In ancient times it was found that solids could be made to adhere strongly by coating each surface to be joined with a thin layer of a liquid which would harden or solidify gradually during contact. Early in this century the selection of suitable adhesives and application techniques was an art depending on the use of the formulations made from fish and animal products or cements made from inorganic thickeners or solutions. The advent of synthetic polymeric adhesives having better and more reproducible properties has progressed a wider use of adherents in the past 40 years, but increased the interest in expanding the art, and has converted it into a science. Despite the advanced technology of today, there are many unanswered questions about the principles underlying the mechanism of adhesion, and there still is excessive empiricism in current application techniques. Guidance is also needed in the search for adhesives suitable under more extreme conditions.

Already important contributions to the subject of adhesion have included the nature of the molecular forces responsible for adhesion, the relation between adhesion and friction, the effects of not matching the physical properties of adhesive and adherent, the effect of voids and precipitations on the development of weak concentrations, and the role played by absorbed films and inadequate wetting on joint strength as well as on the location of the fracture. Obviously, such diversity in the physical and chemical factors important in adhesion had required an interdisciplinary approach in attempting to understand fully and extend the subject. This chapter has been prepared to summarize the fundamental aspects of the subject of adhesion and in particular the effect of chemical constitution on adhesion and adhesion.
dry land solids are pressed together little effort is required to pull them apart, and this occurs because, as Holm and coworkers showed, the real area of contact is generally such a very small fraction of the apparent area.

A thin film of oxide or of organic contamination can decrease greatly the adhesion of solids. If the oxide is removed by appropriate means, the solids can readily be made to adhere on contact. This fact is well exemplified by Anderson's simple experiment in which two gold spheres are pressed together in a high vacuum. Even under these circumstances they will not adhere. However, if one gold half is twisted about its axis while being pressed against the other, some of the adsorbed film and metal oxide is sheared off and area of clean unoxidized gold is exposed, come into intimate contact, and a strong joint is formed.

A striking demonstration of the effect of an organic monolayer on adhesion is McDade and Tabor's experiment with a clean steel ball pressed against a piece of indium metal with a monomolecular film of fatty acid. Although the monolayer prevented adhesion when cold packed, it lost that ability when the two solids were pressed together sufficiently to stretch the monolayer and increase by 50% the average area (A) occupied by the adsorbed molecule of fatty acid (see Fig. 1). Apparently, more asperities of the solids were able to make contact through the stretched film and so good adhesion developed.

Budden, Tabor, and co-workers have proved that in addition to the influence of adsorbed films in decreasing the adhesion of dry solids, there is a loss of adhesion following elastic recovery, or release of elastic strain, on removing the load pressing two solids together. In Fig. 2 the location of areas of elastic deformation behind contacting asperities is indicated by the arrow. Upon removing the load, the elastic strain, which has developed at the base of each asperity, is released, and the resulting internal stresses help to break the adhesion. If these elastic stresses can be removed by annealing the two solids while load is maintained, strong adhesive joints will persist even after removing the load. This mechanism explains the hot-forging of metals at temperatures much below that required to cause any significant diffusion of metal atoms across the junctions.

A wealth of convincing evidence that dry solids always adhere on contact has come from research on the nature of dry friction (or boundary friction). Early investigations by Holm and Tabor, and the now classic series of studies of Budden, Tabor, and co-workers have demonstrated that boundary friction is caused by the adhesion of the two rubbing solids at the points of actual contact. In Fig. 2 the regions of plastically deformed contacting asperities is indicated by the shaded areas. Such adhesion or cold welding occurs on contact of any two solids, making it necessary to apply a force F to overcome friction. In a first approximation F is equal to the true area (A) of all the contacting asperities multiplied by the average shear strength (s) of the junctions. Adhesion between contacting solids is more readily made evident by sliding one over the other than by pulling them apart, because in measuring the frictional force there is no necessity of removing the internal stresses caused by the load in order to detect the existence of the effect.

An extensive literature now exists on the effect of varying the nature of the rubbing solids on their friction as well as on the influence of oxides or other adsorbed films in lowering the friction. Adsorbed monomolecular films of polar–nonpolar (or amphipathic) compounds can greatly decrease the friction between solids, and the physical absorption of such compounds is the most common mechanism encountered in the operation of "lubricant additives" used in lubrication technology. Such oil additives are most effective when they are adsorbed on the rubbing solids at solid–solid contact. For example, a monolayer of a higher fatty acid can lower the coefficient of friction of metals from a range of 0.3–0.5 to a range of 0.05–0.1. Furthermore, it can be amazingly durable under repeated sliding if the two metallic substrates do not form solid solutions or intermetallic compounds. If it were not for the oxide and/or water adsorbed on almost all metals at ordinary temperatures on the earth's surface, it would be impossible to avoid serious adhesion and cold welding on rubbing two of them together. In the absence of organic and inorganic films, any two metals rubbed truly in a high vacuum system will form strong junctions and even cold weld. As a result, the tribology of metals in an extreme vacuum becomes very difficult. In summary, the present-day technology of wear prevention and lubrication under boundary conditions is based largely on the effects of adsorbed organic or inorganic films, oxides, or water in decreasing the adhesion between solids.

In sliding together clean dry plastics, high friction (and even cold welding) is not uncommon. The range of possibilities and the effect of varying the chemical composition of the polymer are well illustrated by comparing in Table 3 the coefficients of static friction of two pieces of polyethylene having different structural similarity similar polymer formed by repeating some of the hydrogen atoms in the polymer with either fluorine or chlorine atoms. Whereas the coefficient of dry friction of polyethylene is about 0.3, it is lowered by fluorination reaching 0.04 when fully fluorinated (as in the case of polytetrafluoroethylene); it is increased by progressive chlorination, rising to 0.9 with 50% chlorine (as in the case of polyvinylidine chloride). As a matter of fact, the existence of such high friction and adhesion between some solid polymers has been utilized in processes for the frictional welding of plastics. Hence, in order to decrease friction and wear in processing, weaving, and application of the woven article, nearly all textile fibers must be treated or finished with lubricants.
A - FUNDAMENTALS

Table 1. Effect of Constitution on Friction and Wettabillity of Unbranched Halogenated Polyethylene.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structural Formula</th>
<th>State Coefficient of Friction</th>
<th>Critical Surface Tension (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl chloride</td>
<td>H - C - C - CH - H</td>
<td>0.00</td>
<td>40</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>H - C - C - CH - H</td>
<td>0.50</td>
<td>39</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>H - C - C - CH - H</td>
<td>0.30</td>
<td>12</td>
</tr>
<tr>
<td>Polyvinyl fluoride</td>
<td>H - C - C - CH - H</td>
<td>0.30</td>
<td>18</td>
</tr>
<tr>
<td>Polyvinylidene fluoride</td>
<td>H - C - C - CH - H</td>
<td>0.30</td>
<td>25</td>
</tr>
<tr>
<td>Polyethyleneether</td>
<td>H - C - C - CH - H</td>
<td>0.30</td>
<td>22</td>
</tr>
<tr>
<td>Polyethyleneether (Teflon)</td>
<td>F - C - C - CH - F</td>
<td>0.04</td>
<td>18</td>
</tr>
</tbody>
</table>

Fig. 3. Interlaced adhesive joint.

