	0.030	1.012	99.64	99.86	602	120	100$^+$	19.9	negative
C-4	90	0.020	1.006	99.60	99.92	570	118	150$^+$	19.3	negative
C-5	116	0.060	1.014	99.60	99.84	564	113	150$^+$	15.5	negative
C-6	178	0.020	1.014	99.50	99.94	570	105	--	11.1	negative
C-7	306	0.080	1.005	99.30	99.90	558	104	--	10.3	negative
Test method	ASTM D-5	ASTM D-6	ASTM D-70	ASTM D-165	ASTM D-4	ASTM D-92	ASTM D-36	ASTM D-113	*	AASHO T-102

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*Csanyi and Fung modified method. Proc. Assoc. of Asphalt Paving Technologists. vol. 23, pp. 64-77, 1954.

Table 4. Characteristics of bituminous materials

Sample no.	Tests									
	Penetration 77/100/5	Loss on heat % at 325° F.	Specific gravity 77° F.	Solubility in CCl_4, %	Solubility in CS_2, %	Flash point ° F.	Softening point, ° F.	Ductility 77° F., cm.	Asphaltene in 86° Be'	Spot test
D-1	51	0.050	0.998	99.41	99.54	638	122	100^+	22.1	negative
D-2	98	0.090	0.990	99.65	99.82	620	119	100^+	19.1	negative
D-3	191	0.020	0.993	99.70	99.89	612	106	100^+	13.3	negative
E-1	92	0.080	1.188	72.94	76.64	505	118	150^+	31.4	positive
E-2	86	0.220	1.174	99.69	99.76	545	112	150^+	16.5	positive
Test method	ASTM D-5	ASTM D-6	ASTM D-70	ASTM D-165	ASTM D-4	ASTM D-92	ASTM D-36	ASTM D-113	*	AASHO T-102

*Csanyi and Fung modified method. Proc. Assoc. of Asphalt Paving Technologists. vol. 23, pp. 64-77, 1954.

After this study had been in progress for some time it was decided to include some positive spot cracked bitumens for the purpose of comparison.

Microscopic glass slides

The non-corrosive, uniform thickness microscopic slides of 3" x 1" x 3/64" size were used. These slides were made of high temperature resistant hard glass that will stand high temperature without breakage. Each slide was carefully cleaned three times in sequence with carbon tetrachloride, acetone and distilled water, then allowed to dry in air protected from dust before they were used. Marks at the quarter points on the bottom side of each slide were made by a diamond marking pencil and served as reference positions where bitumen droplets were applied.

Kinds of aggregates

Two types of aggregates were used: soft limestone and very hard Virginia black trap rock.

The limestone was obtained from the Ray Cook Quarry located in Story County, Iowa. They were composed of stones with the Los Angeles wear of 37 per cent. The color texture is of light pink to grey. Split surfaces of these stones are generally quite smooth. Their apparent specific gravity is 2.76 and the stones have an average absorption of 4.3

per cent.

The black trap rock was obtained from the Arlington Stone Company, Leesburg, Virginia. This aggregate was quarried in London County, Virginia. It consists of plagioclase, feldspar and pysozenes of minocline class, and is considered to be highly hydrophilic in character. They are very hard and tough with the Los Angeles wear of 19 per cent. The split surface is very irregular and corrugated. The apparent specific gravity is 2.99 and the rock has an average absorption of 0.84 per cent.

Both aggregates used for this study were split into small sizes of approximately one inch in diameter, and they were carefully washed twice with distilled water to remove all the fine dust particles.

Method of Procedure

Method of measuring viscosity of bitumens

Absolute viscosities of all the bitumen samples were measured over a range of temperatures from 140° F. to 400° F. by two viscometers. The Koppers Capillary Rise Viscometer was used to measure the viscosities of the samples at temperatures from 140° F. to 180° F., while for temperatures ranging from 150° F. to 400° F. the Brookfield Sychrolectric Viscometer was used.

Koppers Capillary Rise Viscometer measurement. For each bitumen sample, approximately 10 ml. of material was placed in the sample cup, with the sleeve and capillary tube assembled. The unit was immersed in the constant temperature water bath for 30 minutes. The capillary tube was then lowered until the end of the tube was immersed to a depth of 1 cm. in the bitumen sample. It was allowed to remain for another 15 minutes in the bath before the test started. A vacuum equal to 40 cm. of Hg was applied to the top of the capillary tube through the vacuum reservoir. The time required for the bitumen meniscus to rise between 2 to 4 cm. or 4 to 5 cm. graduation marks in the capillary tube was noted. The absolute viscosity of the bitumen at the water bath temperature was calculated by the equation

$$\eta = \frac{g r^2 \rho \Delta t}{8\left[\left(\frac{H}{\rho}+\lambda\right) \log \frac{\left(\frac{H}{\rho}+\lambda-l_1\right)}{\left(\frac{H}{\rho}+\lambda-l_2\right)} - (l_2-l_1)\right]}$$

where η = absolute viscosity in poises

g = gravitational constant, cm. per second per second

r = radius of the capillary bore, cm.

ρ = density of bitumen, g. per ml.

Δt = time of capillary rise, second

H = vacuum applied, cm. of water

l_1 = initial height of bitumen in capillary at start of timed interval, cm.

l_2 = final height of bitumen in capillary at end of timed interval, cm.

λ = depth of immersion of capillary in bitumen, cm. (1.0 cm.).

With some of the constants substituted into the general formula, the viscosity for the capillary rise between 2 to 4 cm. equals:

$$\eta^*_{2-4} = (90.15 \times h \times \Delta_t)\rho$$

for 4 to 5 cm. capillary rise, the viscosity is:

$$\eta^*_{4-5} = (120.10 \times h \times \Delta_t)\rho$$

where h is the vacuum applied in cm. of mercury.

The effect of variation in density of all the bitumens tested over the entire temperature range is less than one per cent of the resulting viscosity measurement. Densities of the bitumens used in the calculation of the viscosity therefore were based only on the values obtained at 140° F.

A total of nine viscosity readings for each bitumen sample were run at every 10° F. interval from 140° F. to 180° F. Tests were repeated at least three times for each temperature interval with maximum allowable deviation of not more than 3 per cent between the three trials. The

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*These two formulae are inaccurate, particularly for low value of h, because they do not take into account the effect of the static head of the fluid column on the value of the driving force h.

average of the three trial readings is reported as the viscosity of the sample at the tested temperature.

Brookfield Sychro-lectric Viscometer measurements. Viscosities of bitumen at higher temperature ranges (150° F. to 400° F.) were measured by the Model LV Brookfield Sychrolectric Viscometer. This equipment measures the drag produced upon a spindle rotating at a definite constant speed while immersed in the bitumen under test. The equipment has four spindles of different sizes and four different rates of shear (proportioned to four rotating speeds). By proper selection of spindle and speed, the viscosity measurement can be obtained as high as 1,000 poises.

To maintain constant rate of shear with each sample tested, only the high viscosity spindle (no. 4 spindle) and the two lower rotating speeds were used on all the samples. However, check readings were occasionally taken with the other spindles and rotating speeds for purpose of checking the flow characters of the bitumens.

For the test, a 500 ml. tall-form Berzelius beaker containing approximately 40 ml. of bitumen was heated in an oil bath until it reached a temperature of 410° F. The Brookfield viscometer, with a calibrated iron-constantan thermocouple attached to the outside surface of the guard for temperature measurement, was lowered into the bitumen to a certain depth. During the test, temperature of the bitumen was gradually reduced by running cool water through the cooling system of the oil bath. At every 10° F. reduction in temperature, as indicated by the pyrometer, a viscosity reading was taken. Tests continued until bitumen temperature reached 150° F. Duplicate trials were made on several samples of each bitumen and the average results were used for the analysis.

To insure that the sample had not been polymerized during the 410° F. oil bath heating, asphaltene content was checked for each original sample and those that had been heated to 410° F. Any change of asphaltene content of more than 2 per cent required repetition of the viscosity test of the sample at a lower temperature, such as 350° F., or as low as 300° F., dependent on the result of the asphaltene content test.

Surface tension measurements

The surface tension of the bitumen was determined by a Ceno-du Nouy Tensiometer Model 70530. This apparatus gives the static values (i.e., the equilibrium values) in dynes per centimeter. The measurements were made over a temperature range of 150° F. to 400° F. except when the asphaltene test indicated that such sample cannot be heated to 400° F.

For surface tension determinations, a pyrex crystallizing glass dish, 2 inches in diameter by $1\frac{1}{2}$ inches in depth, was equipped with a fine iron-constantan thermocouple wire. The tip of the wire extended from the edge to the center of the dish and was about $\frac{1}{4}$ inch from the bottom. About 400 ml. of the bitumen under study was first oven-heated to 410° F. in a covered beaker. As soon as the sample reached the oven temperature, 50 ml. of this heated sample was placed in the test dish. Surface tension measurements were made in the dish, with readings taken at every 10° F. drop in temperature. Values obtained at the various temperatures were corrected according to the methods given by Harkin (28) and Zuidema et al (73).

Contact angle measurement

Two methods of contact angle measurement were used. All angles of contact between the bitumen and microscopic slides were measured by the direct optical method for reason of simple and speedy operation. Angle of contact between bitumen and aggregates, however, were measured indirectly by the calculation of droplet size formed on the aggregate surface.

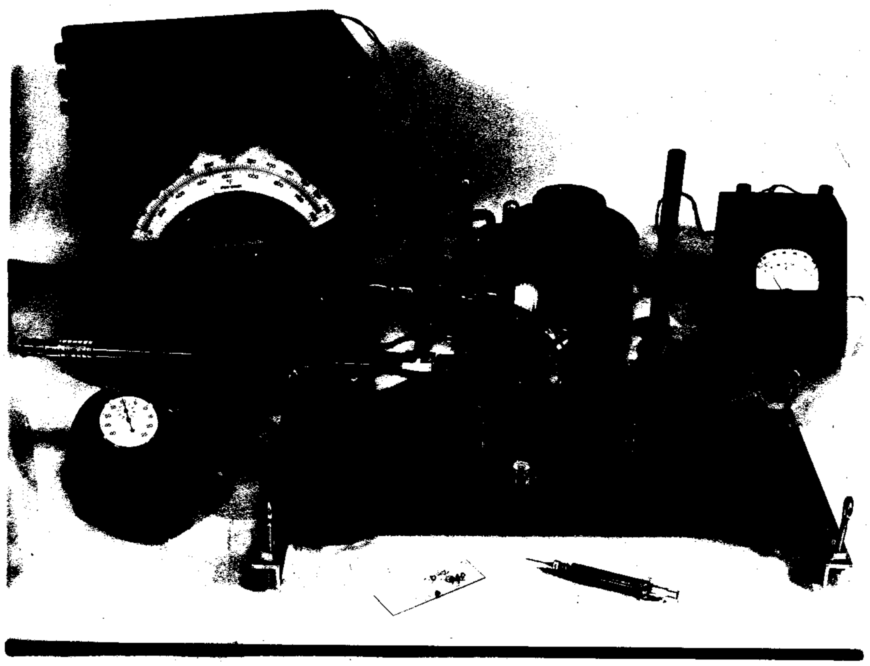
Preparation of slides. Slides used for contact angle measurements were heated by a 250 watt General Electric strip heater, which was mounted on a leveling platform made of asbestos board and aluminum angles. Surface elevations of the heater where the slide was placed, were checked with an 1/1000 inch Ames dial. Any deviation during heating was corrected by adjustment of the four leveling screws of the platform. Slide temperature was carefully controlled with a variac transformer and measured by a pyrometer equipped with a sensitive surface contact thermocouple (Plate 1).

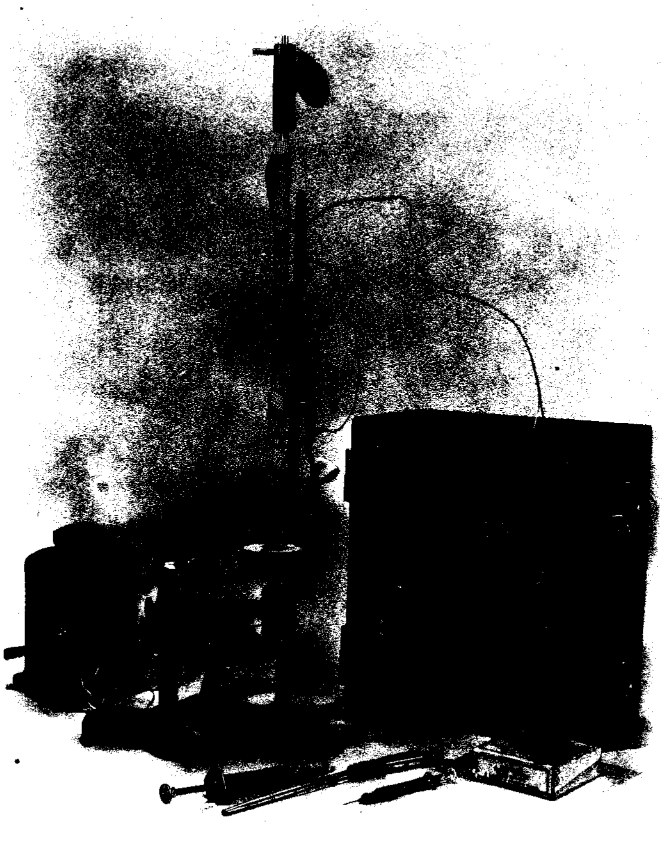
Preparation of aggregate specimen. Aggregates received from the quarries were first reduced to smaller size approximately one inch cube. Measurements of contact angles were made on types of surfaces, namely on a split surface and on a polished surface. The former was prepared by breaking the aggregates under a special design hydraulic hand press (18), while the latter was polished by a metallurgical grinder to a high degree of finish similar to the surface of a glass slide. The aggregate specimens were then weighed individually after they were washed and dried to constant weight.

In order to keep the flat surface of the aggregates in a level position ready for the application of bitumen droplet, a 2-ounce shallow tin can was filled with No. 100 U. S. Sieve silica sand in which each particle of aggregate was embedded. The plane of the aggregate surface was adjusted by a steel ruler placed across the rim of the can at several points and the final surface was checked by an Ames dial at three points within the area where the droplet was placed.

Plate 1. Devices for heating and measuring temperature of glass slides

Plate 2. Devices for applying bitumen droplet





Maintenance of constant temperature of the aggregate specimen during and after the application of bitumen droplets was extremely difficult and time consuming. In the early part of this investigation, the placing of droplets was performed inside a small glass door drying oven set at the required temperature. This temperature was measured on the surface of the aggregate by a surface contact thermocouple placed near the area where the droplet was applied. An alternate method was used in the later part of the study, in which the aggregate specimen was heated under two infra-red heat lamps located approximately ten inches above the surface. As soon as the aggregate reached the required temperature, the bitumen droplet was applied. The specimen can was carefully placed in the pre-heated oven for a time of about three minutes, during which the contact angle came to equilibrium. Results obtained from both methods agreed quite well within the accuracy of the measuring equipment.

Method of applying bitumen droplets. Drops of bitumen at 300° F. were deposited either from a pre-heated syringe (using sizes number 21, 22 and 25 short stem needles), in the volumes of 0.012, 0.010 and 0.008 ml., or from a serological pipette with volume being regulated by a calibrated screw micro-pipetter. Temperature of the bitumen in the pipette was kept constant by a 60 watt electric heating tape, and was measured by the sealed-in fine iron-constantan thermocouple (Plate 2). By touching the tip to the solid surface for a definite length of time, drops of a constant and reproducible size were detached onto the surfaces of the solid. The direction of motion of the discharged liquid bitumen can be controlled by adding or withdrawing some bitumen from the drop, and the proper advancing or receding angles of contact can be formed with ease.

After the droplets formed on the surface of the solids (glass slides or aggregates) and reached the state of equilibrium and further spreading ceased, the solid was immediately removed from the heating strip or from the oven and allowed to cool at room temperature for two hours. It was then placed in a freezer until the time when the angle measurement was made.

Measurement of contact angles. For high viscosity bitumen, the angle of contact on the glass surface was generally large and distinct. Measurement made using the method of image projection was found to be very satisfactory. The apparatus consisted of a 50-watt small SVE strip film projector as the light source, a condensing lens system, an adjustable stage or manipulator and a small picture frame mounted with a thin sheet of opal ground glass. Measurements were carried out at night or in a dark room.

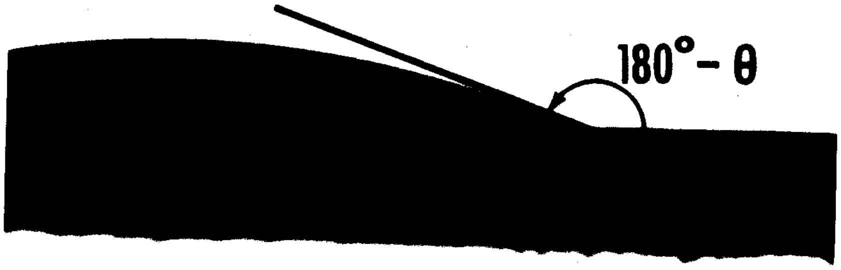
Each slide containing the small bitumen droplet was held in a level position by the manipulator. The exact position of the slide was located by trial. The beam of light from the projector passed through the condensing lens across the plane surface of the slide. A sharp image of the droplet was projected on the back of the opal glass where it was outlined with a pencil on the attached paper. From the outline the angles of contact at both sides were measured by means of a protractor.

When angle of contact is small, the image projection method sometimes gave inconsistent results. Measurements for such angles, and part of larger angles as well, were made under a microscope equipped with protractor eyepiece (Plate 3). The slides under study were held in vertical position by a specially machined plexiglass holder. This holder consisted of a $1\frac{1}{2}$" x $1\frac{1}{2}$" x $\frac{1}{4}$" angle of 3 inches long. Attached to the vertical leg of the angle was a 3" x $1\frac{1}{4}$" x $\frac{1}{4}$" plate. These served as a vise to hold the slide in true vertical position. The assembly was then clamped onto the mechanical stage of the microscope. Angles formed at the extreme edges of the droplet were measured by the protractor eye-piece (Plate 4). For each bitumen sample, 50 droplets were prepared and measured for each 20^{o} F. interval of the entire application temperature range.

The angles of contact formed by bitumen on aggregates cannot be measured by either of the above methods, except

Plate 3. Apparatus for measurement of contact angles formed on glass surface

Plate 4. Bitumen drop on the surface of glass slide as seen through the microscope


180° - θ

those that have been formed on highly polished surfaces. Another method, the principle of spheroidal segment (40), was used. Angles were calculated from the greatest height and radius of the droplet segment. Droplets on the surfaces of aggregate either embedded in fine sand in an ointment can or mounted on a paraffined glass plate, were measured under a high power Leitz Ortholeux research microscope (Plate 5). Fine talcum powder was sprinkled on the surface of the droplet to permit better focussing. The size of the base of the droplet was measured by a micrometer eyepiece, while its greatest height was obtained by successively focussing on the top and the base of the segment. The differences of depths of focus as indicated by the vernier of the fine focussing adjustment gave the greatest height of the droplet.

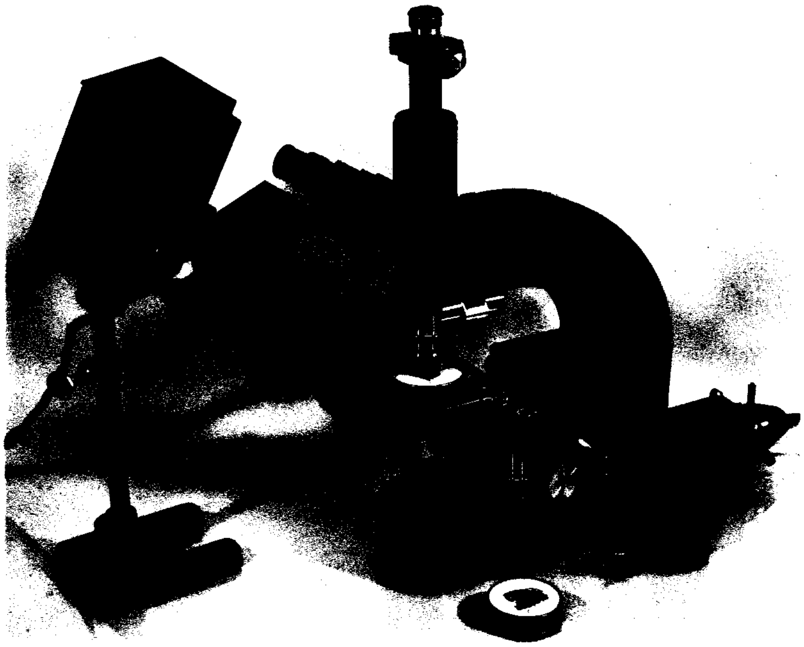
Contact angles formed on a solid can also be calculated from their respective radius and volume. The volume for each droplet can either be measured from the weight added to the solid or from the decrease of weight in the pipette after each drop has been delivered. In most cases, the volume of each drop can be calculated from the displacement of the pipette with reasonable accuracy.

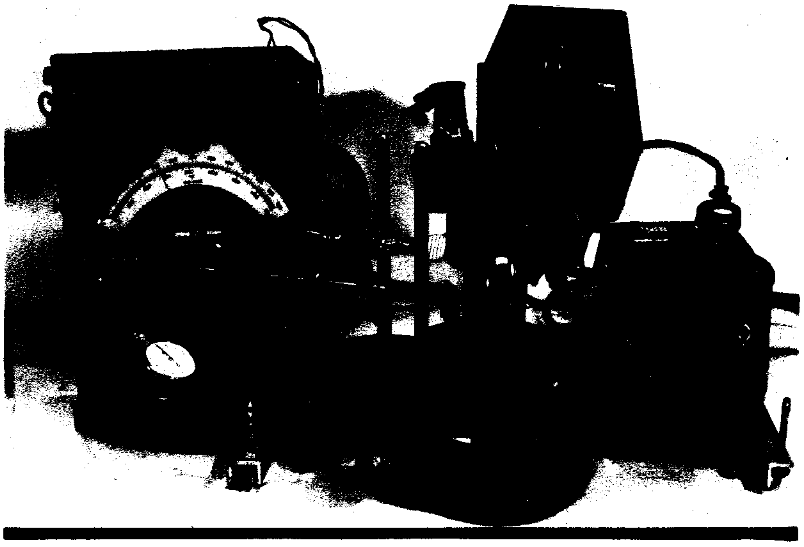
Measurement of the rate of spreading

Extension of a liquid drop on a solid is a combined action of their surface energies. The rate for such

Plate 5. Apparatus for measurement of height and diameter of the droplet

Plate 6. Apparatus for measurement of the rate of spreading





extension and the time needed for the drop to reach equilibrium are means of measuring the wetting ability of the viscous liquid on the solid. Investigation for the rate of spreading of the bitumen on heated solids was made under a low power stereoscope microscope. A Leitz camera lucida was used to reflect the image of a stopwatch on the objective. This attachment was properly mounted on top of the micrometer eyepiece (Plate 6). A series of readings were taken on the micrometer scale for the increasing diameter of the droplet at each second of time interval.

EXPERIMENTAL RESULTS

The object of this research was not to determine the exact values of the contact angles formed by bituminous binders on solids but to study the rheological properties of bitumen that are contributory to the degree of their adhesiveness. All of the pertinent experimental results have been summarized and tabulated in tables and graphical forms in order to aid the discussion and for comparison.

