Adhesion: Mechanisms That Assist or Impede It

An interdisciplinary approach relates present knowledge of adhesion to bioadhesional problems.

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Although much attention has been given to the formation, structure, and properties of biological interfaces, an especially unsettled aspect of the subject is biological adhesion, without which organized tissue would not exist. In contrast, much progress has been made in recent years in our understanding and control of adhesion in man-made systems, resulting in the development of both physical and chemical techniques for controlling adhesion in problems ranging from improving adhesion to impeding it. Therefore, it seems timely to apply what has been learned from studies of man-made junctions to problems in bioadhesion, wherever possible. This is particularly appropriate since adhesive behavior in biological environments has received increased attention recently in research on surgical adhesives, marine fouling, dental restoratives, extracorporeal circuits, and prosthetic implants.

Adhesion between Dry Solids

Adhesion between dry, nonreacting solids in contact is caused by a strong, but extremely localized, field of attractive force emanating from each solid surface. In the absence of ions or strong permanent dipoles in (or near) a solid surface, this field of force varies as the inverse seventh power of the distance away from the solid surface. The *total* attractive force is generally negligible when two plane solids free of net electric charge are separated by distances variously estimated at tens to hundreds of angstroms. Only when there is a large area of intimate (or real) contact between the dry solids can they be made to adhere significantly. Since solid surfaces are rarely ideally planar, the effort needed to pull them apart is usually insignificant because the real area of contact (that is, the total of individual areas of contact between those few opposed asperities in position to touch each other) is generally a very small fraction of the apparent area of contact (*1*, *2*). But if one or both solids is sufficiently soft to permit deformation of the surface, the real area of contact and the adhesion developed under modest loads can be large (*3*, *4*). Because of the extreme localization of the attractive force field, a very thin adsorbed film of oxide or as little as one condensed monolayer of organic contamination can greatly decrease the adhesion of dry solids (*3*, *5*).

Another cause of loss of adhesion is the release of the internal stresses which develop in the area of elastic deformation at the base of every compressed asperity when the load applied to press two hard solids together is removed. As Tabor has demonstrated (*4*), if these elastic stresses can be removed by annealing the two solids while the load is maintained, strong adhesive junctions will persist even after the load is removed. This is further proof that good adhesion can result from the operation of purely physical forces without the necessity of chemical interaction.

A wealth of experimental evidence that contacting, clean, dry solids adhere significantly has come from research on the nature of dry friction. Various well-controlled experiments by Bowden, Tabor, and their co-workers (*2*) have demonstrated that such friction is caused by the adhesion of the two rubbing solids at the areas of real contact between the plastically deformed tips of their contacting asperities. Such adhesion (or cold welding) makes it necessary to apply a force to overcome friction; to a first approximation this force is equal to the true (or real) area of all the contacting asperities multiplied by the average shear strength of the junctions. The principal cause of wear is the breaking of these junctions, usually by a shearing within the weaker of the two contacting asperities.

A massive and reliable literature exists indicating the friction-lowering (and hence the adhesion-lowering) properties of thin films of oxides, water, or organic compounds, all of which are common surface contaminants. Although high friction and wear are common when uncontaminated, dry organic solids are rubbed together, the effect of varying the chemical composition of the organic surface can be great. Figure 1 shows the effect on the coefficient of friction (μ) of substituting halogen for hydrogen in the ethylene monomer of polyethylene-type polymers (*6*). Whereas progressive substitution of fluorine lowered μ from 0.33 to 0.04, an analogous progressive chlorination of the ethylene monomer increased μ to 0.9 when only half of the hydrogen atoms had been replaced [as in poly(vinylidene chloride)]. By comparison, values of μ up to 0.10 are common for well-lubricated metal joints. These results deserve the attention of biological and medical scientists in view of the present or contemplated uses of such polymers in prosthetic implants as well as in biological research.

Behavior of Liquids in Making Adhesive Joints

When two flat, smooth, solid surfaces are spontaneously wetted by a thin layer of a liquid, strong adhesion can result. The reason is evident from Fig. 2 and an application of the classic Laplace-Kelvin equation of capillarity (*7*)

$$p_l - p_v = \gamma_{lv}\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \quad (1)$$

Here p_l and p_v are, respectively, the pressure within the liquid and the pressure in the vapor outside the liquid; R_1 and R_2 are, respectively, the radius and half the thickness of a thin, circular layer of liquid in contact with the solid; and γ_{lv} is the surface tension of the liquid. If $R_2 \ll R_1$, then p_v will be

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greater than p_l; hence, the two plates will be forced together because of the pressure difference $p_v - p_l$. From Eq. 1 it follows that many common liquids which spontaneously wet two such solid surfaces will hold them together. Budgett (*8*) found that when two highly polished, flat steel disks (4.5 centimeters in diameter) were completely wetted by a paraffin oil having $\gamma_{lv} = 28$ dynes per centimeter, a total force of about 20 kilograms was needed to pull the disks apart. The force calculated from Eq. 1 was 30 kilograms.

Such a method of forming an adhesional joint has several serious limitations.

1) The resistance of the joint to shear stresses is determined solely by the viscosity of the liquid film; hence, only if the viscosity is very great could the joint long withstand an external shearing stress.

2) It would be necessary to prepare extremely closely fitted, smooth, solid adherends in order to bring the solid surfaces together closely enough to form a joint having high tensile strength.

3) Freedom of the solid surfaces and the liquid from dust or other particles could be critically important in forming a strong joint.

However, a stronger and much more useful joint would be formed if the viscosity of the intervening thin liquid layer were increased greatly through any of various mechanisms, such as (i) solvent permeation or evaporation, (ii) polymerization, (iii) gelling caused by a dispersed solid or polymer, or (iv) cooling until the liquid solidifies.

Whereas joints with great resistance to tensile stress but low resistance to shearing stress are of little technological usefulness, they may be important in the many relatively mobile, conformable systems found widely in biological systems. The limited requirement for shear strength in such biological joints may be satisfied if the liquid is very viscous. It should be remembered that proteinaceous viscous liquids obtained from fish and animal sources were among the earliest adhesives known to man. Any cross-linking of the liquid adhesive would strengthen the joint, and any depolymerization or thinning through dilution, or as the result of enzymatic action, would weaken it. Since many biological membranes or other biological systems are sufficiently nonrigid to conform to the requirement for coplanarity or efficient mating of contours of the opposed surfaces, it is very probable that intervening liquid films cause many biological surfaces to adhere adequately for nature's purpose.

McBain and his co-workers (*9*) first established the following three requirements for the formation of a useful, strong, adhesive joint: (i) good wetting, (ii) solidification, and (iii) sufficient deformability to reduce the buildup of elastic stresses in the formation of the joint. The second and third requirements have been fully investigated, but the need for the first was not adequately understood until much later (*10–13*).