If $\gamma > 0$, then $p_1 - p_2$ will be a large negative quantity and there will be a greater pressure $p_2$ in the air outside the liquid than the value $p_1$ inside, hence, the two plates will be pressed together under the pressure difference $p_2 - p_1$. 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 Beckett,42 Hardy,88 Hintow and Bowden,22 and more recently by de Blas,121 For example, Beckett 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 adhering joint has several obvious limitations:

(a) the resistance of the joint to shear stress is obtained upon the viscosity of the liquid film; hence, only if the viscosity is great could the shear strength of the joint be large;

(b) it would be necessary to prepare extremely well-fitted, smooth, solid surfaces to form a strong joint;

(c) freedom from dust would be critically important.

If the contact angle of a liquid adhesive with each adherend is not large, a prompt adhesive action is obtained upon pressing them together, even though imperfectly fitted, until they are separated by only a thin liquid layer. Thereafter, a stronger and more useful joint will be formed if the viscosity of the liquid layer is increased greatly through any of various mechanisms such as:

(a) solvent penetration or evaporation (as in sticking on a postage stamp),
(b) polymerization, and (c) cooling until solidification occurs. If properly designed, the resulting joint can have high resistance to both tensile and shear stresses. However, the process of forming an adhesive joint can be readily described, an analysis of the mechanism involved and of the factors limiting the strength and utility of the joint is complex.

In their pioneering studies of adhesion in 1925, McMillan and Hopkinson129 reported that: "Any fluid which wets a particular surface and which is then converted into a tenacious mass by cooling, evaporation, oxidation, ete., must be regarded as an adhesive for that surface." McMillan and Lee130 soon afterward added the requirement that the adherent must be able to deform under this solidification to relieve the elastic stresses developed in the forming of the joint. Their work made evident the following three requirements for an adhesive: (a) wetting, (b) solidification, and (c) sufficient deformability to reduce the buildup of elastic stress in the formation of the joint. These requirements have been fully investigated and reported. The first requirement was studied much later by de Blas121 and Zisman,135-138

Wettability and the Contact Angle

Wettability and wettabillity, we usually mean the adsorption of liquids to solids and the extent to which the liquids spread. In order to advance knowledge of these fundamental properties of matter, it is essential to be careful of the definitions and use of the terms for these properties. Over 170 years ago Thomas Young135 discussed the contact angle of a liquid and the equilibrium of a drop resting on a plane solid surface under the action of the three surface tension shown in Fig. 4. Here $\gamma$ is the surface tension at the interface of the liquid and vapor phases, $\gamma$ at the interface of the solid and the liquid, and $\gamma$ that at the interface of the solid and vapor. Hence, $\gamma = \gamma \gamma \gamma \theta \cos \theta$ (2).

In effect, Young had provided the first good approach for describing wettability, spreading, and their relation to the contact angle.

Fig. 4. Single drop of a liquid on a flat solid.

USE OF LIQUIDS TO PROMOTE ADHESION

For over 50 years it has been known that when two flat, smooth, solid surfaces (the adherends) are separated by a thin layer of a liquid having a zero contact angle, strong adhesion will result. This effect arises from the liquid surface tension ($\gamma$) and the fact that there will be a concave meniscus at the liquid-air interface (see Fig. 3). If the area of contact of the liquid with the solid is $\pi r^2$ and of radius $r$ and thickness $d$, and if the liquid layer is thin enough to be treated as a circular cylinder of radius $r$ and $d$, the Laplace equation of capillarity107 leads to:

$$P = \pi \gamma \frac{d}{r}$$

(1)
First, consider an idealized plane at the liquid-solid interface (Fig. 4). When \( \theta \neq 0 \), the liquid is spread spontaneously or completely on the surface of the solid. We shall define the contact angle between a liquid and a solid to be the angle that the liquid makes with the solid surface. If the contact angle is defined for every solid and liquid, then the solid surface must be to obtain a given reception of the surface. When \( \theta > 0 \), the difference between the contact angle of a liquid and a solid is the contact angle which is the angle formed by the liquid surface and the solid surface. When \( \theta > 0 \), the difference between the contact angle of the liquid and the solid will be \( \theta > 0 \). Therefore, the contact angle between a liquid and a solid must be defined for every solid and liquid. If the contact angle of a liquid is defined for every solid, then the solid surface must be to obtain a given reception of the surface. When \( \theta > 0 \), the difference between the contact angle of the liquid and the solid will be \( \theta > 0 \). Therefore, the contact angle between a liquid and a solid must be defined for every solid and liquid.

Wenzel's relation, which has been investigated fully by H. Wenzel and H. S. Bentley, 11 is a consequence of the first two laws of thermodynamics and the definition of \( \theta \). Wenzel's relation is \[
\cos \theta = \frac{\cos \theta_0}{\cos \theta_0} \tag{3}
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\cos \theta = \frac{\cos \theta_0}{\cos \theta_0} \tag{3}
\]
derived the following expression for a vapor obeying the ideal gas law:

$$\gamma_{ov} - \gamma_{os} = \gamma_{vj} = \frac{R}{T} \gamma_{vl}(T)$$

(10)

where $\gamma_{ov}$ is the pressure of the saturated vapor, $R$ the gas constant, $T$ the absolute temperature, and $\gamma_{vl}(T)$ the Gibbs adsorption excess per unit area of the vapor at the solid-vapor interface.

Two early investigators of the spreading of lacquers on leaves, Cooper and Notall, developed the condition for the spreading of a liquid substance, $S$, on a solid or liquid substrate, $s$:

For spreading $S > 0$

For non-spreading $S < 0$

where

$$S = \gamma_{oi} - \gamma_{ov} + \gamma_{oj}$$

or as the subscripts just introduced, $S = \gamma_{oj} - \gamma_{ov}$

(11)

Soon afterwards Haskin developed a useful concept, named $S$ the "initial spreading coefficient," and from it derived the two relations:

$$S = -\left(\frac{1}{\gamma_{oi}} - \frac{1}{\gamma_{oj}}\right)$$

and

$$S = \frac{W_{A}}{W_{C}}$$

(12)

Here $W_{A}$ is the reversible work of cohesion of the liquid. From the liquid equation applied as a liquid-liquid interface, it is shown that $W_{A}$ is twice the liquid surface tension. Equations (12) and (13) are especially suggestive about the physical causes of spreading; however, like Equations (2) and (3), they are deceptively simple. For example, as Haskin pointed out, an "initial value" of the spreading coefficient exists for the condition that spreading can start; a "final coefficient" is given for the condition that once spreading has occurred the liquid can remain spread. Such experimental information is needed to determine the spreading coefficients.

