

CONSTITUTIONAL EFFECTS ON ADHESION AND ABHESION

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ABSTRACT

It is well known that adhesion between organic solids is the result of intermolecular fields of forces which are highly localized in the vicinity of each solid surface. The effect of varying the chemical constitution of a material on its ability to adhere may be determined to a good first approximation by the nature and packing density of the atoms or molecular radicals in the solid surface. This general conclusion has been established by experiments on the wetting of liquids and solids, by the effect of the constitution of polymeric solids on friction, and by the overriding effect of monomolecular adsorbed films on adhesion. It is shown that the reversible work of adhesion w_A of a liquid to a low-energy solid can be calculated approximately from the contact angle and liquid surface tension because of the minor importance of vapor adsorption in such systems. It is shown that both w_A and the maximum capillary rise in pores and crevices are parabolic functions of the liquid surface tension. The resulting data are discussed in terms of surface constitutive effects, changes in w_A , and in the internal stress concentrations developed as the adhesives solidify. The entire mechanism of operation of so-called mold-release agents follows from considerations regarding the effect of organic structure on the critical surface tension of wetting, γ_c , and from the effects of surface roughness and viscous flow in causing incomplete wetting, gas pockets, and stress concentrations at the interface. Finally, an explanation is offered of De Bruyne's rule on the effect of polarity on the strength of adhesive joints.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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CONSTITUTIONAL EFFECTS ON ADHESION AND ABHESION

ADHESIVE ACTION OF LIQUIDS

For over 40 years it has been known that when two flat, smooth, solid surfaces are separated by a thin layer of a liquid having a zero contact angle, considerable adhesion will result. This effect arises from the liquid surface tension (γ_{LV}^0) and the fact that there will be a concave meniscus at the liquid/air interface. If the area of contact of the liquid with the solid is circular and of diameter R and thickness d , and if the liquid layer is thin enough so that the meniscus can be treated as a circular toroid of radius $r = d/2$, then the Laplace equation of capillarity (1) leads to the relation

$$p_L - p_A = \gamma_{LV}^0 \left(\frac{1}{R} - \frac{1}{r} \right). \quad (1)$$

If $r \ll R$, then $p_L - p_A$ will be a large negative quantity, and hence there will be greater pressure p_A in the air outside the liquid than the value p_L inside, and the two plates will be pressed together under the pressure difference $p_A - p_L$. In short, a thin layer of a liquid which completely wets two flat solids can serve as an adhesive. Equation (1) has been confirmed experimentally by Budgett (2), Hardy (3), Bastow and Bowden (4), and more recently by De Bruyne (5,6). For example, Budgett found that two highly polished steel plates 4.5 cm in diameter, when completely wet by a film of paraffin oil having a surface tension of between 28 and 30 dynes/cm, required a total force of about 20 kg to pull them apart. The calculated force is about 30 kg.

Such a method of forming an adhesional joint has several obvious practical limitations: (a) the resistance of the joint to shear stresses is determined solely by the viscosity of the liquid film, and hence only if the viscosity is very great could the shear strength of the joint be large; (b) it would be necessary to prepare extremely well-fitted, smooth surfaces on the solids to form a sufficiently strong joint; and (c) freedom from dust would be critically important. However, if the contact angle of a liquid adhesive with the adherend is small and if the liquid is viscous, a prompt and useful adhesive action is obtained upon pressing the solids together sufficiently to form a thin liquid layer. Thereafter a more permanent joint will be formed if the viscosity of the liquid layer increases greatly through any of various mechanisms such as (a) solvent permeation or evaporation, (b) polymerization, and (c) cooling until solidification occurs. The resulting joint can in this way be made to have high resistance to both tensile and shearing stresses. However, from the moment of application of the liquid adhesive to the completion of the thickening or solidifying stages, it is important that the contact angle of the adhesive and adherend be zero, or as nearly so as possible, in order that the liquid will spread freely over the adherend and also will flow into any pores and capillaries to create the greatest possible real area of contact of adhesive and adherend. Thus, progress in research on the wetting and spreading of liquids on solids should help illuminate the complex technology of adhesives and adhesion. It is the purpose of this report to discuss the relation of recent research on wetting to adhesion.

PHYSICAL FACTORS INFLUENCING THE CONTACT ANGLE

There still is widespread misunderstanding or ignorance about the effect upon the contact angle of the physical conditions existing during its measurement and about the effect on it of the constitution of liquid and solid. Matters have been made worse by the lack of

appreciation by the majority of past investigators of the necessity of controlling certain physical and chemical variables in order to obtain reproducible and trustworthy data. Publications containing significant, reliable, or up-to-date information on contact angles and their variation with constitution are rare. Therefore, it is essential to review here the present situation before attempting to discuss the effect of wettability on adhesion.

Basic to the subject of "wettability" is Thomas Young's concept (7) of the contact angle θ between a drop of the liquid and a plane solid surface (Fig. 1). When $\theta \neq 0^\circ$, the liquid is nonspreading; when $\theta = 0^\circ$, the liquid is said to completely wet the solid, and it will then spread freely over the surface at a rate depending on the viscosity and surface roughness. Every liquid wets every solid to some extent; that is, $\theta \neq 180^\circ$. In short, there is always some adhesion of any liquid to any solid. On a homogeneous solid surface θ is independent of the volume of the liquid drop so long as the hydrostatic pressure remains a minor factor. Since the tendency for the liquid to spread increases as θ decreases, the contact angle is a useful inverse measure of spreadability or wettability; obviously, cosine θ is a useful direct measure. Since a variety of methods for measuring the contact angle have been described in the literature, progress in understanding wetting phenomena has not been limited in this respect.

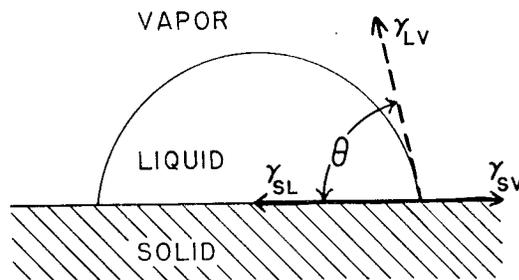


Fig. 1 - Contact angle

Probably the oldest experimental problem in measuring contact angles was the occurrence of large differences between the contact angle θ_A observed when a liquid boundary advances for the first time over a dry clean surface and the value θ_R observed when the liquid boundary recedes from the previously wetted surface. All investigators prior to about ten years ago were much puzzled about which angle is the more significant, θ_A or θ_R . We have devoted much attention to studying, controlling, and interpreting the advancing and receding contact angles and have found that the most common cause of the differences observed is the effect of pores and crevices in the surface of the solid in trapping some of the liquid as it is made to flow over the surface of the solid. When the liquid is forced to recede over that area at a later time, the surface uncovered usually includes wet area; hence, the receding contact angle is always lower than the advancing angle. Whenever sufficient care has been exercised in preparing and handling smooth, clean surfaces and whenever sufficiently pure liquids have been used, no significant differences have been found between the slowly advancing and receding contact angles (8-10).

One particularly interesting condition of a solid surface which can cause significant differences between the advancing and receding contact angles is the situation of a drop of water advancing over the surface of a smooth solid (like glass or platinum) previously coated with a close-packed, vertically-oriented monolayer of a long-chain fatty acid or fatty amine. Because molecules of water can diffuse between the adjacent, helically coiled, hydrocarbon chains of the adsorbed fatty molecules and can remain trapped there, the receding contact angle decreases to about 90 degrees. The advancing contact angle on a previously dry surface is 102 degrees (11,12). If the intermolecular pores of this organic film are previously saturated with water, the advancing and receding contact angles are both 90 degrees. However, if one uses instead a drop of a liquid like methylene iodide having a molecule which is much larger than water, the molecules of liquid are much

less able to diffuse into the pores between the hydrocarbon chains in the film, and the advancing and receding contact angles become equal (13). Effects like these are not at all uncommon in dealing with organic films and coatings.

Wenzel (14) showed over twenty years ago that the roughness, r , of a solid surface is related to the apparent, or measured, contact angle θ' between the liquid and the surface of the solid and to the true contact angle θ between the liquid and the surface at the air/liquid/solid contact boundary as follows

$$r = \frac{\cos \theta'}{\cos \theta}. \quad (2)$$

Here the macroscopic roughness factor r is defined as the ratio of the true area to the apparent area (or envelope) of the solid. Wenzel's relation has been discussed fully by Cassie and Baxter (15) and by Shuttleworth and Bailey (16). This simple relation is a consequence of the definition of r and the first two laws of thermodynamics. Wenzel's relation is especially valuable because surfaces having $r = 1.00$ are rarely encountered. Perhaps the nearest to such a smooth surface is that of freshly fire-polished glass or carefully cleaved mica. Carefully machined or ground surfaces have values of r from 1.5 to 2.0 or greater.

There are several important consequences of Wenzel's equation. Since r is always greater than one when $\theta < 90^\circ$, Eq. (2) indicates $\theta' < \theta$. Since most organic liquids exhibit contact angles of less than 90° on clean polished metals, the effect of roughening the metals is to make the apparent contact angle θ' between the drop and the envelope to the metal surface less than the true contact angle θ . In other words, each liquid will appear to spread more when the metal is roughened. When $\theta > 90^\circ$, Eq. (2) indicates $\theta' > \theta$. Since pure water makes a contact angle of from 105° to 110° with a smooth paraffin surface, the effect of roughening the surface tends to make θ' greater than 110° ; values of 140° have been observed (15).

Surface roughness adds to the difficulty of measuring θ accurately because the experimental methods used measure θ' , and it is often assumed $\theta' = \theta$. In order to make accurate measurements of small contact angles, the solid surface must be much smoother than when measuring large contact angles. Thus, when $\theta = 10^\circ$, the difference between the real and apparent angles will be 5° if $r = 1.02$; hence an even smoother surface will be necessary to keep the percent error low. When $\theta = 45^\circ$, the same 5° difference between θ and θ' will occur when $r = 1.1$. When $\theta = 80^\circ$, the 5° difference in θ and θ' will occur when $r = 2.0$; and hence a high surface finish is not so essential.