Effects of Surface Roughness

Of course, real, solid, "flat" surfaces are not planar; too little attention had been given to the disturbing effects of surface roughness on adhesion. The innumerable small hills, valleys, and crevices in the surface of practically any real solid create problems which must not be neglected if strong, durable, adhesive joints are desired. A viscous liquid can appear to spread well over a solid surface and yet have many gas pockets or voids in small surface pores and crevices where the liquid adhesive has formed a mantle over neighboring peaks without having fully penetrated into the valleys. Even if the liquid adhesive spreads spontaneously over the solid, there is no certainty that intimate contact of liquid and solid interface will have occurred everywhere. This problem is magnified when the liquid rapidly polymerizes or hardens soon after being applied.

When a liquid adhesive solidifies, the loss in joint strength caused by the interfacial voids is much greater than would be expected from the ratio of the interfacial area occupied by voids to the area of the entire joint interface. This result arises from the action of internal and external stress concentrations; each of these types of action has been given increasing attention in the past several decades. Griffith (*14*) showed that adhesive joints may fail at relatively low applied stresses if cracks, air bubbles, voids, inclusions, or other surface defects are present. On application of an external load to the joint, stress concentrations arise that can be much higher than the mean applied stress. Real joints are better represented by Fig. 3 than by Fig. 2. If the gas pockets or voids in the surface depressions of the adherend are all nearly in the same plane and are not far apart (as is shown for the upper adherend of Fig. 3), cracks can readily propagate from one void to the next, and the joint can break as easily as if it had a built-in "zipper." Because this situation is desirable in molding rubber and plastics, in such processes both a smooth finish and a coating of release agent are applied to the surface of the mold (*15*). For a strong adhesive joint, however, the kind of roughness shown on the

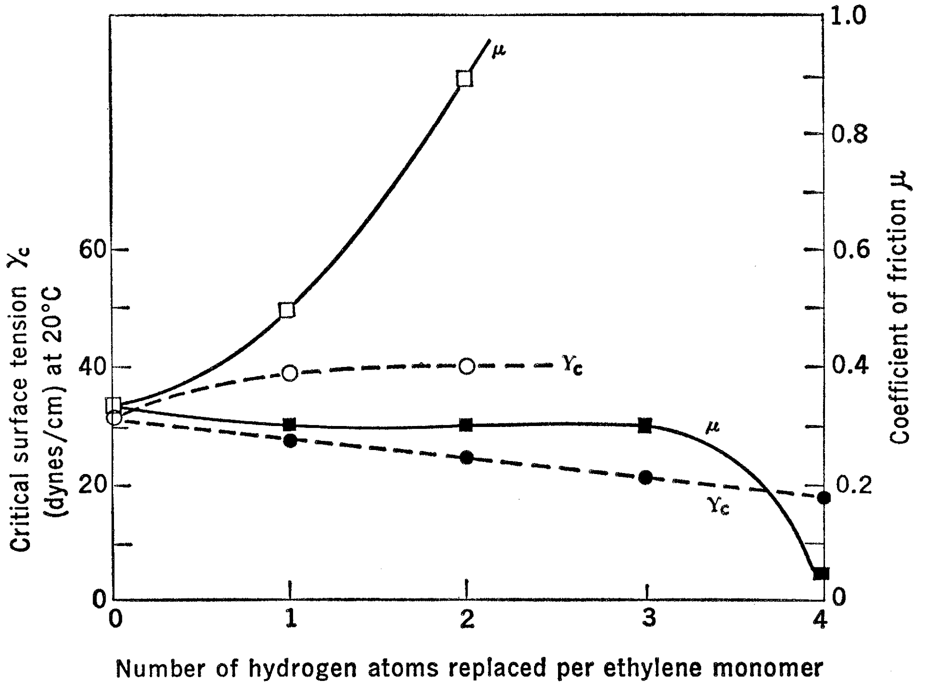


Fig. 1. The effect, on surface properties, of progressive hydrocarbon replacement in polyethylene-type surfaces by chlorine (open symbols) and fluorine (solid symbols). (Squares) Friction; (circles) wettability.

lower adherend would be preferable (provided roughening of the surface did not result in excessive formation of voids) because crack propagation in the resin would have to follow a much longer, nonrectilinear path to connect neighboring voids.

Stress Concentration Problems

Internal stresses and stress concentrations usually develop during solidification of the adhesive. In general, the strength of the adhesive joint is decreased considerably below its theoretical value by the development of these internal stress concentrations; the effect is especially serious in joining adherends with an adhesive such that neither the adherends nor the adhesive has significant ability to shrink during the cooling (due to unmatched thermal expansion coefficients) or curing of the joint. In a lap joint (Fig. 4), 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. As the contact angle (θ) of the adhesive becomes large, the maximum stress concentration increases and moves toward the lineal boundary where the adhesive and atmosphere make contact with the adherend (*16*).

Definitions and Concepts about Wetting and Spreading

The extent to which liquids spread over a solid surface and the adhesion of these liquids to the solid define the wetting properties of the solid. In considering the wetting properties of solid surfaces it is helpful to distinguish two broad classes of solids according to their specific surface free energies (*17*) even though reliable determinations of the surface free energy of a solid in a vacuum (γ_{s°) cannot yet be made for most solids. At ordinary temperatures, solids having strong intermolecular forces always have specific surface free energies ranging from around 100 to 10,000 ergs per square centimeter; the higher values correspond to the hardest materials with very high melting points. The much weaker intermolecular forces in soft, organic solids of low melting point are reflected in their lower specific surface free energies, which range from 10 to <100 ergs per square centimeter. We have classified solids of these two types as solids having "high-energy surfaces" and "low-energy surfaces," respectively (*17*).

In marked contrast, the specific surface free energy of a pure liquid is easily obtained because this is simply its surface tension (γ_{lv}). The specific surface free energies of organic liquids and of most inorganic liquids (exclusive of the liquid metals) at ordinary temperatures are readily measured; they rarely exceed the value for water. Hence, one would expect these liquids to spread spontaneously on contact with solids of high surface energy, since a large decrease in the surface free energy of the system would result from such contact. But since the surface free energies of such liquids are comparable to those of low-energy solids, among the organic liquids should be found many that do not spread readily on low-energy solids (*11*, *13*).

Thomas Young (*18*) was the first to discuss the contact angle of a liquid and the equilibrium of a drop resting on a plane solid surface under the action of three surface tensions. These tensions are indicated in Fig. 5, where γ_{lv° is the surface tension at the interface of the liquid and vapor phases, γ_{sl} is that at the interface of the solid and the liquid, and γ_{sv° is that at the interface of the solid and vapor. Hence,

$$\gamma_{sv^\circ} - \gamma_{sl} = \gamma_{lv^\circ} \cos \theta \qquad (2)$$

In effect, Young provided the first good approach for describing the wettability and spreading of a liquid on a solid and the relation of this property to the equilibrium contact angle.