Assuming that no surface equilibration is involved, the above group of relations are the basic relations which are used in describing the equilibrium contact angle and wetting phenomena. However, in so far as details of molecular structure of the substances and surfaces play an important part, these purely thermodynamic equations would not be expected to suffice to permit us to describe the wetting, spreading, and adhesion of liquids on solids.

An informative approximation for an organic liquid spreading upon an organic solid or liquid surface can be derived from Fig. 12, since it is then often reasonable to assume that $\gamma_{ov}$ is negligibly small in comparison with $\gamma_{oi}$. Therefore:

$$S = \gamma_{oi} - \gamma_{ov}$$

(15)

and

$$\gamma_{oi} > \gamma_{ov}$$

(16)

for spreading to occur. Hence, in all such systems, when spreading occurs the unit 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 $\gamma_{oi}$. However, the small change in energy involved in creating and wetting the solid and liquid necessitates using finely divided solids having large surface areas per gram in order to be able to measure it. This is difficult to do with many organic solids and liquids. It may also introduce many complications if the present edges, holes, surface strains, and impurities.

High and Low-Energy Solid Surfaces

In considering the wetting properties of solid surfaces, we found it helpful to consider a few convenient terms to identify the extremes of the specific surface free energies of solids. As is well known, the specific surface free energies of liquids (excluding the liquid metals) are less than 100 ergs/cm² at ordinary temperature. One of the important interfacial phenomena is the contact angle between the liquid and the solid surface.

Table 2. Classification of Solid Surfaces.

<table>
<thead>
<tr>
<th>High-Energy Surface</th>
<th>Low-Energy Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong hydrogen bonds</td>
<td>Weak hydrogen bonds</td>
</tr>
<tr>
<td>Intermolecular force</td>
<td>Intermolecular force</td>
</tr>
<tr>
<td>Hard</td>
<td>Soft</td>
</tr>
<tr>
<td>High melting point</td>
<td>Low melting point</td>
</tr>
<tr>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Int. $\gamma_{ii} &gt; 100$</td>
<td>Int. $\gamma_{ii} &lt; 200$ ergs/cm²</td>
</tr>
<tr>
<td>Hydrogen (metal, oxide, etc.)</td>
<td>Organic (plastics, polymers, etc.)</td>
</tr>
</tbody>
</table>

For spreading to occur, the value being higher the greater the hardness and the higher the melting point. Soft organic solids have much lower melting points and the specific surface free energies are generally below 200 ergs/cm². Solids having high specific surface free energies may be said to have "high-energy surfaces," and solids having low specific surface free energies may be said to have "low-energy surfaces." 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 specific free energy of the system, and this is most often true. But since the surface free energies of such liquids are comparable to those of low-energy solids, among these liquids should be found those exhibiting nonspreading on low-energy solids.

Spreading on Low-Energy Surfaces

Because of the large percentage error in low contact angles resulting from the surface roughness, for such measurements much care must be exercised in preparing the surfaces of these polymers in extremely clean and gaseous-free condition. Using such solids and pure liquids it was found, in disagreement with past reports on contact angle phenomena, that these systems not only behaved reproducibly but also the advancing and receding contact angles were identical to 90° as the liquid drop was advancing at receding sufficiently slowly to be reproducible to equilibrium.

In general, a rectilinear relation was established empirically between the cosine of the contact angle, $\theta$, and the surface tension, $\gamma_{oi}$. For each homologous series of organic liquids, this relation was found to hold true for the critical surface tension, $\gamma_{li}$, for wetting by each homologous series. In general, a rectilinear relation was established between the cosine of the contact angle, $\theta$, and the surface tension, $\gamma_{oi}$.

When rectilinear bands are obtained in this type of graph, the intercept of the lower limit of the band at $\cos \theta = 1$ is known as the critical
surface tension, $\gamma$, of the solid. Although the intercept is less precisely defined than the critical surface tension of a homologous series of liquids, nevertheless it is an even more useful parameter because it is a characteristic of the solid surface. It has proved a useful empirical parameter whose relative value acts as much as would be expected of $\gamma_0$, the specific surface free energy of the solid.

By comparing values of $\gamma$ for structurally "homologous" or "analogous" solids, such as unbranched polyethylene and its water-chlorinated or fluorinated analogs (see Table 1), and by making the reasonable assumption that the surface composition of the solid polymer was the same as that of the horizontally oriented polymer molecule, it was possible to study the effect of the surface constitution of polymeric solids on the wetting. From the curves of Figs. 6 and 7, $\gamma$ values for polyethylene, poly(ethylene chloride), and polyvinyl chloride are plotted vs $\gamma_0$ in Fig. 9 against the atom percent replacement of hydrogen by chlorine (or fluorine). Although the interpretation of the first chloride atom in the monomer units $\gamma$ rise from 31 to 20 dynes/cm, the addition of a second chlorine lowers $\gamma$ to 10 dynes/cm. On comparing the upper and lower curves, striking differences are evident in the effect on $\gamma_0$ of chlorine or fluorine replacement of hydrogen, both as to the direction of the change and the effect of progressive halogenation. Although polyvinylchloroethylene does not exist, an organic coating with an outermost surface composed of chemically active chlorine atoms was prepared by the reaction method to form an adsorbed, condensed, and oriented monolayer of perfluoro-polymer-polyethylene acid (PEEK) on the clean polished surface of glass or platinum. Not only is the graph of $\gamma$ vs $\gamma_0$ such for a surface similar to those of the above-mentioned chlorinated polyethylenes, but the corresponding value of $\gamma_0$ (43 dynes/cm) is shifted in the direction of higher values.

Effect of Constitution on $\gamma_0$

In Table 4 are presented, in another and more fundamental way, the results of our comparative studies of the wettabilities of numerous well-defined, low-energy, solid surfaces. Since the same results were obtained regardless of the nature of the polished solid substrate on which the perfluoro-polymer-polyethylene acid monolayer was adsorbed, it must be concluded that the wettabilities of three monolayer-coated surfaces is determined by the nature and packing of the outermost atoms, or exposed groups of atoms, in the coating, and not by the nature and arrangements of atoms in the solid substrate. It has been found that the extreme localization of the fields of force of the outermost bound atoms responsible for the adhesion of liquids to organic solids.

Results of wetting studies on clean, smooth, plasticizer-free, polymeric solids of general interest are summarized in Table 3. A range in $\gamma_0$ of 40 to 45 dynes/cm has been found for a series of hydrophobic surfaces of the monomeric type and for dry clean wood. These values of $\gamma_0$ are reasonably close to that of 43 dynes/cm reported for the oxygen-rich surface of polyethylene teraphthalate. Nylon, with its many exposed amide groups, has the highest $\gamma_0$ value of the common plastics reported.