Effect of Temperature on Viscosity

It is a recognized fact that bitumen is readily affected, as to its constitution and properties, by the action of heat. At relative high temperature, bitumens tend to lose their plastic flow and approximate Newtonian liquids. Evaluation of these complex flow properties required proper selection of the rate of shear that can be applied to the sample under test. This is particularly important in the use of the rotational torsion viscometer. Figures 2 and 3 indicate the effect of the rate of shear on some bitumens at relatively low temperature. The use of the lower rate of shear, corresponding to the lower speed of rotation in the Brookfield Viscometer, was necessary to measure all of the bitumens

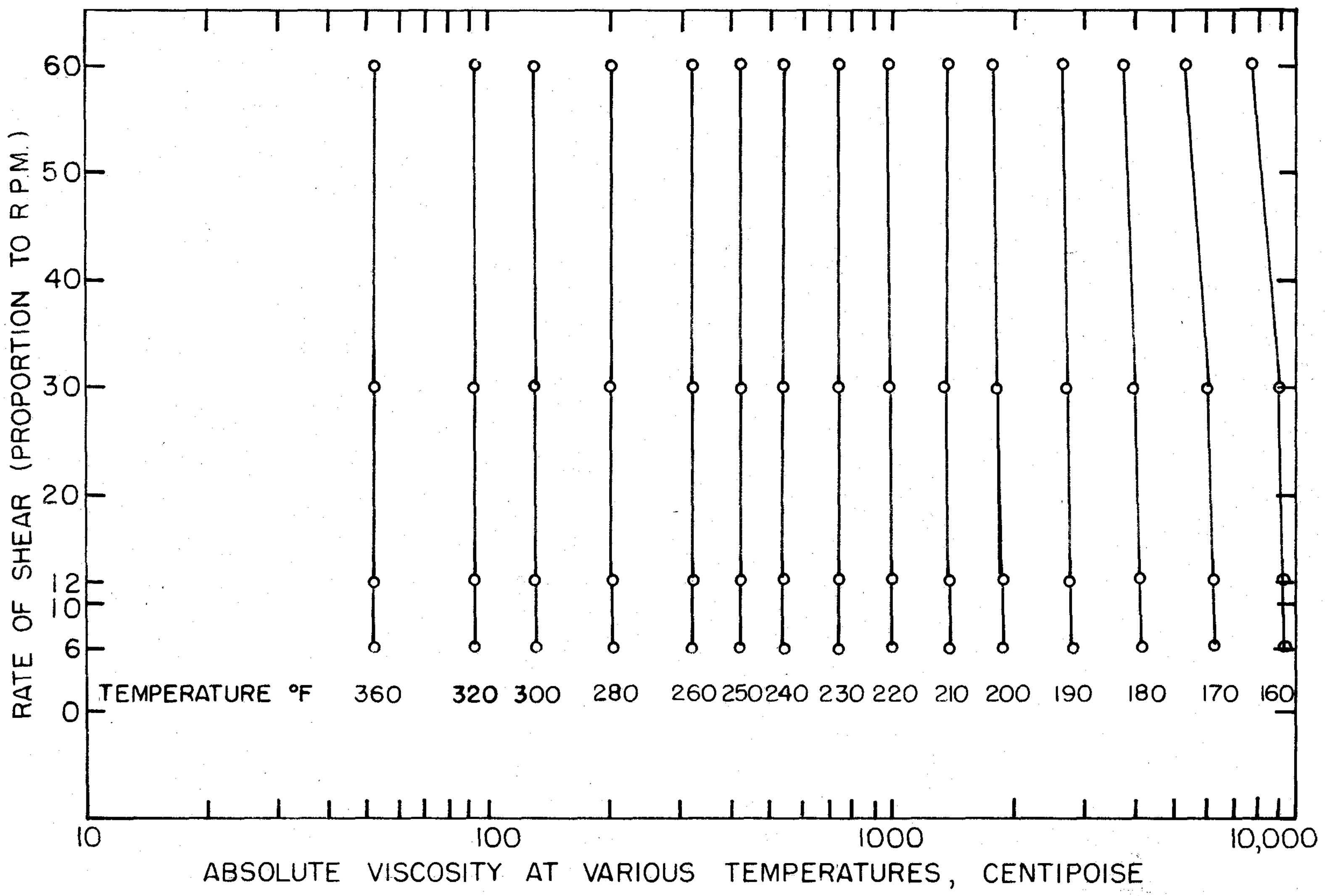


Fig. 2. Effect of rate of shear on the consistency of A-9 bitumen at various temperatures (Brookfield Synchro-lectric viscometer readings)

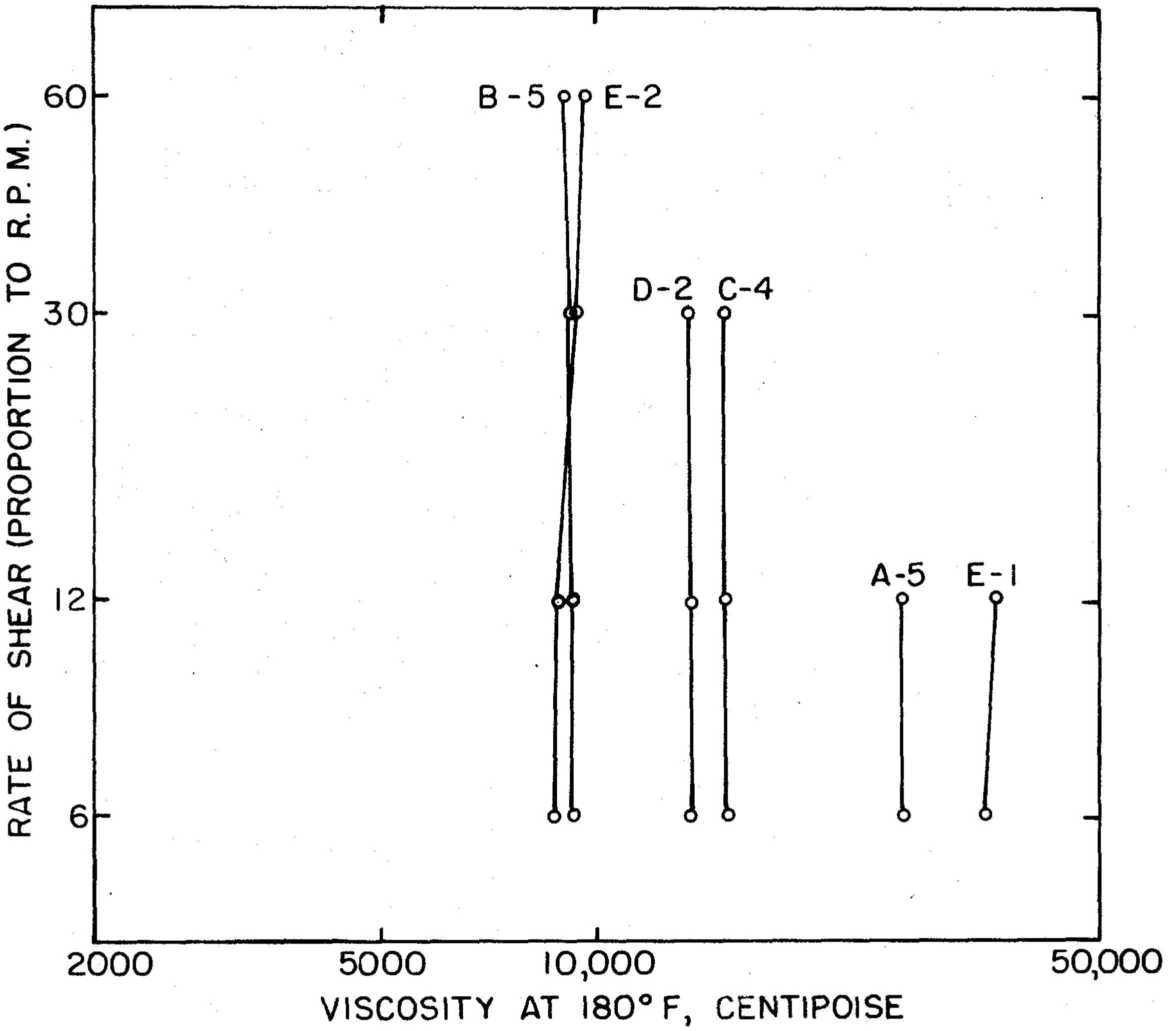


Fig. 3. Effect of rate of shear on the consistency of six bitumens

Table 5. Viscosities of six similar penetration bitumens as measured by three viscometers at temperature of 180° F.

Sample	A-5	B-5	C-4	D-2	E-1	E-2
Brookfield Synchro-lectric Viscometer At 6 R.P.M.	26,500	9,200	15,000	13,500	34,000	8,700
12 R.P.M.	26,200	9,200	15,000	13,500	35,800	8,900
30 R.P.M.	--	9,150	15,000	13,200	--	9,350
60 R.P.M.	--	9,000	--	--	--	9,700
Koppers' Capillary Rise Viscometer	27,000	9,200	14,800	13,800	36,700	8,300
Saybolt Furol Viscometer (converted)	26,800	9,450	15,600	14,000	42,000	8,500

under study. The results are shown in Table 5. These checked reasonably well with those obtained by Kopper's and Saybolt Furol Viscometers.

The relation between log viscosity and temperature for all the bitumens are shown in Figures 4 through 8. They are the average value from a number of tests.

The plots of log-log viscosity versus log. absolute temperature (459.58 + ° F. in degrees Rankine, or Fahrenheit absolute) gave a straight line over the range of tested temperatures from 150° to 380° F. These linear

Fig. 4. Variation of absolute viscosity with temperature for series A bitumens

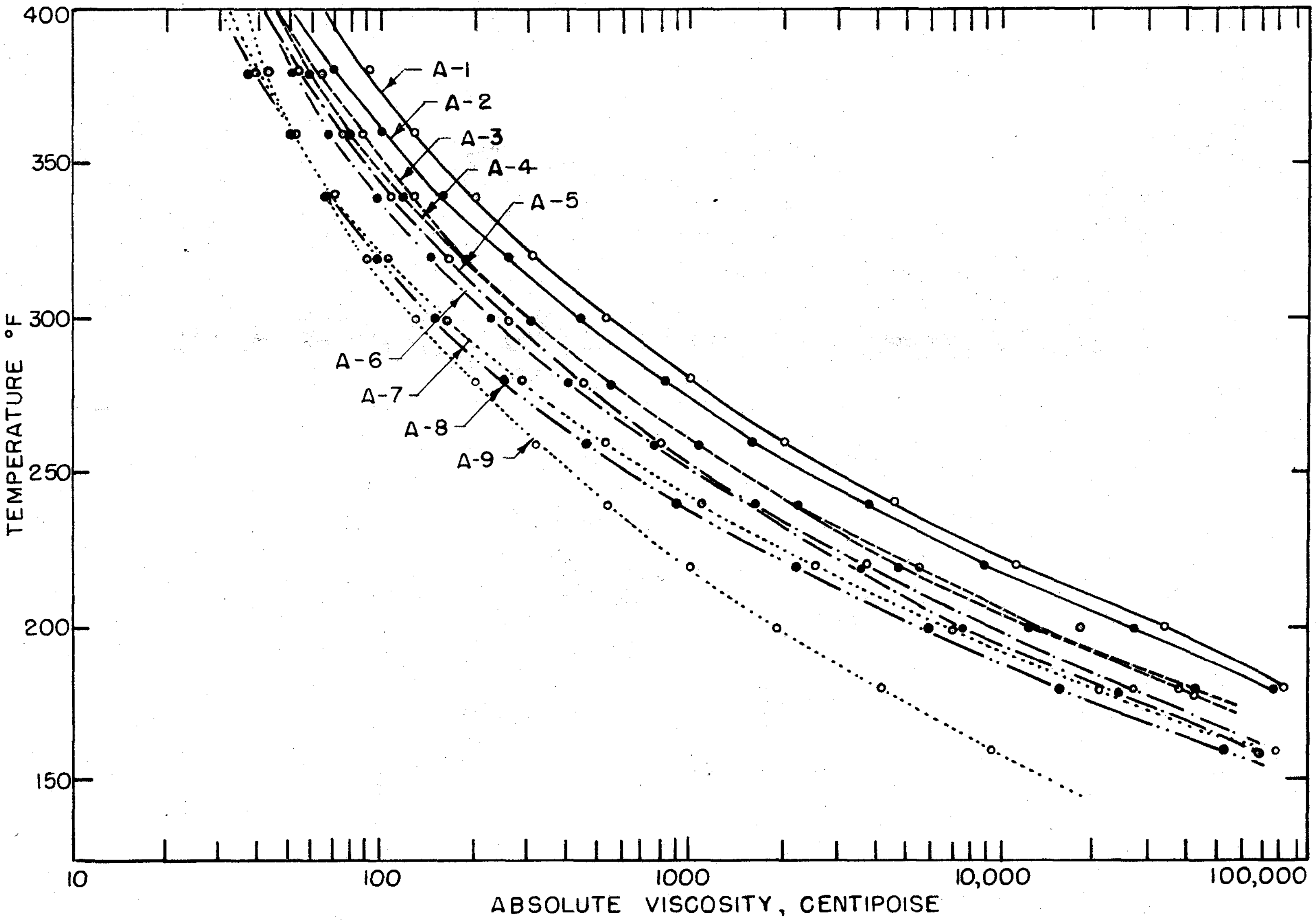
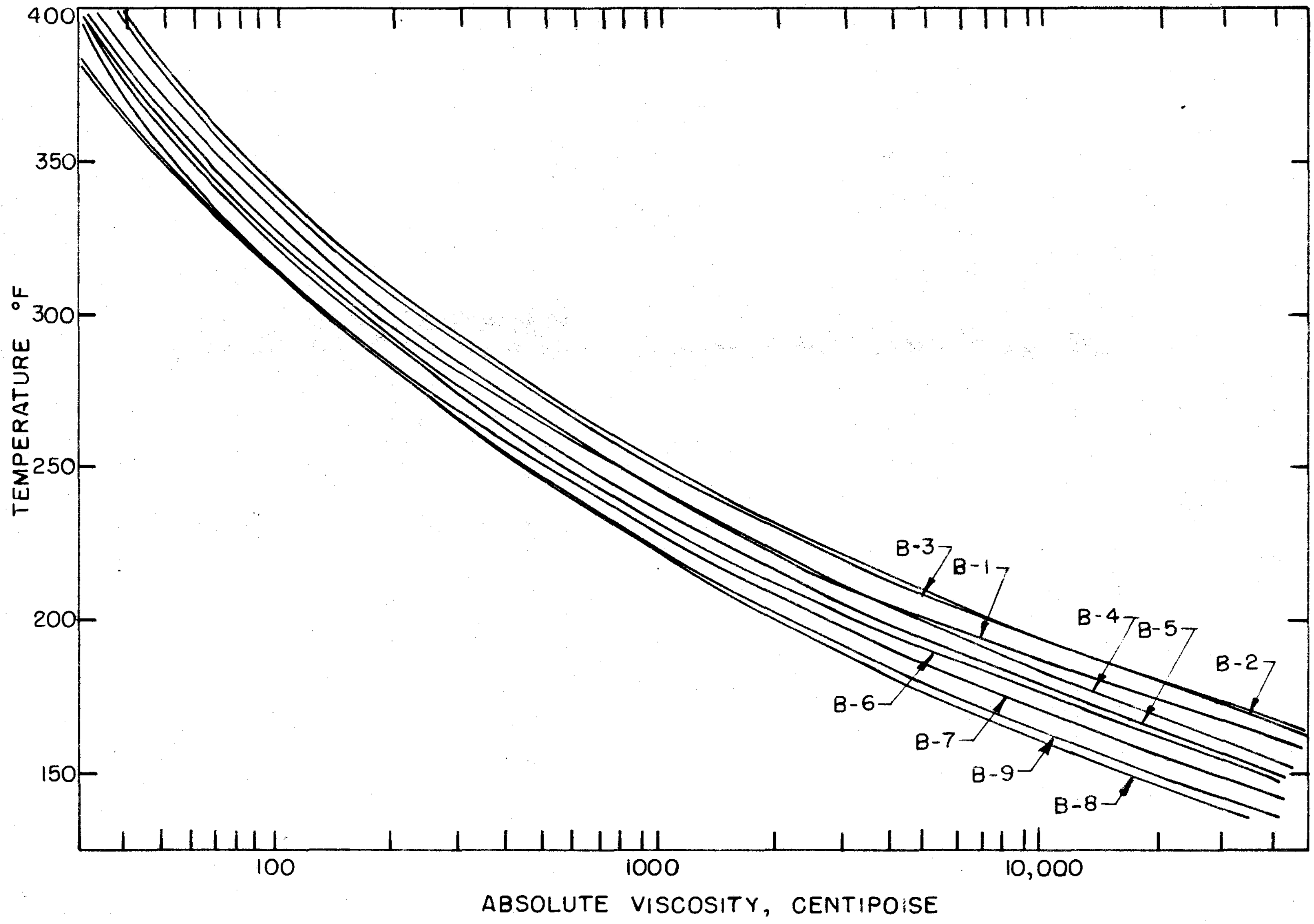

A-1
A-2
A-3
A-4
A-5
A-6
A-7
A-8
A-9
400
350
300
250
200
150
TEMPERATURE °F
10
100
1000
10,000
100,000
ABSOLUTE VISCOSITY, CENTIPOISE

Fig. 5. Variation of absolute viscosity with temperature for series B bitumens


400
350
300
250
200
150
TEMPERATURE °F
100
1000
10,000
ABSOLUTE VISCOSITY, CENTIPOISE
B-3
B-1
B-4
B-5
B-2
B-6
B-7
B-9
B-8