First, let us consider the liquid-solid interface to be a plane. When $\theta = 0$, the liquid is said to spread spontaneously or completely on the surface of the solid; when $\theta \neq 0$, the liquid is said to be nonspreading. However, because we always find some liquid-to-solid adhesion, we can say that every liquid can wet every solid to some extent. On a sufficiently smooth and homogeneous solid surface, θ is independent of the volume of the liquid drop. Since the tendency for a given mass of liquid to spread (and adhere) increases as θ decreases, the contact angle is a useful inverse measure of wettability; cosine θ is an obvious direct measure. As θ decreases, a liquid drop will spread and come in contact with a larger area of

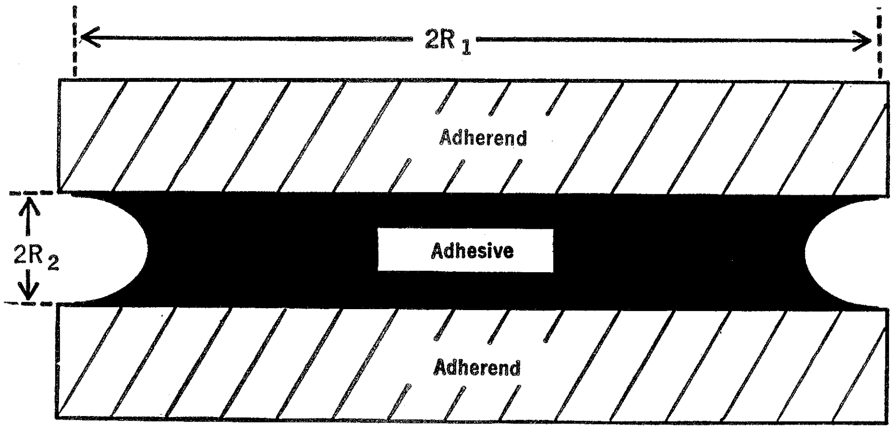


Fig. 2. Idealized adhesive joint.

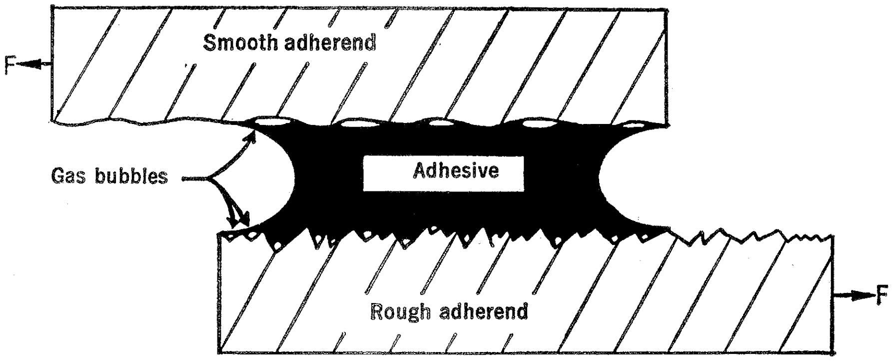


Fig. 3. Effect of surface roughness on coplanarity of gas bubbles.

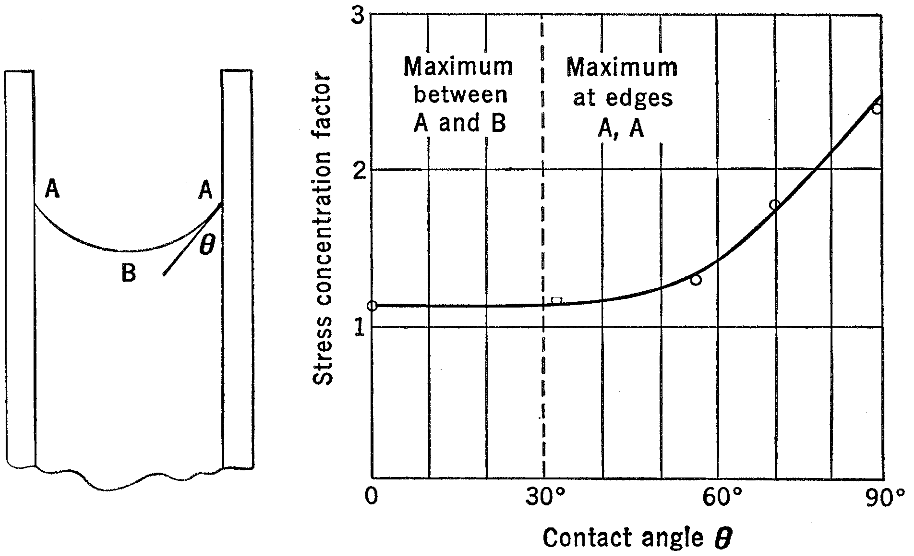


Fig. 4. Variation of stress concentration maxima in lap joint adhesive with angle of contact. [After Mylonas (*16*)]

the surface; as θ vanishes, the area covered by the liquid drop becomes increasingly great; therefore, when $\theta = 0$, spontaneous spreading will occur over the accessible solid surface.

The oldest experimental problem in measuring contact angles results from the difference between the advancing contact angle (θ_A), the angle observed when a liquid boundary advances over a clean, dry, solid surface, and the receding contact angle (θ_R), the angle observed when the liquid boundary recedes from a previously wetted surface. When a difference is observed between these two angles, the most common cause is the entrapment of liquid in the valleys, crevices, and pores of the solid surface as the liquid advances over it. When the liquid recedes, the surface uncovered usually includes wet areas; hence, for this case, θ_R is smaller than θ_A. However, when care is exercised to prepare solids with sufficiently smooth, clean, homogeneous surfaces, no significant differences are found between the contact angles exhibited by a pure liquid whether advancing or receding over the solid (*11*, *13*).

Wenzel (*19*) investigated the way in which the gross or macroscopic roughness of a solid surface was related to (i) the apparent (or measured) contact angle (θ') between the liquid and the envelope to the surface of the solid and (ii) the true contact angle (θ) between the liquid and the surface at the air-liquid-solid contact boundary. Using as the measure of the roughness (r) the ratio of the true area of the solid to the apparent or envelope area, he found the simple relation

$$r = \frac{\cos \theta'}{\cos \theta} \tag{3}$$

Wenzel's equation is important because r varies widely in practice; instances where $r = 1.00$ are rare indeed. Perhaps the nearest thing to such a smooth surface is that of glass freshly polished by fire, or a very carefully cleaved single crystal of mica. Even carefully machined and ground metal surfaces usually have r ranging from more than 3.0 to not less than 1.5. Several consequences of Wenzel's equation (Eq. 3) are especially important. It indicates that when $\theta < 90$ degrees, $\theta' < \theta$. Since most organic liquids exhibit contact angles of less than 90 degrees on clean polished metals, the effect of randomly roughening the metals is to make the apparent contact angle, θ', between the drop of liquid and the envelope to the metal surface less than the true contact angle θ. In other words, each liquid will appear to spread more after the metal surface has been roughened. Equation 3 indicates that when $\theta > 90$ degrees, $\theta' > \theta$. Since pure water makes a contact angle of from 105 to 110 degrees with a smooth paraffin surface, the effect of roughening the paraffin makes θ' greater; values of 140 degrees have been observed. Various investigators have discussed the effect of roughness on θ in more detail (*20*); their work is especially interesting in describing contact-angle hysteresis on surfaces having an orderly roughness, such as the surfaces of woven textiles.