BASIC THERMODYNAMIC CONSIDERATIONS

Thomas Young (7) pointed out over 150 years ago that the three surface tensions γ_{sv}° , γ_{sl} , and γ_{lv}° existing at the phase boundaries of a drop of liquid at rest on a solid surface, as in Fig. 1, must form a system in static equilibrium. The resulting relation, which has been derived more satisfactorily by Sumner (17) by a simple thermodynamic argument using the analogous specific free surface energies rather than the surface tensions, is

$$\gamma_{sv}^\circ - \gamma_{sl} = \gamma_{lv}^\circ \cos \theta. \quad (3)$$

Here the subscripts sv° and lv° refer to the solid and liquid in equilibrium with the saturated vapor, respectively. It should be noted that the contact angle used here must be the value measured under conditions of thermodynamic equilibrium. Also it should be noted that when $\theta = 0$, we can only conclude

$$\gamma_{sv}^\circ \geq \gamma_{sl} + \gamma_{lv}^\circ.$$

Dupré (18) over a half a century later showed that w_A , the reversible work of adhesion per unit area of one liquid with another liquid (or with a solid), is related to the various specific free surface energies as follows:

$$w_A = \gamma_{S^\circ} + \gamma_{LV^\circ} - \gamma_{SL} . \quad (4)$$

Here S° refers to the solid in a vacuum. If we are interested in the work $w_{A'}$ to pull the liquid off the surface leaving the equilibrium adsorbed film, then

$$w_{A'} = \gamma_{SV^\circ} + \gamma_{LV^\circ} - \gamma_{SL} . \quad (5)$$

By elimination of γ_{SL} from Eqs. (3) and (5), we obtain

$$w_{A'} = \gamma_{LV^\circ} (1 + \cos \theta) . \quad (6)$$

From an application of this relation to a liquid/liquid interface made up of two layers of the same liquid, the specific reversible work of cohesion w_c of the liquid is simply

$$w_c = 2\gamma_{LV^\circ} . \quad (7)$$

It wasn't until 1937 that Bangham and Razouk (19) first recognized the surface energy change resulting from the adsorption of vapor on the surface of the solid could not be generally neglected and derived the following equation for w_A from Eqs. (3) and (4):

$$w_A = (\gamma_{S^\circ} - \gamma_{SV^\circ}) + \gamma_{LV^\circ} (1 + \cos \theta) . \quad (8)$$

Here γ_{SV° is the specific free surface energy of the solid immersed in the saturated vapor of the liquid; hence $\gamma_{S^\circ} - \gamma_{SV^\circ}$ is the specific free energy decrease on immersion of the solid in the saturated vapor of the liquid. We will use their symbol f_{SV° to represent this free energy change, i.e.,

$$f_{SV^\circ} = \gamma_{S^\circ} - \gamma_{SV^\circ} . \quad (9)$$

Thus Eq. (8) can be written

$$w_A = f_{SV^\circ} + \gamma_{LV^\circ} (1 + \cos \theta) . \quad (10)$$

Hence, from Eq. (6),

$$w_A - w_{A'} = f_{SV^\circ} . \quad (11)$$

Bangham and Razouk also pointed out that if the surface concentration of the adsorbed vapor from the liquid is Γ and the chemical potential is μ , then

$$\Gamma = - \left(\frac{\partial \gamma}{\partial \mu} \right) \quad (12)$$

or

$$\gamma_{S^\circ} - \gamma_{SV^\circ} = \int_{p=0}^{p=p_0} \Gamma d\mu , \quad (13)$$

where p is the vapor pressure and p_0 the saturated vapor pressure. In the special case where the vapor behaves like a perfect gas, $d\mu = RT d \ln p$, so that

$$f_{SV^\circ} = \gamma_{S^\circ} - \gamma_{SV^\circ} = RT \int_p^{p_0} \Gamma d \ln p = RT \int_p^{p_0} \frac{\Gamma}{p} dp . \quad (14)$$

Hence, f_{SV° will always have a positive value. This makes it evident that in general $w_A > \gamma_{LV^\circ} (1 + \cos \theta)$.

Cooper and Nuttall (20) originated the well-known conditions for the spreading of a liquid substance "b" on a solid (or liquid) substance "a:"

$$\begin{aligned} \text{For spreading} & \quad S > 0, \\ \text{for nonspreading} & \quad S \leq 0, \\ \text{where} & \quad S = \gamma_a - (\gamma_b + \gamma_{ab}) \end{aligned} \quad (15)$$

or in the above notation for a solid

$$S = \gamma_{S^\circ} - (\gamma_{LV^\circ} + \gamma_{SL}). \quad (16)$$

Harkins soon afterward developed and applied these relations more fully in a series of papers (21-24), identified S the "initial spreading coefficient," and derived the illuminating relations

$$S = W_A - W_c \quad (17)$$

and

$$S = - \frac{\partial F}{\partial \sigma}, \quad (18)$$

where F is the free energy of the system and σ the surface area.

Assuming there is no surface electrification, Eqs. (3-18) are the basic equilibrium thermodynamic relations for wetting and spreading phenomena.

An informative approximation can be derived from Eq. (16) for the case of an organic liquid spreading upon an organic solid surface since it is then reasonable to assume that γ_{SL} is negligibly small in comparison with γ_{LV° . Therefore,

$$S = \gamma_{S^\circ} - \gamma_{LV^\circ} \quad (19)$$

and

$$\gamma_{S^\circ} > \gamma_{LV^\circ} \text{ for spreading.} \quad (20)$$

Hence, in all such systems when spreading occurs the specific free surface energy of the liquid is less than that of the solid.

Wettability can also be measured by the reversible work of adhesion W_A or by the heat of wetting per unit area h_{SL} . However, the small change in energy involved in contacting most solids and liquids necessitates using finely divided solids having large surface areas per gram in order to measure the heat of wetting. This is difficult to do with many organic solids of interest here; it also introduces many new complications. In addition to the known sensitivity of such measurements to traces of impurities, there must be added the effect of the presence of sharp edges, holes, surface strains, and imperfections. These problems with most highly divided solids have plagued all investigators of this subject. We have preferred to employ more carefully defined solid surfaces and to use cosine θ as the measure of wetting.

LOW- AND HIGH-ENERGY SURFACES

It has been very helpful to define convenient names for the two extremes of the specific surface free energies of solids. The specific surface free energies of all liquids (excluding the liquid metals) are less than 100 ergs/cm² at ordinary temperatures. But hard solids have surface free energies ranging from around 5000 to about 500 ergs/cm², the values being higher the greater the hardness and the higher the melting point. Examples are the ordinary metals, metal oxides, nitrides and sulfides, silica, glass, ruby, and diamond.

In contrast, soft solids have much lower melting points and their specific surface free energies are generally under 100 ergs/cm². Examples are waxes, most solid organic polymers, and, in fact, most organic compounds. Solids having high specific surface free energies may be said to have "high-energy surfaces," and solids having low specific surface free energies have "low-energy surfaces" (8-10).

Because of the comparatively low specific surface free energies of organic and most inorganic liquids, one would expect them to spread freely on solids of high surface energy since there would result a large decrease in the surface free energy of the system, and this is most often found to be true. But the surface free energies of such liquids are comparable to those of low-energy solids; hence, systems showing nonspreading should be and are most commonly found among such combinations. Research has shown that whenever one of these liquids did not spread on a high-energy surface, some kind of adsorption process had taken place before or during the contact of liquid and solid owing to a coating which had been deposited on the solid making it behave like a low-energy surface.

THE CRITICAL SURFACE TENSION OF WETTING (γ_c)

Systematic studies of the contact angles for a wide variety of pure liquids on low-energy solid surfaces (25-27) and on high-energy solid surfaces (28,29) have revealed many regularities in the wettability. The solids studied include smooth organic crystals and polymers, as well as high-energy surfaces such as metals and glass which had been modified by the adsorption of a monolayer of oriented organic molecules. In general, a rectilinear relation has been established empirically (8-10) between the cosine of the contact angle θ and the surface tension γ_{LV}° for each homologous series of organic liquids. This had led to the useful concept of the critical surface tension γ_c of wetting for each homologous series, as defined by the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight line plot of $\cos \theta$ vs γ_{LV}° .

The regularities in the contact angles exhibited by pure liquids on low-energy surfaces are illustrated by the data for the homologous series of liquid n-alkanes on several types of fluorinated solid surfaces. In Fig. 2 each curve represents the wetting behavior of a single surface by a number of n-alkanes. Curve A is a plot for smooth, clean polytetrafluoroethylene (Teflon); the lower the surface tension of the alkane liquid, the larger is $\cos \theta$, and the more wettable the surface. For all values of the surface tension of the liquids below a critical value, γ_c , the contact angle is zero. Curve B presents recent data (30) for the new copolymer of tetrafluoroethylene and hexafluoropropylene (F.E.P. Teflon), and curve C is for a still newer material, polyperfluoropropylene (31). Curves D, E, and F describe the wetting behavior of a normally completely wettable, high-energy surface (clean, smooth platinum) modified previously by the adsorption of an oriented, close-packed, unimolecular layer of a perfluoroalkanoic acid. The similarity of these graphs of the wetting properties is remarkable, and careful investigations of such systems and graphs have made it possible to prove that the presence of a condensed adsorbed monolayer of organic polar-nonpolar molecules always transforms a high-energy surface into one with the wetting properties characteristic of a low-energy surface of the same surface composition and packing.

From the intercept of the rectilinear graph of Fig. 2, it is evident that γ_c has a value of about 18.5 dynes/cm for the n-alkanes on the surface of Teflon. Values of about 17 and 15 dynes/cm are obtained from curves B and C because the introduction of the perfluoromethyl group as a side chain in the polymer reduces γ_c , the reduction becoming greater the higher the surface concentration of exposed $-\text{CF}_3$ groups. An adsorbed, close-packed monolayer of a perfluorinated acid (curves D, E, and F) is an example of such a surface (32,33). The values of γ_c for such surfaces are, therefore, much lower than for surfaces comprised only of $-\text{CF}_2-$ groups. The closer the packing of the aliphatic chains of the adsorbed molecules, the closer the packing of the exposed terminal $-\text{CF}_3$ groups, and hence

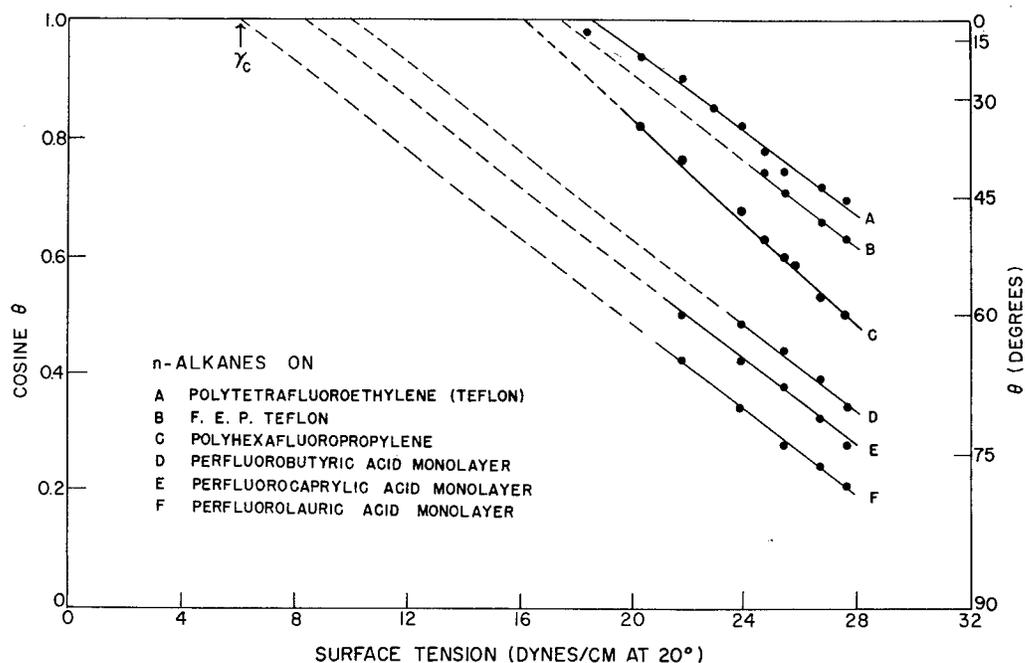


Fig. 2- Contact angles for a series of liquid n-alkanes on several types of fluorinated solid surfaces. The critical surface tension γ_c of wetting is the intercept of the horizontal line $\cos \theta = 1$ with the extrapolation of the straight line plot of $\cos \theta$ vs γ_{LV}° .

the lower γ_c . Thus, the value for a condensed monolayer of perfluorolauric acid (curve F) is only 6 dynes/cm, and this surface is the least wetted by the alkanes (or by any other liquids) of any surface yet encountered.