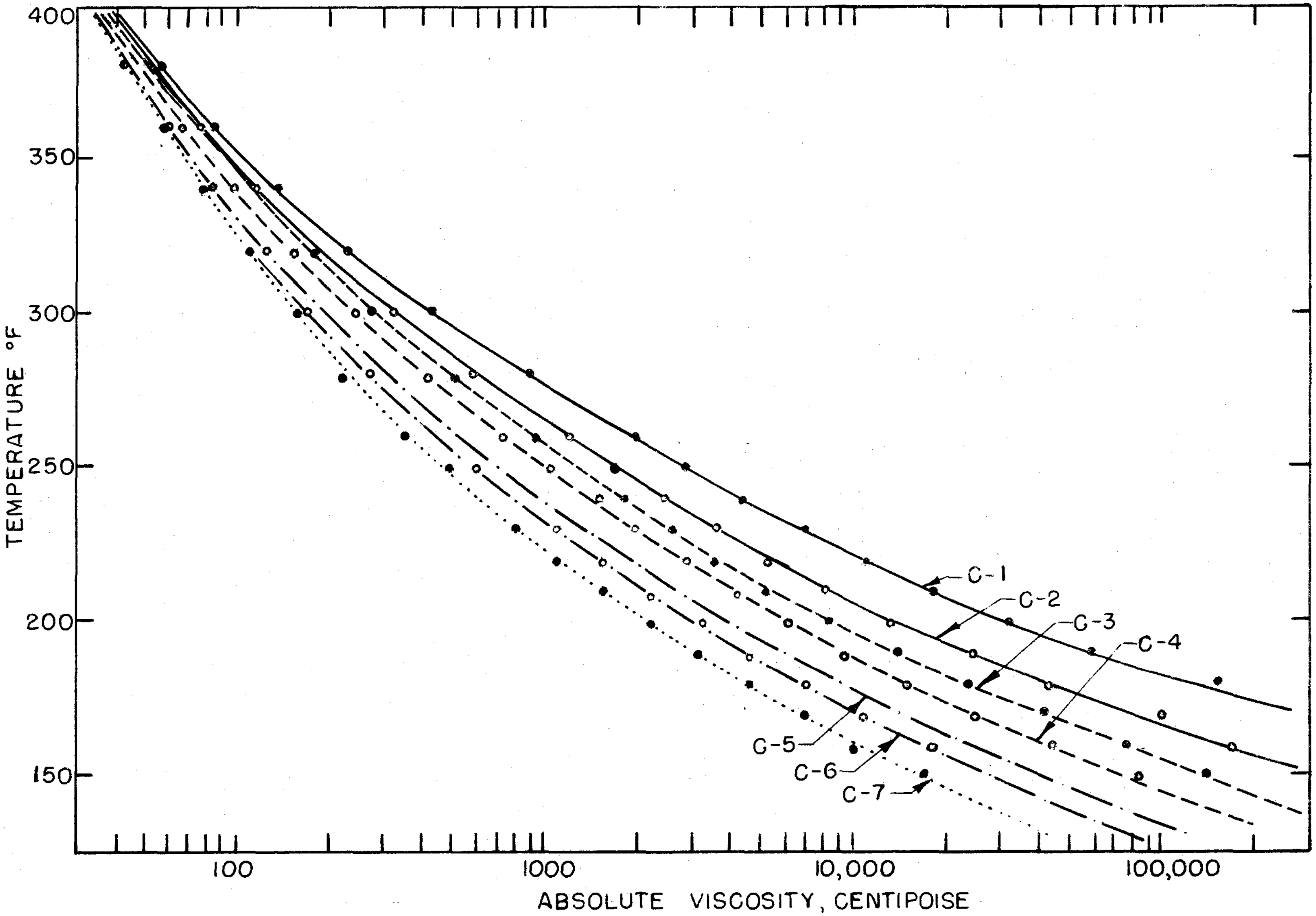


Fig. 6. Variation of absolute viscosity with temperature for series C bitumens

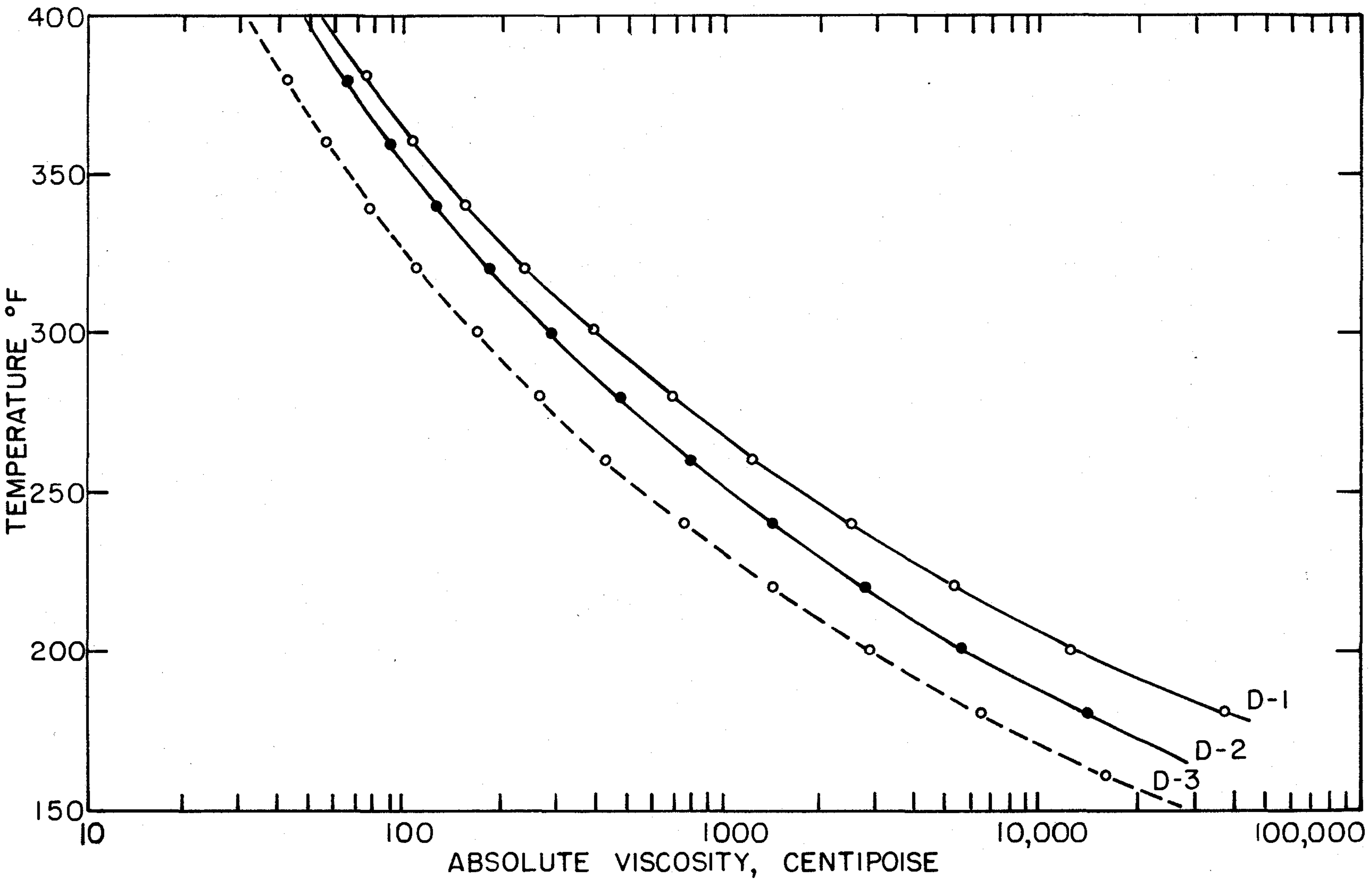
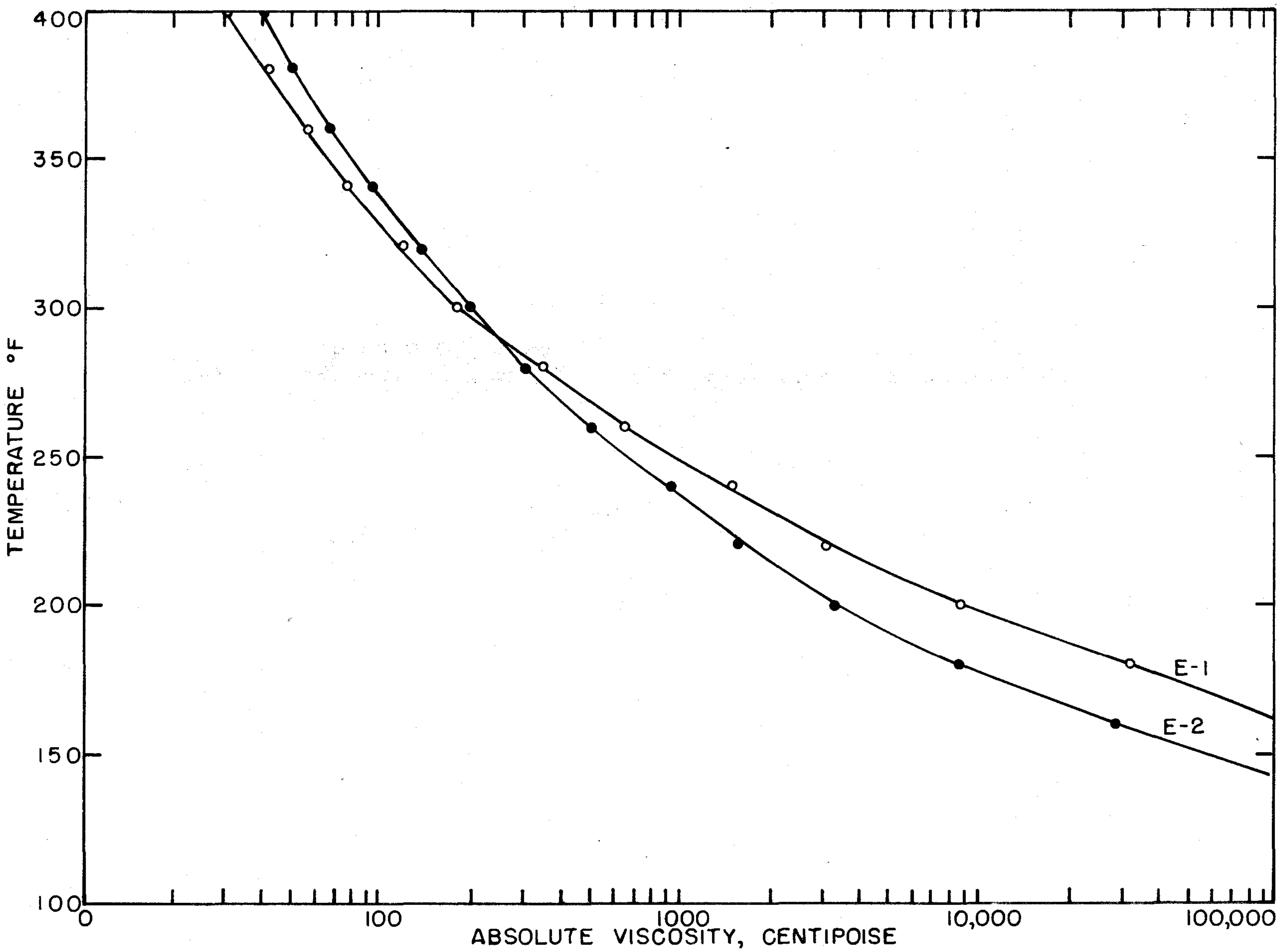


Fig. 7. Variation of absolute viscosity with temperature for series D bitumens

Fig. 8. Variation of absolute viscosity with temperature for series E bitumens


400
350
300
250
200
150
100
TEMPERATURE °F
0
100
1000
10,000
100,000
ABSOLUTE VISCOSITY, CENTIPOISE
E-1
E-2

viscosity-temperature curves are shown on Figures 9 through 13. An empirical equation representing this relationship can be established in the form of

$$\log \eta = AT_R^{-m}$$

where η is the viscosity in centipoise

A is a constant

m is a constant

T_R is the absolute temperature in Rankine.

The two constants A and m for all the bitumens as calculated from the observed results are shown in Table 6.

Viscosities measured at various temperatures of five bitumens with similar penetration are shown in Table 7. Results indicated that there is a direct relationship between the per cent of asphaltene and viscosity. At the low temperature range, significant variations in viscosities with respect to the asphaltene contents were observed.

Effect of Temperature on the Surface Tension

The variation of the surface tension of the bitumen with temperature is of importance in the study of contact angles. In relation to viscosity, surface tension affects the facility with which the bitumen wets the solid and adjusts the droplets' size and shape. An attempt to determine the surface tension of semi-solid to solid states of the bitumens is possible only when they are in the molten

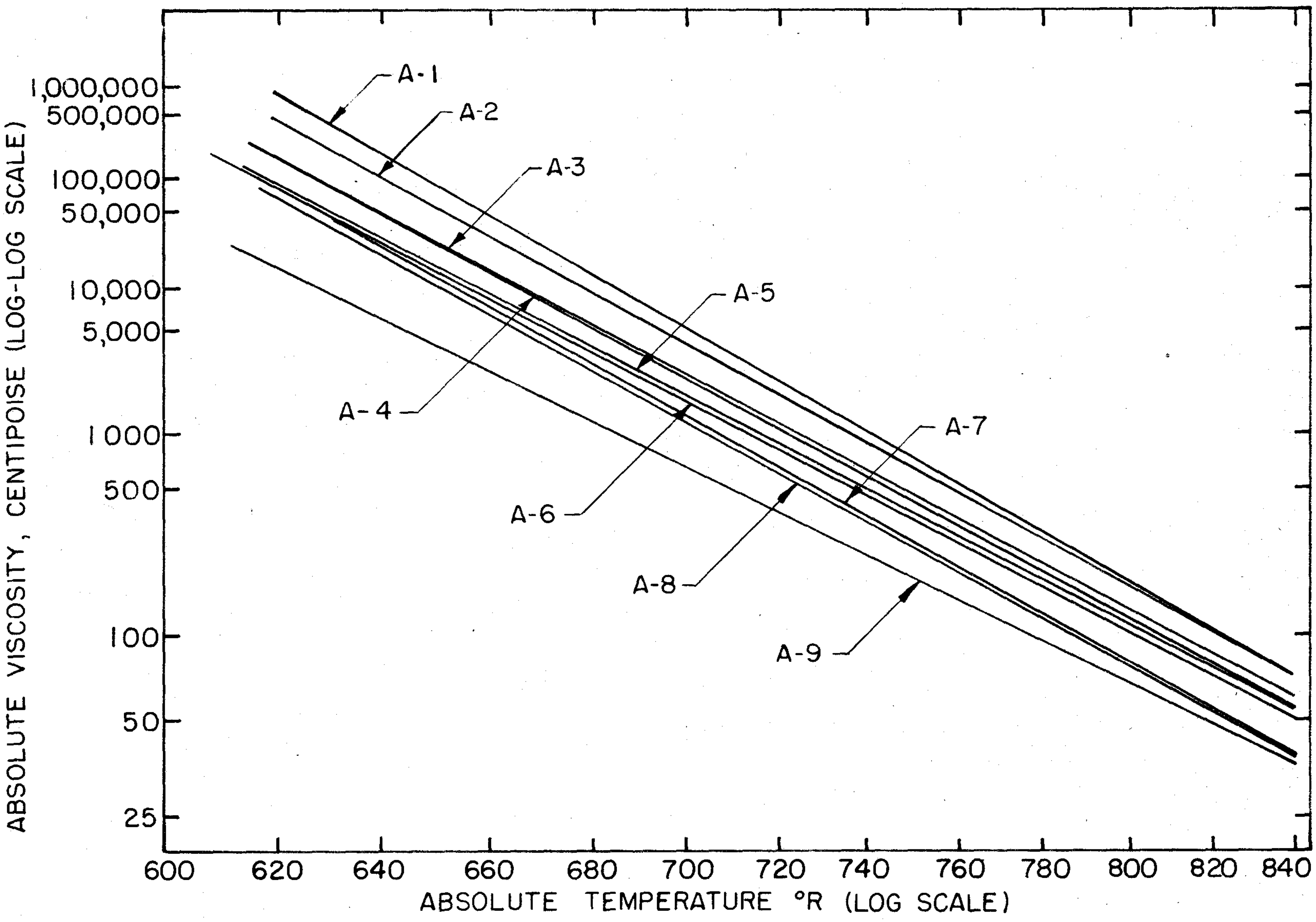


Fig. 9. Plot of log-log absolute viscosity vs. log absolute temperature for series A bitumens

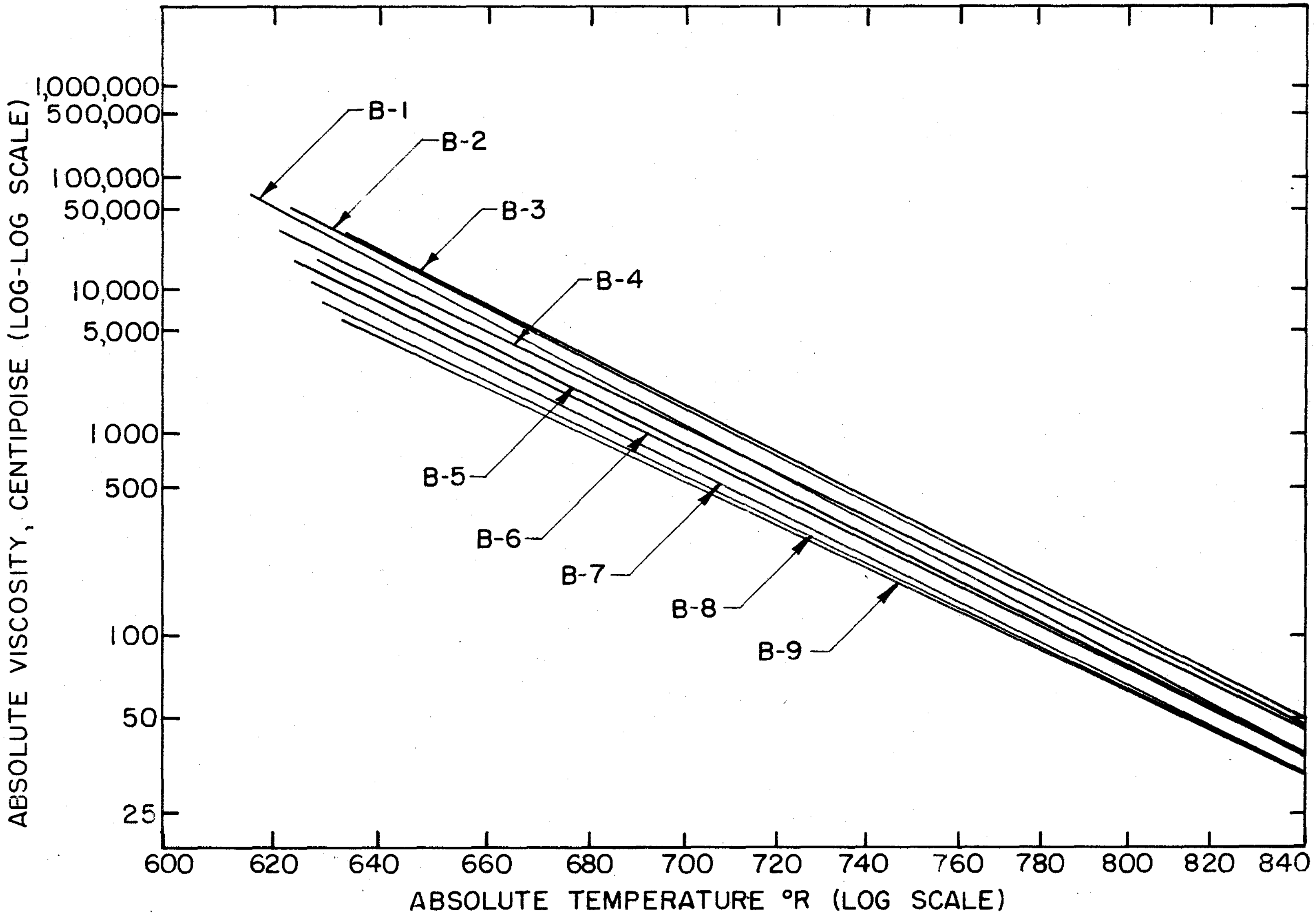


Fig. 10. Plot of log-log absolute viscosity vs. log absolute temperature for series B bitumens

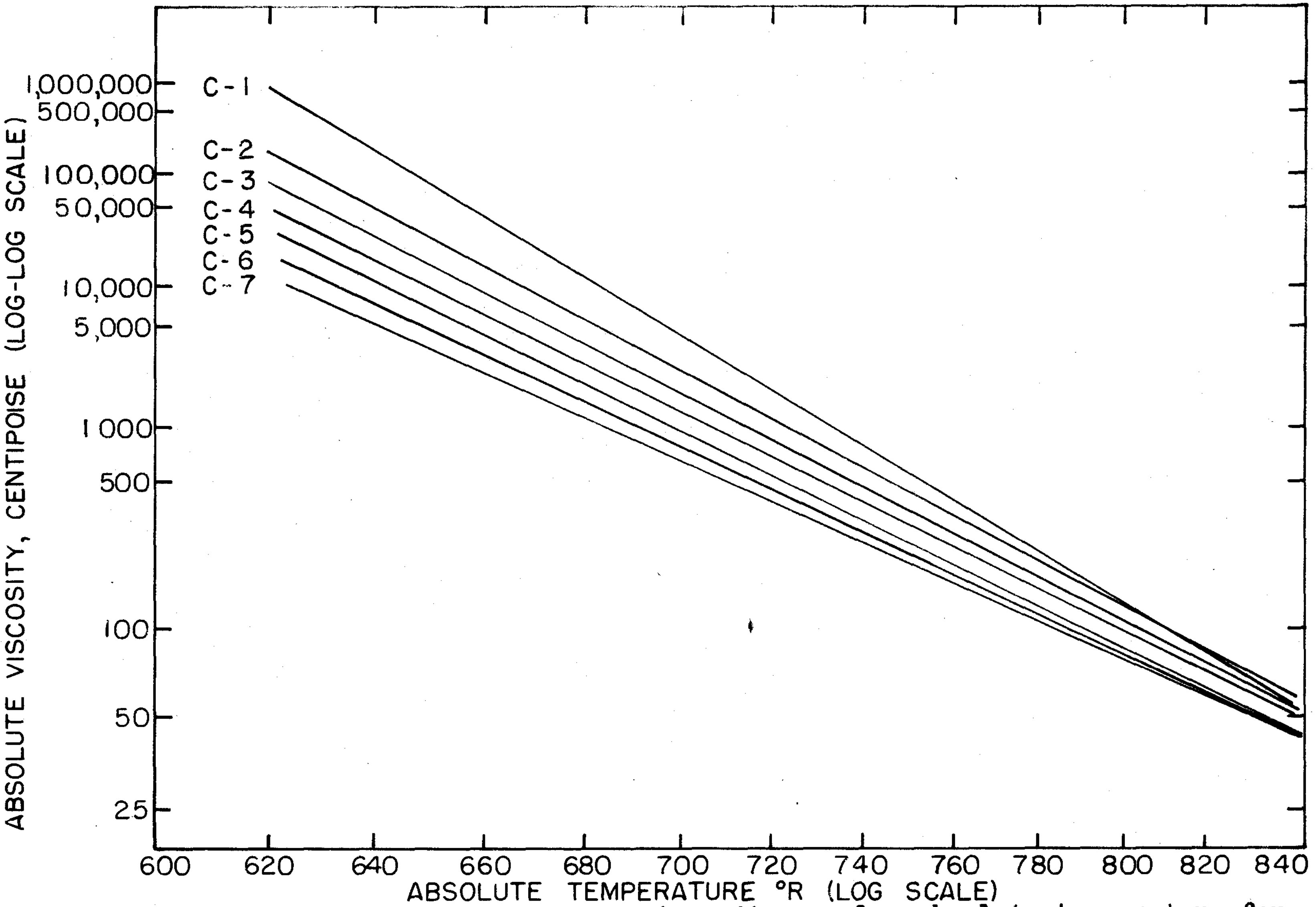


Fig. 11. Plot of log-log absolute viscosity vs. log absolute temperature for series C bitumens

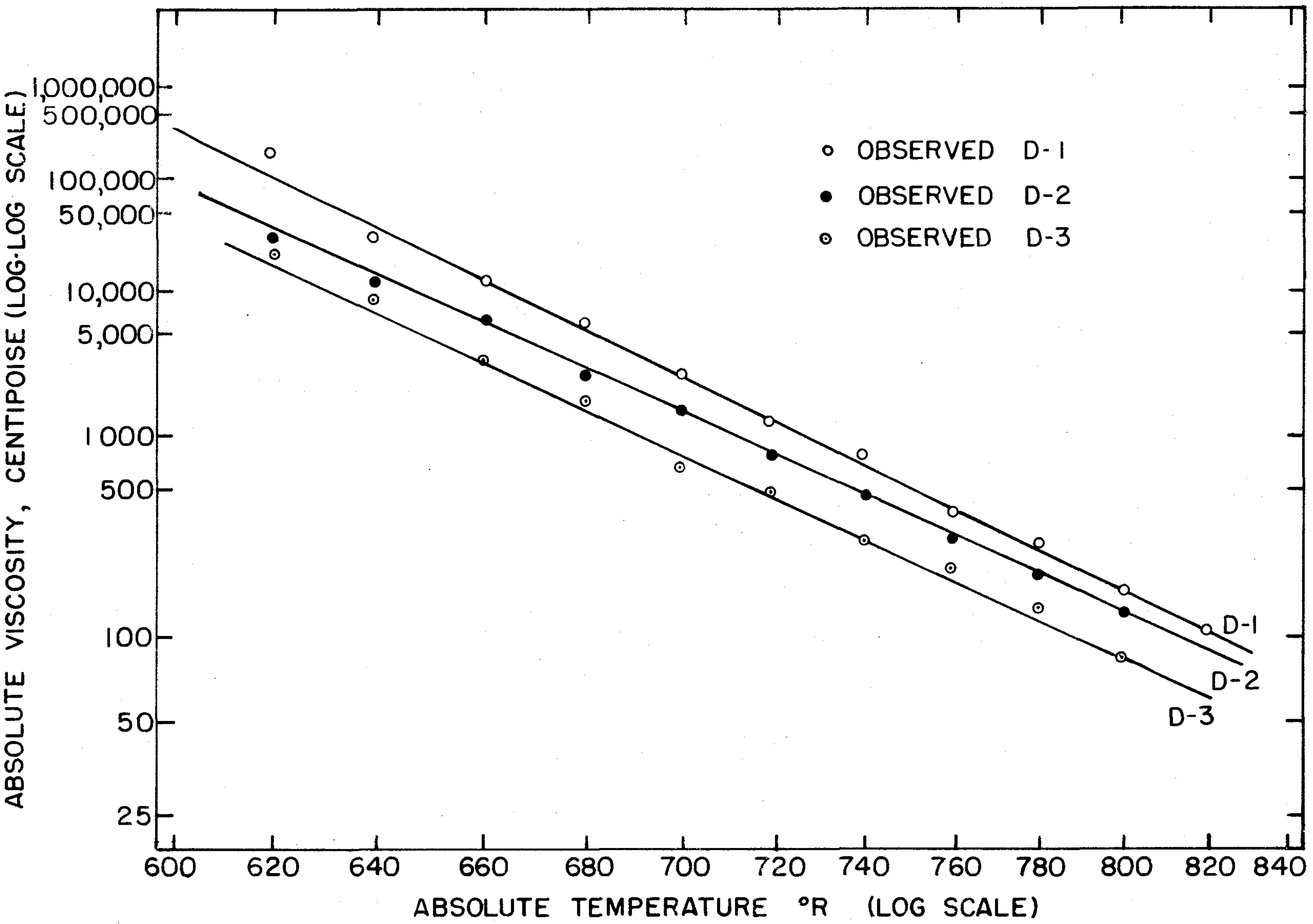


Fig. 12. Plot of log-log absolute viscosity vs. log absolute temperature for series D bitumens

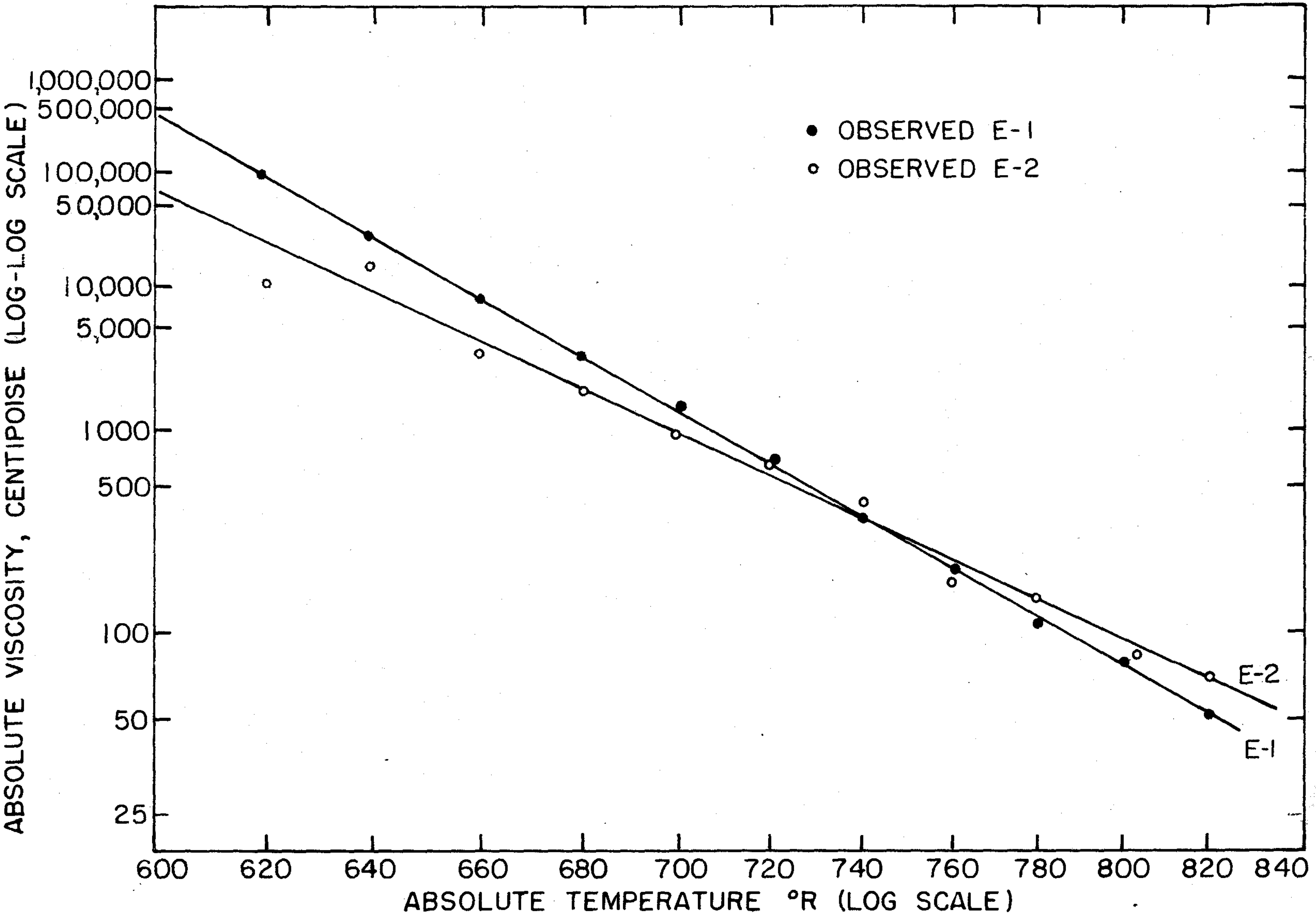


Fig. 13. Plot of log-log absolute viscosity vs. log absolute temperature for series E bitumens

Table 6. Constants for the viscosity-temperature equations $\text{Log } \eta = A \cdot T_R^{-m}$

Sample no.	m	A	Sample no.	m	A
A-1	3.382	1.522×10^{10}	C-1	4.019	9.822×10^{11}
A-2	3.593	5.985×10^{10}	C-2	3.718	1.256×10^{11}
A-3	3.468	2.466×10^{10}	C-3	3.401	1.528×10^{10}
A-4	3.633	7.231×10^{10}	C-4	3.316	8.410×10^{9}
A-5	3.448	2.092×10^{10}	C-5	3.217	4.221×10^{9}
A-6	3.471	2.408×10^{10}	C-6	3.132	2.372×10^{9}
A-7	3.675	8.876×10^{10}	C-7	2.929	6.131×10^{8}
A-8	3.656	7.614×10^{10}			
A-9	3.035	1.187×10^{10}	D-1	3.283	7.429×10^{9}
			D-2	3.013	1.179×10^{9}
B-1	3.519	3.112×10^{10}	D-3	3.110	2.021×10^{9}
B-2	3.347	1.052×10^{10}			
B-3	3.410	1.581×10^{10}	E-1	3.769	1.654×10^{11}
B-4	3.238	4.901×10^{9}	E-2	3.099	1.946×10^{9}
B-5	3.314	7.945×10^{9}			
B-6	3.286	6.487×10^{9}			
B-7	3.294	6.629×10^{9}			
B-8	3.153	2.549×10^{9}			
B-9	3.170	2.875×10^{9}			

Table 7. Comparison of the viscosity at various temperatures of five similar penetration bitumens

Sample	A-5	B-5	C-4	D-2	E-1	E-2
Penetration	90	86	90	98	92	86
% asphaltene 86/88 Be' Naphtha	21.7	19.5	19.3	19.1	31.4	16.5
Temperature ° F.	Absolute viscosity in centipoise					
400	42	32	36	50	30	40
380	54	41	50	71	43	57
360	75	54	67	93	58	70
340	108	75	98	128	79	93
320	165	110	150	190	120	130
300	260	170	245	280	180	192
280	450	280	415	464	330	290
260	800	490	730	800	630	500
240	1,600	900	1,500	1,500	1,300	890
220	3,650	1,700	2,900	2,800	3,050	1,500
200	8,400	3,750	6,100	5,600	8,700	3,300
180	26,500	9,200	15,000	13,200	34,000	8,700
160	86,300	25,000	44,260	34,000	105,000	28,000
140	292,000	79,500	162,000	102,800	468,000	96,500

state, and of course a certain number of assumptions are necessary. Corrections and extrapolation might be assumed to be more simple, although there is an increased chance of error if a long interval of high temperature is encountered. The results of these measurements of surface tension under various temperature conditions are shown in Figures 14 through 18.