Surface roughness increases the difficulty of measuring θ accurately. The experimental methods used to measure the contact angle generally measure θ', and all too often it is assumed that $\theta' = \theta$. Analysis of Eq. 3 reveals the following relationship: the smaller the contact angle to be measured, the greater the solid-surface smoothness needed in order to obtain a given precision of measurement. When the contact angle is large, a high surface finish is not so essential.

Effects of Constitution on Wetting

Only in the past two decades have we learned much about the relation of the constitution of solids and liquids to the equilibrium contact angle. Various pure liquids and solids were examined under controlled experimental conditions, frequent use being made of homologous families of liquid compounds. The solid organic surfaces used were chemically well-defined polymers pressed into the form of smooth polished plates. Guided by the results of such experiments, we turned to polished, clean, solid surfaces of glass or metals and coated each with an adsorbed, condensed, organic monolayer. Through use of such solids and of liquids which had been carefully freed of surface-active impurities, reproducible contact angles were obtained; furthermore, the advancing and receding contact angles of each solid-liquid pair were identical so long as the liquid drop was advancing or receding sufficiently slowly to be reasonably close to equilibrium conditions.

A rectilinear relation was established empirically between the cosine of the contact angle and the surface tension for each homologous series of organic liquids (*11*, *13*, *21*). Figure 6 illustrates the results observed with the *n*-alkanes on polytetrafluoroethylene (Teflon) (*17*). The critical surface tension (γ_c) for wetting by a homologous series of liquids was defined as the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight-line plot of $\cos \theta$ against γ_{lv°. Even when $\cos \theta$ is plotted against γ_{lv° for a variety of nonhomologous liquids, the plotted points fall close to a straight line or collect around it in a narrow rectilinear band. For certain surfaces, such as that of polytetrafluoroethylene, the points fell on a curve for values of γ_{lv° above 50 dynes per centimeter, but in these cases the curvature was due to the formation

Table 1. Critical surface tension (γ_c) of various polymeric solids.

Polymeric solid	γ_c (dyne/cm at 20°C)
Poly(1,1-dihydroperfluorooctyl methacrylate)	10.6
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Starch	39
Poly(methylmethacrylate)	39
Poly(vinyl chloride)	39
Poly(vinylidene chloride)	40
Poly(ethylene terephthalate)	43
Cellulose	45
Poly(hexamethylene adipamide)	46

of weak hydrogen bonds between such liquids and the solid surface (*13*). When there was no hydrogen bonding with the atoms in the solid surface, as was true in the case of polyethylene or of poly(vinyl chloride), the data points for cos θ plotted against γ_{lv° for any low-energy surface always fell on a straight line or within a narrow rectilinear band. Whenever 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 a homologous series of liquids, it is an even more useful parameter because it is a characteristic of the solid surface alone; it has proved a useful empirical parameter which is symbatic with the free surface energy γ_{s°.

Table 2. Critical surface tensions (γ_c) of low-energy surfaces.

Surface constitution	γ_c (dyne/cm at 20°C)
Fluorocarbon surfaces	
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ and $-CF_2-$	17
$-CF_2-CF_2-$	18
$-CF_2-CFH-$	22
$-CF_2-CH_2-$	25
$-CFH-CH_2-$	28
Hydrocarbon surfaces	
$-CH_3$ (crystal)	20–22
$-CH_3$ (monolayer)	22–24
$-CH_2-CH_2-$	31
$\underset{\cdots}{-}CH\underset{\cdots}{-}$ (phenyl ring edge)	35
Chlorocarbon surfaces	
$-CClH-CH_2-$	39
$-CCl_2-CH_2-$	40
$=CCl_2$	43

By comparing the γ_c values of structurally "homologous" or "analogous" solids, such as an unbranched polyethylene and its various chlorinated or fluorinated analogs, and by making the reasonable assumption that the surface composition of the solid polymer is the same as that of the extended polymer molecule oriented parallel to the surface, it was possible to investigate the effect of the surface constitution of such polymeric solids on their critical surface tensions. Striking differences are evident from the two curves in Fig. 1 representing wetting behavior. Thus, we see that, whereas fluorination of polyethylene decreases γ_c, chlorination raises it (compare the solid and open circles of Fig. 1). Strikingly similar effects for halogen substitution are noted in the two frictional graphs as well (compare the solid and open square representing μ values in Fig. 1).

Results of many investigations of clean, smooth, plasticizer-free, polymeric solids of general interest are summarized in Table 1. Values of γ_c for a series of hydroxyl-rich surfaces including cellulose composites (various dry, clean woods) and starch polymers range from 40 to 45 dynes per centimeter (*22*). These values of γ_c are reasonably close to the value of 43 dynes per centimeter reported for the oxygen-rich surface of Dacron or Mylar [poly(ethylene terephthalate)]. Nylon 66, with its many exposed amide groups, has the highest γ_c value (46 dynes per centimeter) of the common plastics reported.

A wide variety of similar measurements of cos θ relative to γ_{lv} proved that the value of γ_c for low-energy organic surfaces, as well as for high-energy surfaces coated with condensed organic monolayers, was determined essentially by the nature and packing of the outermost or exposed surface atoms of the solid; it was independent of the chemical nature and arrangements of the atoms and molecules beneath that solid surface or surface coating (*11–13, 21*). Moreover, uniform, condensed single monolayers of stearic acid, primary octadecyl amine, or octadecyl alcohol, even though only about 24 angstroms thick, were sufficient to reduce the wetting properties to the same value of γ_c (characteristic of CH_3-rich surfaces), regardless of the nature of the solid substrate. This result provided strong evidence that the attractive field of force emanating from the metallic or nonmetallic solid substrate was minor at this distance. Because the field of force became unimportant at a distance of very few atom diameters, atoms not in the first few surface layers of the solid made little contribution to the adhesion. There was good evidence that when the constitution of the solid, or of the adsorbed monolayer, was such that either ions or large, uncompensated, permanent dipoles were located in the outermost portion of the surface monolayer, the residual field of force of the surface was much less localized (*13, 21, 23*).

The effect of surface constitution on γ_c for low-energy solid surfaces is summarized in Table 2. The surfaces are identified with respect to probable exposed atoms or organic radicals and are arranged in the order of increasing γ_c within the subgroup. Results of major interest to surface and polymer chemistry can be deduced readily from Table 2 (for a full discussion of these results, see *13, 15, 23*). In general, the observed effectiveness of covalent atomic substituents (attached to carbon atoms) tending to increase γ_c can be expressed by the inequality series

$$F < H < Cl < Br < I < O < N \qquad (4)$$

Surface Chemical Interferences and Aids in Adhesion

An adequate understanding of adhesive action should provide an explanation of poor as well as good adhesion, hence an explanation of the properties of "abhesives," which are materials commonly applied, as thin coatings, to one solid to prevent—or greatly decrease—adhesion of that solid to another solid after the two have been brought into intimate contact. Abhesives are used in molding, casting, or rolling operations; therefore, it is common in industry and the arts to refer to them as "parting," "mold-release," or "antistick" agents.