Even when $\cos \theta$ is plotted against γ_{LV}° for a variety of nonhomologous liquids, the graphical points lie close to a straight line or tend to collect around it in a narrow rectilinear band (Fig. 3). On some low-energy surfaces this band exhibits curvature for values of γ_{LV}° above 50 dynes/cm (8-10,34). But in those cases such curvature results when weak hydrogen bonds form between the molecules of liquid and those in the solid surface. This is most likely to happen with liquids of high surface tension, because these always are hydrogen-donating liquids. Therefore, the valuable working hypothesis was evolved that the graph of $\cos \theta$ vs γ_{LV}° for any low-energy surface is always a straight line (or a narrow rectilinear band) unless the molecules in the solid surface form hydrogen bonds or otherwise strongly associate with the liquid (34).

When rectilinear bands are obtained in this type of graph, the intercept of the lower limb of the band at $\cos \theta = 1$ is chosen as the critical surface tension γ_c of the solid. Although this intercept is less precisely defined than the critical surface tension of an homologous series of liquids, nevertheless, it is an even more useful parameter, because it is a characteristic of the solid only. It has been found to be an empirical parameter which gives good relative characterization of γ_s° , the specific surface free energy of the solid.

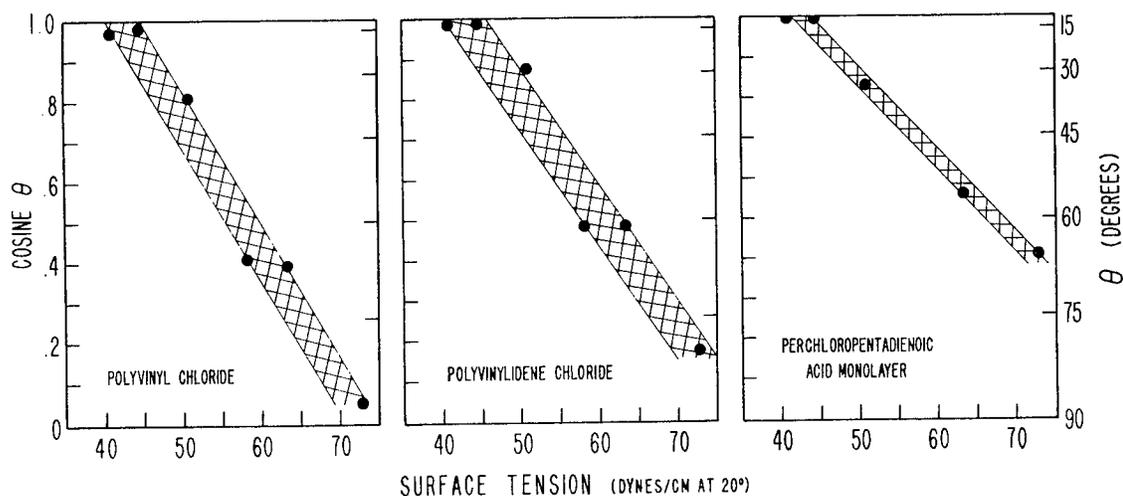


Fig. 3 - Wettability of various liquids on surfaces of polyvinyl chloride, polyvinylidene chloride, and a closed-packed monolayer of perchloropentadienoic acid on platinum

EXTREME LOCALIZATION OF SURFACE FORCES EVIDENCED IN WETTING

From our many investigations we have established that the wettability of low-energy organic surfaces, or of high-energy surfaces coated by organic films, is determined by the nature and packing of the surface atoms of exposed groups of atoms of the solid and is otherwise independent of the nature and arrangements of the underlying atoms and molecules (12, 25-27). These findings exemplify the extreme localization of the attractive field of force around the solid surfaces and covalent-bonded atoms which are responsible for the adhesion of a great variety of liquids to solids. The basic explanation is that the surface atoms in both solids and such liquids generally attract each other by highly localized attractive force fields such as the London dispersion forces (35), which vary in intensity inversely as the sixth power of distance. The influence of such a field of force becomes unimportant at a distance of only a few atom diameters; hence, there is little contribution to the force of adhesion by atoms not in the surface layers. However, when the constitution of the solid, or of the adsorbed monolayer, is such that either ions or large, uncompensated, permanent dipoles are located in the outermost portion of the surface monolayer, the residual field of force of the surface is much less localized. A recent example will be found in the unexpectedly strong wetting behavior of a solid coated with an adsorbed terminally fluorinated monolayer of a fatty acid or amine (36). Langmuir (37,38) many years ago called attention to the extreme localization of surface forces encountered in observing the mechanical properties of insoluble organic monolayers on water, and he often referred to this concept as "the principle of independent surface action." Our studies of wetting demonstrate that although there are understandable exceptions to this principle, it is usually true.

SURVEY OF VARIATION OF γ_c WITH CONSTITUTION OF SOLIDS

The widespread occurrence of the rectilinear relationship between $\cos \theta$ and γ_{LV}° in the now large body of experimental data, and the fact that these graphs do not cross, had made it possible to use γ_c to characterize and compare the wettabilities of a variety of low-energy surfaces.

Table 1
Critical Surface Tensions γ_c of Some Low-Energy Surfaces

Surface Constitution	γ_c (dynes/cm at 20° C)
Fluorocarbon Surfaces	
-CF ₃ *	6
-CF ₂ H*	15
-CF ₃ and -CF ₂ - (ratio 1 to 2)	16.2
-CF ₂ -CF ₂ -	18.5
-CH ₂ -CF ₃	20
-CF ₂ -CFH-	22
-CF ₂ -CH ₂ -	25
-CFH-CH ₂ -	28
Hydrocarbon Surfaces	
-CH ₃ (single crystal face)	22
-CH ₃ *	22 - 24
-CH ₃ (monolayer of polymethylsiloxane)	24
-CH ₂ -CH ₂ -	31
·CH· (phenyl ring edge)	35
Chlorocarbon Surfaces	
-CClH-CH ₂ -	39
-CCl ₂ -CH ₂ -	40
=CCl ₂ *	43

*Close-packed adsorbed monolayer

In Table 1 are presented the resulting values of γ_c obtained from recent studies (26, 27) of the contact angles of a number of well-defined, low-energy, solid surfaces. In the first column is given the constitution of the atoms or organic radicals in the solid surface arranged in the order of increasing values of γ_c . Some of the salient features of Table 1 are highly informative and deserve a brief review here.

Fluorocarbon Surfaces

The surface of lowest energy ever found, and hence lowest γ_c , is that comprised of closest packed -CF₃ groups (32,33). The effect of the replacement of a single fluorine atom by a hydrogen atom in a terminal -CF₃ group is to more than double γ_c . Thus, the value γ_c of 6 dynes/cm obtained for a condensed adsorbed monolayer of perfluorolauric acid is to be compared with that of 15 dynes/cm (34) for a condensed adsorbed monolayer of ω -monohydroperfluoroundecanoic acid (CF₂H-(CF₂)₉COOH).

A parallel and regular increase in γ_c has been observed with progressive replacement of fluorine by hydrogen atoms in the surfaces of bulk polymers. In Table 1 the data for Teflon (-CF₂-CF₂-), polytrifluoroethylene (-CF₂-CFH-), polyvinylidene fluoride (-CF₂-CH₂-), and polyvinyl fluoride (-CFH-CH₂-) are listed in the order of increasing values of γ_c ; however, this is also the order of decreasing fluorine content. Each of these polymers can be considered a fluorinated derivative of polyethylene; a plot of γ_c against the atom percent replacement of hydrogen in the monomer by fluorine results in a straight line (Fig. 4); the decrease in γ_c is approximately 3 dynes/cm for each successive 25% replacement.

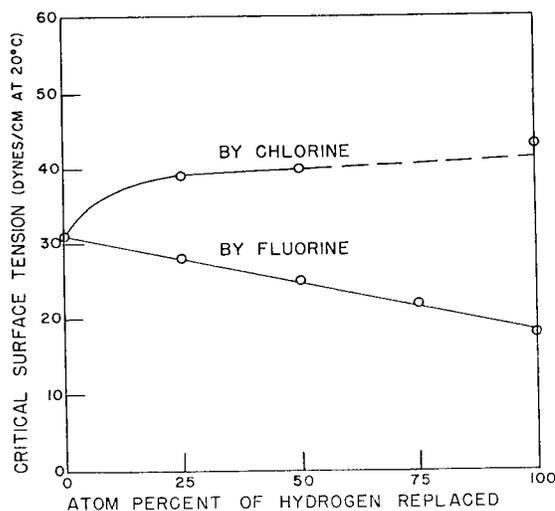


Fig. 4 - The effect of progressive halogen substitution on the wettability of polyethylene-type surfaces

Hydrocarbon Surfaces

Results in Table 1 of studies of the wetting of hydrocarbon surfaces reveal that the lowest values of γ_c and the largest contact angles are found in a surface comprising close-packed oriented methyl groups. The low value of γ_c of about 22 dynes/cm results when the methyl groups are packed in the close-packed array found in the easiest cleavage plane of a single crystal of n-hexatriacontane (10). The less closely packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a value of γ_c of 22-24 dynes/cm (12,39). The great sensitivity of the contact angle, and hence of γ_c , to such subtle changes in the packing of the methyl groups comprising the surface of the solid is not only remarkable, but has much significance in technological aspects of wetting and adhesion. It should be noted that the transition from a surface comprised of $-\text{CH}_3$ groups to one of $-\text{CH}_2-$ groups results in an increase in γ_c of some 10 dynes/cm; this is to be compared with the increase of 12 dynes/cm, observed in going from a surface of $-\text{CF}_3$ to one of $-\text{CF}_2-$ groups.

The presence of aromatic carbon atoms in the hydrocarbon surface also serves to increase γ_c . Thus, the introduction of a significant proportion of phenyl groups in the surface in going from polyethylene to polystyrene raises γ_c from 31 to 33 dynes/cm. A further increase to 35 dynes/cm results when the surface is composed solely of phenyl groups, edge on, as in the cleavage surface of naphthalene or anthracene single crystals (25).

