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GENERAL ENGINEERING LABORATORY

SURFACE CHEMISTRY OF ADHESION, ABHESION AND LUBRICATION

by

F. F. Carini

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GENERAL ELECTRIC

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I. Introduction

A knowledge of the surface properties of chemical materials is paramount in making better lubricants, adhesives and protective or decorative coatings. In the past, less attention has been paid to the interface characteristics than to the study of the various phases, i.e., solid, liquid and gas alone. The emphasis is now shifting to increased examination of the surface properties of systems in order to help explain phenomena in the fields of adhesion, and lubrication. Information on surface characteristics is now available which points the way to improved products in these areas and new application of these materials.

1. Adhesion involves the art of sticking materials together. There are numerous examples of the use of adhesives to join metallic, organic and ceramic materials. These will be amplified under the section "Applications" which follows, along with a discussion of how a knowledge of surface properties can be used to improve the effectiveness of paint and protective coatings.

2. Abhesion involves that property of a surface which reduces the tendency for sticking to occur. Some cases where abhesion is desirable would be

   (1) In the casting industry, where stearates are used to provide a surface coating to allow the casting to be removed from the mold and,

   (2) In bakeries where silicones are used to coat the pans to prevent the dough from sticking to the pans.

   Other areas where such action is needed are in the automatic ice making machines and in the cooking ware industry.

3. Lubrication involves those surface treatments which reduce the friction between bodies moving with respect to one another. In the field of boundary lubrication, it is a recognized fact that the adsorption of some constituent of the lubricant on the surface of the metals is one of the requisites for adequate lubrication. Adequate boundary lubrication is generally associated with the formation of a metal soap on the surface of the metals. Extreme pressure lubricants also act by a reaction between the lubricant and the metal to form a readily deformable surface so that no galling will occur.

It might be well to review some of the interactions which can occur between systems such as are used in adhesion and lubrication. Actually, quite often in practice, more than one of these systems comes into play, so that the interaction is quite complex. Some of these interactions, which will be termed chemical interactions are ion-ion, ion-dipole, atom-ion, and ion-metal. These forces are usually stronger than the purely physical forces such as dipole-dipole and dipole-metal; however, there is often a combination of both chemical and physical factors to achieve the ultimate in adhesion.

The intrinsic strength of an adhesive bond can be no stronger than the sum of the molecular forces interacting. The forces mentioned above are included as making up the maximum adhesion shown schematically in Figure I.

Factors Involved in Adhesion

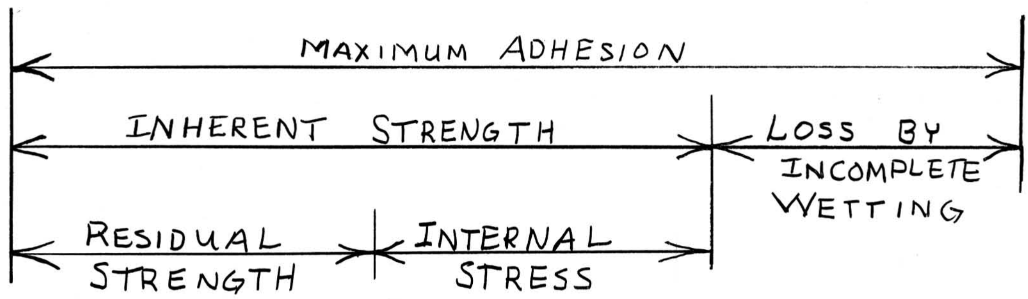


Figure I

The inherent strength of the bond is lower than the maximum adhesion due to the loss caused by incomplete wetting. The factors affecting the maximum adhesion and inherent strength will be discussed more completely in this paper. Some of the factors influencing internal stresses will be listed.