A tabulation of the values of γ_c for each of the much-used types of release films or coatings, such as fatty alcohols, silicones, and fluorocarbons, reveals that the films having the most general effectiveness have the lowest values of γ_c (*12, 13, 15*). Each such abhesive coating converts the solid into a low-energy surface. When a liquid is placed on that coated surface, the more γ_{lv° exceeds γ_c, the greater the equilibrium contact angle will be. As θ becomes larger, more interfacial voids develop, and such poor adhesion results that, after the liquid has solidified in the mold, the application of a modest external stress suffices for effective separation from the wall of the mold. Therefore, the basis of abhesive action is the surface-energy decrease induced in the high-energy surface by the adsorption of a monolayer of a polar amphipathic compound having an outermost terminal group such as $-CH_3$ or $-CF_3$.

Hence, it should now be evident that, in order to obtain optimum adhesive strength in a joint, it is essential that the interface with each adherend be kept as free as possible from low-energy organic films. In this way the incidence and size of interfacial voids may be kept to a minimum. This conclusion may be of importance in biological systems, for it means that an apparently subtle change in the surface composition of a biological membrane can greatly decrease (or increase) its wettability and also its adhesiveness. An outermost substituent which decreases γ_c (such as $-CH_3$ or $-CH_2-$) would *decrease* adhesiveness, whereas one which increases γ_c (such as phenyl, $-OH$, $-SH$, $-COOH$, or $-NH_2$) would *increase* adhesiveness.

Many high-energy solids, such as glass, silica, alumina, metals, metal oxides, and a great variety of organic polymeric solids like cellulose, polysaccharides, polypeptides, and proteins, readily adsorb water. When a polymolecular or "duplex" film of water is present on such surfaces, all but the most firmly adsorbed portion (often only a monolayer) can be removed by gentle heating, by drying in a vacuum, or by use of a water-displacing agent at ordinary temperatures (*24*). Removing the last monolayer of adsorbed water can be difficult, however.

Recent investigations have demonstrated that adsorbed water greatly decreases the surface energy of glasses, silica, alumina, and metals (*25*). At room temperature one condensed monolayer of adsorbed water will convert these high-energy solid surfaces into low-energy surfaces. As more than a monolayer of water is adsorbed, γ_c decreases somewhat and approaches the critical surface tension of a bulk water surface (about 22 dynes per centimeter at 20°C). Therefore, if any liquid devoid of hydrophilic groups (such as a hydrocarbon, chlorocarbon, bromocarbon, or iodocarbon) comes in contact with such a moist surface, it will not spread and will have a fairly large contact angle. But liquids containing accessible hydrophilic groups will tend to spread more readily upon such moist surfaces. If the organic liquid is sufficiently hydrophilic, it may spread so vigorously as to displace the bulk adsorbed water (*24*), and in the most extreme situation it may even displace or desorb all but the last monolayer of water. Good examples of this large group of compounds are the liquid polar-nonpolar hydrocarbon derivatives such as the alcohols, glycols, ketones, acetates, acetoacetates, and ether alcohols, as well as certain volatile liquids with unusually low surface tensions, such as the Freons and the dimethyl silicone trimer and tetramer. Because there are so many water-displacing agents among the polar-nonpolar, hydrophilic organic compounds, it is prob-

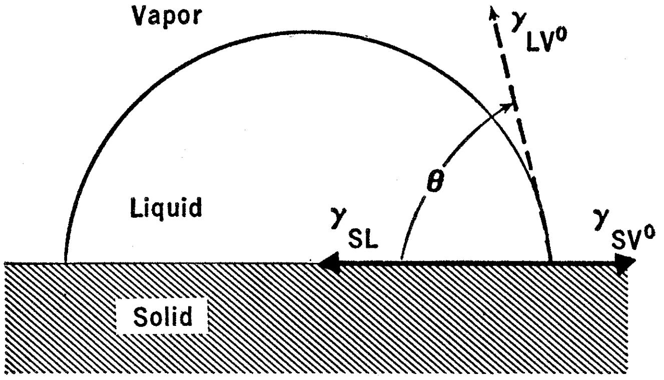
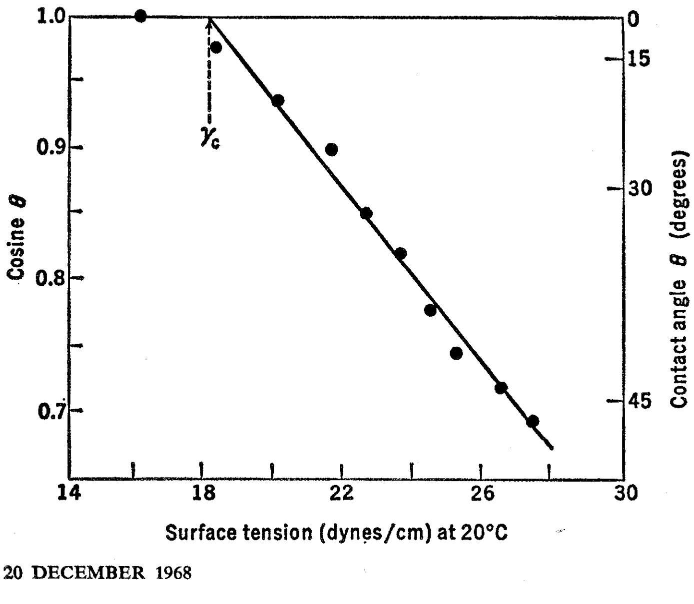
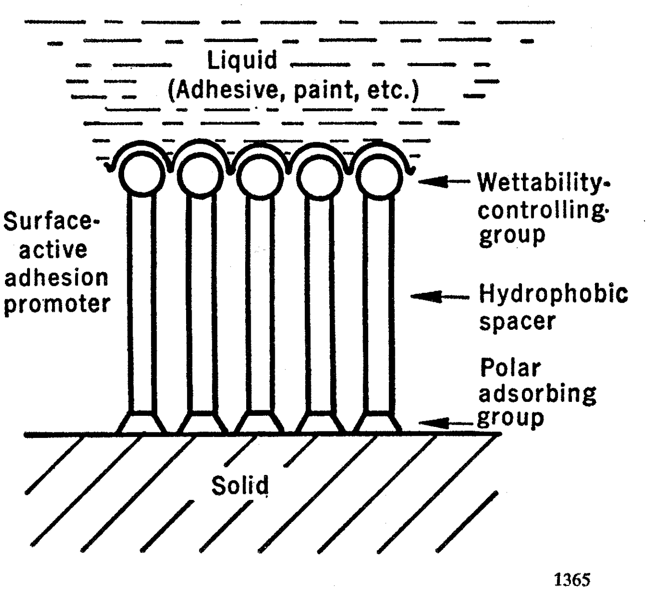


Fig. 5 (left). Schematic diagram of a finite contact angle formed by a sessile drop resting on a solid surface.