Chlorocarbon Surfaces

Graphs of $\cos \theta$ vs γ_{LV} for the chlorinated hydrocarbons: polyvinyl chloride ($-\text{CH}_2-\text{CHCl}-$) and polyvinylidene chloride ($-\text{CH}_2-\text{CCl}_2-$) are narrow, rectilinear bands (Fig. 3). The corresponding polytrichloroethylene polymer has not been studied. The completely chlorinated analogue, polytetrachloroethylene, never has been prepared, and probably cannot be, owing to steric hindrances resulting from the large atomic diameter of covalent chloride. In Fig. 4 values of γ_c for polyethylene, polyvinyl chloride, and polyvinylidene chloride (40) are plotted against the atom percent replacement of hydrogen by chlorine, since the two chlorinated polymers can be considered derived from polyethylene by 25 and 50 atom percent replacement, respectively. Although the introduction of the first chlorine atom in the monomer causes γ_c to rise from 31 to 39 dynes/cm, the addition of a second chlorine only increases γ_c to 40 dynes/cm. There are striking differences, therefore, in the effects on γ_c observed with fluorine and chlorine replacement of hydrogen, both as to the effect of progressive halogenation and the direction of the change.

Although polytetrachloroethylene does not exist, an organic coating with an outermost surface comprised of close-packed covalent chlorine atoms has been prepared by adsorbing a condensed, oriented monolayer of perchloropentadienoic acid ($\text{CCl}_2=\text{CCl}-\text{CCl}=\text{CCl}-\text{COOH}$) on the clean polished surface of glass (40). Not only is the graph of $\cos \theta$ vs γ_{LV} for such a surface quite similar to those of the above-mentioned chlorinated polyethylenes, but the corresponding value of γ_c (43 dynes/cm) is shifted in the appropriate direction (i.e., to higher values of γ_c). Extrapolation of the line defined by the experimental points for the two chlorinated polymers in Fig. 4 to the value of γ_c for 100% hydrogen replacement indicates a value of 42 dynes/cm. Thus, the hypothetical polytetrachloroethylene surface should have a critical surface tension of wetting of 42 dynes/cm, which is only 1 dyne/cm less than the experimental value found for the perchloropentadienoic acid monolayer. This shows how closely the latter surface approximates a fully chlorinated polymeric solid surface in its wetting properties. When the condensed monolayer was adsorbed on polished platinum, the results were the same.

An interesting but more specialized example of the relation of γ_c to constitution is the plot in Fig. 5 of $\cos \theta$ of water vs percent chlorination of polyethylene. This graph is a good straight line over the range of 0 to 100% (40).

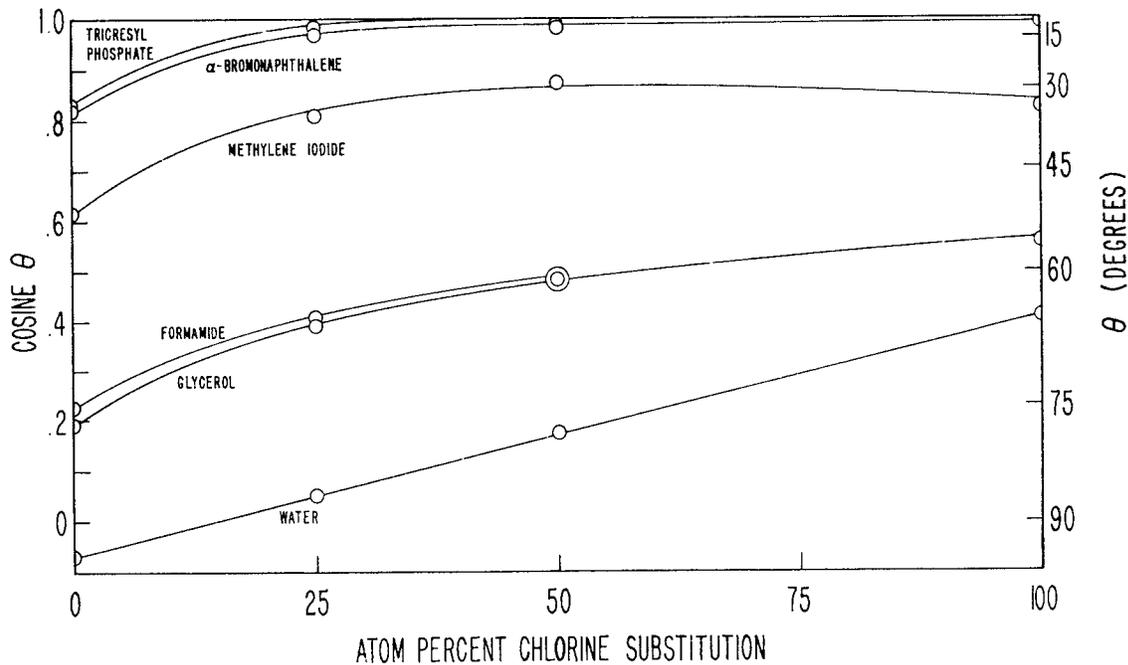


Fig. 5 - Wettability for various liquids vs atom percent chlorine substitution in the solid surface

CRITICAL SURFACE TENSIONS OF SOLID POLYMERS

Results of wettability studies on clean, smooth, plasticizer-free polymeric solids of general interest have been summarized in Table 2. In agreement with the predictions to be made from Table 1 and the surface composition to be expected for each polymeric solid, the introduction of covalent chlorine atoms markedly increases the wettability of the polymer. Thus, in a series of copolymers of polytetrafluoroethylene and polytrifluoro-chloroethylene (40), there is a regular increase in γ_c with chlorination in going from the fully fluorinated surface ($\gamma_c = 18.5$ dynes/cm) to that having 25 atom percent chlorine

Table 2
Critical Surface Tensions γ_c of Common Polymeric Solids

Polymer	γ_c (dynes/cm at 20° C)
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Polyvinylidene fluoride	25
Polyvinyl fluoride	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Polyvinyl alcohol	37
Polyvinyl chloride	40
Polyvinylidene chloride	40
Polyhexamethylene adipamide	46

substitution ($\gamma_c = 31$ dynes/cm). Similarly, a large increase in γ_c of 8 dynes/cm was observed on replacing 25% of the hydrogen atoms in polyethylene by chlorine.

Included in Table 2 is the value for polyvinyl alcohol ($\gamma_c = 37$ dynes/cm) which was reported recently by Ray, et al. (41,42). The same investigators reported a range in γ_c of 40 to 45 dynes/cm for a series of hydroxyl-rich surfaces of the starch polymer type. These values of γ_c are reasonably close to that of 43 dynes/cm reported for the oxygen-rich surface of polyethylene terephthalate (43).

Contact angles and surface tensions for studies of the wetting of the smooth surfaces of various waxes, resins, and cellulose derivatives have been reported by F. E. Bartell, et al. (44-46). If the cosines of their contact angles are plotted against γ_{LV} , good straight lines are obtained. The values of γ_c for their resin surfaces rich in exposed oxygen-containing groups fit in well with the data presented here on the relative wettability of oxygen-rich surfaces.

Nylon, with its many exposed amide groups, has the highest value of γ_c of the common plastics reported (43). Since γ_c for all the polymers of Table 2 are well below the surface tension of water (72.8 dynes/cm), all are hydrophobic.

EFFECT OF CONSTITUTION ON WETTING OF HIGH-ENERGY SOLID SURFACES

In order to explain the wettability of high-energy surfaces, it first proved necessary to unravel two additional surface-chemical problems. The first was encountered when it was discovered that liquids such as octanol-1, octanol-2, 2-ethylhexanol-1, trichlorodiphenyl, and tri-*o*-cresyl phosphate exhibited appreciable contact angles on clean, hydrophilic, high-energy surfaces such as platinum, stainless steel, glass, fused silica, and α -Al₂O₃ (synthetic sapphire) no matter what extremes of purification were used. A long investigation (28) revealed that each liquid was nonspreading on these high-energy surfaces

because the molecules adsorbed on the solid to form a film whose critical surface tension of wetting was less than the surface tension of the liquid itself. In short, each liquid was unable to spread upon its own adsorbed and oriented monolayer. These liquids were therefore named "autophobic" liquids. From this it follows that polar liquid compounds which are not autophobic have surface tensions which are less than the critical surface tension of wetting of their adsorbed monolayers. Examples from among the many nonautophobic liquids are the aliphatic hydrocarbons, the aliphatic ethers and polyethers, the polymethylsiloxanes and the perfluoro-alkanes.

The other problem that had to be solved was to explain why all pure liquid esters spread completely upon the metals studied, yet some spread on glass, silica, and α - Al_2O_3 and others did not. Long-continued research (29) finally revealed that the basic cause of these differences in spreadability was ester hydrolysis which occurred immediately after the liquid ester adsorbed upon hydrated surfaces such as those of glass, fused silica, and α - Al_2O_3 . This is not unreasonable since the polar group of the ester would be expected to adsorb in immediate contact with the solid surface unless prevented by steric hindrance, and since in the surface the molecules of the water of hydration (being oriented) should be more effective in causing hydrolysis than bulk water. Through surface hydrolysis two fragments of the ester result. The fragment which has a greater average lifetime of adsorption remains and eventually coats the surface with a close-packed monolayer of that molecular species. Eventually the surface becomes blocked or "poisoned" by the coating of the hydrolysis product, and the hydrolysis reaction ceases. Hence, the volume concentration of hydrolyzed ester is so small that it cannot be observed by applying ordinary analytical methods. When the resulting monolayer has a critical surface tension of wetting less than the surface tension of the ester, nonspreading behavior is observed; i.e., the ester is unable to spread upon the adsorbed film of its own hydrolysis product. Dozens of esters having a great variety of structures have been studied, and in every instance of nonspreading on glass, fused silica, and α - Al_2O_3 , we have been able to give a similar explanation of the behavior.

As an example, the high boiling compound bis(2-ethylhexyl)sebacate spreads freely on metals but is unable to spread on fused silica, boro-silicate glass, or α - Al_2O_3 . On these hydrated nonmetallic surfaces the diester hydrolyzes to form 2-ethylhexanoic acid. The critical surface tension of wetting of a close-packed monolayer of 2-ethylhexanoic acid is about 28 dynes/cm (28). Since the surface tension of this diester is 31.1 dynes/cm at 20°C, $\gamma_{LV}^\circ > \gamma_c$ and the diester cannot spread on the film of its hydrolyzed product. When in contact with metals at ordinary conditions of relative humidity, the adsorbed diester is not in contact with hydrated water and so cannot hydrolyze; nevertheless, the molecule adsorbs on the surface, lying as flat as possible to allow the greatest number of polarizable atoms to contact the adsorbing surface (29). The resulting adsorbed monolayer, because of the presence of the ester groups, must have a critical surface tension of wetting greater than that of polyethylene; in other words, γ_c is considerably greater than 31 dynes/cm. Hence, $\gamma_{LV}^\circ < \gamma_c$, and the diester must spread freely over its own adsorbed film and over the metal surface.

With this background of research it became possible to explain many of the spreading properties of liquids on solids. For example, one can readily explain the nearly universal spreading properties of the polydimethylsiloxanes. These liquids spread on all high-energy surfaces because the surface tensions of 19 to 20 dynes/cm (29) are always less than the critical surface tensions of their own adsorbed films. This follows because an adsorbed close-packed monolayer of such a liquid has an outermost surface of methyl groups which are not as closely packed as the methyl groups in a single crystal of a paraffin. Since γ_c of hexatriacontane is about 22 dynes/cm (10), the value of γ_c for the silicone monolayer must exceed that value; actually it is about 24 dynes/cm. Hence, γ_{LV}° is always below γ_c , and the polydimethylsiloxanes cannot be autophobic.