Table 3. Crustal Surface Tensions $\gamma_0$ of Various Linear Polymers.

<table>
<thead>
<tr>
<th>Polymeric Solid</th>
<th>$\gamma_0$ (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>10.6</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>16.2</td>
</tr>
<tr>
<td>Polyvinylidene</td>
<td>18.5</td>
</tr>
<tr>
<td>Polyethylene-derivative</td>
<td>22.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>25.0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>20.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>31.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>35.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>37.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>39.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>45.0</td>
</tr>
<tr>
<td>Polyethylene-oxide</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Some results of major interest on surface and polymer chemistry can be deduced readily from these data.

Table 4. Critical Surface Tensions $\gamma_0$ of Low-Energy Surfaces.

<table>
<thead>
<tr>
<th>Surface Constitution</th>
<th>$\gamma_0$ (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorocarbon surfaces</td>
<td></td>
</tr>
<tr>
<td>C-F</td>
<td>6</td>
</tr>
<tr>
<td>C-F</td>
<td>15</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>17</td>
</tr>
<tr>
<td>C-F and C-F</td>
<td>18</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>22</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>25</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>35</td>
</tr>
<tr>
<td>Hydrocarbon surfaces</td>
<td></td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>20</td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>24</td>
</tr>
<tr>
<td>C-H and C-H</td>
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</tr>
<tr>
<td>C-H and C-H</td>
<td>35</td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>39</td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>40</td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>42</td>
</tr>
<tr>
<td>C-H and C-H</td>
<td>43</td>
</tr>
<tr>
<td>Fluorocarbon surfaces</td>
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<td>C-F and C-H</td>
<td>40</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>42</td>
</tr>
<tr>
<td>C-F and C-H</td>
<td>43</td>
</tr>
</tbody>
</table>
Table 4, and they deserve discussion. The surface of lowest energy ever found (and hence the one having the lowest $\gamma$) is that composed of close-packed terminally fluorinated (CF-3) groups. The replacement of a single fluorine atom by a hydrogen atom in a terminal CF-3 group produces more than twice the $\gamma$. A parallel and regular increase in $\gamma$ has been observed with progressive replacement of fluorine by hydrogen atoms in the surfaces of both polymeric and polyelectrolytes. Data for polyethylenimine [CF3-CF2-CF2-NH2] and polyvinylpyridine [CF3-CF2-CF2-CH2-CH2-NH2] are listed in the order of increasing values of $\gamma$; however, this is also the order of decreasing fluorine content.

Among the hydrocarbon surfactant molecules, a close-packed oriented methyl group is the lowest value. In 24 dyne/cm results when the methyl groups are in close-packed order. The lowest value of 22 dyne/cm results when the methyl groups are in the closest packing found in the earliest cleavage plane of a single crystal of a higher paraffin such as hexadecane.

The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. The least packed arrangement found in a condensed adsorbed monolayer of a high molecular weight fatty acid is characterized by a $\gamma$ value of about 12 dyne/cm. 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conclusion that bringing the low-energy surface of polytetrafluoroethylene (or polyethylene) into contact with this film-coated water did not cause a significant change in the orientation or packing of the film adsorbed at the water-air interface.

The surface tension of water is significant in this context, as it is one of the key factors affecting the wetting behavior of materials. The surface tension of water at 25°C is approximately 72 dynes/cm.

In order to understand the wettability properties of high-energy surfaces, new surface-technical problems have been solved. When a surface is wetted, it is often observed that the surface tension of water is reduced due to the presence of surfactants or other surface-active agents. The wetting behavior of a surface can be quantified by the contact angle, which is the angle between the surface and the liquid.

Wetting of High-Energy Solids

In order to understand the wettability properties of high-energy surfaces, two new surface-technical problems have been solved. When a surface is wetted, it is often observed that the surface tension of water is reduced due to the presence of surfactants or other surface-active agents. The wetting behavior of a surface can be quantified by the contact angle, which is the angle between the surface and the liquid.

The wetting behavior of solid surfaces is influenced by various factors, including the surface energy, the concentration of surface-active agents, and the presence of surfactants. In general, the lower the surface energy of a solid, the more difficult it is to wet.

Generalizations about Wetting and Spreading on Solids

The results of these investigations can be generalized as follows: the wetting of a solid by a liquid is a function of the surface energy of the solid and the liquid, and the surface tension of the liquid. The wetting behavior of a solid can be influenced by the presence of surface-active agents, which can reduce the surface tension and improve wetting.

In conclusion, the wetting behavior of solid surfaces is a complex phenomenon influenced by various factors, and understanding this behavior is crucial for applications such as adhesion, lubrication, and coating.

Reversible Work of Adhesion of Liquids to Solids

The work of adhesion, also known as the reversible work of adhesion, is the energy required to separate two surfaces in contact. The work of adhesion is a measure of the strength of the intermolecular forces between the solid and the liquid.

In summary, the wetting behavior of solid surfaces is a complex phenomenon influenced by various factors, and understanding this behavior is crucial for applications such as adhesion, lubrication, and coating.
Table 8. Literature Values of $f_{sv}$ for Metallic High-Energy Surfaces.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
<th>$f_{sv}$</th>
<th>$\gamma_{sv}$</th>
<th>$\gamma_{lv}$</th>
<th>$\gamma_{lv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>Water</td>
<td>101</td>
<td>174</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>n-Heptane</td>
<td>108</td>
<td>132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>n-Heptapal</td>
<td>108</td>
<td>132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>Benezene</td>
<td>110</td>
<td>140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>Octane</td>
<td>107</td>
<td>133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>n-Heptape</td>
<td>29</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>n-Heptape</td>
<td>37</td>
<td>71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>n-Heptape</td>
<td>49</td>
<td>88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>n-Heptape</td>
<td>53</td>
<td>93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>n-Heptape</td>
<td>168</td>
<td>313</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>n-Heptapal</td>
<td>20</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>n-Heptape</td>
<td>83</td>
<td>120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Data from Ref. 25 unless otherwise indicated.
* See Ref. 58.
* See Ref. 96.

will be equal to or greater than twice the surface tension of the liquid. A simple calculation shows that if the field of contact of the adhesion is 30 dynes, then the average tensile strength of the adhesive is 2000 kg/m^2. This value is much greater than the tensile strength of common organic adhesives. For example, Kao and Matsuoka have obtained for polyethylene a tensile strength of 183 kg/m^2. Therefore, the joint must be broken by cohesive failure (that is, failure in the bulk phase of the adhesive). Since the correlation of $f_{sv}$ and $\gamma_{lv}$ is given in Eq. (8), a simple calculation of the adhesion energy, even greater than $\gamma_{sv}$, is apparent that when the adhesive makes a tensile contact angle with the adhered, the theoretical adhesion strength will always be much more than the observed tensile or shear strength of the adhesive.