The surface tension and temperature curves show the same linear variation with an abrupt transition point at temperatures between 200-250° F. The relationship between the viscosities and their surface tensions at the same temperatures are shown in Figures 19 through 21. These tests were made to ascertain if any significant variations in these curves occurred.

Contact Angle Measurements

It is true that a degree of wetting can be readily determined by measuring the angle of contact formed under the various known viscosities and surface tensions of the bitumens. Data collected by the physical chemists has proven that the final shape of a liquid droplet formed on solid surface is governed by factors such as the viscosity, density, surface tension, surface character, adsorption and other physical characteristics of the liquid and solid. The

Fig. 14. Plot of surface tension vs. temperature for series A bitumens

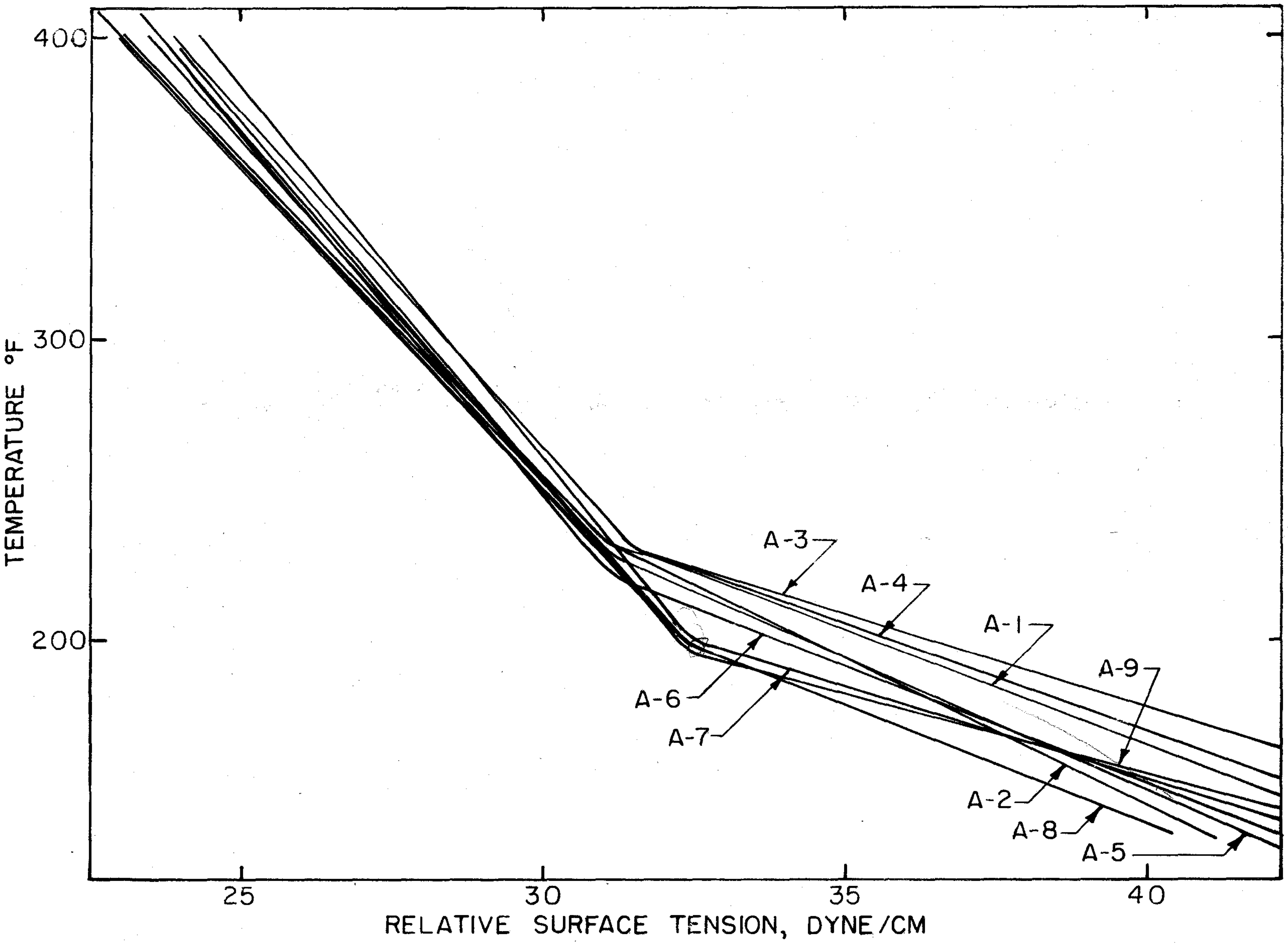

TEMPERATURE °F
400
300
200
25
30
35
40
RELATIVE SURFACE TENSION, DYNE/CM
A-3
A-4
A-1
A-9
A-6
A-7
A-2
A-8
A-5

Fig. 15. Plot of surface tension vs. temperature for series B bitumens

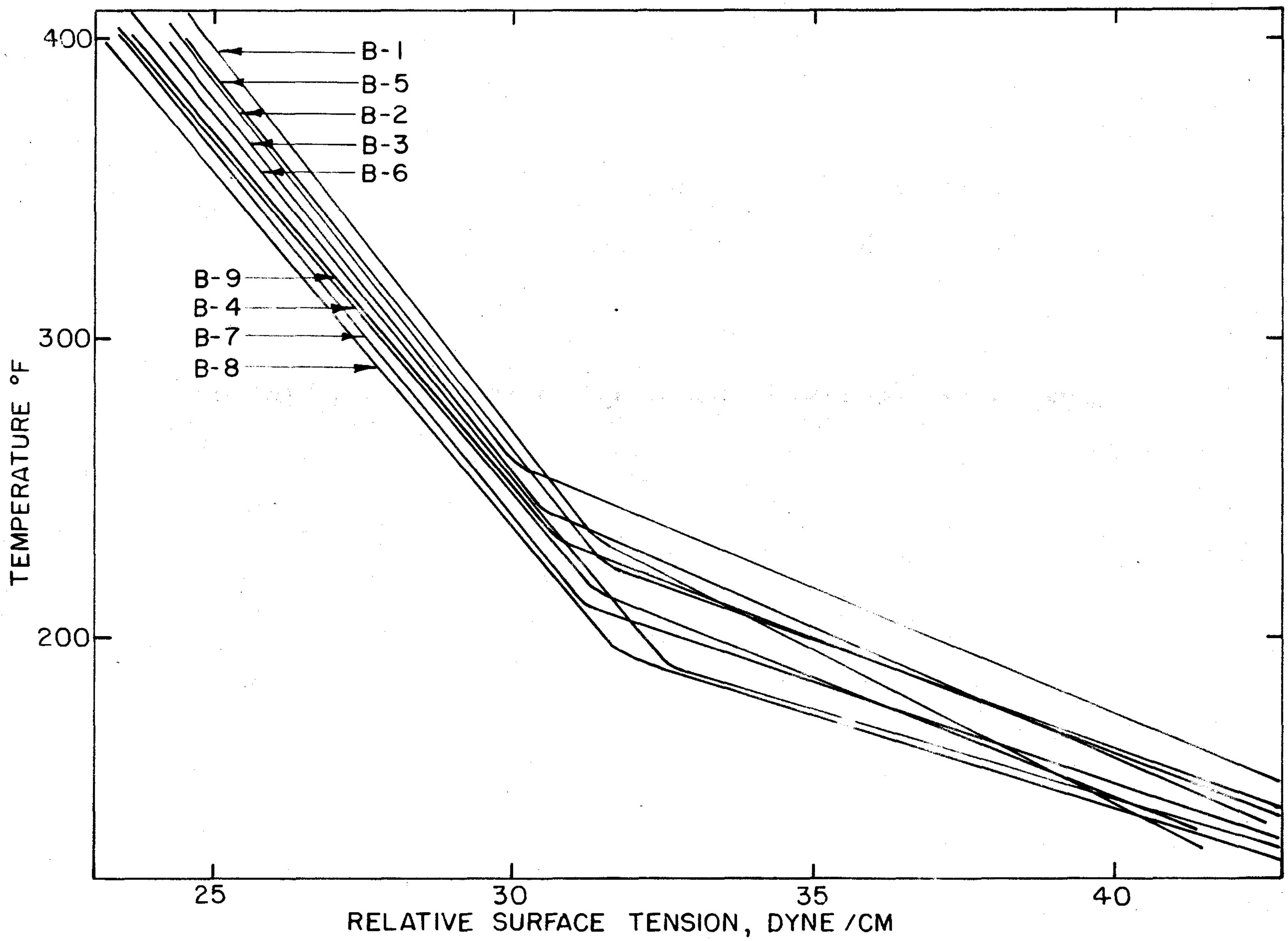
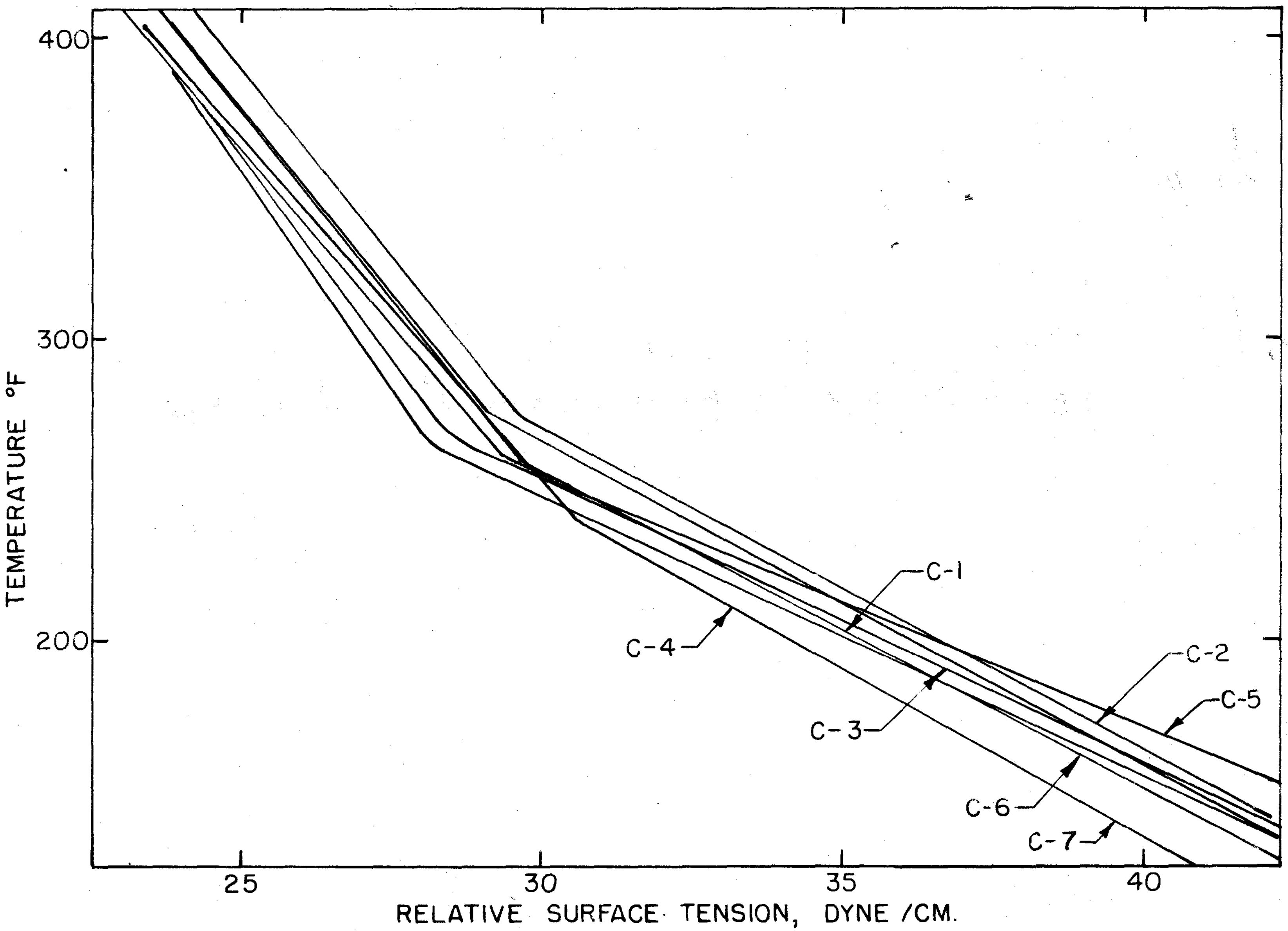

B-1
B-5
B-2
B-3
B-6
B-9
B-4
B-7
B-8
400
300
200
TEMPERATURE °F
25
30
35
40
RELATIVE SURFACE TENSION, DYNE/CM

Fig. 16. Plot of surface tension vs. temperature for series C bitumens


400
300
200
TEMPERATURE °F
25
30
35
40
RELATIVE SURFACE TENSION, DYNE /CM.
C-1
C-2
C-3
C-4
C-5
C-6
C-7

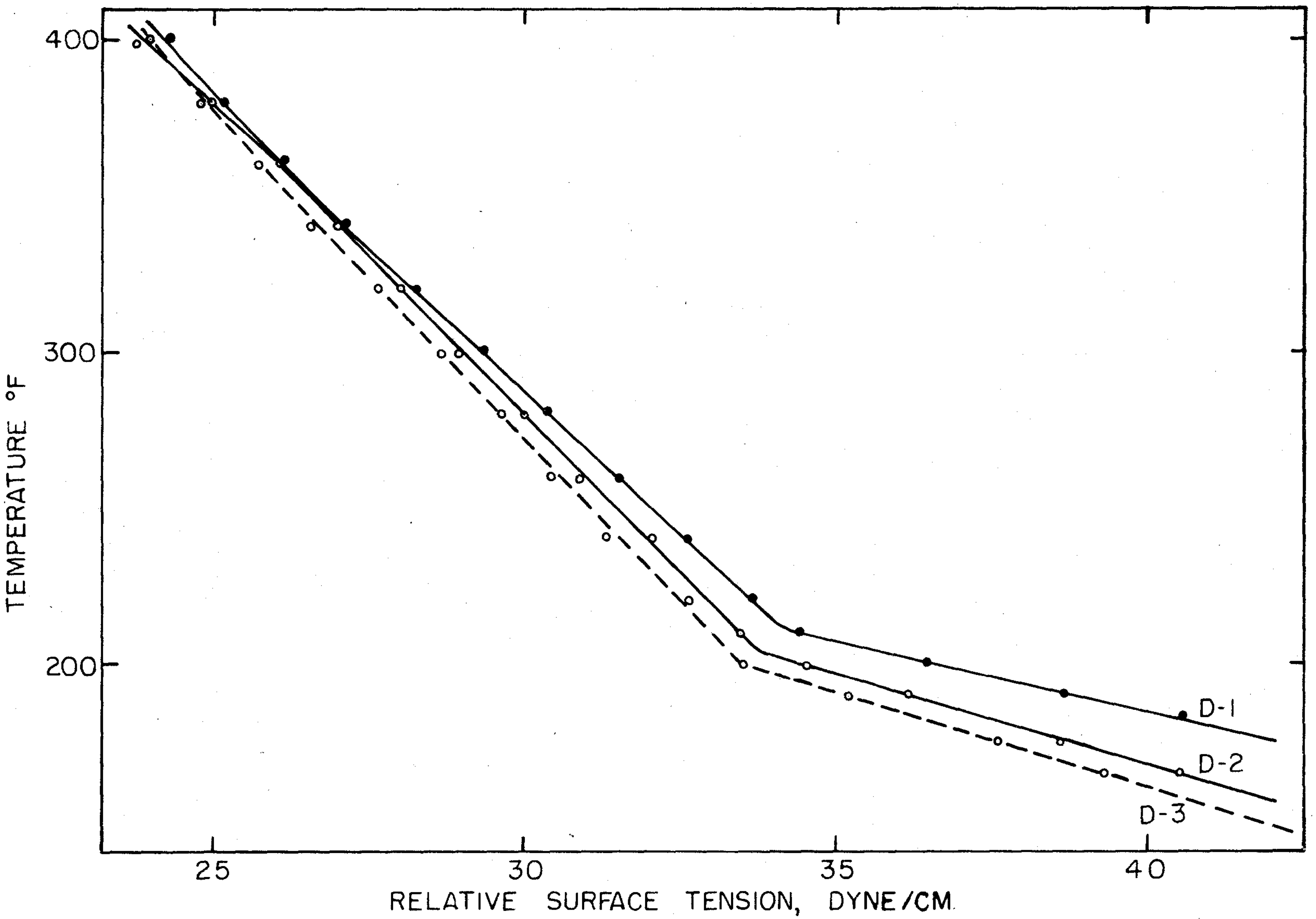
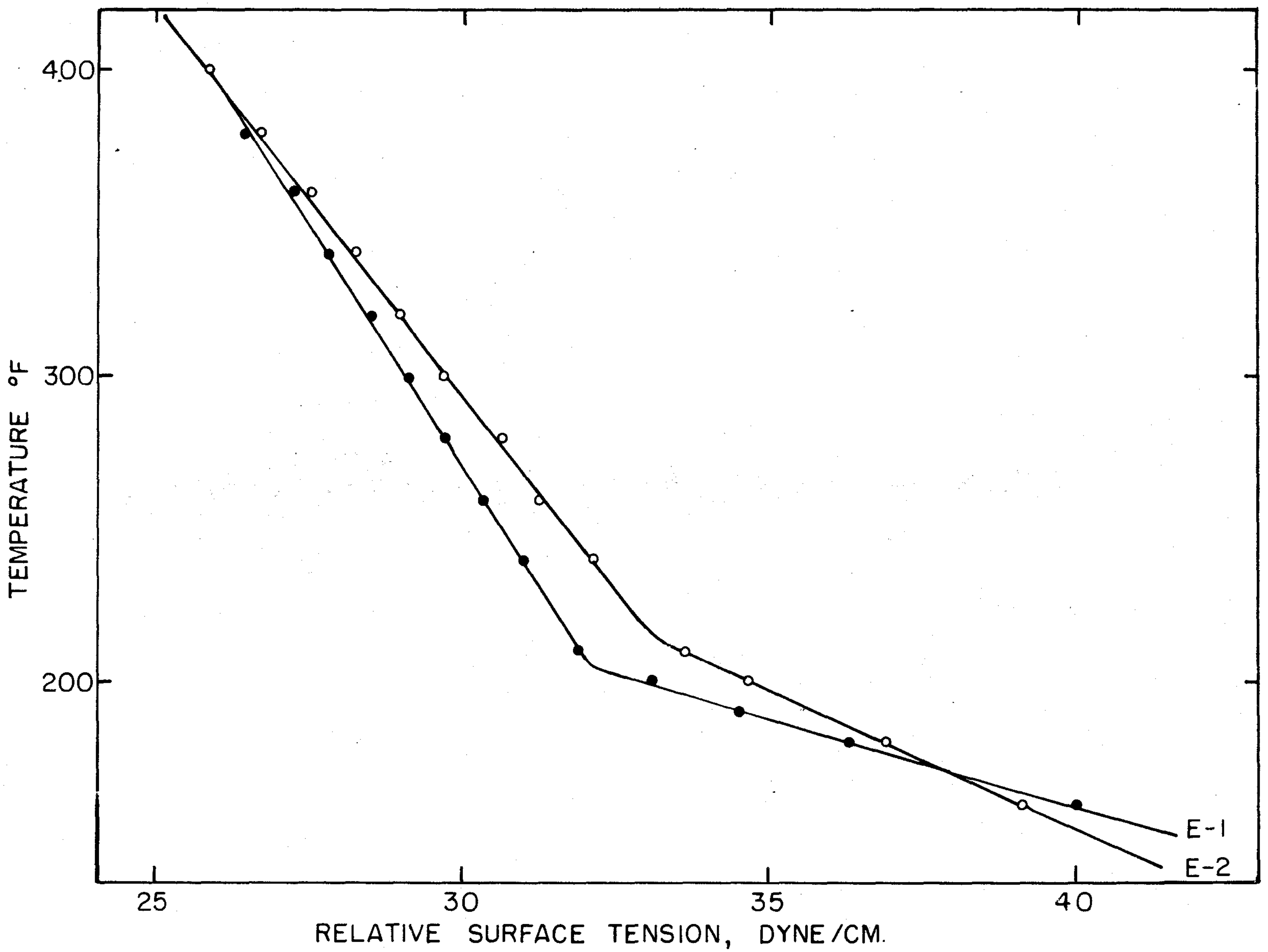