The critical surface tension of polyethylene of 31 dynes/cm (10) must be about the same as that of a monolayer of paraffin molecules adsorbed lying flat on a metal (28). Since the surface tensions of liquid aliphatic hydrocarbons are always less than 30 dynes/cm, and hence less than γ_c , such liquids are always able to spread on their own adsorbed films. Thus the paraffin oils also cannot be autophobic.

Many liquid compounds release polar decomposition products able to adsorb and form low-energy surfaces. As we have pointed out many times (29,32-34,47,48) the nonspreading property can be produced in nearly all pure liquids by the addition of a minor concentration of a suitable adsorbable polar compound.

Our results on the mechanism of spreading can be generalized as follows: every organic liquid, or other liquid, having a low specific surface free energy always spreads freely on specularly smooth, clean, high-energy surfaces at ordinary temperatures unless the film adsorbed by the solid is so constituted that the resulting film-coated surface is a low-energy surface having a critical surface tension less than the surface tension of the liquid. Because of the highly localized nature of the forces between each solid surface and the molecules of the organic liquid and also between the molecules of each liquid, a monolayer of adsorbed molecules is always sufficient to give the high-energy surface the same wettability properties as the low-energy solid having the same surface constitution.

ON ADHESION TO HIGH-ENERGY SOLID SURFACES

Bangham and Razouk's Eqs. (8) and (14) have been employed by Boyd and Livingston (49) and by Harkins and several coworkers (50-52) in order to calculate W_A for water, propanol, propyl acetate, acetone, benzene, and n-heptane on the surfaces of silica (SiO_2), anatase (TiO_2), barium sulfate, stannic dioxide (SnO_2), ferric oxide (Fe_2O_3), graphite, mercury, copper, silver, lead, iron, and tin. For each of these systems f_{SV}° was computed from the adsorption isotherm of the vapor on the solid. Tables 3 and 4, which summarize their results, show that in every case f_{SV}° can not be neglected in comparison with W_A . It should be noted that each of these solids is a highly adsorptive, finely divided material, and excluding graphite, each is a hydrophilic, high-energy surface. The results obtained with graphite may have been greatly affected by capillary condensation or other adsorption mechanisms peculiar to finely powdered solids; hence, the applicability of the f_{SV}° term in Eq. (8) to the adhesion of graphite is questionable.

Tabor (53) has pointed out that W_A' for any system having $\theta = 0$ will be given by twice the surface tension of the liquid; hence a simple calculation assuming the field of the attractive force causing adhesion vanishes in about 3 Ångströms shows that the average tensile strength of the adhesive joint must be much greater than the tensile strength of common adhesives. Therefore, the joint must break by cohesive failure (in the bulk phase of the adhesive) rather than at the adherend/adhesive interface. Since the correction term f_{SV}° in Eq. (8) simply makes the adhesional energy even greater than $2\gamma_{LV}$, it can be concluded that when the adhesive makes a zero contact angle with the adherend, the thermodynamic adhesive strength at the solid/liquid interface will always be much more than the observed tensile or shear strength of the adhesive.

ON CALCULATING THE WORK OF ADHESION FOR LOW-ENERGY SOLID SURFACES

It is an unfortunate fact that f_{SV}° has not yet been measured for any well-defined, smooth, low-energy, solid surface. It is important not to assume from the results summarized in Tables 3 and 4 that the value of f_{SV}° for low-energy surfaces will also be an important correction term in Eq. (8). On the contrary, there is much indirect experimental evidence that whenever a liquid exhibits a large contact angle on a solid there is negligible

Table 3
Literature Values of f_{sv}° for Nonmetallic High-Energy Surfaces*
(ergs/cm² at 25°C)

Solid	Liquid	$f_{sv}^\circ = \gamma_s^\circ - \gamma_{sv}^\circ$	W_A
TiO ₂	Water	300 (196†)	370 (340†)
TiO ₂	n-Propanol	114 (108†)	138 (154†)
TiO ₂	Benzene	85	114
TiO ₂	n-Heptane	58 (46†)	78 (86†)
SiO ₂	Water	316	388
SiO ₂	n-Propanol	134	158
SiO ₂	Acetone	109	133
SiO ₂	Benzene	81	110
SiO ₂	n-Heptane	59	79
BaSO ₄	Water	318	390
BaSO ₄	n-Propanol	101	125
BaSO ₄	n-Heptane	58	78
Fe ₂ O ₃	n-Heptane‡	54	94
SnO ₂	Water	292 (220 †)	364 (364 †)
SnO ₂	n-Propanol	104 (117 †)	128 (163 †)
SnO ₂	Propyl acetate †	104	151
SnO ₂	n-Heptane‡	54	94
Graphite	Water	64	136
Graphite	n-Propanol	95	118
Graphite	Benzene	76	96
Graphite	n-Heptane	57‡	97‡

*Data from Ref. 49 unless otherwise indicated.

†Ref. 51.

‡Ref. 52.

Table 4
Literature Values of f_{sv}° for Metallic High-Energy Surfaces*
(ergs/cm² at 25°C)

Solid	Liquid	$f_{sv}^\circ = \gamma_s^\circ - \gamma_{sv}^\circ$	W_A
Mercury	Water	101	174
Mercury	n-Propanol	108	132
Mercury	Acetone	86	110
Mercury	Benzene	119	148
Mercury	n-Octane	101	123
Copper	n-Heptane †	29	69
Silver	n-Heptane †	37	77
Lead	n-Heptane †	49	89
Iron	n-Heptane †	53	93
Tin	Water †	168	312
Tin	n-Heptane †	50	90
Tin	n-Propanol †	83	129

*Data from Ref. 49 unless otherwise indicated.

†Ref. 50.

‡Ref. 51.

adsorption of the vapor. Recent measurements by Bewig and Zisman (54) using a new Volta potential method of studying adsorption have demonstrated that negligible adsorption of most vapors occurs on smooth, clean surfaces of polytetrafluoroethylene. Extensive room temperature adsorption measurements with a McBain-Bakr balance over the entire vapor pressure range of p/p_0 up to 1.0 by Martinet (55) have recently led to the conclusion that the vapor adsorption for the many substances studied is a small fraction of a monolayer. Hence, f_{SV}° must be a very small term compared with W_A' , for all liquids have γ_{LV}° much greater than γ_c . The same conclusions can be extended for the same temperatures to other low-energy solids such as polyethylene, polystyrene, polyvinyl chloride, etc., and to all liquids having surface tensions much greater than the γ_c of the solid.

It is important to emphasize here that if a substantial fraction of a condensed monolayer of any of these vapors could adsorb on the solid surface, the surface constitution (and hence γ_c) of the solid surface would necessarily be transformed thereby to that of the adsorbed film. For example, if tetrachloroethane ($\gamma_{LV}^\circ = 36.3$) were to adsorb as an appreciable fraction of a monolayer on the surface of a single crystal of hexatriacontane, the critical surface tension of wetting would of necessity be raised from the original value of 22 to that of 43 dynes/cm for the chlorine-rich surface because its surface composition would be similar to that of the perchloropentadienoic monolayer described previously. Thus we can conclude that f_{SV}° must be negligible for liquids like water, glycol, methylene iodide, etc., having surface tensions considerably larger than γ_c ; presumably, it becomes a more significant correction for liquids having values of γ_{LV}° close to or less than γ_c . For example, f_{SV}° may not be negligible for decane ($\gamma_{LV}^\circ = 23.9$) on hexatriacontane ($\gamma_c = 22$) or for α -methylnaphthalene ($\gamma_{LV}^\circ = 33.7$) on polyethylene ($\gamma_c = 31$). As a general proposition, when $\theta > 0$, the liquid on a low-energy solid surface is in equilibrium with much less than an adsorbed monolayer.

Turning to any high-energy surface converted to a low-energy surface by the adsorption of a suitable condensed organic monolayer, the same conclusions about the negligible value of f_{SV}° apply as those given in the preceding paragraph with the one reservation that f_{SV}° may become more significant if the molecule of the liquid is small enough to be able to penetrate readily through the condensed monolayer and so adsorb on the high-energy surface beneath. An example of such a situation is the penetration of water vapor through a close-packed monolayer of octadecylamine to adsorb on the glass substrate.

IMPORTANCE OF W_A' IN ADHESION

From the preceding discussion it is concluded that for any low-energy solid surface: (a) liquids having γ_{LV}° much greater than γ_c , will have W_A essentially equal to W_A' ; (b) as γ_{LV}° closely approaches γ_c but exceeds it, $W_A - W_A'$, may become more significant; and (c) for liquids having γ_{LV}° less than or equal to γ_c , $W_A - W_A'$, may become appreciable.

It can also be concluded that the difference $W_A - W_A'$ will not be negligible for high-energy surfaces unless both the vapor pressure and adsorptivity are very low or unless the liquid on contact with the solid lays down a low-energy adsorbed film; in such cases rules (a), (b), and (c) will apply. However, in the latter case if the molecules of the liquid can readily diffuse through the adsorbed film to adsorb on the high-energy substrate beneath, $W_A - W_A'$ may become appreciable.

The preceding conclusions permit some interesting conclusions about the reversible work of adhesion of liquids to solids by the application of the results of investigations over the past decade on wetting and constitution. Since W_A' is the reversible work of adhesion under conditions when there is always maintained a thermodynamic equilibrium of solid and liquid, and W_A is the reversible work of adhesion in removing the solid to an evacuated enclosure, it would be appropriate to name the former the equilibrium reversible work of adhesion and to name the latter either the absolute reversible work of adhesion or the

maximum reversible work of adhesion. The symbols used by Boyd and Livingston (49)

$$W_A = W_{S^\circ/LV^\circ} \quad (21)$$

and

$$W_{A'} = W_{SV^\circ/LV^\circ} \quad (22)$$

would be somewhat more indicative of the physical significance of W_A and $W_{A'}$, but will not be used here because of the inconvenience of printing them.

OPTIMUM VALUES OF WORK OF ADHESION

Assuming we are dealing with the adhesion of a liquid and a perfectly plane solid surface, the equilibrium reversible work of adhesion $W_{A'}$ is given by:

$$W_{A'} = \gamma_{LV^\circ}(1 + \cos \theta). \quad (23)$$

However, our experiments show that for any homologous series of liquid compounds, for all values of $\gamma_{LV^\circ} \geq \gamma_c$ the contact angle is related to γ_{LV° by

$$\cos \theta = a - b \gamma_{LV^\circ}. \quad (24)$$

Since γ_{LV° approaches γ_c as θ approaches zero, we can write Eq. (23) as

$$\cos \theta = 1 + b(\gamma_c - \gamma_{LV^\circ}). \quad (25)$$

Upon eliminating $\cos \theta$ between Eqs. (23) and (25), the following is obtained

$$W_{A'} = (2 + b \gamma_c) \gamma_{LV^\circ} - b \gamma_{LV^\circ}^2. \quad (26)$$

This is the equation of a parabola with the concave side toward the surface tension axis; it has a maximum value of $W_{A'}$, occurring at

$$\gamma_{LV^\circ} = \frac{1}{b} + \frac{1}{2} \gamma_c. \quad (27)$$

Finally, the maximum value of $W_{A'}$ is given by

$$W_{A'} = \frac{1}{b} + \gamma_c + \frac{1}{4} b \gamma_c^2. \quad (28)$$

For example, with smooth polyethylene $\gamma_c = 31$ and $b = 0.026$ (10); hence the maximum of $W_{A'}$ occurs at $\gamma_{LV^\circ} = 54$ dynes/cm and is about 76 ergs/cm².