Unfortunately, reliable data is not available on the values of $\gamma_{lv}$ for well-defined, smooth, low-energy, solid surfaces. But one should not assume from the results in Tables 5 and 6 that the value of $\gamma_{lv}$ will also be an important correction term for low-energy solids. On the contrary, there is good experimental evidence that whenever a liquid exhibits a large contact angle on a solid, there is negligible absorption of the vapor. Measurements by Rehrl and Zusman using a contact potential method of studying absorption have demonstrated that negligible adsorption of most vapors occurs on smooth, clean surfaces of polyethylene, polyethylene. Adsorption measurements with a McPherson balance over the entire vapor pressure range of Hg, up to 1.0 L/sec, and a subsequent investigation by Gustafsson have led to the conclusion that the vapor absorption at ordinary temperatures for many substances studied is a small fraction of a monolayer. Hence $\gamma_{lv}$ must be a very small term compared to $\gamma_{sv}$ for all liquids having $\gamma_{sv}$ greater than $\gamma_{lv}$.

The same conclusions can be extended for the same temperatures to other low-energy solids such as polyethylene, polyethylene, polyvinyl chloride, etc., and to all liquids having surface tensions greater than the value of $\gamma$ of each of these solids. If a substantial fraction of a condensed monolayer of any of these vapors adherent to a smooth surface, the surface tension of the liquid, then $\gamma_{lv}$ of the solid surface would naturally be transformed to that of the adsorbed film, and the wetting properties would have to be those of a higher energy surface. Therefore, it can be concluded that $\gamma_{lv}$ must be negligible for liquids having surface tensions considerably

Fig. 11. Work of adhesion $\gamma_{wl}$ in absence of vapor adhesion on polyethylene chloride, polyethylene chloride, and polyethylene. For example, with a sufficiently smooth surface tension for liquids having values of $\gamma_{lv}$ close to or less than $\gamma_{sv}$, further measurement of $\gamma_{lv}$ would be negligible.

It is of interest to compute the value of $\gamma_{wl}$ for the many liquid-solid combinations reported in the past. Figures 11 to 13 show...
greater than that for the apparent surface area. However, the larger the contact angle the more difficult it becomes to detect 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 or voids in hollows and crevices. Such difficulties with the formation of gas bubbles and pores are, of course, greatly amplified in dealing with viscous adhesives which solidify slowly after being applied to the joint. Hence in practice the true value of \( W_A \) lies somewhere between the value obtained from Eq. (19) and 2 times this value. Where there are accessible pores, crevices, and cavities in the surface of the adherend, the liquid adhesive will penetrate to some extent and increase adhesion, the process ceasing when an adequate supply of liquid ceases to be available or when the liquid viscosity increases too much or solidification occurs. Obviously, in order to obtain the maximum adhesion, the adhesive should penetrate and fill each capillary.

As an approximation it may be assumed that the capillary size equation

\[
h = \frac{1}{\rho} \left( \frac{\tan \theta}{\pi} \right)
\]

(23)
can be used (\( R \) is the equivalent radius of the capillary, \( \kappa = 2/9 \pi, \) and \( \rho \) is the density of the liquid) and also that the liquid will wet the capillary wall according to the condition 12 given in relation of Eq. (17). Eliminating \( \cos \theta \) from the two equations, the results for the parabola

\[
h = \frac{1}{\rho R} \left( \frac{h}{h + \gamma_1} - 1 \right)
\]

(24)

Evidently \( h \) has a maximum when

\[
\gamma_1 = \frac{1}{2} \left( \gamma_2 + \gamma_3 \right)
\]

(25)

For example, in the case of smooth polyethylene, the maximum capillary size will occur when \( \gamma_1 = \frac{1}{2} (37 + 38.4) = 37.7 \) dynes/cm. Hence, the maximum size occurs when \( \gamma_3 \) is 37.7 dynes/cm more than \( \gamma_1 \). It is questionable that the rise in the line pores and crevices connected to the interface can be treated precisely in the above way in practice; it is also difficult that the contact angle is uniform over the interior of the crevices and pores. However, this simple analysis reveals that \( W_A \) will go through a maximum as \( \gamma_3 \) increases when a porous interfacial surface is involved.  

3. INFLUENCE OF CONSTITUTION ON ADHESION

Effects of Solidification of the Liquid Adhesive

When a liquid adhesive solidifies, the reversible work of adhesion of the adhesive to the adherend would still be close to the value computed in the preceding calculations for the adhesive to the liquid state if it were not for the development of stresses or concentration effects. This conclusion follows from the highly localized nature of the attractive field of force causing adhesion. Since this attractive force is effective for little more than the depth of one molecule in both the adhesive and the adherend, it will be unaffected by changes of state as long as allowance is made for any resulting alteration in the surface density of molecular orientation occurring at the joint interface.  

Furthermore, the formation can be estimated from the change of density on solidification, but the latter may be difficult to compute since recrystallization effects could originate through a crystallization process starting from some nucleus not located in the interface. Internal stresses and stress concentrations usually develop on solidification of the adhesive, the most common cause being the difference in the thermal expansion coefficient of the adhesive and adherend. In many applications of adhesives this matching process is not readily done or is neglected because it is not critical. However, in general, the theoretical strength of the adhesive joint is considerably decreased by the development of internal stress concentrations.

The effect of internal stresses developed in solidification and of stress concentrations during application of a joint have been given much attention. An excellent discussion of this area of research has been given by Sneddon.  

In particular interest here are the plasticine studies of Myhans and Bydler.  

It led to the conclusion that in a lap joint, point wetting of the adherend tends to produce greater stress concentration at the free surface of the adhesive where failure is most likely to be initiated. As the contact angles become large, the maximum stress concentration increases and moves toward the final boundary where the adhesive and atmosphere make contact with the adherend, the stress concentration factor increasing from about 1.2 to 2.5 (Fig. 14).

Furthermore, Gillott has shown that failure of the adhesive may occur from a relatively small applied stress if there are air bubbles, voids, inclusions, or surface defects; it occurs because stress concentrations result which are much higher than the mean stress applied across the specimen. This conclusion is especially important when considered in terms of the probable effect of poor wetting on the development of stresses in air pockets at the adhesive adherend interface.

It has already been shown that if \( \theta = 0 \), the theoretical joint strength exceeds the tensile strength of the adhesive by a factor of two or more. In practice, the theoretical joint strength is not attained; evidently, one main cause is the development of stress concentrations during solidification of the adhesive. When \( \theta = 0 \), there may be gas pockets formed at the adhesive adherend interface which stresses concentrations...
can build up; if the adhesive is too viscous when applied, it may never penetrate the accessible surface before polymerization. Of course, this situation is aggravated if θ ≠ 0.