Fig. 6 (below, left). Wettability of polytetrafluoroethylene by the *n*-alkanes.

Fig. 7 (below, right). Schematic representation of a surface-active coupling agent.





able that, in the application of some liquid resin systems to make adhesive joints, an addition agent, impurity, or diluent functions as a water-displacing agent. When such an agent is used, it may be possible to obtain good wetting and adhesion by the resin even if the relative humidity is high. However, if any hydrophilic groups are added to the resin molecules to give the resin the ability to spread spontaneously on water and to give it also some water-displacing ability, the substitution should not be carried too far because then the resin will become more susceptible to water permeation and to displacement, by water, after it has been adsorbed on the adherend.

Since a polymolecular adsorbed film of water offers little resistance to shearing stresses, the presence of such a layer of water on the adherend surface will normally greatly decrease the strength of the adhesive joint formed. An exception is the special case where the adhesive is a gradually thickening aqueous solution, such as a viscous aqueous silicate solution (for example, a cement), or a polymer-thickened aqueous solution. But if an organic liquid adhesive, while polymerizing, is not able to react with, dissolve, or displace all of the adsorbed water on the adherend, the joint, after it has "set," will be weak. Such problems are common where joints must be made under conditions of great humidity or under water. Of course, these problems are commonplace in biological and dental systems.

Still another problem encountered after a good adhesive joint has formed is its gradual deterioration as a result of prolonged immersion in water or prolonged exposure to a very humid atmosphere. This problem is all too often encountered in the failure of protective coatings on wood, brick, or concrete. Another example of the same problem is the deterioration of a composite plastic reinforced with a hydrophilic solid fiber such as glass. A similar problem is the gradual deterioration of dental fillings made from cements or from organic composite materials. To understand how barnacles and other marine organisms can maintain such strong adhesion to foreign surfaces while submerged in water is still a challenge.

No general solution to such problems exists; however, several approaches are known. Obviously, long exposure to moisture requires that the adhesive used to make the joint be chemically resistant to decomposition by water. The use of an appropriate "coupling agent" in forming the joint is also helpful; since use of such agents is increasing rapidly, they deserve a brief discussion.

Promotion of Adhesion by Coupling Agents

A coupling agent is a special type of surface-active agent intended to promote adhesion; it functions by adsorbing on, and altering, the surface of the solid to facilitate its interaction with the liquid adhesive by either chemical or physical processes. A number of materials (*26, 27*) are being used as coupling agents for glass-fiber-reinforced plastics. These agents are believed to react chemically with both the adherend and the adhesive. But high joint strength can be achieved if there is a sufficiently intimate molecular contact between adhesive and adherend; thus surface-active coupling agents can be designed which do not require chemical interaction with both phases (*28*). Several new classes of such compounds have been synthesized and investigated at the Naval Research Laboratory (*29–31*). These compounds are sufficiently surface-active to adsorb strongly on many types of solid, high-energy adherends. The resulting adsorbed monolayer presents an outermost surface on which the liquid adhesive will spread spontaneously even at high humidities without chemically combining with the film-coated surface.

Since many organic adhesives are applied as solutions or dispersions which are thinned with solvents having low surface tensions, it might be supposed that such adhesives would invariably spread spontaneously on adherends having high-energy surfaces, and that the use of a coupling agent to improve wetting would be unnecessary. Such is usually not the case, however, because the high-energy surfaces are highly susceptible to the adsorption of interfering low-energy films of the type discussed above. In practice, such adhesives do not always spread readily or uniformly over many kinds of metals and other inorganic surfaces. A hitherto unrecognized and important function of the adsorbed film of adhesion promoter can be to prevent such contamination by serving as a preliminary protective coating for the clean, high-energy solid prior to application of the liquid adhesive. A second function is to prevent the adsorption of any contaminant which may have migrated from the liquid adhesive toward the high-energy surface of the adherend. In either case, the adsorbed monolayer of coupling agent should prevent surface contamination by organic substances, or by water, which could interfere with spontaneous spreading by the liquid adhesive, interpose a weakly bound layer at the interface, or introduce a plane of easy parting after the adhesive had solidified (*28, 30*).

Figure 7 presents schematically the role of a surface-active coupling agent in an adhesive joint. The desired wetting properties are obtained by incorporating an appropriate atomic group (or organic radical) at the outer end of the oriented adsorbed molecule. The opposite end of the molecule can comprise one or more polar groups each of which is able to adsorb, quite independently, on the adherend surface by strong physical or chemical adsorption. The coupling agent would thus be highly resistant to displacement by solvents or by surface-active components in the liquid adhesive. Since the small size of the water-vapor molecule makes permeation of organic coatings by moisture a constant threat to the integrity and longevity of adhesive joints, the outer surface of the coupling-agent film should be more hydrophobic than hydrophilic. Finally, where there is a chemical reaction between coupling agent and adherend, the product should have optimum resistance to immersion in water; it should be insoluble in water and should be as hydrolytically stable as possible.

For example, highly adsorptive chlorine-containing compounds can be chosen which, when adsorbed, have covalent chlorine atoms in the outermost film surface, form a very hydrophobic coating, are resistant to chlorine hydrolysis, and have critical surface tensions of wetting of 40 dynes or more per centimeter (*11–13*, *32*). Obviously the choice of the adsorbing group to be used for coupling the agent to the solid surface will depend on the nature of that solid and on whether or not any chemical interaction with the adherend surface can provide high resistance to water-degradation of the joint. Thus, for oxygen-rich surfaces, a variety of substituted silanes (*26*) and many types of coordination complexes with chromium (*27*) have been used; compounds with related structures are still being developed. Similarly, the use of substituted amines on glasses, paper, and cellulose has been proposed. Chlorophenyl-substituted mono-, di-, and tricarboxylic acids are already being applied to metal surfaces and have been proposed for application to surfaces of metal oxides and to the hydroxyapatite constituent of teeth (*29, 30*). The specific types of surface-active coupling agents discussed above were designed to be added to an adhesive joint of current interest. However, effective coupling agents may already be present in biological systems in the form of the naturally occurring amino acids, carboxylic acids and salts, amines, and even the lower-molecular-weight proteins or polypeptides. Manifestly, synthetic materials chosen for biological use would have to be nontoxic and nonirritating.

Some Implications for Bioadhesion

The correlation of γ_c with biological interactions can be illustrated by brief discussion of three examples: (i) the contact interaction of blood with foreign surfaces; (ii) the interaction of isolated cells with foreign surfaces; (iii) the selective behavior of highly developed organisms on solids.