Obviously perfectly flat solids are not used in the practice of making adhesive joints. Each adherend will have a true surface area which will be r times greater than the apparent or envelope area; hence the work of adhesion would be expected to be r times greater than that for the apparent surface area. However, the larger the contact angle the more difficult it becomes to make the liquid flow over the surface of each adherend to fill completely every crevice and pore in the surface. More often there are air pockets trapped in the hollows and crevices. Such difficulties with the formation of gas bubbles and pores are, of course, greatly amplified in dealing with viscous adhesives which rapidly solidify (by one process or another) shortly after being applied to form the joint. Hence in practice the true value of $W_{A'}$ is somewhere between the value given in Eq.(23) and r times that.

Where there are pores, crevices, and capillaries in the surface of the adherend, the viscous liquid adhesive will penetrate more or less and so increase adhesion if there is an adequate supply of the liquid. However, to obtain the maximum adhesion, the adhesive should obviously penetrate into the small spaces to reach the equilibrium position. Let us assume that the capillary rise equation

$$h = \frac{k \gamma_{LV}^{\circ} \cos \theta}{\rho R} \quad (29)$$

can be used, where R is the equivalent radius of the capillary, $k = 2/981$, and ρ is the density of the liquid. Also assume that the liquid still wets the capillary wall according to the $\cos \theta$ vs γ_{LV}° relation of Eq. (29). Eliminating $\cos \theta$ from the two equations, there results the following equation for the parabola:

$$h = \frac{k \gamma_c}{\rho R} (b + \gamma_c + 1) - \frac{(bk)}{R\rho} \gamma_{LV}^{\circ 2}. \quad (30)$$

Evidently, h has a maximum when γ_{LV}° has the value

$$\gamma_{LV}^{\circ} = 1/2 \left(\gamma_c + \frac{1}{b} \right). \quad (31)$$

For example, in the case of smooth polyethylene, the maximum capillary rise will occur when $\gamma_{LV}^{\circ} = 1/2 (31 + 38.4) = 34.7$ dynes/cm. Hence, the maximum rise occurs when γ_{LV}° is 3.7 dynes/cm more than γ_c . In practice it is questionable if the rise in the fine pores and crevices connected to the interface can be treated precisely in the above way; it is also doubtful that the contact angle against the wall of any crevice or pore is the same as that of the flat portion of the adherend surface. The main value of this analysis is to reveal again that $W_{A'}$ may go through a maximum as γ_{LV}° increases even when a porous interfacial surface is involved.

Because of the preceding conclusions, it is of interest to compute the value of $W_{A'}$ for the many liquid/solid combinations reported from our laboratory in the past ten years. In Tables 5-9 will be found calculated values of $W_{A'}$, arranged downward in rows according to decreasing values of the liquid surface tension and in columns from left to right according to increasing values of γ_c . Some of these data are graphed in Figs. 6-9 to show how $W_{A'}$ varies as a function of γ_{LV}° .

In every case there results a parabolic curve with a maximum. However, in a few instances, such as in Fig. 6 with polytrifluoroethylene, the decrease of $W_{A'}$ after reaching the maximum value is greatly moderated by the effect of the hydrogen bonding action of the liquids of high surface tension, i.e., water, glycerol, and formamide each of which is an effective hydrogen-donating compound. Similar effects are seen in Fig. 9 in the curve for the close-packed monolayers terminated by $-CF_2H$ groups and $-CF_3$ groups. In the latter case if one excludes the data points for the hydrogen donating liquids, the curve is seen to form an excellent parabola with its maximum occurring at about 40 dynes/cm.

In Table 9 will be found arranged in increasing order of magnitude the maximum values of $W_{A'}$ as read from the graphs from Figs. 6-9. For the sake of comparison, the corresponding values of γ_c are given in the second column. It will be noted that although $W_{A'}$ is usually in the same order as γ_c , there are two notable exceptions: polyvinylfluoride and polyvinylidene fluoride have larger values of $W_{A'}$ than would be expected from their values of γ_c . The cause is the greater effectiveness in hydrogen bonding manifested by these fluorocarbon polymers than the more fully fluorinated polymers on one hand and the unfluorinated hydrocarbon polymers on the other. This effect raised the curves in Fig. 6 for these two polymers for all values of γ_{LV}° greater than 50 dynes/cm. However, if we compare $W_{A'}$ for nonhydrogen bonding liquids, such as methylene iodide, α -bromonaphthalene, and trichlorodiphenyl, the same order is found as their respective values of γ_c . Thus it appears that γ_c is a more generally useful index of surface wettability and adhesiveness than is the maximum value of $W_{A'}$.

Table 5
Comparison of W_A' for Various Liquids on Fluorinated Solid Surfaces (20°C)

Liquid	Liquid Surface Tension (γ_{LV}°) (dynes/cm)	$W_A' = \gamma_{LV}^\circ(1 + \cos \theta)$ in (ergs/cm ²)						
		Polyhexafluoropropylene ($\gamma_c = 16.2$)	Polytetrafluoroethylene ($\gamma_c = 18.5$)	Polytrifluoroethylene ($\gamma_c = 22$)	Polychlorotrifluoroethylene ($\gamma_c = 31$)	Polyvinylidene fluoride ($\gamma_c = 25$)	Polyvinyl fluoride ($\gamma_c = 28$)	Polyethylene ($\gamma_c = 31$)
Water	72.8	43.2	50.3	70.3	72.8	82.9	85.4	67.7
Glycerol	63.4	-	52.4	72.2	72.2	79.8	89.2	75.5
Formamide	58.2	43.2	56.2	72.2	66.3	88.2	92.4	71.3
Methylene iodide	50.8	48.2	51.6	67.4	73.1	73.9	84.2	82.1
α -Bromonaphthalene	44.6	-	57.6	66.2	74.4	77.7	82.0	81.1
Tricresyl phosphate	40.9	-	51.5	67.7	70.3	77.0	77.0	74.8
Benzyl phenylundecanoate	37.7	-	52.6	64.8	67.8	71.6	73.8	71.0
t-Butyl naphthalene	33.7	-	48.0	58.7	65.8	65.8	66.9	67.2
Bis-(2-ethylhexyl) phthalate	31.2	-	45.4	60.1	62.2	61.0	62.0	62.3
Bis-(2-ethylhexyl) sebacate	31.1	-	45.7	60.7	-	61.4	61.7	-
n-Hexadecane	27.6	40.5	46.8	49.7	-	52.8	Spr.	Spr.

Table 6
Comparison of W_A' for Various Liquids on Chlorinated Solid Surfaces (20°C)

Liquid	Liquid Surface Tension (γ_{LV}°) (dynes/cm)	$W_A' = \gamma_{LV}^\circ(1 + \cos \theta)$ in (ergs/cm ²)			
		Polyethylene ($\gamma_c = 31$)	Polyvinyl Chloride ($\gamma_c = 39$)	Polyvinylidene Chloride ($\gamma_c = 40$)	Perchloropentadienoic Acid Monolayer ($\gamma_c = 43$)
Water	72.8	67.7	76.6	85.4	103
Glycerol	63.4	75.5	88.2	94.2	98.8
Formamide	58.2	71.3	81.8	86.4	-
Methylene iodide	50.8	82.1	91.9	95.2	92.9
α -Bromonaphthalene	44.6	81.1	88.4	88.6	>89
Tricresyl phosphate	40.9	74.8	80.6	81.2	>82
Benzyl phenylundecanoate	37.7	71.0			

Table 7
Comparison of $W_{A'}$ for Various Liquids on Nylon, Mylar,
and Polystyrene (20°C)

Liquid	Liquid Surface Tension (γ_{LV}°) (dynes/cm)	$W_{A'} = \gamma_{LV}^\circ(1 + \cos \theta)$ in (ergs/cm ²)		
		Polystyrene ($\gamma_c = 33$)	Polyethylene Terephthalate ($\gamma_c = 43$)	Polyhexamethylene Adipamide ($\gamma_c = 46$)
Water	72.8	71.6	84.1	97.7
Glycerol	63.4	73.2	85.1	95.1
Formamide	58.2	74.2	86.4	95.6
Thiodiglycol	54.0	79.4	91.5	96.6
Methylene iodide	50.8	92.4	90.8	89.2
Trichlorodiphenyl	45.3	87.6	88.6	88.1
α -Bromonaphthalene	44.6	87.7	87.7	87.4

Table 8
Comparison of θ and $W_{A'}$ for Various Liquids on High Energy Surfaces
Coated with Monolayers of "Adhesives" (20°C)

Liquid	Liquid Surface Tension (γ_{LV}°) (dynes/cm)	$-\text{CF}_3(\gamma_c = 6)^*$		$-\text{CF}_2\text{H}(\gamma_c = 15)^\dagger$		$-\text{CH}_3(\gamma_c = 24)^\ddagger$		$\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array} (\gamma_c = 24)^\S$	
		θ (deg)	$W_{A'}$ (ergs/cm ²)	θ (deg)	$W_{A'}$ (ergs/cm ²)	θ (deg)	$W_{A'}$ (ergs/cm ²)	θ (deg)	$W_{A'}$ (ergs/cm ²)
Water	72.8	105	53.9	97	63.9	102	57.7	101	58.9
Glycerol	63.4	102	50.2	89	64.6	94	59.0	98	54.6
Methylene iodide	50.8	103	39.4	-	-	66	71.5	70	68.2
α -Bromonaphthalene	44.6	92	43.0	-	-	58	68.2	56	69.5
Tricresyl phosphate	40.9	83	45.9	65	58.2	61	60.7	61	60.7
Benzyl phenylundecanoate	37.7	92	36.4	62	55.4	56	58.8	-	-
Hexachlorobutadiene	36.0	81	41.6	69	48.9	38	64.4	-	-
<i>t</i> -Butyl naphthalene	33.7	86	36.0	68	46.4	47	56.7	49	55.8
Bis-(2-ethylhexyl) phthalate	31.2	78	37.7	40	55.1	45	53.3	44	53.6
Bis-(2-ethylhexyl) sebacate	31.1	79	37.1	-	-	44	53.5	-	-
<i>n</i> -Hexadecane	27.6	78	33.4	67	38.5	39	49.0	36	50.0

Key:

* The film of $-\text{CF}_3$ is a perfluorolauric acid condensed monolayer on platinum (32,33).

† The film of $-\text{CF}_2\text{H}$ is a ω -monohydroperfluoroundecanoic acid condensed monolayer on platinum (34).

‡ The film of $-\text{CH}_3$ is a *n*-octadecylamine condensed monolayer on platinum or glass (12,39).