In adhesive technology, it is common practice to roughen the surface to be adhered, or “give it tooth,” and to obtain a stronger joint. This practice can be justified theoretically with certain important considerations. If gas pockets or voids in the surface depressions of the adherend are all neatly in the same plane and are not far apart (as on the upper adherend of Fig. 15), there may be crack propagation from one pocket to the next, and the joint may break as if it had a built-in “zipper.” Therefore, if roughness must be accepted, the kind of roughness shown on the lower adherend would be preferable because crack propagation along a plane would be less probable.

**MECHANISM OF ADHESIVE ACTION**

An adequate theory of adhesive action should be able to explain not only its ability to form good joints but also the fundamental reasons why an interface of two materials is particularly strong and why the interface is held together. The strength of an adhesive bond is a complex function of various factors, such as the type of adhesive, the type of materials being bonded, and the conditions under which the bond is formed.

**Table 7. Critical Surface Tension of Wetting at Surfaces Coated with Adhesives.**

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>θ (deg at 30°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-Condensed</td>
<td>67°C (min at 30°C)</td>
</tr>
<tr>
<td>Polymethylsiloxane film</td>
<td>34</td>
</tr>
<tr>
<td>Fatty acid monomer</td>
<td>24</td>
</tr>
<tr>
<td>Polyelectrolyte film</td>
<td>16</td>
</tr>
<tr>
<td>HCl-F2C5H4-CH2Cl monomer</td>
<td>15</td>
</tr>
<tr>
<td>Polynaphthalene-6 or -8</td>
<td>10</td>
</tr>
<tr>
<td>Polyaniline acid monomer</td>
<td>6</td>
</tr>
</tbody>
</table>

**Fig. 15. Effect of surface roughness in causing entrapment of gas bubbles.**

**Table 8. Adhesion of Ice to Organic Solids.**

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Contact Angle, Degrees</th>
<th>Kbz (cm)</th>
<th>V (×10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>100</td>
<td>181 to 309</td>
<td>1.5</td>
</tr>
<tr>
<td>Steel acid</td>
<td>100</td>
<td>450 to 510</td>
<td>1.5</td>
</tr>
<tr>
<td>Polyvinyl</td>
<td>75</td>
<td>450 to 510</td>
<td>10</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>ca. 20</td>
<td>520 to 560</td>
<td>0.20</td>
</tr>
</tbody>
</table>

8 From Ref. 106.
GUILTIRES PRINCIPLES IN MAKING ADHESION JOINTS

The preceding analysis of adhesion and adhesives makes it evident that for optimum joint strength, it is essential to keep the contact angle between the liquid adhesive and the adherent as small as possible in order to minimize the buildup of stress concentrations and to obtain good spreading. Obviously, the interface of each adherent must be kept smooth and free as possible of low-energy surface films and dust in order to prevent excessive flow into pores and crevices. Maximum spreading and capability will be obtained with surface films of 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 separations prevail, the adhesion to either high-energy or low-energy surfaces will usually be strong, and generally failures of the joint will be in coalescence. If the surface of the adhered is to be roughened, it must be done so as to keep any surface gas pockets formed from being coalescent or nearly so over a large region. Under these conditions, roughening tends to increase the probability that small gas pockets would be produced at the interface between the solid surface and the ice. The resulting surface distribution of gas pockets will serve to cause stress concentrations at the interface upon application of external stressing stresses, and the ice should break at the joint by a sort of two-dimensional zipper effect, the bubbles at the interface serving as the elements of the zipper. In other words, as in Fig. 15, in such coatings some types of roughnesses can be an advantage. However, under any circumstances, if the ice is frozen and thawed a number of times in succession, the water will creep into the pores of the surface by a vapor adsorption-condensation process, and once the cracks and pores are filled and the water trapped in them has frozen, the adhesion of the ice will tend to increase. For example, ice can in this way be made to adhere strongly to a mica plate. This result also exemplifies the fact that any stronger than \( \gamma_{av} \) of the adherent, a strong joint can be formed when a large real area of contact is created.


due to certain non-uniform conditions, they can be difficult to produce or to make strong and durable. This is a condition of joint behavior observed in practice or in the more controlled conditions of the laboratory. It is of considerable importance, if only that it rarely occurs and is due to the true failure of the series of stages leading to failure. This situation has also important role in increasing some of the more severe coatings as well as various methods of corrosion prevention. The effect of small pores or cracks is that impermeation, even of micro-size on water or solvent permeability, and the subsequent attack on the strength or corrosion of solid surfaces, had not been understood. Griffiths \(^5\) was the first to discuss and demonstrate convincingly how small imperfections like bubbles of enclosed gas, particles of other solids, and microscopic pores or crevices in solid glass could cause crack initiation, growth, and acceleration to eventually cause failure and a serious decrease in the strength of a solid under sustained external loads.

Despite later proposed, and good evidence to prove, that crystal imperfections in an apparently simple cubic solid lattice (such as rock salt) could provide the ultimate in low-energy systems, departure from equilibrium can arise through the evaporation of a solvent or diffusing of the lattice. Griffiths' lattice theory, which takes account of the lattice imperfections, was first to consider the role of various types of lattice imperfections in determining the mode and rate of failure of a variety of crystalline solids.

Irwin \(^5\) later developed the subject of fracture mechanics as a logical extension of the conclusions from Griffith's and later investigations' work; as a consequence, there is a rapidly growing research effort by physicists and engineers in the fracture mechanics and stress analysis of crack initiation and propagation and their relation to the mode of failure. These analyses of crack paths and the mechanism of plastic solids and composite junctions. In addition to these mechanisms, plastic flow and time-dependent viscous flow, especially commonly found in plastics or in polymeric materials, have been shown to play an important part in determining the ultimate strength and the temperature on the mode and time for failure in plastics. \(^9,10\) as well as adhesive and adhesive-tape joints. \(^10\)

Much literature is continuing to appear about this area of research. Although these concepts and methods of tackling problems of the solid state have been illuminating and have provided useful research, there is still much to be done to apply to the many other classes of real materials. A complete solution for the concept of failure in adhesive joints or in protective coating is still not available. It is already well established that joints and, especially those at the interfaces in loaded joints, play an important role in increasing the internal rate of failures of glass fiber-tetin composite materials. It is well as the other composite materials. The main difference is the type of protective coating systems containing dispensed pigments and fillers during the stages of drying, curing, or aging. Research on adhesive joints and adhesion is made more difficult to handle theoretically because the joints are rarely formed under equilibrated conditions. In order to manage such a situation experimentally, one must prevent the build-up of momentum or any loss of energy in the system through controlled motion of parts, heat generation, conduction, or radiation. It is easy to conceive of the ideas of forming a joint under equilibrium conditions, but generally it is not possible except under highly specialized and limited conditions. In many common adhesive systems, departure from equilibrium can arise through the evaporation of a solvent or diffusion of the lattice. Griffiths' lattice theory, which takes account of the lattice imperfections, was first to consider the role of various types of lattice imperfections in determining the mode and rate of failure of a variety of crystalline solids.