Fig. 17. Plot of surface tension vs. temperature for series D bitumens

Fig. 18. Plot of surface tension vs. temperature for series E bitumens


400
300
200
TEMPERATURE °F
25
30
35
40
RELATIVE SURFACE TENSION, DYNE/CM.
E-1
E-2

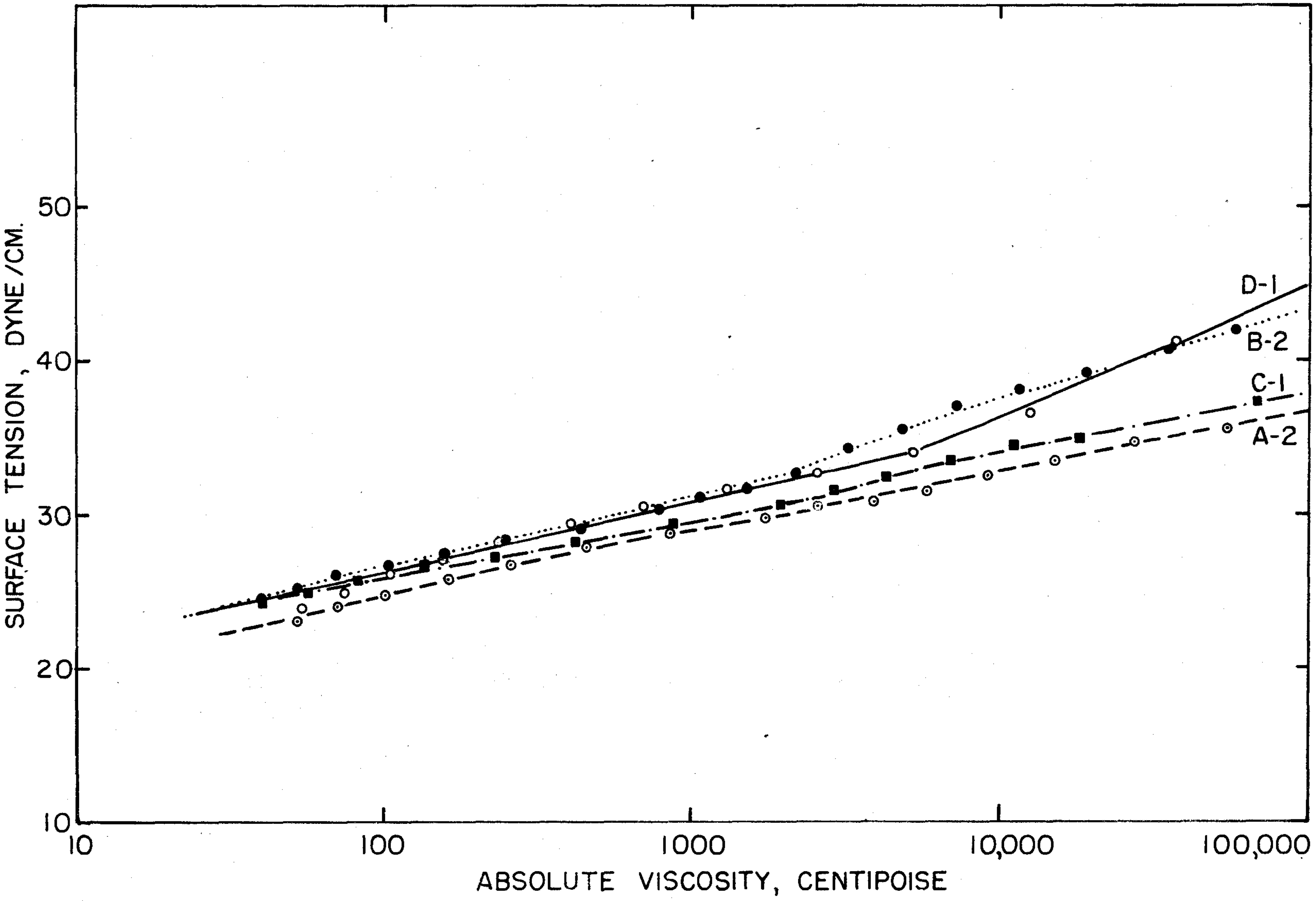


Fig. 19. Relationship between surface tension and absolute viscosity of 50-60 penetration bitumens

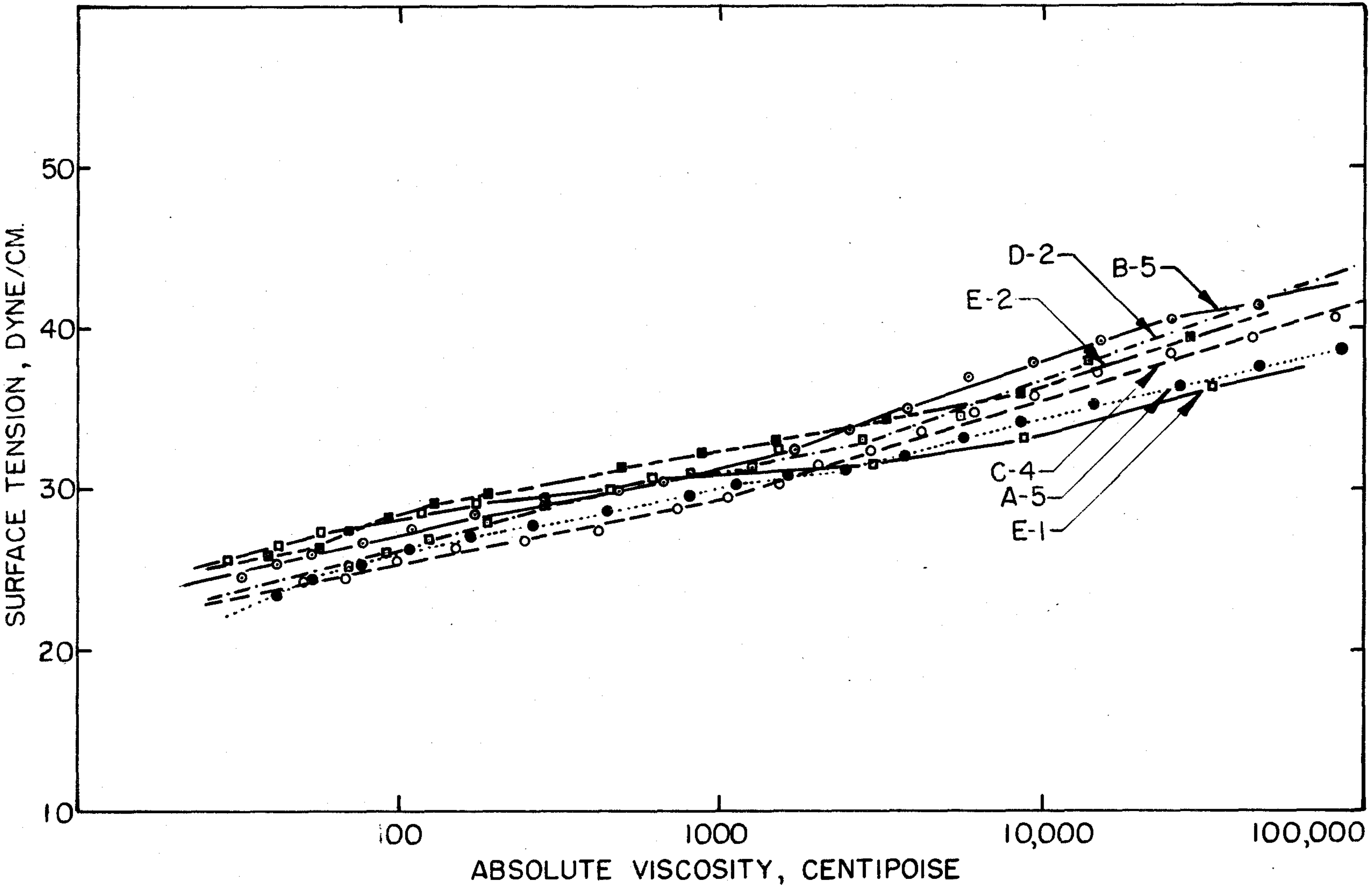
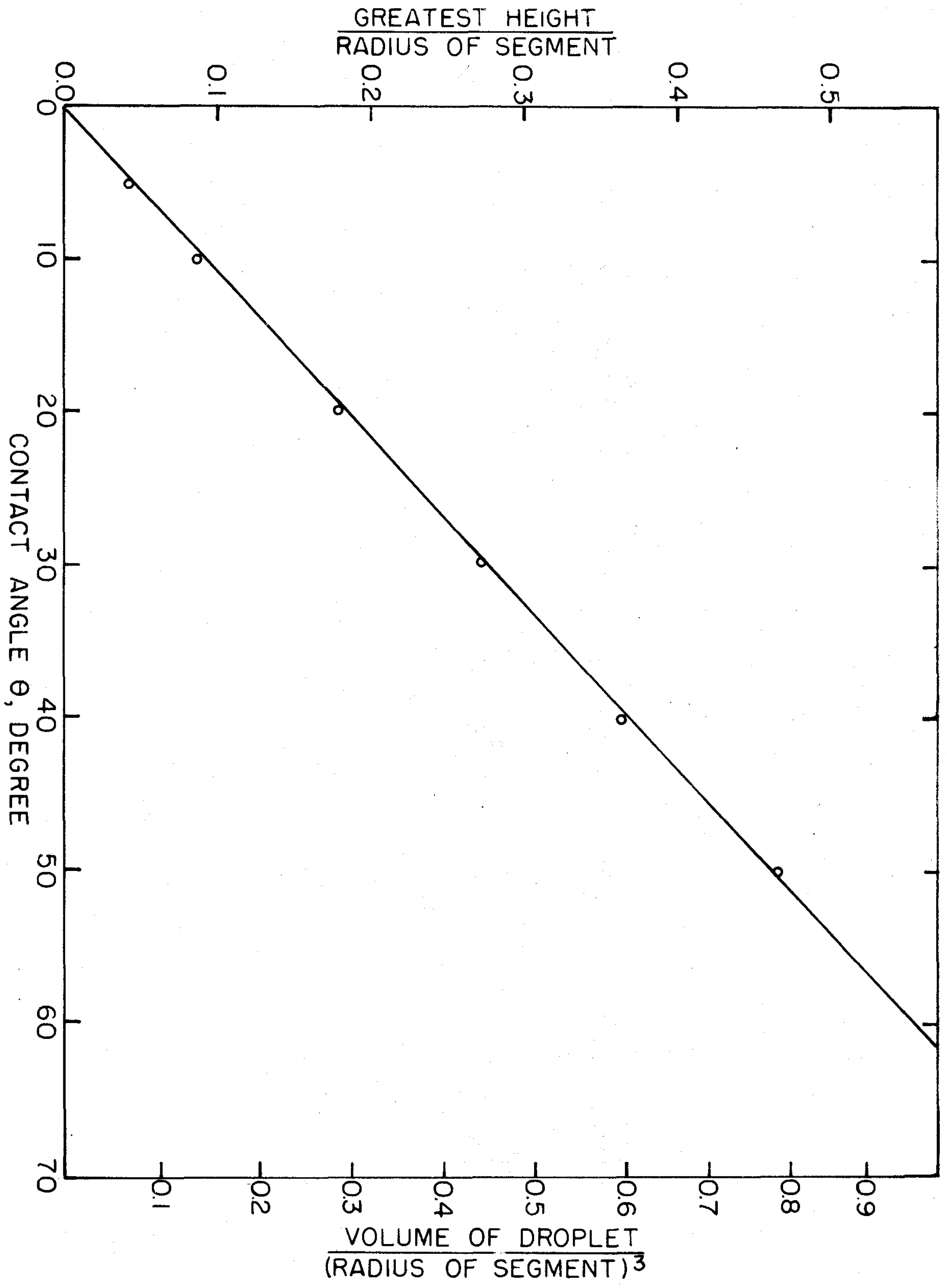


Fig. 20. Relationship between surface tension and absolute viscosity of 85-100 penetration bitumens

absolute control of all of these factors is either impossible or impracticable. It is even difficult to select truly representative specimens from a hydrophobic limestone and a hydrophilic black trap that were used in this study. With only a few important variables which can be controlled, results of contact angle measurements on the aggregates are very inconsistent, particularly when angles under study are formed at lower temperatures (below 200° F.). Contact angles formed on glass surfaces by bitumens at various temperatures furnish reasonable data on the rheological effects of bitumen on a solid, which simulates the condition of an ideal aggregate surface. Data obtained on smooth glass surfaces can be used to predict the relationship between bitumen and aggregates under conditions in which some variables have been eliminated. The statistical results of the contact angles as measured on glass surfaces are shown in Figures 24 through 28.

Disregarding the kind of surfaces on which the angle of contact is measured, the time element for the droplet to reach the equilibrium state is of material importance. Since it was found in most cases (Figure 23) that a duration of three minutes was necessary. This time was adequate for a droplet on an aggregate surface to reach the state of equilibrium under temperature conditions over 200° F.

Fig. 22. Relationship between contact angle and size of spherical segment


GREATEST HEIGHT / RADIUS OF SEGMENT
0.0
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50
60
70
CONTACT ANGLE θ, DEGREE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
VOLUME OF DROPLET / (RADIUS OF SEGMENT)^3

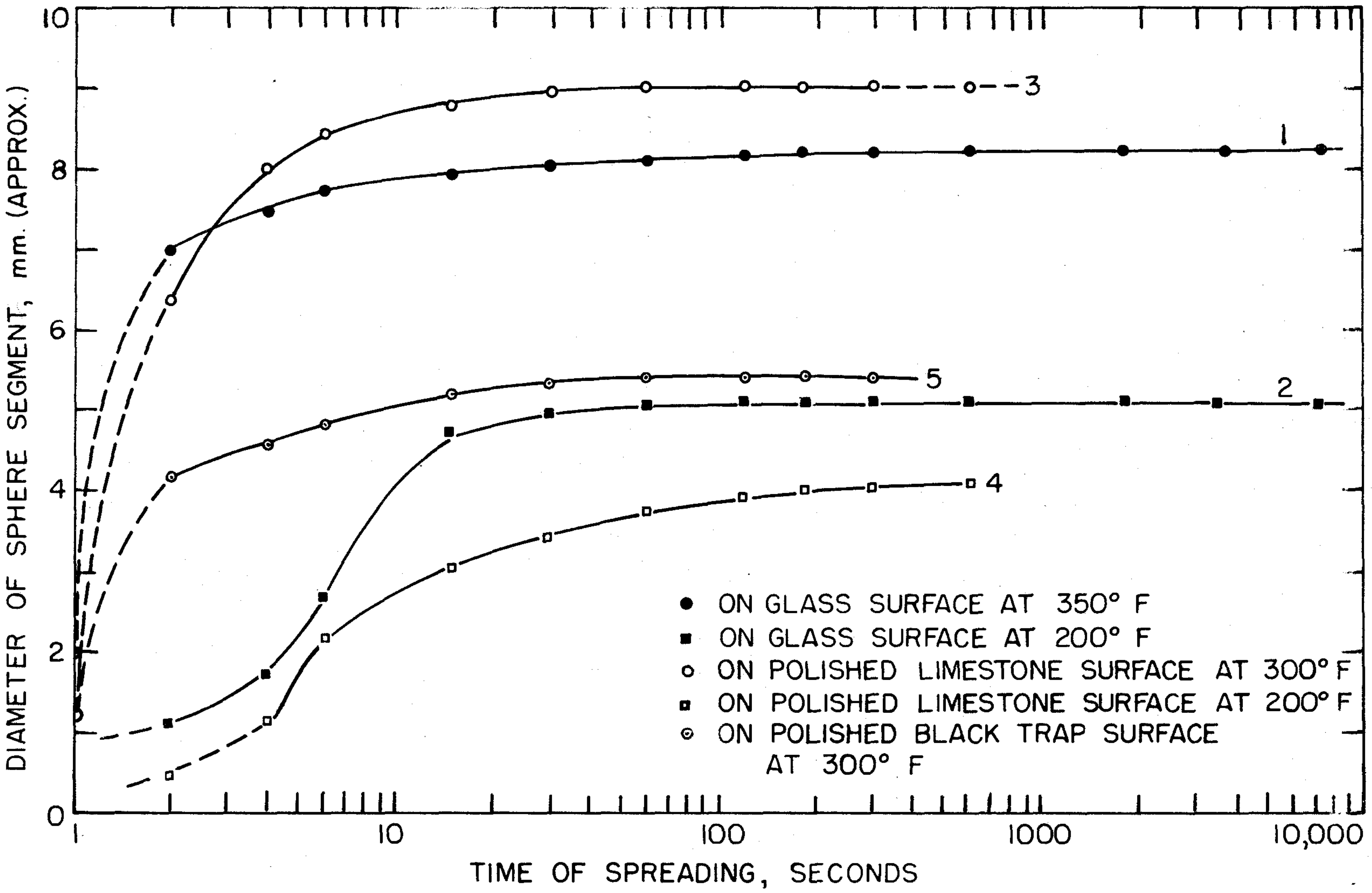


Fig. 23. Rate of spreading of D-2 bitumen over solids

Fig. 24. Plot of temperature vs. contact angle on glass surface of series A bitumens

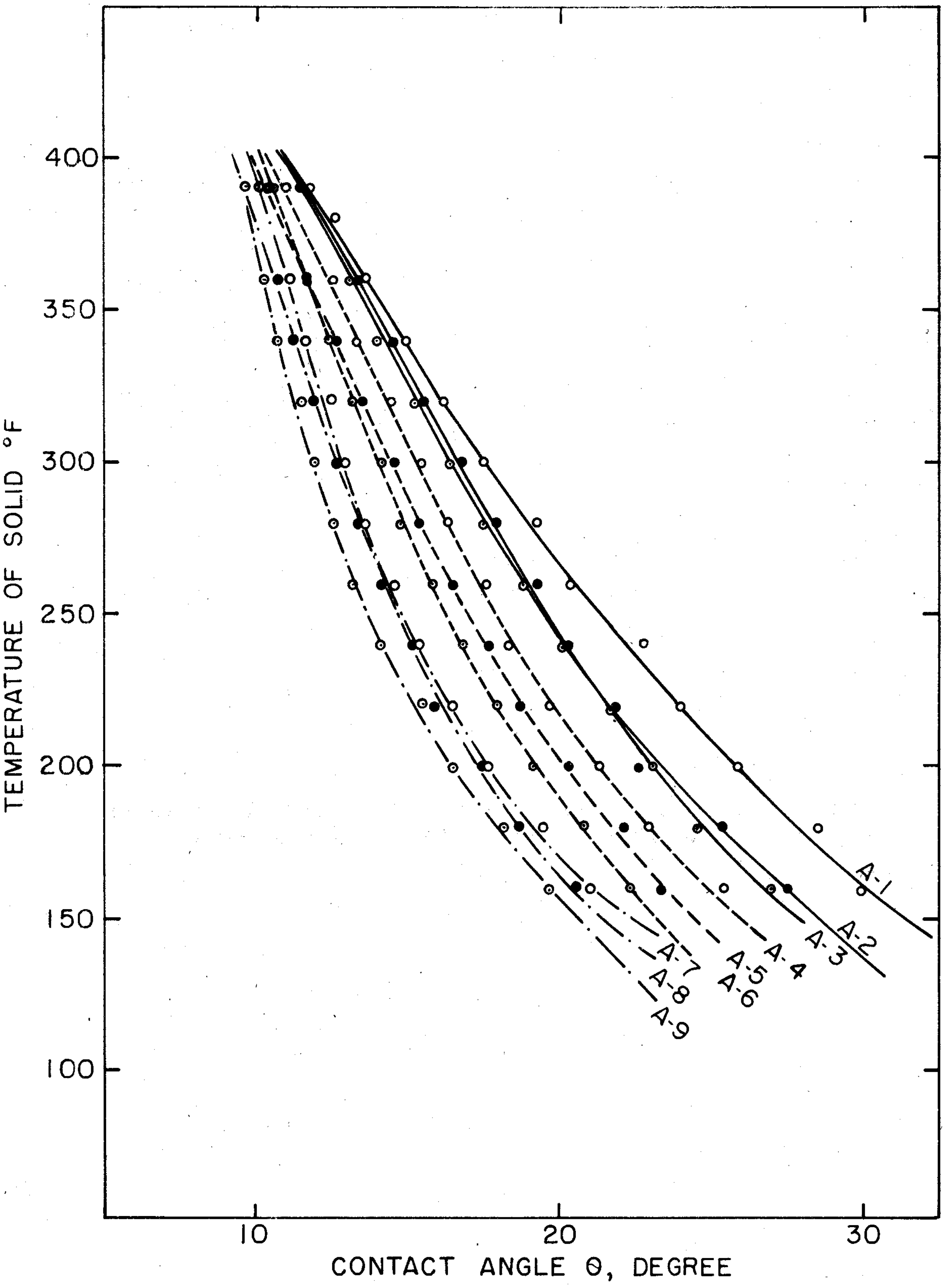

TEMPERATURE OF SOLID °F
400
350
300
250
200
150
100
10
20
30
CONTACT ANGLE Θ, DEGREE
A-1
A-2
A-3
A-4
A-5
A-6
A-7
A-8
A-9

Fig. 25. Plot of temperature vs. contact angle on glass surface of series B bitumens