§ The film of $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{CH}_3 \end{array}$ is a glass slide coated by baking at 300°C after contact with DC 200 fluid in benzene.

Table 9
Maximum Values of w_A' for Various Polymeric Solids
(20°C)

Polymeric Solids	γ_c (dynes/cm)	w_A' (ergs/cm ²)
Polyhexafluoropropylene	16.2	52.5
Polytetrafluoroethylene	18.5	58.0
Polytrifluoroethylene	22	72.5
Polystyrene	33	78.0
Polyethylene	31	82.0
Polyethylene terephthalate	43	88.0
Polyvinylidene fluoride	25	88.5
Polyvinyl fluoride	28	92.0
Polyvinyl chloride	39	92.0
Polyvinylidene chloride	40	92.0
Polyhexamethylene adipamide	46	97.0

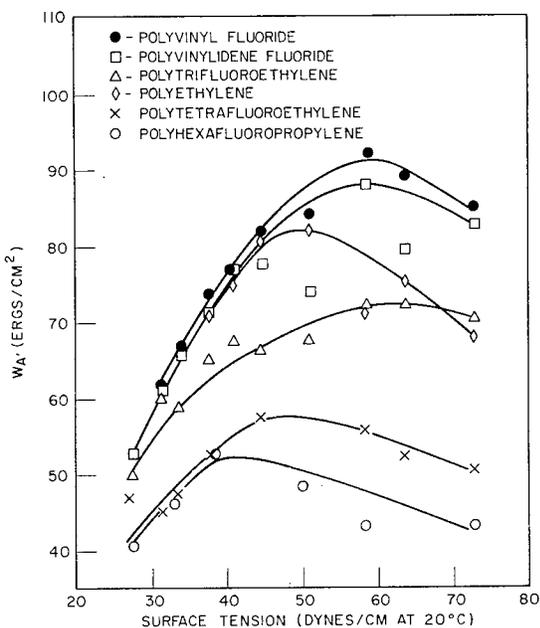


Fig. 6 - Effect on w_A' of fluorinating polyethylene

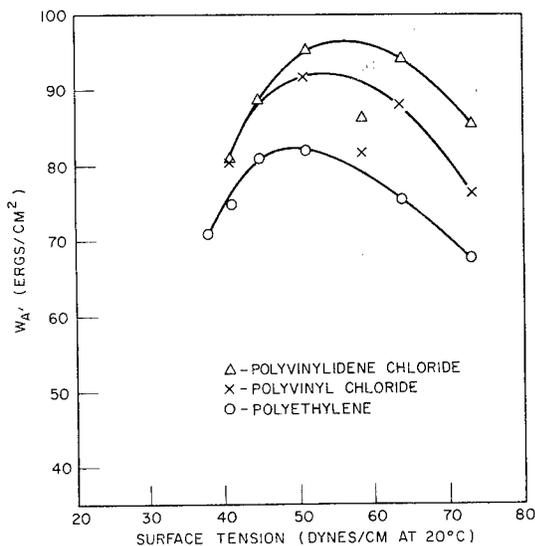


Fig. 7 - Effect on w_A' of chlorinating polyethylene

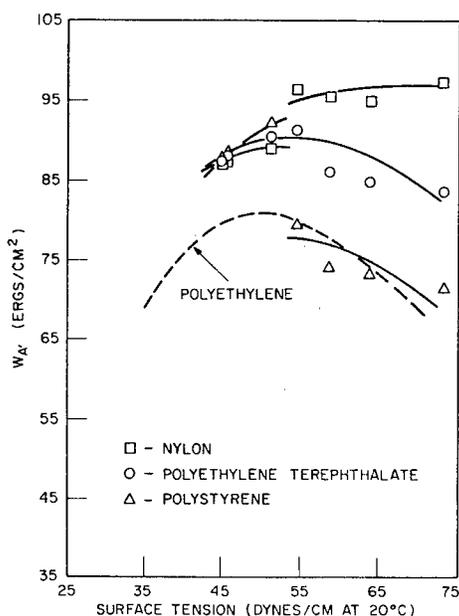


Fig. 8 - Effect on W_A' of liquid surface tension for some common plastics

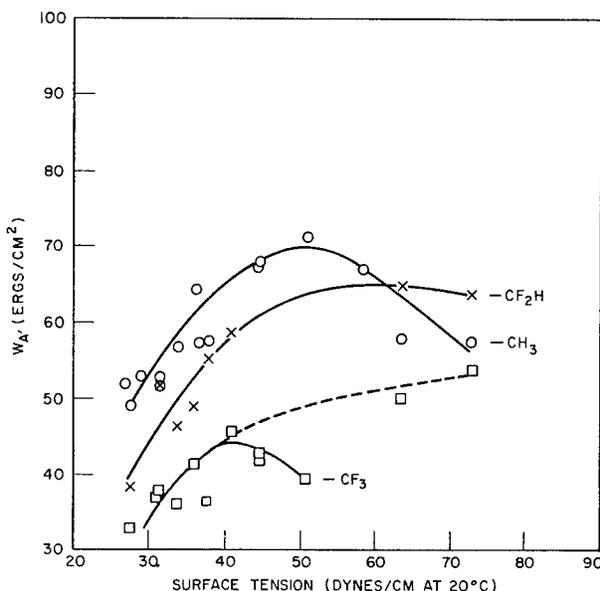


Fig. 9 - Effect on W_A' of adsorbing a condensed monolayer

If one wishes to calculate W_A' in order to estimate W_A , it should usually suffice to employ the values given in Tables 5-8, or even the maximum values of W_A' given in Table 9. However, if W_A is desired for a low-energy surface prepared by coating a high-energy surface with an organic monolayer, it would be better to take values of W_A' from Table 8 for nonhydrogen bonding liquids like methylene iodide, etc. In this way, one will avoid problems arising from permeability of the monolayer by water, glycerol, or formamide to adsorb strongly on the high-energy substrate under the monolayer. By following this procedure the estimated values of W_A' for -CH₃, -CF₂H, and -CF₃ coated surfaces, such as those described in Table 8, are approximately 70, 58, and 44 ergs/cm², respectively.

Upon surveying the data in Tables 5-8, it is evident that the greatest variation in W_A' among all the low-energy solid surfaces reported here is at the most three-fold. Of course, organic solids such as polymers containing other types of polar groups as well as chlorine, bromine, iodine, and aromatic radicals would be expected to raise W_A' and γ_c , and therefore it is presumed that some organic materials have values of W_A' in excess of 100 ergs/cm².

ON THE CHANGES IN W_A' UPON SOLIDIFICATION OF THE LIQUID ADHESIVE

When a liquid adhesive solidifies, there will usually develop internal stresses which will concentrate around holes, inclusions, or imperfections in the solid adhesive or at the interface between the adherend and the adhesive. If it were not for these stress concentrations and the usual change of density upon solidification, the reversible work of adhesion of the solid adhesive and the adherend would still be close to the value computed in the preceding calculations for the adhesive in the liquid state. This conclusion is based upon the generally accepted fact that the cause of adhesion is the residual field of force emanating from the adherend and attracting the molecules of the adhesive in the vicinity of the interface. The intense localization of this field of force, which has been referred to several

times already, causes this attractive force to be felt essentially only one molecule deep in both the adhesive and the adherend; hence, it will be unaffected by changes of state so long as correction is made for any resulting changes in the surface density or molecular orientation occurring at the joint interface. The former could be estimated from the change of density on solidification, but the latter may be difficult to compute since reorientation effects could originate through a crystallization process starting from some nucleus located deeper within the adhesive. Internal stresses and stress concentrations usually develop on solidification, the most common cause being the difference in the thermal expansion coefficients of the adhesive and adherend. In some applications, such as in sealing glass tubing to metal wires, the necessary precautions are usually taken to match carefully the thermal expansion coefficients of adhesive and adherend. However, in most applications of adhesives, this matching process is not (or can not be) done. Hence the strength of the adhesive joint is usually considerably decreased by the development of internal stresses.

As Mylonas (56), De Bruyne (5), and Tabor (53) have emphasized, in a lap joint poor wetting of the adherend tends to produce a greater stress concentration at the free surface of the adhesive where failure is most likely to be initiated. Mylonas found that large contact angles cause the maximum stress to occur at the edge where the adhesive makes contact with the adherend, the stress concentration increasing from about 1.2 when $\theta = 30^\circ$, 1.4 when $\theta = 60^\circ$, and around 2.5 when $\theta = 90^\circ$. Furthermore, Griffith (57) has shown that failure of the adhesive may occur at a relatively small applied stress if there are air bubbles, solid inclusions, or surface defects; and it occurs because localized stresses result which are much higher than the mean stress applied across the specimen. This is important when considered in view of the probable effect of poor wetting on the development of air pockets at the adhesive/adherend interface.

MECHANISM OF ACTION OF ABHESIVES

"Abhesives" are films or coatings which are applied to one solid to prevent (or greatly decrease) the adhesion to another solid in intimate contact with it. Such materials are employed in molding, casting, or rolling operations, therefore it is common to refer to the film as the "parting agent," "mold-release" agent, or "antistick" agent. Examples of materials commonly used for such purposes are the polydimethylsiloxanes; the long-chain fatty acids, amines, amides, and alcohols; the various types of highly fluorinated fatty acids and alcohols; and the Teflon or F.E.P.-Teflon films deposited by coating the mold with an aqueous dispersion of Teflon particles, drying it, and finishing with a brief bake at a high temperature. In such uses of many of these materials, a condensed monolayer usually will suffice to obtain the optimum effect. In view of the background information already presented here, it is evident that each of these films converts the solid beneath into a low-energy surface having values of γ_c of around 24 for the polymethylsiloxanes, 22 to 24 for the fatty materials, about 15 for the highly fluorinated aliphatics terminating with a $-CF_2H$ group, 18 for the Teflon coating, and 6 to 10 for the perfluoroalkyl acids and alcohols. Hence, any liquid or plastic material placed on a solid covered by such a film or coating will exhibit an equilibrium contact angle which will be larger as $\gamma_{LV} - \gamma_c$ becomes larger.

Much experience has shown that when θ is large enough, such poor adhesion results that a modest external stress suffices for effective mold-release. However, the excellent and easy parting action observed needs additional explanation. As was pointed out earlier, the value of W_A' for the various low-energy surfaces reported here exhibits a maximum variation from the least adhesive liquid to the most adhesive of not over three-fold. This appears too small a range to explain the great effectiveness and easy parting action of a good abhesive. Note that the value of W_A' is for a perfectly flat, smooth surface. The roughness factor r of the uncoated surface of the mold could suffice to raise W_A' by a factor of from 1.5 to 3 or more, depending on the surface finish; however, if the material

to be molded is or becomes viscous rapidly during injection or application, poor wetting will cause pockets to be produced at the interface of the material molded and the adhesive, and thereby the adhesion will be greatly decreased by some unknown fraction $1/g$. Also, when θ exceeds 30° , the resulting stress concentration of from 1.2 to 2.5-fold at the adhesive/plastic interface will act to decrease adhesion by a fraction $1/s$ where s varies from 1.2 to 2.5. Therefore, the adhesional work per sq cm of the apparent or envelope area at the molding interface will be $(r/gs)W_A'$. Evidently, for the best adhesive action, the release agent should be such as to have the largest possible value of θ for the substances to be molded against it. The large values of θ encountered with the various organic types of liquids on such low-energy surfaces as those shown in Table 8 make it evident why these film-forming materials are so effective as adhesives.