On de Boop's Adhesion Rule

deployed \(^5\) in 1939 the following rough-and-ready rule for adhesives: "Provided we use pure or simple water, then when there is a good deal of evidence that strong joints can never be made by polyadhe..."
with non-polar adhesives or to adhere with polar adhesives. This rule has been explained and qualified by the writer, as follows: The statement that polar adhesives do not form strong joints with non-polar adhesives is not necessarily true if the non-polar adhesives are very hydrophilic materials, whereas many polar adhesives are somewhat hydrophobic and so can even absorb some water. Hence, in a normally humid atmosphere, poor wetting and spreading of the non-polar adhesive would occur on contact with the slightly moist surface of the polar adhesive. Many polar liquid adhesives will be able to absorb the atmospheric water, forming a film through the surface chemical action of the film of water adsorbed on the surface of the polar adhesive; hence, adequate wetting and spreading of the adhesive may occur under ordinary atmospheric conditions. This mechanism can be enhanced sometimes by appropriate additives. It is therefore understandable that the dehuyse adhesion rule, although a useful guide, is not always correct and should be used with caution.

Since wetting is determined by the surface composition of the adherend, it is evident that we can modify the adhesion by coating or otherwise adsorbing on the surface of the adherend a monolayer or more of a suitable agent or adhesive. In this way, we can decrease joint strength. If we wish to increase joint strength, the surface chemical composition of the adherend can often be chemically modified to increase its adhesion. For example, polystyrene or polyethylene can be oxidized with chromic acid, boiling, ultraviolet irradiation, or a ionizing radiation, which cause surface oxidation of the polyester or polyethylene which will always increase the contact angle and the wetting and adhesiveness of the liquid. Many common adhesives while liquid have values of $\gamma$ which exceed $\gamma_w$, but polyethylene, polyethylene oxide, makes the difference $\gamma_w - \gamma$ and decreases the contact angle. The results of chemical and surface oxidation was shown by dehuyse to cause a large increase in joint strength. In Fig. 16 is his graph of joint strength vs. contact angle of water with the treated polyethylene using an epoxy resin as the adhesive. As the water contact angle increases with surface oxidation of the polymer, its results are now fully explained.

Recent Advances about $\gamma$ and Surface Structure

In 1950 R. Fox and M. S. Anderson discovered that a group of co-workers in the United States, plotted against the liquid surface tension $\gamma_w$ of a homologous family of polar liquids, is a straight line intercepting the horizontal line $\cos \theta = 1$ at a definite $\gamma_w$. Such a relationship was always observed whenever a homologous family of polar liquids was used. If a variety of liquids is chosen, the contact angle of each is likely to be different, and the surface tension of each will be different. Hence, all within a homologous series, it is a straight line. As the surface tension of the polyethylene or polyethylene oxide increases, the contact angle decreases and the wetting and adhesiveness of the liquid increases. Hence, the dehuyse adhesion rule is no longer valid. In some of the subsequent experiments of polyethylene and polystyrene, the contact angle was observed to be different, but the results of these experiments were not conclusive. The results of these experiments are not conclusive. However, they are consistent with the dehuyse adhesion rule, but they are also consistent with the dehuyse adhesion rule. At W. H. K. Ho and I have recently
In a series of three related papers with Stahlecker (Fig. 21) and Bennett (Fig. 22), the effect of adsorbed water on the wetting of high-energy solid surfaces such as soda-lime glass, Pyrex, quartz, sapphire, and a variety of pure polished metals (Table 9), we were able to demonstrate the large effect of even one adsorbed monolayer of water on the solid upon surfaces by many classes of organic liquids as well as many hydrocarbon polymers. Examples in practice occur in wetting and rinsing of fibers, filters, and preforms, unless they are dried first by heating or evaporation treatments.

A paper with Timmons and several associates, using radiotracer carbon-labeled strontium adsorbed as extruded monolayer on polished clean metal, revealed a steady trend in the relation between the contact angle exhibited by a sessile drop of pure liquid strontium to the percentage surface coverage of the adsorbed film of strontium. The recent results (Fig. 22) obtained by Timmons' group using a steady probing by Levine and Zisman in 1957 that the large contact angle exhibited by the strontium isoleucine molecule on an adsorbed condensed monolayer of a fatty polar nonpolar compound should make it more useful than the water contact angles for estimating the surface density of the packing of methyl terminal groups comprising the adsorbed surface film.

Table 8. Comparison of Φ for High-Energy Surfaces Equilibrated at Different Humidities

<table>
<thead>
<tr>
<th>High-Energy Surface</th>
<th>5% RH</th>
<th>0% RH</th>
<th>85% RH</th>
<th>100% RH</th>
<th>105% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>45</td>
<td>45</td>
<td>45</td>
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<td>45</td>
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<tr>
<td>Iron</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Tungsten</td>
<td>45</td>
<td></td>
<td>45</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Metal oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrO (crystal)</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>SrO (powder)</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>44</td>
</tr>
</tbody>
</table>

Fig. 21. Effect of the partial pressure of water vapor on the critical surface tension of soda lime glass.
A · FUNDAMENTALS

VARIATION IN CONTACT ANGLE WITH SURFACE COVERAGE

Fig. 72. Variation in the contact angle of methylene iodide with the percentage coverage by stearic acid.

In a recent paper by Brummet and Zisman in 1970, and another prepared concurrently by Schrader, many workers in the area of wetting and adhesion have demonstrated the importance of the contact angle in the determination of the wetting properties of materials. The contact angle of a liquid on a solid surface is a measure of the cohesive and adhesive forces acting between the liquid and the solid. The contact angle is defined as the angle between the solid surface and the tangent to the liquid surface at the point of contact.

Many workers have studied the relationship between the contact angle and the properties of the solid surface, such as the surface energy, the roughness of the surface, and the chemical nature of the surface. The contact angle is also affected by the properties of the liquid, such as its surface tension and viscosity.

The contact angle is an important parameter in the study of wetting phenomena, and it is used to characterize the wetting behavior of a liquid on a solid surface. The contact angle is also used to evaluate the adhesion of a liquid to a solid surface, and it is a useful parameter in the design of coatings and adhesives.

3. INFLUENCE OF CONSTITUTION ON ADHESION

Localization of the molecular field of force during wetting of organic solids or films, we have published many examples of how to calculate \( \gamma \) for a surface covered with a variety of organic groups. Brummet and Zisman did this for two classes of compounds, aliphatic and aromatic, having both chain branching and chlorine substituents. The values of \( \gamma \) for each group of materials in the sequence plane were used to determine the percentage of the total surface area of the solid covered by such groups and the resulting \( \gamma \) was corrected.