When blood comes in contact with foreign solid surfaces, there are specific adsorptive interactions which can initiate important events such as the formation of a thrombus and blood coagulation. Two well-recognized processes may occur: (i) the adsorption of proteins leading to coagulation; (ii) the adhesion of platelets, at first to the solid and then to each other. The growing mass of platelets forms a thrombus, which adheres to the solid surface.

Surface attraction of the solid is involved in three ways: in the adsorption of proteins, in the initial adhesion of the platelets, and to some extent in control of the adhesional lifetime of the thrombus. The lifetime (and therefore the aggregate size) of the thrombus should decrease with decreasing γ_c of the foreign surface because of the poorer adhesion to lower-energy surfaces. Consequently, the smaller size of the thrombus upon detachment from such a surface should result in a decreased likelihood of embolism downstream. Lyman and his co-workers (*33*), studying the relation of blood-coagulation induction times to γ_c, reported an encouraging inverse correlation. Since thrombus formation involving cell adhesion is a parallel process in vivo, very likely there is also a correlation of platelet adhesion with γ_c.

Concerning the interaction of isolated cells from a variety of tissues with foreign surfaces, there secms to be general agreement that adhesion and spreading of cells can be a direct function of the solid-surface energy. For example, Taylor (*34*) and Weiss and Blumenson (*35*), using serum-free media, have demonstrated that cells attach and spread more readily on high-γ_c materials like glass and less readily on low-γ_c materials like Teflon and silicone-coated surfaces. Taylor's results on cellulose acetate and various proteins are difficult to interpret without determination of the value of γ_c for each material by methods other than the comparison of hydrophobic contact angles.

Since it has been observed that dead cells can exhibit as much variety in their adhesional behavior as living cells (*34, 36*), the initial stages of adhesion must be greatly influenced by the simple surface-chemical mechanisms discussed above. This is important to note, since cell aggregation studies have shown that the initial contact of cells with each other is essentially a random process, any cell being potentially capable of adhering to any other cell (*36*). Subsequently, however, metabolic activity and cell movements may play the dominant role in determining the persistence of individual adhesive joints and the relative competition among adhesive joints in an aggregating cell mass.

Although the correlations with surface constitution seem promising, they hold only for serum-free media; recent work demonstrates that these simple relations disappear in the presence of proteins adsorbed on the solids (*35*). For example, cells will adhere well on both Teflon and glass surfaces in the presence of horse serum (*35*). We can understand such interferences because our work has demonstrated that an adsorbed monolayer will completely change the wettability and adhesiveness of the solid substrate.

Since single cells respond to differences in the surface properties of various solid substrates, it is not surprising that small organisms do likewise. Marine larvae, for instance, exhibit varied behavior in their settling and ultimate adhesion to solid surfaces and are known to respond specifically to the presence of different adsorbed films (*37*) and particularly to proteins (*38*).

While the foregoing examples are encouraging and well-documented, they pertain to laboratory simulations of biological systems. Since the presence of proteins plays a major role in even such model systems, in real biological systems, where numerous proteins (as well as other surface-active materials) are present, the difficulties are compounded. Thus, if considerations of surface energy are to be useful, it will be in the sense that they define properties of the underlying substrate which may influence the conformation of the adsorbed species making up the new, outermost molecular layer.

There is a real possibility that changes in the surface properties of cells mediate the various stages of cell adhesiveness. For example, any of the numerous surface-chemical interferences with adhesion that are discussed above might diminish the strength of cell-to-cell joints and lead to the increased invasiveness that characterizes malignant cells.

It is also possible that the blood vessels change their internal surface properties with aging, perhaps suffering surface-chemical alterations which lead to increased critical surface tensions and thus to increased adhesion, to the vessel walls, of material circulating in the blood. A related difficulty is the current debate regarding the "wettability" of the vascular endothelium and the relation of this wettability to blood flow. Perel'man (*39*), in agreement with Moolten *et al.* (*40*), maintains that the endothelial lining is "nonwettable," while Zubairov and his co-workers (*41*) and Copley (*42*) reject this thesis on the basis of essentially similar experiments, all involving the creation of a polar-nonpolar interface in the blood vessel. We believe that the rapid and spontaneous adsorption of proteins and other blood surfactants at such an interface will surely result in a γ_c and a wettability different from those of the unmodified vessel wall.

We can anticipate major influences, in biological environments, not only from the water and from the numerous hydrogen-bonding and surface-active molecules present but also from the variety of configurational changes known to occur with biopolymers. For example, although hydrogen-bonding ability is a general feature of the surface of a membrane of such a simple polyamide as a nylon (*43*), both polypeptides and proteins will either exhibit or mask their hydrogen-bonding abilities depending on the conformation of the polyamide chain, the location of the side groups, and the nature of the adjacent liquid phase. Variation in the wetting by hydrogen-bonding liquids with conformational changes has been demonstrated in the alpha-to-beta transition of the model polypeptide, polymethylglutamate (*43*), and in the collagen-to-gelatin transition (*43*). If one could manage to induce or modify specific configurations of proteins at the site of interest, adhesion could be either hindered or assisted.

The knowledge gained from studies of simple systems may well provide a useful starting point for better understanding of biological adhesion, which is the necessary prerequisite to beneficial interference with living systems.

Note added in proof. Since this article was written, Lyman, Brash, and their colleagues (*44*) have demonstrated a direct correlation between the number of platelets adherent to plastic surfaces and the critical surface tensions of the surfaces involved.