As a general proposition, any low-energy surface or film will be more effective as a release agent or adhesive the lower its value of γ_c or the lower W_A' . It also can be concluded from the preceding discussion that the smoother the finish of the outer coating of the adhesive, or the lower the surface tension and viscosity of the material being molded, or the lower its contact angle with the adhesive, the greater will be the external stress required to cause the desired parting action.

Frequently it is desired to reduce considerably the free surface energy or γ_c of a plastic solid in order to decrease its adhesion to another solid, and none of the film-forming adhesives listed in Table 8 can be used for one reason or other. This may happen because the release coating should be an integral part of the plastic object. An effective approach can often be developed by including in the plastic, while still in the liquid state, a small concentration of an additive agent which is surface-active in the liquid and so is able to accumulate to some extent as an adsorbed film. The molecular structure of the additive agent should be such as to have the proper "organophobic-organophilic balance" with both types of groups located at opposite extremes of the molecule. Suitable organophobic groups, as might be guessed from perusal of Table 8, would be those which have a perfluorinated chain, dimethyl silicone structure, or paraffin chain. The general problem of surface activity in nonaqueous liquids has been discussed in a recent series of publications from our Laboratory (58-61).

ON THE "ADHESION RULE"

De Bruyne (62) proposed in 1939 the following "rough-and-ready" rule for adhesives: "Provided we use pure or simple substances as adhesives then there is a good deal of evidence that strong joints can never be made by polar adherends with nonpolar adhesives or to nonpolar adherends with polar adhesives." Tabor (53) has indicated this rule is now well established. Some further clarification of this rule can be given from the following surface-chemical considerations: The statement that polar adhesives do not form strong joints with nonpolar adherends would follow of necessity from the fact that a liquid polar adhesive usually has a higher surface tension γ_{LV} than the critical surface tension of γ_c of wetting of a nonpolar adherend, and hence poor wetting would be encountered. This would cause the previously mentioned difficulties with gas pocket formation during spreading, stress concentrations at the joint if θ becomes large, etc. A nonpolar adhesive liquid would usually have a lower surface tension γ_{LV} than the critical surface tension γ_c of wetting of the polar adherend; hence good wetting and spreading should result. However, many nonpolar adhesives are very hydrophobic materials, whereas many polar adherends are somewhat hydrophilic, or can even absorb some water. Hence, in a normally humid atmosphere, poor wetting and spreading of the nonpolar adhesive would occur on contact with the slightly moist surface of the polar adherend. Many polar liquid adhesives will be able to either absorb the atmospheric water or to displace through surface-chemical action the film of water adsorbed on the surface of the polar adherend; hence, adequate wetting and spreading of the adhesive may occur under ordinary atmospheric conditions. This mechanism can be enhanced sometimes by appropriate additives.

Since wetting is determined by the surface constitution of the adherend, it is evident that we can modify the limitation indicated by the above rule of De Bruyne by coating or otherwise absorbing on the surface of the adherend a parting agent or adhesive, if we wish to decrease joint strength; if we wish to increase the joint strength, we can chemically treat the adherend surface to raise its γ_c . An example of the latter is the now widely used surface oxidation of polyethylene to increase γ_c and the wettability and hence increase adhesion and printability.

CONCLUSIONS

For optimum or theoretical joint strength, it is essential to keep the contact angle as small as possible in order to minimize the buildup of stress concentrations and to obtain good spreading. Obviously, the interface of each adherend must be kept as smooth and free as possible of low-energy surface films and dust in order to prevent forming gas pockets and occlusions. In applying liquid adhesives the viscosity should be as low as possible in order to increase the extent of capillary flow into pores and crevices. Maximum spreading and capillarity will be obtained with adhesives having the highest surface tension compatible with obtaining a low contact angle. When conditions of complete wetting and freedom from the formation of gas pockets and occlusions prevail, the adhesion to either high- or low-energy surfaces will usually be ample, and generally failures of the joint will be in cohesion. Under such ideal conditions the problem of obtaining optimum joint strength is not a surface chemical problem. However, the problem of obtaining these ideal conditions is emphatically a surface chemical problem.

Adhesives are materials which form low-energy surface coatings on application to high-energy solid surfaces. Such coated surfaces exhibit large contact angles upon the application of liquid polymers and plastics, and this results in limited spreading and capillarity with the frequent formation of gas pockets at the interface. When solidification occurs the joints formed break easily in adhesional failures because the built-in points of stress concentrations around gas pockets at the interface guide crack formation.

Serious problems can develop in making adhesional joints if water is present on the adherend or is produced as the result of reaction in the adhesive. Under some circumstances a few monolayers of water adsorbed on the adherend can be tolerated because they are readily displaced by the adhesive or absorbed in the adherend or adhesive; however, bulk water can not be tolerated because of either its low shear strength or its adverse effect on spreading of the adhesive.

REFERENCES

1. Poynting, J.H., and Thomson, J.J., "Properties of Matter," 13th ed., London, Chas. Griffin, p. 152, 1934
2. Budgett, H.M., Proc. Roy. Soc. A86:25 (1911)
3. Hardy, W.B., "Collected Scientific Papers," Cambridge Univ. Press, 1936
4. Bastow, S.H., and Bowden, F.P., Proc. Roy. Soc. A134:404 (1931)
5. De Bruyne, N.A., Research 6:362 (1953)
6. De Bruyne, N.A., Nature 180:262; Aug. 10, 1957
7. Young, T., Phil. Trans. Roy. Soc. (London) 95:65 (1805)
8. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 5:514 (1950)
9. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:109 (1952)
10. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:428 (1952)
11. Baker, H.R., Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 56:405 (1952)
12. Shafrin, E.G., and Zisman, W.A., "Hydrophobic Monolayers and Their Adsorption from Aqueous Solution," p. 129 in "Monomolecular Layers," Am. Assoc. Adv. Sci., Wash., D.C., 1954
13. Levine, O., and Zisman, W.A., J. Phys. Chem. 61:1068 (1957)
14. Wenzel, R.N., Ind. and Eng. Chem. 28:988 (1936)
15. Cassie, A.B.D., and Baxter, S., Trans. Faraday Soc. 40:546 (1944)
16. Shuttleworth, R., and Bailey, G.L.J., Disc. Faraday Soc., No. 3:16 (1948)
17. Sumner, C.G., "Symposium on Detergency," Chem. Publ. Co., N. Y., p. 15, 1937
18. Dupré, A., "Theorie Mechanique de la Chaleur," p. 369, Paris, Gauthier-Villars, 1869
19. Bangham, D.H., and Razouk, R.I., Trans. Faraday Soc. 33:805 (1937)
20. Cooper, W.A., and Nuttall, W.H., J. Agric. Sci. 7:219 (1915)
21. Harkins, W.D., and Grafton, E.H., J. Am. Chem. Soc. 42:2534 (1920)
22. Harkins, W.D., and Ewing, W.W., J. Am. Chem. Soc. 42:2539 (1920)
23. Harkins, W.D., and Feldman, A., J. Am. Chem. Soc. 44:2665 (1922)

24. Harkins, W.D., Chem. Rev. 29:408 (1941)
25. Fox, H.W., Hare, E.F., and Zisman, W.A., J. Colloid Sci. 8:194 (1953)
26. Zisman, W.A., "Relation of Chemical Constitution to the Wetting and Spreading of Liquids on Solids" in "A Decade of Basic and Applied Science in the Navy," Wash., D.C., U. S. Government Printing Office, p. 30, 1957
27. Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 64:519 (1960)
28. Hare, E.F., and Zisman, W.A., J. Phys. Chem. 59:335 (1955)
29. Fox, H.W., Hare, E.F., and Zisman, W.A., J. Phys. Chem. 59:1097 (1955)
30. Bennett, M.K., and Zisman, W.A., J. Phys. Chem. 64:1292 (1960)
31. Bennett, M.K., and Zisman, W.A., J. Phys. Chem., to be published
32. Schulman, F., and Zisman, W.A., J. Colloid Sci. 7:465 (1952)
33. Hare, E.F., Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 58:236 (1954)
34. Ellison, A.H., Fox, H.W., and Zisman, W.A., J. Phys. Chem. 57:622 (1953)
35. London, F., Trans. Faraday Soc. 33:8 (1937)
36. Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 61:1046 (1957)
37. Langmuir, I., J. Am. Chem. Soc. 38:2286 (1916)
38. Langmuir, I., "Third Colloid Symposium Monograph," New York, Chem. Catalogue Co., Inc., pp. 48-75, 1925
39. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:428 (1952)
40. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 58:260 (1954)
41. Ray, B.R., Anderson, J.R., Scholz, J.J., J. Phys. Chem. 62:1220 (1958)
42. Scholz, J.J., Ray, B.R., and Anderson, J.R., J. Phys. Chem. 62:1227 (1958)
43. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 58:503 (1954)
44. Bartell, F.E., and Greager, O.H., Ind. and Eng. Chem. 21:1248 (1929)
45. Bartell, F.E., and Zuidema, H.H., J. Am. Chem. Soc. 58:1449 (1936)
46. Bartell, F.E., and Ray, B.R., J. Am. Chem. Soc. 74:778 (1952)
47. Bigelow, W.C., Pickett, D.L., and Zisman, W.A., J. Colloid Sci. 1:513 (1946)
48. Bigelow, W.C., Glass, E., and Zisman, W.A., J. Colloid Sci. 2:563 (1947)
49. Boyd, G.E., and Livingston, H.K., J. Am. Chem. Soc. 64:2383 (1942)
50. Harkins, W.D., and Loeser, E.H., J. Chem. Phys. 18:556 (1950)

51. Loeser, E.H., Harkins, W.D., and Twiss, S.B., J. Phys. Chem. 57:251 (1953)
52. Basford, P.R., Harkins, W.D., and Twiss, S.B., J. Phys. Chem. 58:307 (1954)
53. Tabor, D., Rept. Prog. Appl. Chem. , Soc. Chem. Ind., London, 36:621 (1951)
54. Bewig, K.W., and Zisman, W.A., "Low Energy Reference Electrodes for Investigating Adsorption by Contact Potential Measurements," Presented at Spring Meeting, Div. Colloid and Surface Chemistry, Am. Chem. Soc., St. Louis, March 21, 1961, to be published
55. Martinet, J.M., "Adsorption des Composés Organique Volatile par le Polytétrafluor Ethylene," Commissariat a L'énergique Atomique, Rapport CEA 888, Centre D'Études Nucléaires de Socloy, 1958
56. Mylonas, C., Proc. VII Int. Congr. Appl. Mech., London, 1948
57. Griffith, A.A., Phil. Trans., A221:163 (1920)
58. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 63:1121 (1959)
59. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 63:727 (1959)
60. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 64:150 (1960)
61. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 64:157 (1960)
62. De Bruyne, N.A., The Aircraft Engineer, XVIII, No. 12, 53, Dec. 28, 1939

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