However, such an approach in relating the measured value of \( \gamma \) to the surface constitution works reasonably well for oriented adsorbed monolayers or for essentially linear polymeric coatings which are not too hindered sterically from allowing the molecules to assemble and pack on the surface in an obviously most probable arrangement.

Since the surface contribution is the overwhelmingly important one in determining the value of \( \gamma \), it is helpful for both research and applications to have convenient tabulations of the values of \( \gamma \) as a function of the nature of the surface composition. We have made reference tables in several ways: (a) by listing values of \( \gamma \) in the order of increasing values for the various kinds of monomolecular-covered surfaces, (b) by tabulating the values for the various polymeric solid surfaces, and (c) by tabulating values of \( \gamma \) contributions for the different conveniently selected organic groups or radicals. These tables are found in various publications.11,13,35,36

Krukoff has prepared a chart useful as a guide for new work13, which was published in 1975. It included here in a simplified form as Appendix I.

Many other investigators have published tables of values of \( \gamma \), including those obtained by Lee using a stepped series comprising of pure alcohols, ethers, menthol, glycerol, formamide, urotropine, and four polyglycols. Some of these latter values probably need to be used with some caution because all these liquids form hydrogen bonds readily.

Many investigators have difficulties in finding many points made in our paper. There has been apparent a rather general tendency for too restricted a variety of liquids in contact angle studies in order to save valuable time and effort. Especially common have been investigations made with improperly purified liquids, contaminated surfaces, or inadequately cleaned and polished solid surface. For example, Zisman and I published a paper on the wetting of polyethylene and polyvinylchloride by aqueous solutions whose surface tension was increased by adding water to pure ethyl or butyl alcohol. We demonstrated that, although the resulting graph of \( \gamma \) vs. liquid surface tension (Fig. 22 and 23) were interesting and allowed one to obtain useful data, there were several drawbacks, which were discussed. Ever since then, many investigators have used this approach without always understanding the limitations imposed in contact angle studies by using a group of hydrogen-bonding liquids.
Effect of Surface Treatments by Oxidation, Electrical Discharge, and Radiation

It is astonishing how many problems of adhesion and of surface deterioration of plastics and rubber can be solved by using the results of both our related research on the surface chemistry of wetting and adhesion. It is easier to be interested in the surface of an adhesive, or to choose an adhesive that is about as complex as the surface of a large number of solids, as are the adhesives and the substrate. These adhesives can be used to change the wetting properties of the materials or to change the composition of the surface coating. In dealing with linear polymers and adhesives, a lack of uniformity of the composition may be a limiting factor in this practice. In the case of the surface coating, the surface properties of the organic coatings at the molecular level have become key issues. Thus, the need for understanding the wetting and adhesion of various materials such as the polyethylene, polypropylene, polyvinyl chloride, and other polymers has been satisfied when these surfaces were treated briefly with oxidizing agents, electrical charge, UV, and even x-radiation. Usually the resulting changes to the surface layer could be detected with extraordinary rapidity and delay by observing the change in the equilibrium contact angle of water or of some other wetting agent in a function of the intensity and duration of radiation or other surface chemical treatment. The same approach has been used to follow and study the commensurability of the ultraviolet photochemical degradation of a plastic as was shown very convincingly with pure polyethylene by R. Fox, T. B. Price, and D. S. Cahn who in turn work the contact angle indicated definite surface constitutive changes in 100 minutes of exposure of the substrate to light at room temperature and temperature, and the same sensitivity was found with UV spectroscopy. In contrast, the patterns of net expulsions were observed in about five hours exposure. There have been many papers since to show how the contact angle is the most critical surface tension in adhesion toward the other adhesion materials and that this can be used to observe the modification of the wetting and adhesion through surface modification of a variety of polymers and plastics.

In order to understand more about the behavior of real particles, one must recognize the often complex nature of the surface of the adherends as well as the adhered-adhesive interface. Frequently the joint consists of only two adherends and one adhesive. Many adherends are coated with surface oxides which may or may not be hydrated and are capable of playing an important role in determining whether the joint will be good in the oxide, in one of the adherends, or by adhesive failure in the junction between the oxide coating and the metal adherend. In other systems, contaminants such as adsorbed traces of organic plasticizers, low polymers, monomers, or inorganic dust on the surface may affect the final state of failure. In dealing with linear polymers as adherends, a lack of uniformity of the composition may be a limiting factor in this practice. In the case of the surface coating, the surface properties of the organic coatings at the molecular level have become key issues. Thus, the need for understanding the wetting and adhesion of various materials such as the polyethylene, polypropylene, polyvinyl chloride, and other polymers has been satisfied when these surfaces were treated briefly with oxidizing agents, electrical charge, UV, and even x-radiation. Usually the resulting changes to the surface layer could be detected with extraordinary rapidity and delay by observing the change in the equilibrium contact angle of water or of some other wetting agent in a function of the intensity and duration of radiation or other surface chemical treatment. The same approach has been used to follow and study the commensurability of the ultraviolet photochemical degradation of a plastic as was shown very convincingly with pure polyethylene by R. Fox, T. B. Price, and D. S. Cahn who in turn work the contact angle indicated definite surface constitutive changes in 100 minutes of exposure of the substrate to light at room temperature and temperature, and the same sensitivity was found with UV spectroscopy. In contrast, the patterns of net expulsions were observed in about five hours exposure. There have been many papers since to show how the contact angle is the most critical surface tension in adhesion toward the other adhesion materials and that this can be used to observe the modification of the wetting and adhesion through surface modification of a variety of polymers and plastics.

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approaches 100%. Increased condensation of water on the surfaces of both metals and metallic oxides will initiate the hydrolysis of some adsorbed ligands, and so the wetting properties of these surfaces will become more like those of highly hydrated surfaces as glass, silica, and glass. Obviously, data is needed on the values of $v_{fr}$ for a variety of low-energy solid surfaces; with these data the values of $v_{fr}$ given here, one would no longer have to estimate it, and hence the knowledge of adhesion would become more precise.

The empirical nature of $v_{fr}$ is obvious, and it would be helpful to replace $v_{fr}$ by parameters having a sound interpretation in thermodynamic or statistical mechanical considerations. Unfortunately, the effect of constitution on either $v_{fr}$ or $v_{fr}$ is still unknown, and neither quantity can be studied until a satisfactory experimental method for measuring each has been found. A more precise theory of wetting of low-energy surfaces should at least include $v_{fr}$. Probably the lateral spread in the data points of our graphs of $\cos \theta$ or $\gamma_{fr}$ for a given solid surface is due to the variation of $v_{fr}$ among the liquids used.

Finally, our investigations have been concerned with the wetting of a solid by one liquid, and nothing has been said about the complex problems of the competitive wetting and adhesion of two immiscible liquids with respect to a given solid surface. However, it is obvious that the empirical laws here for the simpler systems should prove helpful in learning more about the more complex systems.

References