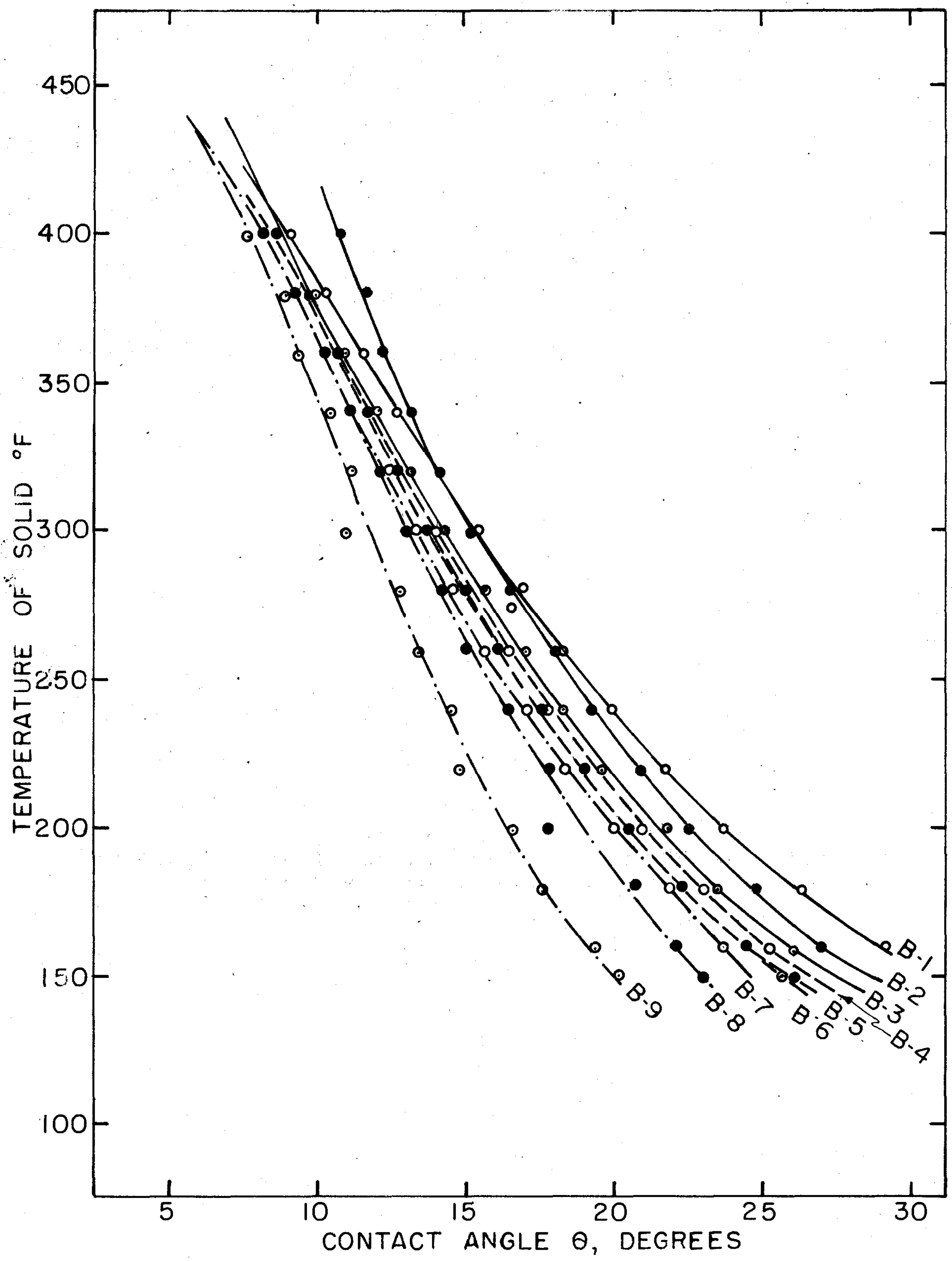
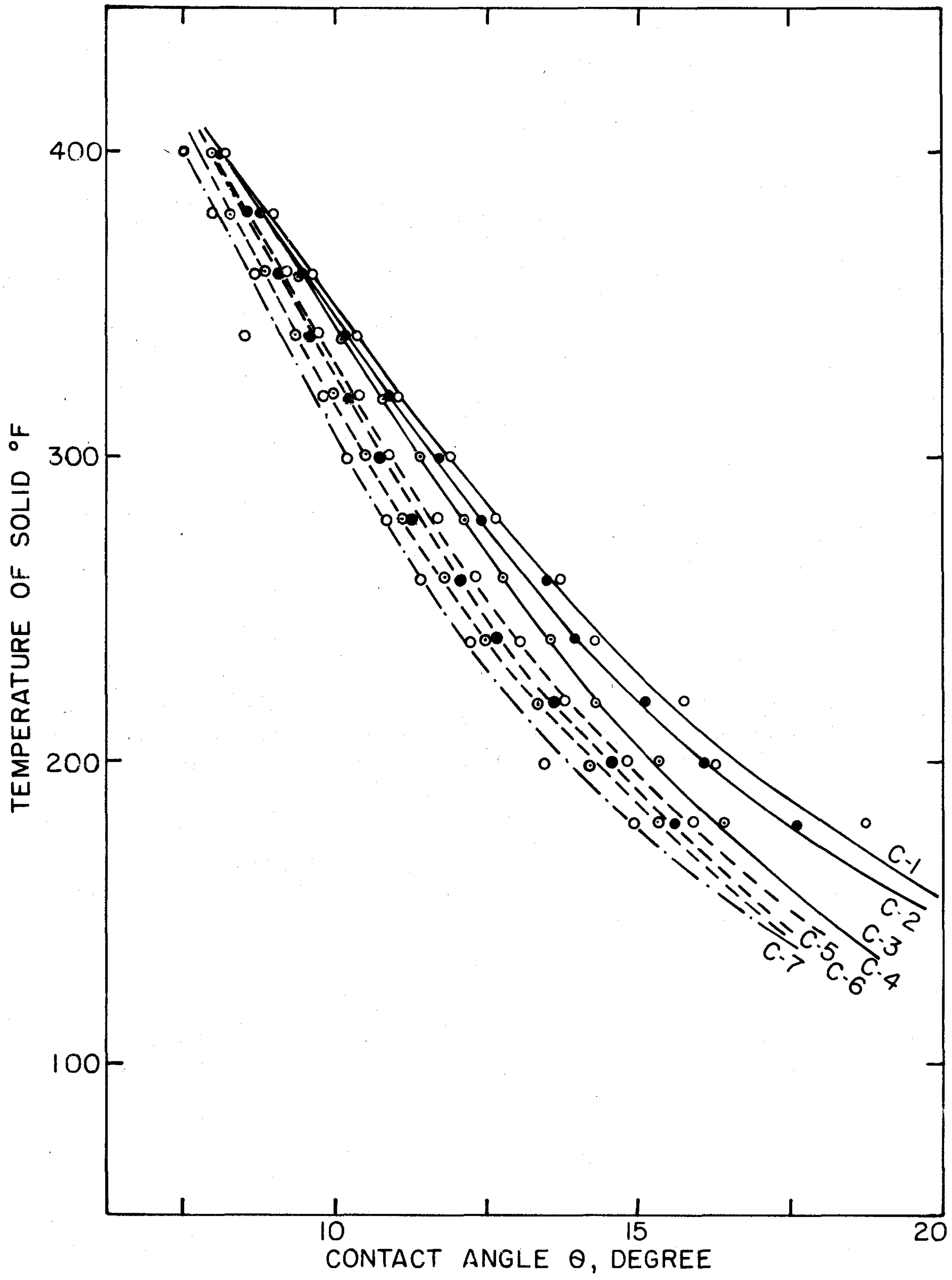
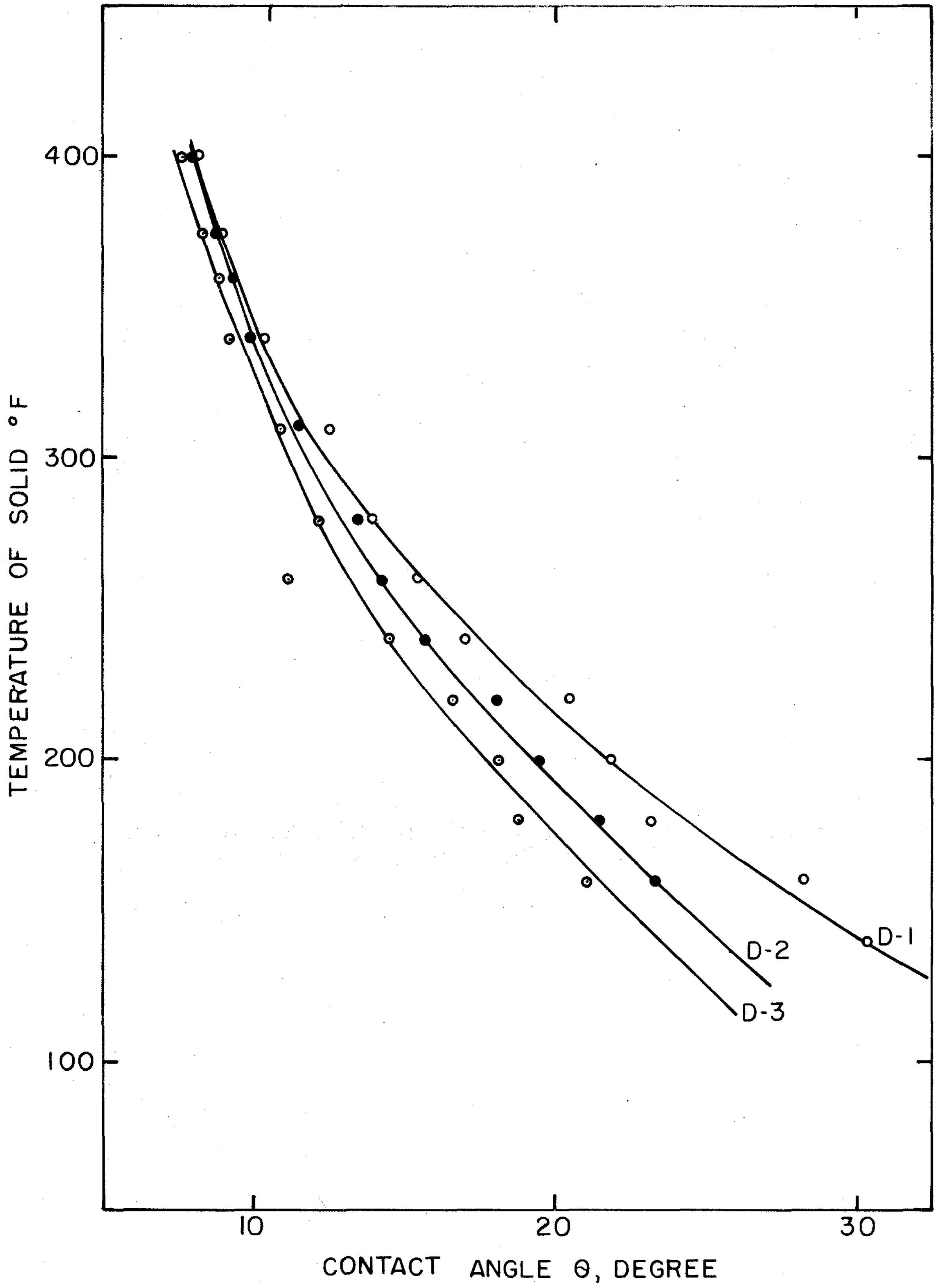

TEMPERATURE OF SOLID °F
450
400
350
300
250
200
150
100
CONTACT ANGLE Θ, DEGREES
5
10
15
20
25
30
B-1
B-2
B-3
B-4
B-5
B-6
B-7
B-8
B-9

Fig. 26. Plot of temperature vs. contact angle on glass surface of series C bitumens


TEMPERATURE OF SOLID °F
400
300
200
100
CONTACT ANGLE θ, DEGREE
10
15
20
C-1
C-2
C-3
C-4
C-5
C-6
C-7


TEMPERATURE OF SOLID °F
400
300
200
100
10
20
30
CONTACT ANGLE Θ, DEGREE
D-1
D-2
D-3

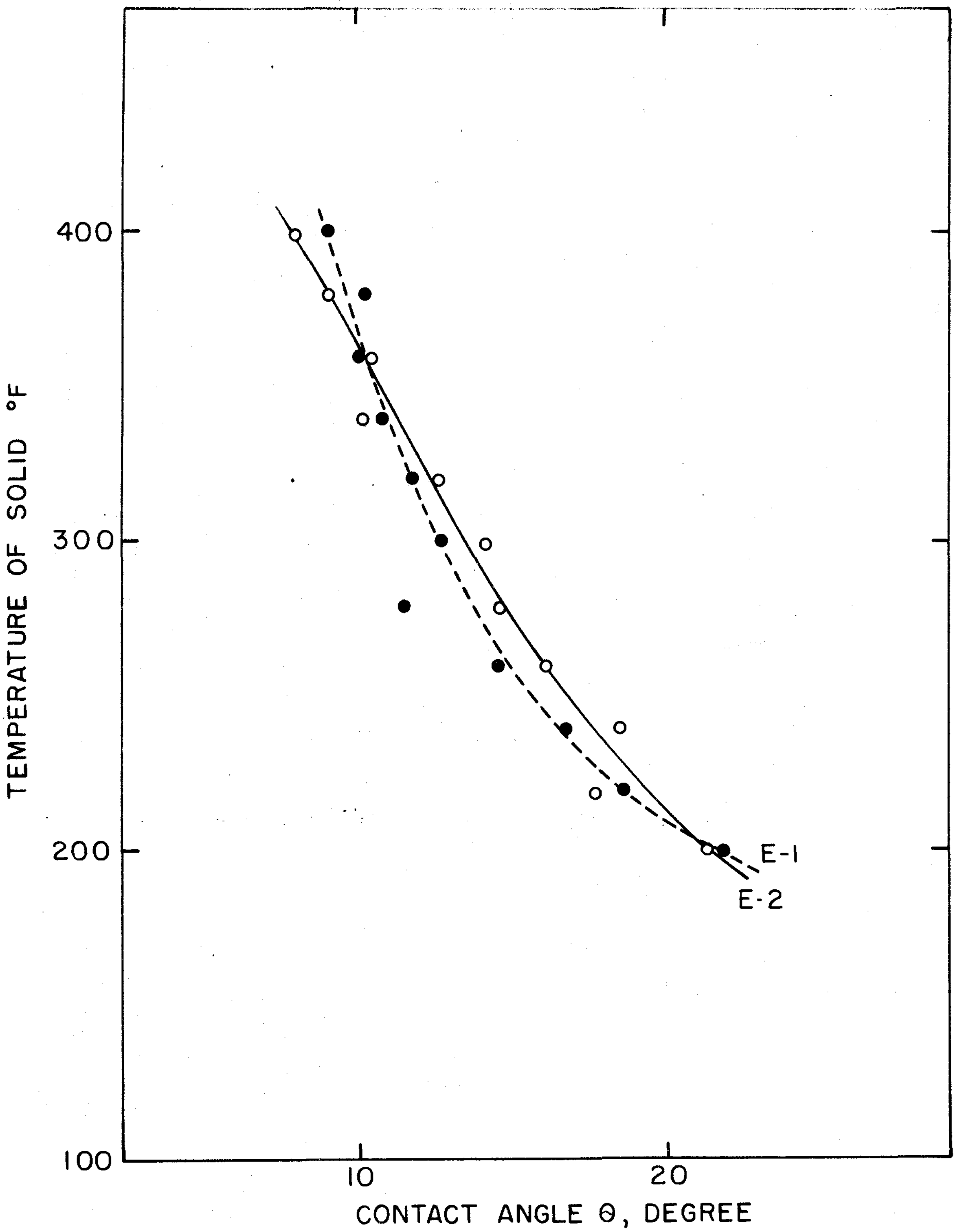


Fig. 28. Plot of temperature vs. contact angle on glass surface of series E bitumens

Measurements of the contact angles on glass surfaces with the protractor eyepiece usually gave satisfactory results. On aggregate surfaces, the indirect measurement of the droplet diameter together with the height or volume were found to be more convenient. Figure 22 shows the conversion curve of height/radius or volume/(radius)^3 ratios to angle of contact.

Tests to simulate the conditions of basic or acidic characteristics of an aggregate were also performed on glass slides, by coating the surface of the glass slide with the 10 per cent normal solution of sodium hydroxide or 10 per cent normal solution hydrochloride acid. The approximate pH readings on the surfaces of the slides were 10.4 and 2.7 respectively. Results on the effect of surface characteristics are shown in Figure 29.

Figures 30 to 32 show the relationships between the contact angle on the glass surfaces and the viscosities of the bitumen at time of contact. These results are from the interpretations of the curves of viscosity-temperature and contact angle-temperature. Such plots are entirely empirical and are intended only to study whether there is any direct relationship between contact angle and viscosity of the bitumens. However, results shown in Figures 33 and 34 are separate experiments conducted with the bitumen on slides whose temperatures were carefully controlled so that

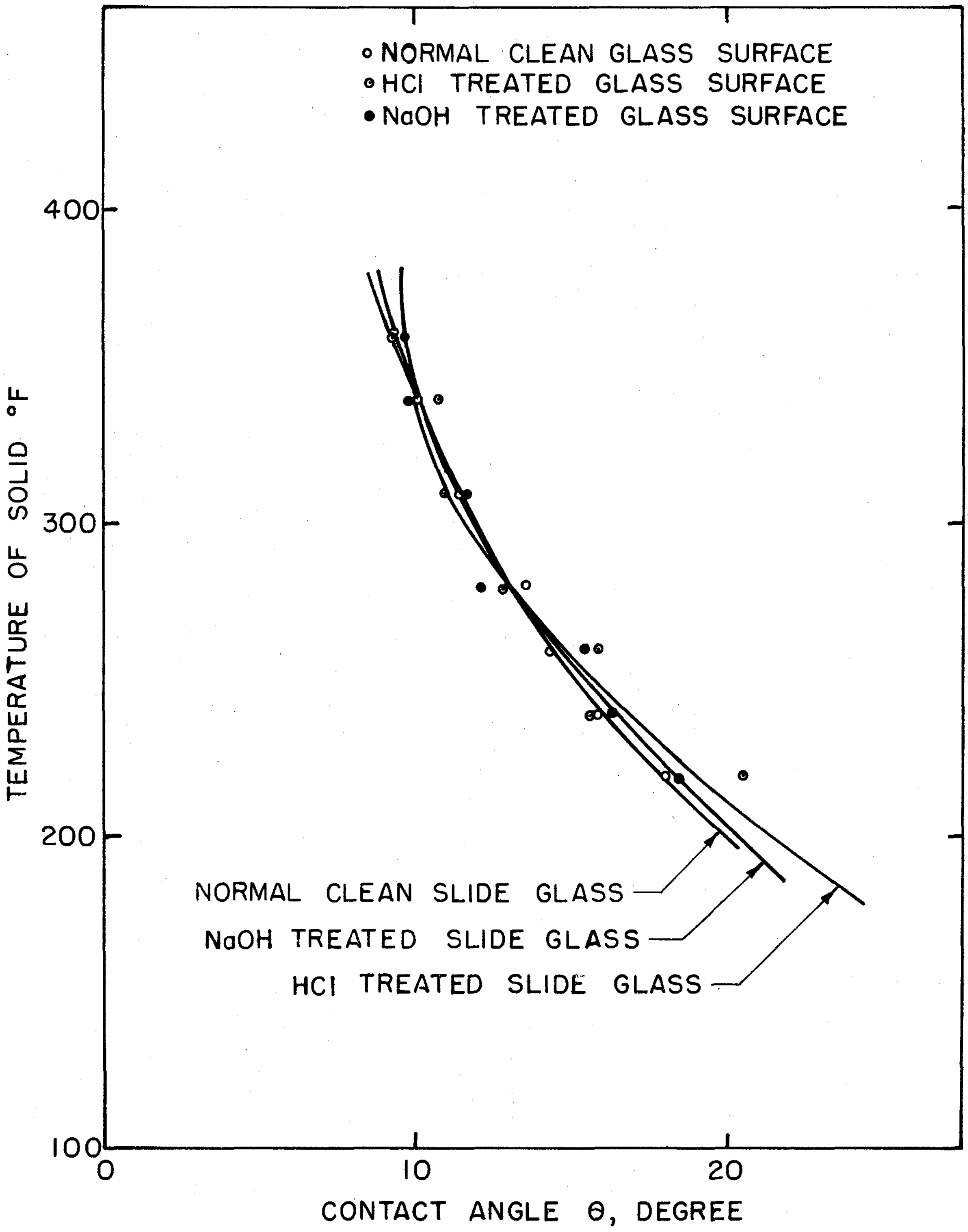


Fig. 29. Plot of temperature vs. contact angle on chemically treated glass surfaces

Fig. 30. Relationship between absolute viscosity and contact angle on glass surface of 50-60 penetration bitumens

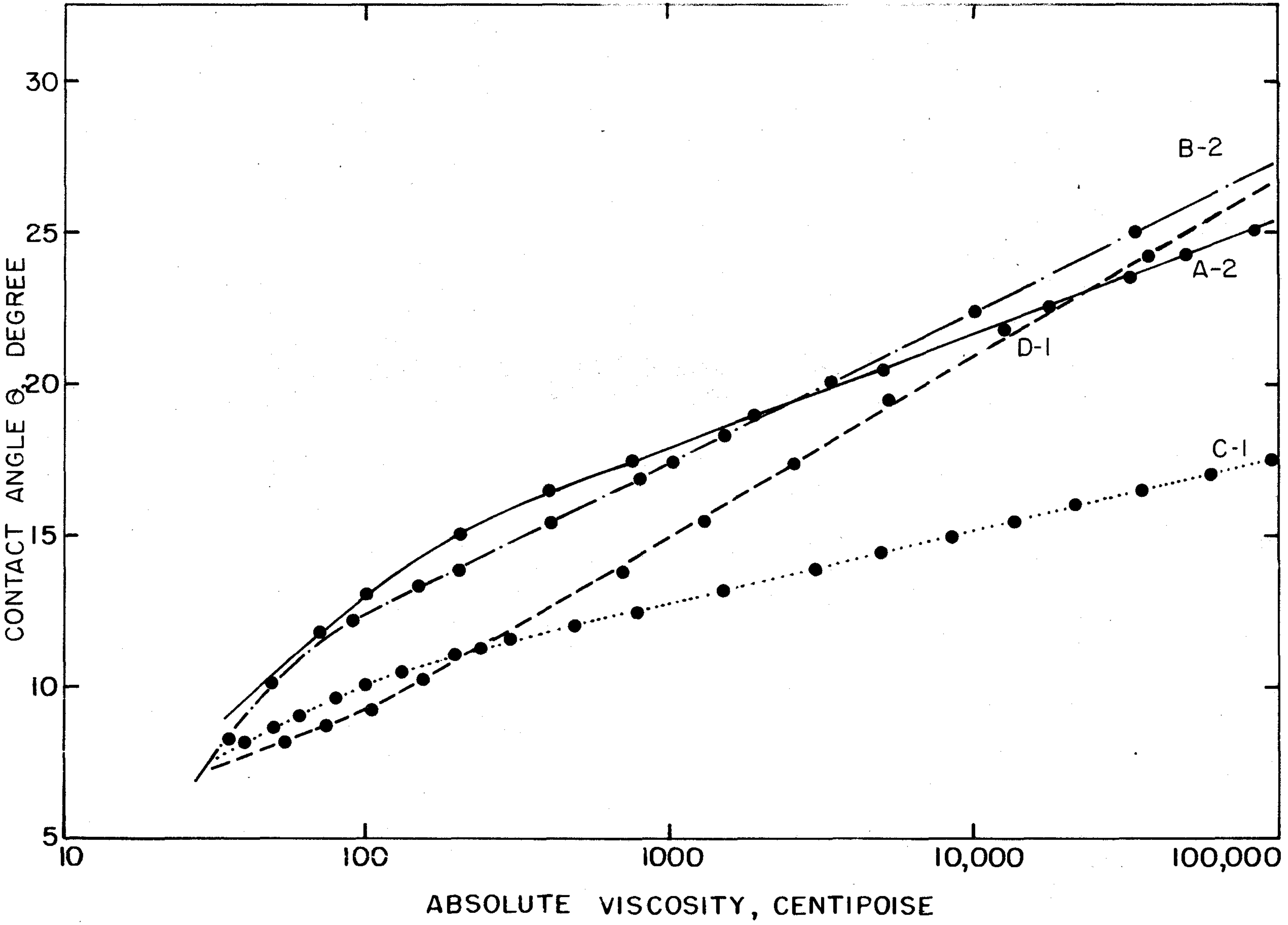
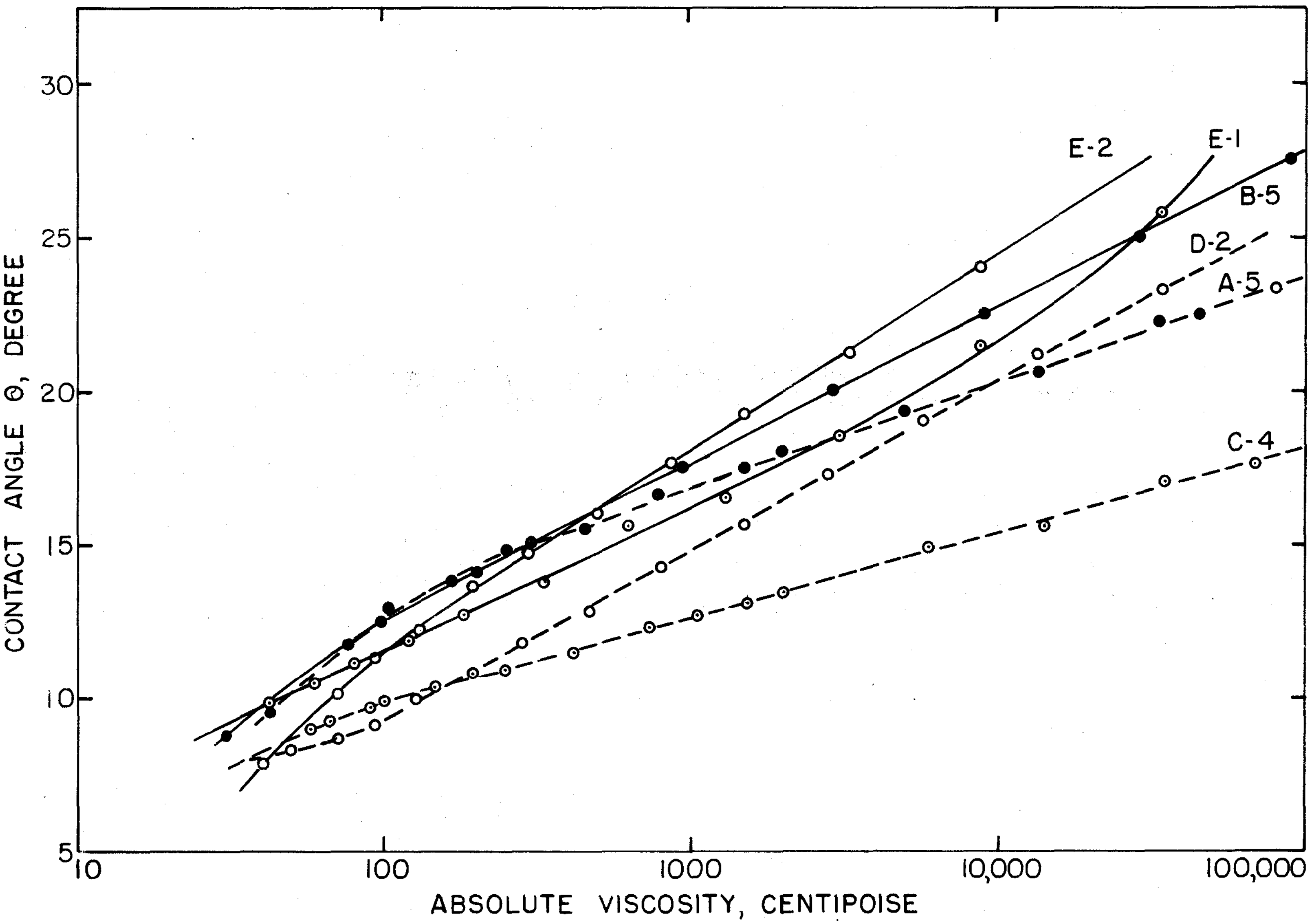