References

1. R. Holm, *Die Technische Physik der Electrischen Kontacte* (Springer, Berlin, 1941).
2. F. P. Bowden and D. Tabor, *Friction and Lubrication of Solids*, pt. 1 (Oxford Univ. Press, London, 1950); *ibid.*, pt. 2 (Oxford Univ. Press, London, 1964).
3. J. S. McFarlane and D. Tabor, *Proc. Roy. Soc. London Ser. A* **202**, 224 (1950).
4. D. Tabor, in *Adhesion*, D. D. Eley, Ed. (Oxford Univ. Press, London, 1961), chap. 5.
5. F. P. Bowden and J. E. Young, *Proc. Roy. Soc. London Ser. A* **208**, 311 (1951); O. Levine and W. A. Zisman, *J. Phys. Chem.* **61**, 1068 (1957); ———, *ibid.*, p. 1188; R. L. Cottington, E. G. Shafrin, W. A. Zisman, *ibid.* **62**, 513 (1958).
6. R. C. Bowers, W. C. Clinton, W. A. Zisman, *Mod. Plastics* **31**, 131 (1954).
7. N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford Univ. Press, London, ed. 3, 1941), p. 9.
8. H. M. Budgett, *Proc. Roy. Soc. London Ser. A* **86**, 25 (1911).
9. J. W. McBain and D. G. Hopkins, *J. Phys. Chem.* **29**, 88 (1925); J. W. McBain and W. B. Lee, *Ind. Eng. Chem.* **19**, 1005 (1927).
10. N. A. deBruyne, *Nature* **180**, 262 (1957).
11. W. A. Zisman, *A Decade of Basic and Applied Science in the Navy* (Government Printing Office, Washington, D.C., 1957), p. 30.
12. ———, in *Adhesion and Cohesion*, P. Weiss, Ed. (Elsevier, New York, 1962), p. 176.
13. ———, *Advan. Chem. Ser.* **43**, 1 (1963).
14. A. A. Griffith, *Phil. Trans. Roy. Soc. London Ser. A* **221**, 163 (1920).
15. W. A. Zisman, *Ind. Eng. Chem.* **55**, 19 (1963).
16. C. Mylonas, in *Proc. Int. Congr. Appl. Mech., 7th, London* (1948).
17. H. W. Fox and W. A. Zisman, *J. Colloid Sci.* **5**, 514 (1950).
18. T. Young, *Phil. Trans. Roy. Soc. London* **95**, 65 (1805).
19. R. N. Wenzel, *Ind. Eng. Chem.* **28**, 988 (1936).
20. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.* **40**, 546 (1944); R. Shuttleworth and G. L. Bailey, *Discussions Faraday Soc.* **3**, 16 (1948); F. E. Bartell and J. W. Shepard, *J. Phys. Chem.* **57**, 211 (1953); R. E. Johnson, Jr., and R. H. Dettre, *Advan. Chem. Ser.* **43**, 112 (1963).
21. E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.* **61**, 1046 (1957).
22. V. R. Gray, *Forest Prod. J.* **12**, 452 (1962).
23. E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.* **66**, 740 (1962).
24. H. R. Baker, P. B. Leach, C. R. Singleterry, W. A. Zisman, *Ind. Eng. Chem.* **59**, No. 6, 29 (1967); M. K. Bernett and W. A. Zisman, *J. Phys. Chem.* **70**, 1064 (1966).
25. E. G. Shafrin and W. A. Zisman, *J. Amer. Ceram. Soc.* **50**, 478 (1967); M. K. Bernett and W. A. Zisman, "Effect of Adsorbed Water on Wetting Properties of Borosilicate Glass, Quartz, and Sapphire," *Naval Res. Lab. Rep. No. 6705* (1968); M. K. Bernett and W. A. Zisman, "Effect of Adsorbed Water on Critical Surface Tension of Wetting on Metal Surfaces," *Naval Res. Lab. Rep. No. 6727* (1968).
26. E. P. Plueddeman, H. A. Clark, L. E. Nelson, K. R. Hoffman, *Mod. Plastics* **39**, 135 (1962); S. Sterman and J. G. Marsden, *Ind. Eng. Chem.* **58**, 33 (1966).
27. F. Hauserman, *Advan. Chem. Ser.* **23**, 338 (1959).
28. W. A. Zisman, *Ind. Eng. Chem.* **57**, 26 (1965).
29. J. G. O'Rear, P. J. Sniegoski, F. L. James, "Chlorophenyl-alkyl-substituted carboxylic acids and silanes designed as adhesion promoters," paper presented at the 154th national meeting of the American Chemical Society, Chicago, 1967 (*Advan. Chem. Ser.*, in press).
30. E. G. Shafrin and W. A. Zisman, "Preparation and wettability of terminally chlorophenyl-substituted carboxylic acid films," paper presented at the 154th national meeting of the American Chemical Society, Chicago, 1967 (*Advan. Chem. Ser.*, in press).
31. W. D. Bascom, "The wettability of ethyl- and vinyltriethoxy-silane films formed at organic liquid/silica interfaces," paper presented at the 154th national meeting of the American Chemical Society, Chicago, 1967 (*Advan. Chem. Ser.*, in press).
32. A. H. Ellison and W. A. Zisman, *J. Phys. Chem.* **58**, 260 (1954).
33. D. J. Lyman, W. M. Muir, I. J. Lee, *Trans. Amer. Soc. Artificial Internal Organs* **11**, 301 (1965).
34. A. C. Taylor, *Exp. Cell Res. Suppl.* **8**, 154 (1961); ———, in *Biological Interactions in Normal and Neoplastic Growth*, M. J. Brennan and W. L. Simpson, Eds. (Little, Brown, Boston, 1962).
35. L. Weiss and L. E. Blumenson, *J. Cell. Physiol.* **70**, 23 (1967).
36. L. Weiss, *J. Theoret. Biol.* **6**, 275 (1964).
37. D. J. Crisp and J. S. Ryland, *Nature* **185**, 119 (1960).
38. D. J. Crisp and P. S. Meadows, *Proc. Roy. Soc. London Ser. B* **158**, 364 (1963).
39. I. M. Perel'man, *Colloid J. (USSR) English Transl.* **27**, 422 (1965).
40. S. E. Moolten, L. Vroman, G. M. S. Vroman, B. Goodman, *Arch. Internal Med.* **84**, 667 (1949).
41. D. M. Zubairov, A. V. Repeikov, Timberbaev, *Fiziol. Zh. SSSR* **49**, 85 (1963).
42. A. L. Copley, in *Flow Properties of Blood and Other Biological Systems*, A. L. Copley and G. Stainsby, Eds. (Pergamon, New York, 1960).
43. R. E. Baier and W. A. Zisman, "Critical surface tension of wetting for protein analogues," paper presented at the 153rd national meeting of the American Chemical Society, Miami Beach, 1967.
44. D. J. Lyman, J. L. Brash, S. W. Chaikin, K. G. Klein, M. Carini, *Trans. Amer. Soc. Artificial Internal Organs* **14**, 250 (1968).

NEWS AND COMMENT

Strategic Studies: British Center Said To Attract Nixon's Interest

London. Apparently in line with President-elect Nixon's pledge to engage a wide range of advisers for his administration, a Nixon emissary, former congressman Robert Ellsworth, recently spent an afternoon here visiting a research organization known as the Institute for Strategic Studies (ISS).

Ellsworth's time abroad was brief, and seems to have been for no other official purpose than to look in on ISS. He said his object was merely to become acquainted with ISS's operational methods, and ISS staff members say they discussed nothing but that. What, if anything, is going to come out of the visit has not been revealed to outsiders. But what makes the episode a bit curious is that the director of ISS, Alastair Buchan, who is on 3 months' leave to a Canadian university, saw Ellsworth in the United States prior to his visit here, and the ISS staff says that it knew nothing of Ellsworth's visit until the morning of the day he showed up for a noon-to-5 p.m. discussion. Probably the whole matter can be explained in terms of crossed signals and the incoming administration's desire to learn something about one of the more esteemed and unusual institutions of strategic scholarship. Nevertheless, if the administration is going to seek advice abroad, it is worth looking at what is possibly the first foreign organization to engage its interest.

ISS, little known to the general public but extraordinarily well connected to western military and political circles, is a British incorporated, nongovernmental, London-based organization founded in 1958. Listed as the founders were seven Britons, including Denis W. Healey, who is now Minister of Defence; there was also a retired admiral who was a director of Vickers-Armstrong, and the then-editor of the