CONTACT ANGLE Θ, DEGREE
30
25
20
15
10
5
10
100
1000
10,000
100,000
ABSOLUTE VISCOSITY, CENTIPOISE
B-2
A-2
D-1
C-1

Fig. 31. Relationship between absolute viscosity and contact angle on glass surface of 85-100 penetration bitumens


E-2
E-1
B-5
D-2
A-5
C-4
30
25
20
15
10
5
10
100
1000
10,000
100,000
CONTACT ANGLE Θ, DEGREE
ABSOLUTE VISCOSITY, CENTIPOISE

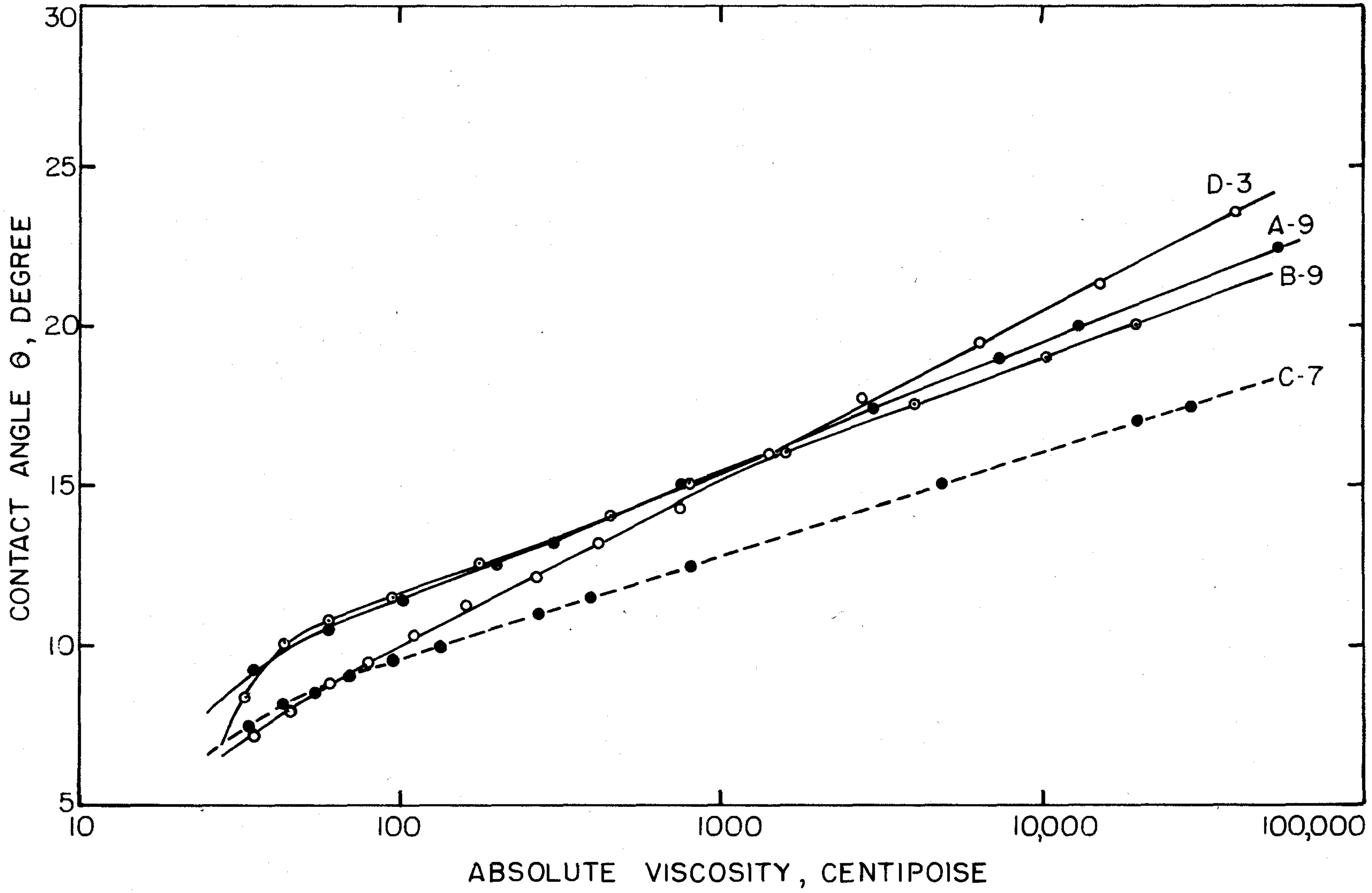
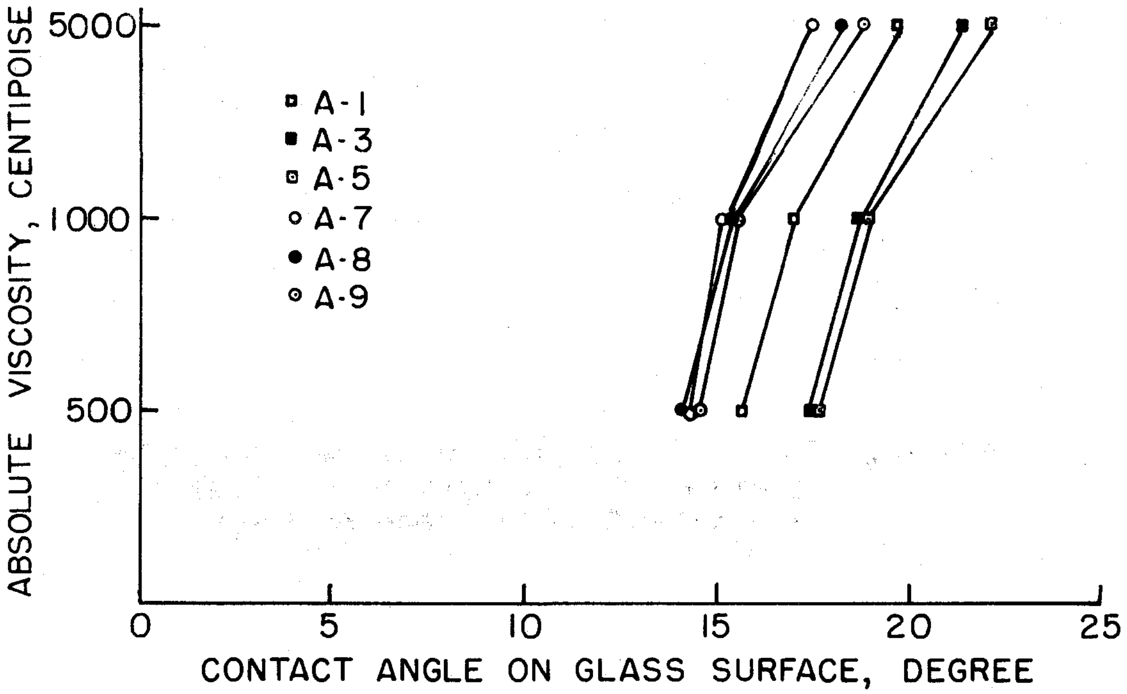
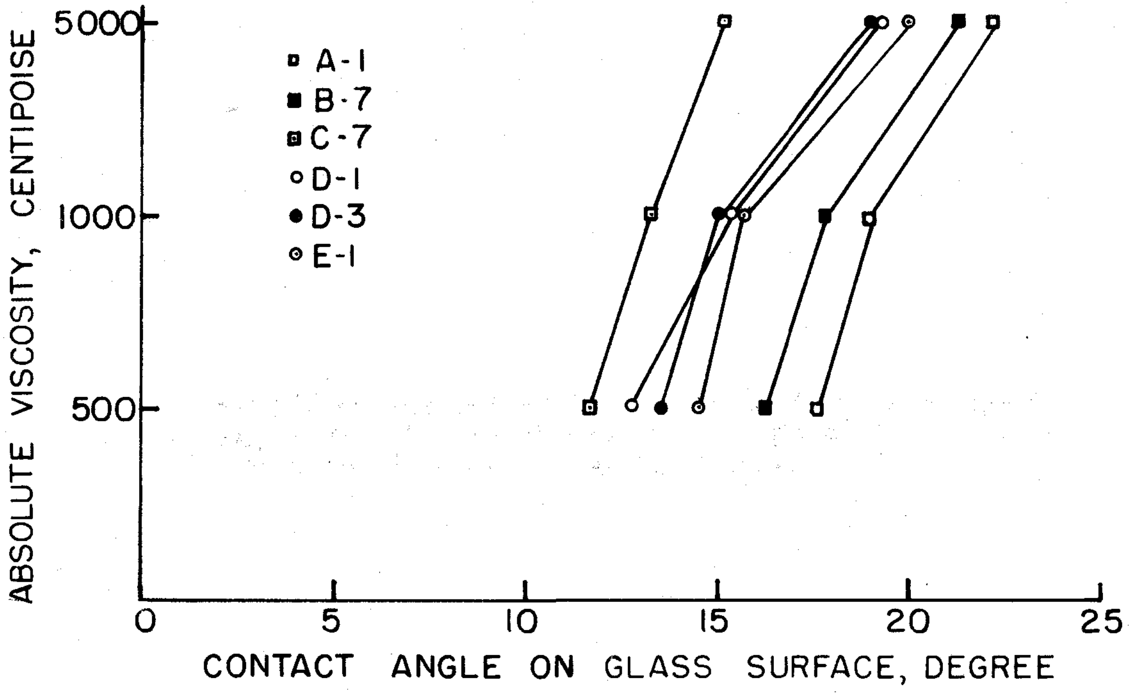


Fig. 32. Relationship between absolute viscosity and contact angle on glass surface of 200-300 penetration bitumens

Fig. 33. Variation of contact angles formed by bitumens of identical viscosities (bitumens from the same source)

Fig. 34. Variation of contact angles formed by bitumens of identical viscosities (bitumens from different sources)


ABSOLUTE VISCOSITY, CENTIPOISE
5000
1000
500
A-1
A-3
A-5
A-7
A-8
A-9
0
5
10
15
20
25
CONTACT ANGLE ON GLASS SURFACE, DEGREE


ABSOLUTE VISCOSITY, CENTIPOISE
5000
1000
500
A-1
B-7
C-7
D-1
D-3
E-1
0
5
10
15
20
25
CONTACT ANGLE ON GLASS SURFACE, DEGREE

the viscosity of the bitumen will be very close to 500, 1000 and 5000 centipoises as set by the comparison tests.

The theoretical plots between surface tensions and contact angles of a few selected bitumens are shown in Figures 35 to 37. It is generally true that the effect of temperature to surface tension is not very critical. Experiments on droplets formed by controlled surface tension seem to be unnecessary. Possible discrepancy between theoretical and actual will be within the limits of the accuracy of the measuring equipment.

Statistical results from the hundreds of angle measurements formed on aggregates with both polished and split surfaces deviate considerably under the same temperature. The results of this are shown in Tables 8 through 12.

Evaluation of Adhesion Tension between Bitumens and Solids

As already discussed in the previous chapter, neither the interfacial tension between solid and air or water is known, nor is there as yet a direct method of determining them. However, the difference between these two tensions yields the adhesion tension, which be calculated from the known angle of contact and the surface tension of the bitumen under question. The value of this adhesion tension has always been considered as another primary way of estimating

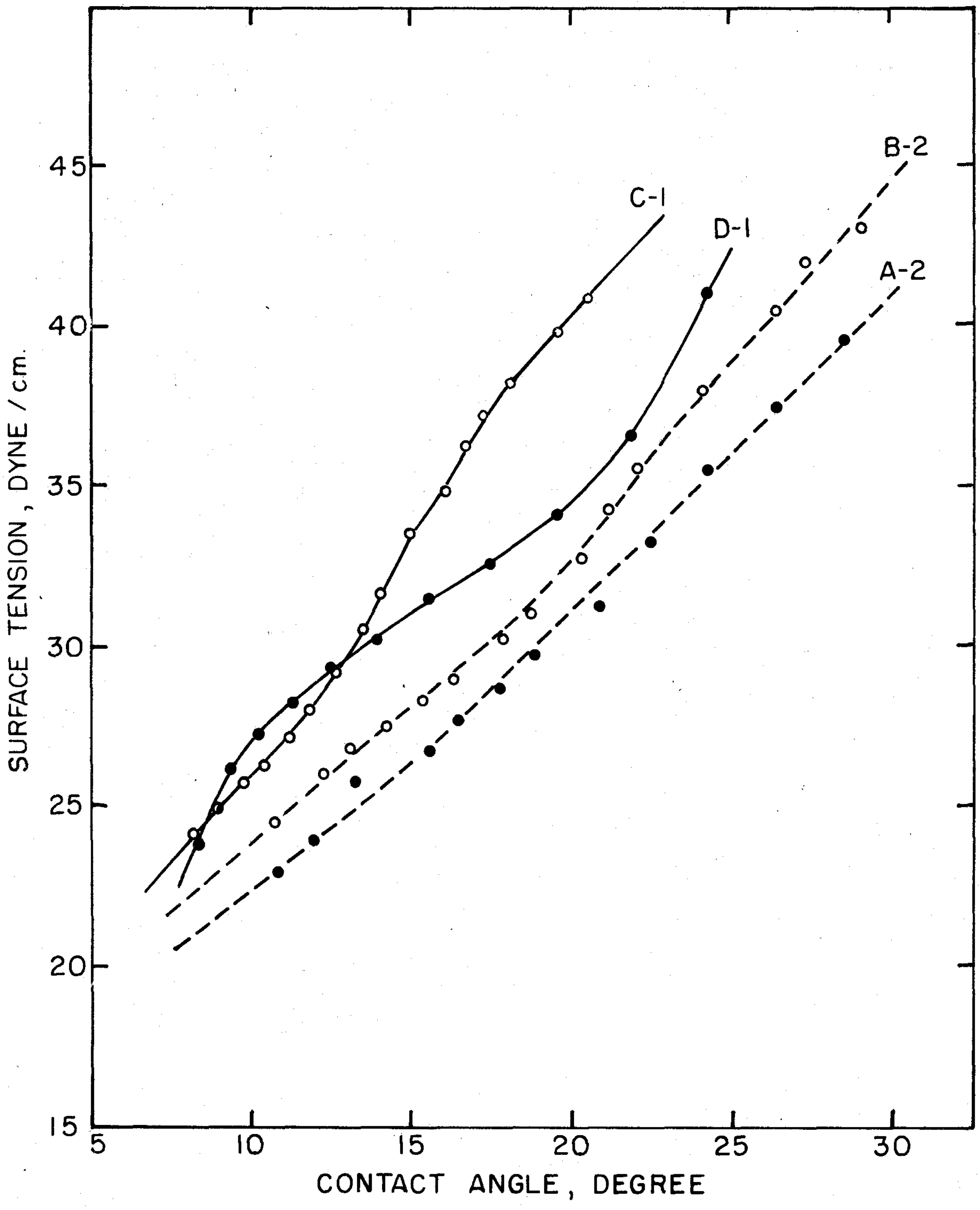


Fig. 35. Relationship between surface tension and contact angle on glass surface of 50-60 penetration bitumens

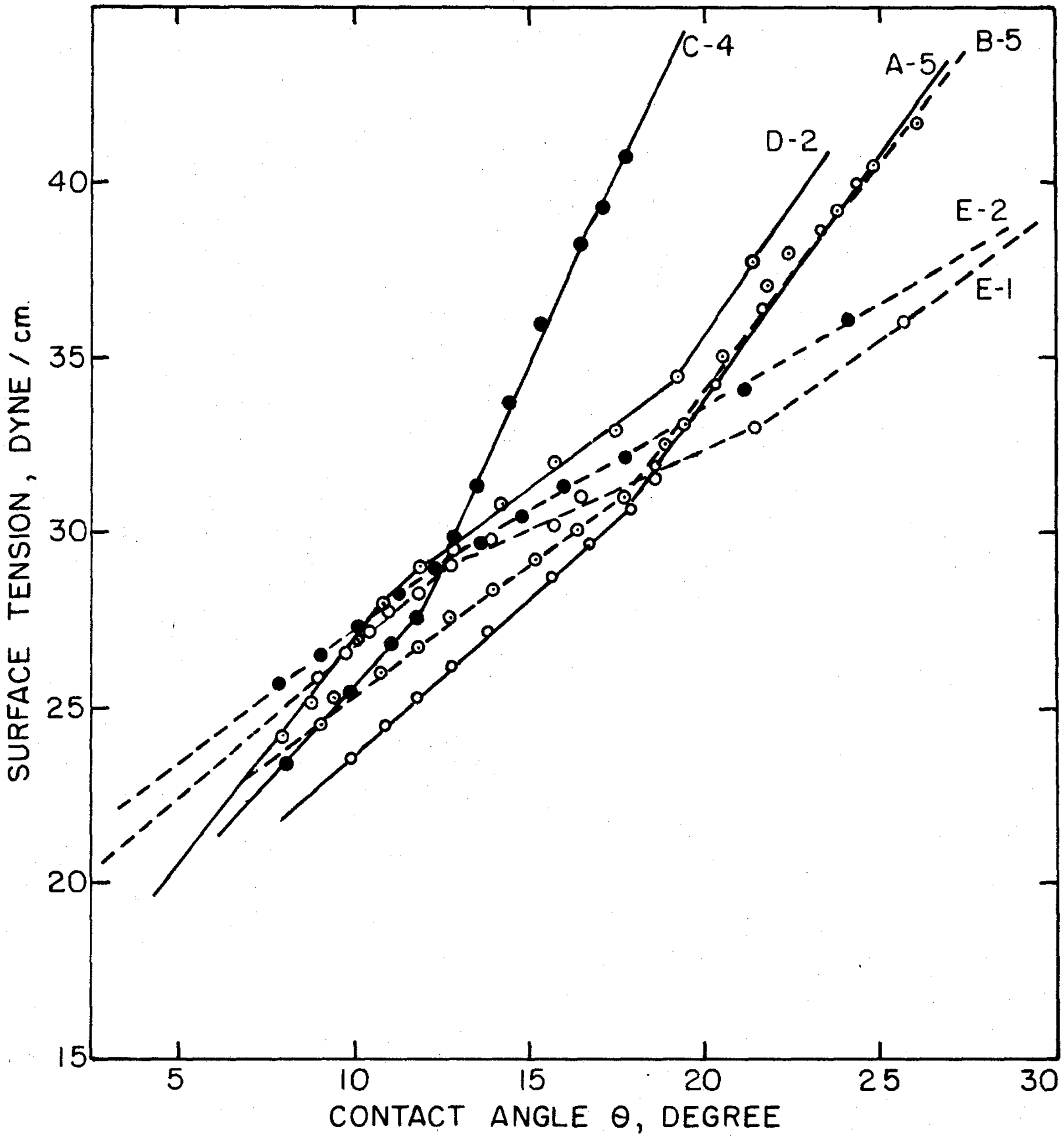


Fig. 36. Relationship between surface tension and contact angle on glass surface of 85-100 penetration bitumens

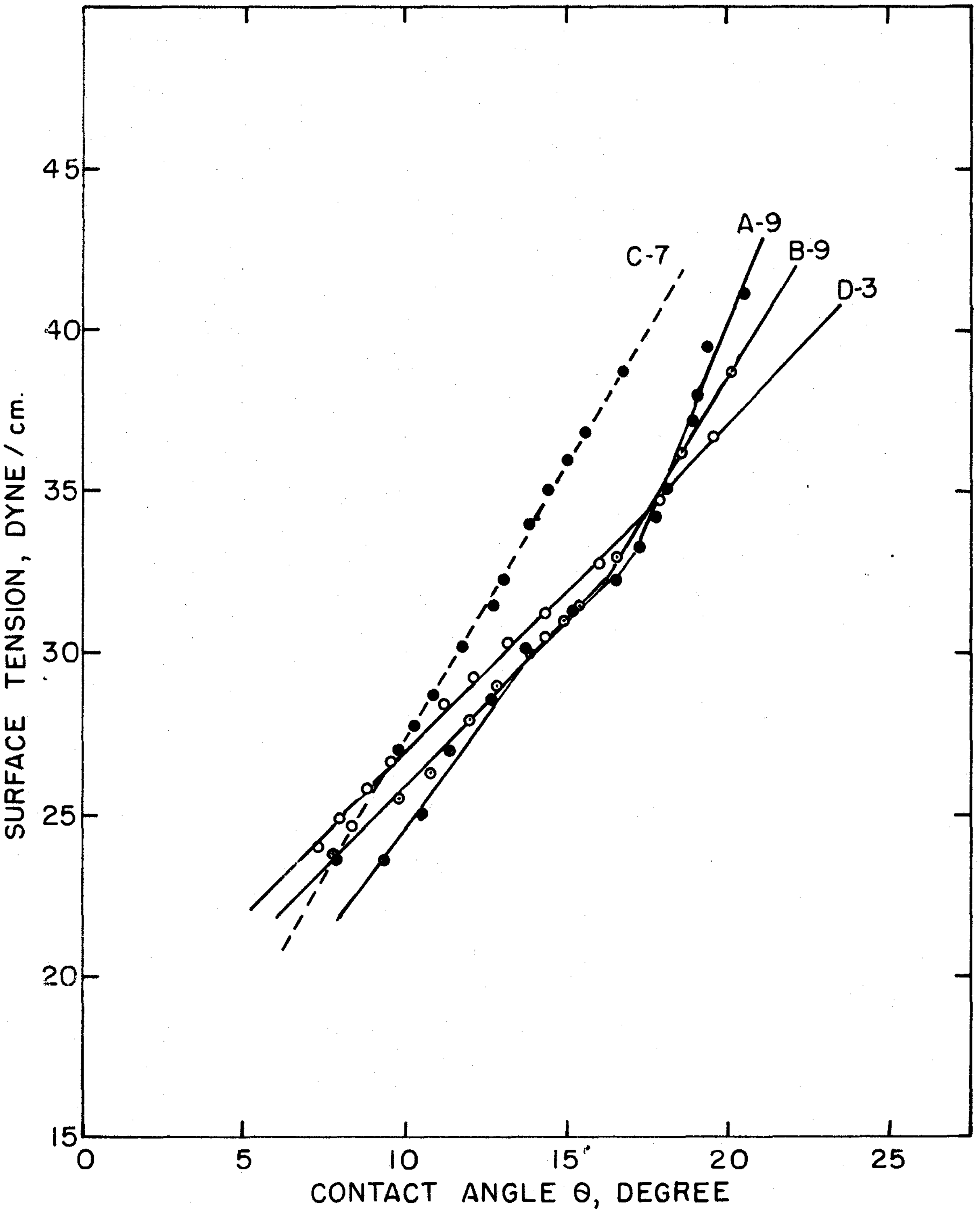


Fig. 37. Relationship between surface tension and contact angle on glass surface of 200-300 penetration bitumens

Table 8. Contact angles formed by series A bitumens on aggregates with polished and split surfaces

Bitumen		Application temperature		% of Asphaltene 86/88'Be Naphtha	Limestone		Black trap	
Code	Penetration	Bitumen	Aggregate		Polished surface	Split surface	Polished surface	Split surface
A-1	33	300°F.	350°F.	27.9	11°23'	11°10'	15°38'	14°27'
			300		15°14'	14°48'	20°23'	21°53'
		250	250		20°53'	21° 7'	24°48'	27° 9'
			200		30°29'	34°51'	38°19'	41°18'
			150		*32°-48°	*36°-57°	*43°-56°	*44°-60°
A-5	90	300	350	21.7	7°34'	8°21'	10°48'	10°18'
			300		10°56'	11°21'	13°13'	14°27'
		250	250		12°34'	12°43'	19°52'	20°14'
			200		25°40'	26°53'	32°44'	34°52'
			150		38°11'	38°47'	46°30'	47° 0'
A-7	123	300	350	18.8	6°30'	5°48'	7°54'	7°30'
			300		7°48'	9° 0'	11°24'	12° 0'
		250	250		11°30'	13°14'	16° 0'	15°30'
			200		23° 0'	25°30'	28°30'	30°14'
			150		33°27'	34°30'	40°14'	41° 0'
A-9	217	300	350	17.6	6°30'	6° 0'	6°45'	7° 0'
			300		7° 0'	7°10'	8°14'	8°42'
		250	250		9°20'	9° 0'	10°51'	11° 4'
			200		20°43'	20°30'	26°40'	27° 0'
			150		32° 0'	33°30'	36°23'	38°41'

*Wide variation in measured angles

Table 9. Contact angles formed by series B bitumens on aggregates with polished and split surfaces

Bitumen		Application temperature		% of Asphaltene 86/88'Be Naphtha	Limestone		Black trap	
Code	Penetration	Bitumen	Aggregate		Polished surface	Split surface	Polished surface	Split surface
B-1	45	300°F.	350°F.	4.9	7°21'	8° 0'	10° 0'	12°30'
			300		13°34'	14°22'	15°57'	15° 0'
		250	250		24°48'	23°14'	28°30'	30°29'
			200		36°30'	38°42'	39° 0'	41°24'
			150		45°32'	47°50'	49°30'	54°17'
B-5	86	300	350	19.5	8°36'	9°40'	11°38'	10°18'
			300		10°40'	11°24'	18°50'	18°30'
		250	250		21°32'	20°50'	27° 0'	27°12'
			200		33°10'	32°27'	37° 0'	38° 6'
			150		40° 0'	44°12'	48° 0'	49°34'
B-7	141	300	350	18.4	6°19'	5°21'	5°54'	6°30'
			300		8° 0'	8°29'	11°23'	10°50'
		250	250		16°30'	16° 0'	22° 8'	24°19'
			200		22° 6'	24°17'	31°43'	30°56'
			150		31° 0'	31°14'	38°27'	40° 0'
B-9	216	300	350	9.8	5° 0'	4°30'	5°12'	5° 0'
			300		6°19'	8°13'	10° 2'	10° 0'
		250	250		14°38'	16° 0'	19°54'	21°13'
			200		20°13'	20° 0'	24° 6'	27°42'
			150		25°30'	27°24'	32° 0'	33°21'

Table 10. Contact angles formed by series C bitumens on aggregates with polished and split surfaces

Bitumen		Application temperature		% of Asphaltene 86/88°Be Naphtha	Limestone		Black trap	
Code	Penetration	Bitumen	Aggregate		Polished surface	Split surface	Polished surface	Split surface
C-1	54	300°F.	350°F.	21.8	7°27'	7° 0'	10°53'	11° 0'
			300		10°30'	10°43'	19°30'	24°13'
		250	250		21°11'	24°14'	29°32'	27°10'
			200		34°50'	33°40'	44°30'	44° 0'
			150		40°28'	41° 0'	58°24'	55°41'
C-4	90	300	350	19.3	6° 0'	6°30'	7°50'	8°10'
			300		8°40'	7°54'	14°24'	13°30'
		250	250		19°18'	19° 0'	22°11'	22°30'
			200		21°40'	23°28'	33°12'	35° 0'
			150		36°40'	37°16'	41°27'	40°30'
C-7	306	300	350	10.3	4°12'	4° 0'	5°30'	4°40'
			300		6° 0'	5°28'	7°30'	7°17'
		250	250		17°21'	14° 3'	19°33'	20°30'
			200		23°50'	22° 0'	28°14'	29°30'
			150		30° 0'	28°27'	31°37'	34° 0'

Table 11. Contact angles formed by series D bitumens on aggregates with polished and split surfaces

Bitumen		Application temperature		% of Asphaltene 86/88'Be Naphtha	Limstone		Black trap	
Code	Penetration	Bitumen	Aggregate		Polished surface	Split surface	Polished surface	Split surface
D-1	51	300°F.	350°F.	22.1	7°48'	7° 0'	12°33'	11° 0'
			300		13°27'	15°21'	19°43'	16°30'
		250	250		20°30'	21°32'	26° 3'	26°17'
			200		31°14'	29°50'	42°30'	45°42'
			150		48°17'	48°35'	58°19'	57°13'
D-2	98	300	350	19.1	6°11'	6°48'	9°21'	13°28'
			300		9° 7'	11° 5'	15°17'	19°20'
		250	250		22°32'	24°41'	27°33'	28°14'
			200		28°29'	27°12'	37°30'	39°34'
			150		40°14'	41° 2'	50°31'	51°35'
D-3	191	300	350	13.3	3°25'	4°10'	6°14'	7°24'
			300		7°41'	6°30'	10° 0'	14°53'
		250	250		18°27'	16° 0'	21°30'	20°24'
			200		20°20'	19°30'	30°19'	37°35'
			150		31°19'	34°17'	40°10'	46°23'

Table 12. Contact angles formed by series E bitumens on aggregates with polished and split surfaces

Bitumen		Application temperature		% of Asphaltene 86/88'Be Naphtha	Limestone		Black trap	
Code	Penetration	Bitumen	Aggregate		Polished surface	Split surface	Polished surface	Split surface
E-1	92	300°F.	350°F.	31.4	10°30'	9° 0'	11°13'	10°45'
			300		13°48'	18°13'	19°24'	22°13'
		250	250		27°22'	26°14'	28°45'	30°25'
			200		48° 0'	54°26'	53°17'	52°28'
			150		*50°-69°	*62°-74°	*55°-79°	*56°-78°
E-2	86	300	350	16.5	7°47'	8°12'	6°34'	6°14'
			300		10° 0'	10°29'	11°43'	12°49'
		250	250		21°47'	24°16'	27° 6'	31°43'
			200		30° 7'	30°21'	43°36'	50° 4'
			150		*38°-52°	*34°-53°	*49°-65°	*52°-66°

*Wide variations in measured angles

the degree of adhesion between a solid and a bitumen when the question of stripping is in doubt. No attempt has been made to include this problem in the present study, but for comparative purposes, the calculation of the adhesion tensions on solid by several bitumens at a given temperature are calculated by the following formula:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos\theta$$

and $\gamma_{SA} - \gamma_{SL}$ = adhesion tension = $\gamma_{LA} \cos\theta$

and the results are given in Tables 13 and 14, and 15.

Table 13. Typical adhesion tensions for bitumens against glass surfaces

Bitumen sample	Temperature of solid ° F.	Surface tension at solid temperature dyne per cm.	Contact angle θ degree	Cos θ	Adhesion tension dyne per cm.
A-1	300	27.7	17.5	0.954	26.4
	250	30.0	21.4	0.931	27.9
	200	35.4	25.8	0.900	31.9
A-5	300	28.0	14.5	0.968	27.1
	250	30.2	16.0	0.961	29.0
	200	34.2	20.3	0.938	32.1
A-9	300	27.8	12.0	0.978	27.2
	250	30.0	13.7	0.972	29.2
	200	32.3	16.5	0.959	31.0
B-1	300	28.7	15.2	0.965	27.7
	250	30.7	19.0	0.946	29.0
	200	34.5	23.7	0.916	31.6
B-5	300	28.5	14.8	0.967	27.6
	250	30.5	16.8	0.957	29.2
	200	35.0	20.5	0.937	32.8
B-9	300	27.8	11.8	0.979	27.2
	250	30.0	14.0	0.970	29.1
	200	32.3	16.5	0.959	31.0
C-1	300	28.0	12.0	0.978	27.4
	250	30.5	14.0	0.970	29.6
	200	36.1	16.6	0.958	34.6
C-4	300	26.9	11.0	0.982	26.4
	250	29.7	12.6	0.976	29.0
	200	35.1	14.7	0.967	33.9
C-7	300	28.0	10.2	0.984	27.6
	250	30.1	11.7	0.979	29.5
	200	34.1	13.5	0.972	33.1
D-1	300	29.3	12.4	0.977	28.6
	250	32.0	16.5	0.959	30.7
	200	36.5	21.7	0.929	33.9

Table 13. (Continued)

Bitumen sample	Temperature of solid ° F.	Surface tension at solid temperature dyne per cm.	Contact angle θ degree	Cos θ	Adhesion tension dyne per cm.
D-2	300	29.0	11.8	0.979	28.4
	250	31.5	15.0	0.966	30.4
	200	34.5	19.2	0.944	32.6
D-3	300	28.6	11.1	0.981	28.1
	250	31.0	13.8	0.971	30.1
	200	33.5	18.0	0.951	31.9
E-1	300	29.1	12.7	0.976	28.4
	250	30.7	15.6	0.963	29.6
	200	33.0	21.8	0.928	30.6
E-2	300	29.6	13.5	0.972	28.8
	250	31.7	16.8	0.957	30.3
	200	34.6	21.3	0.932	32.2

Table 14. Typical adhesion tension for bitumens against limestone surfaces

Bitumen sample	Temperature of solid ° F.	Surface tension of bitumen at solid temperature, dyne per cm.	Contact angle θ degree		Cos θ		Adhesion tension dyne per cm.	
			(1)*	(2)*	(1)*	(2)*	(1)*	(2)*
A-1	300	27.7	15.2	14.8	0.965	0.967	26.7	26.8
	250	30.0	20.9	21.1	0.934	0.933	28.0	28.0
A-5	300	28.0	10.9	11.3	0.982	0.980	27.5	27.4
	250	30.2	12.6	12.7	0.976	0.975	29.5	29.4
A-9	300	27.8	7.0	7.1	0.993	0.992	27.6	27.6
	250	30.0	9.3	9.0	0.987	0.988	29.6	29.6
B-5	300	28.5	10.6	11.4	0.983	0.980	28.0	27.9
	250	30.5	21.5	20.8	0.989	0.991	30.2	30.2
C-4	300	26.9	8.7	7.9	0.989	0.991	26.6	26.7
	250	29.7	19.3	19.0	0.944	0.946	28.0	28.1
D-2	300	29.0	9.1	11.1	0.987	0.981	28.6	28.4
	250	31.5	22.5	24.7	0.924	0.909	29.1	28.6
E-1	300	29.1	13.6	18.2	0.971	0.950	28.3	27.6
	250	30.7	27.4	26.2	0.888	0.897	27.3	27.5
E-2	300	29.6	10.0	10.5	0.985	0.980	29.2	29.0
	250	31.7	21.8	24.3	0.929	0.912	29.4	28.9

*(1) -- Polished surface
(2) -- Split surface

Table 15. Typical adhesion tension for bitumens against black trap surfaces

Bitumen sample	Temperature of solid °F.	Surface tension of bitumen at solid temperature, dyne per cm.	Contact angle θ degree		Cos θ		Adhesion tension dyne per cm.	
			(1)*	(2)*	(1)*	(2)*	(1)*	(2)*
A-1	300	27.7	20.4	21.9	0.937	0.928	25.9	25.7
	250	30.0	24.8	27.1	0.908	0.890	27.2	26.7
A-5	300	28.0	13.2	14.4	0.974	0.968	27.3	27.1
	250	30.2	19.9	20.2	0.940	0.938	28.4	28.3
A-9	300	27.8	8.2	8.8	0.990	0.988	27.5	27.5
	250	30.0	10.9	11.0	0.982	0.981	29.5	29.4
B-5	300	28.5	18.8	18.5	0.946	0.948	27.0	27.0
	250	30.5	27.0	27.2	0.891	0.889	27.2	27.1
C-4	300	26.9	14.4	13.5	0.969	0.972	26.1	26.1
	250	29.7	22.2	22.5	0.926	0.924	27.5	27.4
D-2	300	29.0	15.3	19.3	0.965	0.944	28.0	27.4
	250	31.5	27.5	28.2	0.887	0.881	27.9	27.8
E-1	300	29.1	19.4	22.2	0.943	0.926	27.4	26.9
	250	30.7	28.7	30.4	0.877	0.863	26.9	26.5
E-2	300	29.6	11.7	12.8	0.979	0.975	29.0	28.9
	250	31.7	27.1	31.7	0.890	0.851	28.2	27.0

*(1) -- Polished surface
(2) -- Split surface

DISCUSSION

Factors affecting the degree of adhesion between bitumens and aggregates are numerous. In this investigation, emphasis was centered mainly on the rheological properties of bitumens and the effects of surface characteristics of aggregate upon adhesion.

Comparison of the viscosities of five series of bitumens confirmed the general belief that bitumens behave as non-Newtonian liquids at relatively low temperatures. Certain flow curves (Figures 2 and 3) do not give a perfect straight line function, indicating that the bitumen remains Newtonian in character up to a certain rate of shear, after which a temporary decrease or increase in the viscosity is brought about by the shearing stress. For normal bitumens, series A-D, decreasing viscosities are prevalent at higher rate of shear. In the cracked bitumens, series E, the reverse is true. Changes in viscosities with the rate of shear are probably due to the dissociation of the molecular structures in the micelles. The variation in shear consequently will alter the degree of dispersion in their colloidal state.

In this study, bitumens were applied at low consistencies. The resulting flow characteristics approached the Newtonian character. The measurement of viscosity by using the Brookfield viscometer is feasible since the result is well correlated with the data obtained from other apparatus commonly used for measuring viscosity (Table 5).

At temperatures above 350° F., no detectable difference was observed in viscosity among all five series of bitumens. This indicates clearly that under such temperature condition, in spite of the difference in asphaltene contents, grades, sources or degree of thixotropy, there is no change in the flow properties of the bitumens. When the temperature is low, a marked difference was found in the viscosity for bitumens of equal penetration but from different sources. Bitumens A-3, B-3 and C-2, for example, all have similar penetration. Their viscosities measured at 200° F. are 27,000, 7,200 and 31,000 centipoises respectively. B-3 bitumen was 3.7 to 4.2 times less viscous than the A-3 and C-2 bitumens. At 150° F., viscosities were found to be 735,000, 82,000 and 1,900,000 centipoises respectively. Here the viscosity of B-3 bitumen was nine to 23 times lower than A-3 and C-2. At higher temperature such as 400° F., their viscosities were practically equal to each other at 40 centipoises. The same holds true for other bitumens with the exception of the cracked bitumens, where their viscosities are changeable and inconsistent. It seems evident that penetration test alone is not adequate for identifying the relative physical and chemical characters of bitumens.

The straight line curve obtained from the plot of logarithm viscosity versus absolute temperature on the log-log co-ordinates is extremely useful. An empirical equation is thus established for each grade of bitumen as:

$$\log \log \eta = \log A - m \log T_{absolute}.$$

The significant constant in this equation appeared to be m rather than A. Constant m is the tangent of the angle made by the logarithmic curve with the axis of the abscissa. It serves as an index to measure the temperature susceptibility of bitumens. Constant A is the logarithm of the absolute temperature when the logarithmic curve is extrapolated to unit viscosity. Curves plotted in Figures 9 to 12 were calculated from this empirical formula. The results are in perfect agreement with the actual observed data. For cracked bitumen E-2, however, the observed and calculated viscosities do not coincide with each other. The deviation may be due to errors in the measurement or that the equation is not valid for this bitumen having thixotropic character. The advantage of this equation is that it furnishes a convenient means of predicting the viscosity of all kinds of bitumens at temperatures within the range of 140° F. to 400° F., an information which is of particular interest to the bituminous paving technologists.

Temperature exhibits pronounced effect on the surface tension of bitumens in liquid and semi-solid states. Between

200° F. to 250° F. abrupt transitions were observed in the surface tension curves (Figures 14 to 18). These transition points generally appeared at low temperature when the penetration of the bitumen is high. The linear proportion at the two ends of each curve indicates that the surface tension is directly proportional to the temperature below and above the transition temperature. The breaks in all these curves suggested that at specific temperature, changes in the molecular structures are taking place. This same phenomenon did not appear in each viscosity curve, therefore such changes probably did not occur inside the colloidal system of the bitumen but at the surface boundary.

In view of the important effects that surface tension and viscosity exert upon the physical characteristics of bitumens, plots of viscosity versus surface tension for bitumens of similar penetration were made. Results on Figures 19 and 20 showed the perfect straight line relationship in most of the bitumens, especially series A and C. The uniform variation means that such bitumens are very homogeneous in physical character. On the contrary, the curves for the two cracked E series bitumens were very irregular in shape. Such variation revealed their heterogeneous quality . The comparison of the high penetration bitumens (Figure 21) showed only slight variation in qualities among them. In spite of these variations, the bitumens seem to have an identical response to the changes of viscosities or surface tensions. The relatively straight line curve of C-7 bitumen indicates the good quality possessed by the series C bitumens over the other four series.

For perfect adhesion between liquid bitumen and a solid, two stages are involved. First is the wetting of the solid by the liquid and the second is the interaction of the surface energies of the two substances across the area of contact. As discussed before, one of the factors that affect the progress of the first stage is the rheological properties of the bitumen; the second stage can be analyzed by studying the effect of the solid surface characteristics and the adhesion tension between the bitumens and solids. The useful means to evaluate such effects is the study of the equilibrium contact angle formed on the solid surfaces. Results indicate that the contact angle formed by a small bitumen droplet on solid surface is directly related to the characteristics of the solid and the bitumen. This angle, if not subjected to any external forces, will not change in value when the state of equilibrium is reached.

The study on the rate of spreading of bitumen on different solids is valuable. The slope in the first portion of the spreading curve revealed a significant relationship between the consistency of bitumens and the surface characteristics of solids. With two experimental bitumen droplets of identical size and viscosity, the relative adhesion quality of two aggregates at the same temperature can be estimated by comparing the spreading areas covered by the droplets since we know that the size of contact angle is inversely proportional to the spreading area.

The effect of temperature upon the solid and bitumen is equally important in the formation of contact angles. Any change in temperature not only alters the consistency of the bitumen, but also energizes the effect of the surface polarity in the solid. Smooth glass surfaces serve as an ideal aggregate, upon which the effects produced by roughness, absorption and polarity in actual aggregates were eliminated. Differences in the size of contact angles obtained thus serve as an index to predict the adhesive qualities of the different bitumens. The C series has consistent physical properties. They formed smaller contact angles and consequently provide better adhesion to aggregates.

Temperature seems to produce significant effect upon the formation of contact angle. The family of curves (Figures 24 to 28) for the bitumens from the five different sources behave similarly. At high temperature range, identical contact angles were observed. As temperature decreases, contact angles varied according to their penetrations and sources. The critical temperature at which unequal change of angles took place seems to be at the vicinity of 250° F. Above this temperature, angles change per degree temperature was relatively small. Below this temperature, the slopes of all the curves were flatter indicating that any slight change of temperature either in bitumen or solid will increase the angle of contact greatly and thus reduces the force of adhesion.

The effect of temperature upon bitumens is actually the alteration of their viscosity. It is quite clear from the plots of viscosity versus contact angle (Figures 30 to 34) that their relationships are in straight line function. The two cracked bitumens, E-1 and E-2 were found to be exceptions. Under equal viscosity, bitumens of similar penetration showed a marked difference in the size of contact angles. With viscosity of less than 40 centipoises, their angles are different by two degrees. At higher viscosity range, the difference may amount up to ten degrees. Again, bitumens from the C series seem to possess the best adhesion to aggregates.

The chemical nature of aggregates is often considered as another major factor that affects the quality of adhesion between bitumens and aggregates. Limited data conducted on the chemically treated glass surfaces (Figure 29) approximated to the general belief that acidic stones gave poorer adhesion with common bituminous paving materials. It seems that if with the presence of moisture similar to actual pavement aggregates, a more significant difference may obtain concerning the adhesion quality on the NaOH and HCl treated glass surfaces.

The technique for the determination of contact angles formed on aggregate surfaces is theoretically sound and useful. The small drop of bitumen can be applied successfully to the small area of the irregular surface which assumed the advancing angle of contact. The aggregates studied were the hydrophobic limestone and the highly hydrophilic Black Traps. Data obtained (Tables 8 to 12) were well correlated with the findings performed on glass surfaces. On split and polished surfaces of both aggregates, contact angles do not vary greatly among bitumens of similar penetration at temperature above 250° F. Below this temperature, considerable effects were observed. Contact angles formed on the Black Trap aggregates, however, were generally larger than those on limestone surfaces even though other pertinent factors were constant. Such variation may account for their differences in surface textures and chemical nature.

Good adhesion, as we know, is dependent on the surface tension and the contact angle formed by the bitumens on solid surfaces. Evaluation for such relationship is generally calculated in terms of their adhesion tension. In Tables 13 to 15 the calculated adhesion tensions indicate no significant differences between the different kinds of bitumens on the three types of solid surfaces. It seems that in our case it is not appropriate to use these values to determine the adhesion qualities of the bitumens in question. Temperatures were found to exert pronounced effects on the contact angles but only small changes upon the surface tension of the bitumens. For comparative study of adhesion, the measurement of contact angles alone seems to be able to furnish us some information concerning the adhesion quality and the degree of wetting of bitumens.

SUMMARY AND CONCLUSIONS

This investigation was concerned mainly with the rheological properties of bitumens and the effect of surface characteristics of aggregates to the degree of adhesion.

Conclusions may be summarized as follows:

1. Five series of bitumens, four normal and one cracked, were used in this study. They are non-Newtonian in character but exhibit the properties of simple liquid at temperatures above 200° F.

2. Under the same temperature, bitumens of equal penetration do not give the same viscosity or equal angle of contact on the same aggregate. Therefore, the use of penetration test alone is inadequate to determine the physical and chemical properties of a bitumen.

3. An empirical formula can be established for the relationship between viscosity and temperature:

$$\log \eta = AT_{abs.}^{-m}$$

where η is the absolute viscosity in centipoise, $T_{abs.}$ is the absolute temperature in rankine, A and m are constants. The exponent m can be used to detect the temperature susceptibility. This formula is applicable for all the bitumen series except the cracked one.

4. The change in systems from semi-solid to liquid state were observed from the abrupt transition points in the surface tension-temperature curves. The locations of the point of transition vary slightly according to the types of bitumen. They all occurred within the temperature range of 200° to 250° F. This range is extremely useful for the determination of proper mixing temperature in paving construction.

5. Specific adhesion can be evaluated between bitumen and aggregate by means of the measurements of their angle of contact. The smaller the contact angle, the better is their mutual affinity.

6. For comparing the adhesive characteristics among the bitumens, smooth glass surfaces were used to serve as ideal aggregates, upon which all the effects due to roughness, absorption and polarity in natural aggregates were eliminated.

7. Contact angles vary with the change of temperature of the aggregates. The critical temperature of such change appeared to be 250° F.

8. The percentage of asphaltene content is found to be another important factor that affects the adhesive quality of the bitumens. The higher the percentage, the lower the adhesion tension produced on the aggregates.

9. The petrological nature of the aggregates do affect the degree of adhesion for the same bitumen. The hydrophobic

limestones consistently formed smaller contact angles than the hydrophilic Black Traps. The same phenomenon correlated with the findings on the chemically treated glass surfaces. With the same kind of bitumen, acidic glass are found to possess larger contact angle than the basic glass.

10. If no external forces are involved, the equilibrium angle of contact once formed on the aggregate surface will not alter. Thus the initial wetting will decide the final adhesion tension.

11. The degree of roughness in the aggregates affects adhesion more severely than the effect due to their petrological differences.

12. The C-series bitumens seem to give the best adhesion to the two aggregates than the remaining four series.

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