II. Applications

A. Adhesion

1. Metal to Metal

Developments in adhesives have progressed at a phenomenal rate in the past fifteen years. This growth has been due, in part, to an increased understanding of the many variables which affect the performance of adhesive joints and the development of synthetic resins which have the high strength required of an adhesive. Until recent times very little attention was paid to the face that the process is dependent on the behavior of thin films of the adhesive in relation to the adherend surface properties rather than the bulk properties. This point was demonstrated by McBain (1) using de Khotinsky cement as the adhesive in preparing couples of copper-copper, tungsten-tungsten and copper-tungsten. The copper joint had a strength of 5,110 psi and the tungsten couple, 300 psi. One would expect that the mixed couple would break at the lower strength, 300 psi; however, this joint measured 780 psi, which shows that, due to the extraordinary behavior of thin films and surface forces, bonds of quite high strength can be formed. While qualitative predictions can be made of a particular system, adhesive or substrate, adhesion must be studied in relation to the surface properties of the materials being bonded; that is, the interaction of the materials is the important parameter of the system.

In the past several years, there have been some quite startling uses of organic adhesives in load bearing structures. One of these applications is in the airframe industry where rivets have been, to a large degree, eliminated in the joining of aluminum. According to the ANC-5 bulletin, the allowable beaming strength of 1/8" 25ST aluminum is 2,812 pounds for a 1/4" diameter rivet. Compare this with the joint (2) made with a vinyl-phenolic resin, FM-47, which has a minimum strength of 4,858 psi when the aluminum has been given the requisite pretreatment. In this case, a 1/2" overlapped adhesive joint replaces a riveted joint when the rivets have been placed only 1 inch apart. This stronger structure has been made possible by the proper treatment of the aluminum surface to provide the aluminum oxide required to form the strongest bonds.

Delmonte (3) has reported that synthetic resin-rubber adhesive develop shear strength in excess of 3,000 psi for bonding steel. These strengths are comparable to the strengths required for some spot-welded structures. Indeed, it is now possible to replace spot welding with adhesives in some applications. Titanium, at times, can be quite difficult to bond together; however, Muchnick (2) has found that joints between titanium couples can have shear strength in excess of 6,000 psi where the surfaces have been adequately cleaned and where the surface structure is optimum for bond formation.

The Army Chemical Center (4) has reported some data comparing the bond strength of 50-50 soft solder with that of an epoxy resin, Araldite 115, in joining a galvanized steel screen to cold rolled steel. Table I gives the tensile strength of the bonded couples after being exposed to various atmospheric conditions for thirty-five days.

Table I

Tensile Strength of Araldite 115

Adhesive	100°F (Dry)	113°F (85% R.H.)	-65°F
Solder	210	227	214
Araldite 115	276	224	283

It can be seen, from Table I, that the Araldite 115 forms a stronger bond than the solder at the extreme temperatures tested. In addition to this, it was found that a cost reduction of more than 50 per cent could be realized because of the difference in cost of the resin as compared to the heavier solder.

2. Metal-Organic

Another large area in which adhesion plays an important role is in the field of protective, decorative or insulating coatings for metals. These may range from the extremely thin coatings such as are used as the dielectric material on foil for capacitors to the relatively thick foamed plastic material used for thermal insulation. All these must adhere well to the metal substrate and therefore depend on the formation of strong bonds to the prepared metal surface. The surface properties of the metals are especially important in this application, because no pressure can be used to help cause the chemical interaction needed for bonding. The adhesion depends solely on the activity of the system.

In some cases, to make use of the desirable properties of the synthetic resins, the surface of the object to be coated must be especially treated to form a strong bond to the surface. These special preparations are exemplified by the process for coating with Teflon. In this case, both the substrate and the organic material must be treated to make surfaces as highly reactive as possible. The metal is degreased and given a chemical treatment to make the metal surface reactive to an epoxy resin. The Teflon is chemically treated with sodium in liquid ammonia and then the organic Teflon bonds firmly to the epoxy-coated metal surface.

Another example of the importance of surface reactivity is indicated by the work of K. Brookman (5). He worked on the adherence of paints to aluminum surfaces. He found that he could correlate the degree of adherence with the increase in the apparent thickness of the aluminum oxide layer on the aluminum due to the chemical reaction between the reactive hydroxyl (-OH) and carboxyl (-COOH) groups and the metal substrate. This reactivity can also be followed by the extent of adsorption of the resin for the aluminum oxide. This will be covered more completely later.

B. Abhesion

To obtain abhesive surfaces one must treat the surface such that little or no chemical reaction can occur between the substrate and its environment. The most widely known example is the nonwetting of paraffin by water.

The techniques of treating surfaces with silicones such as "dry film" take advantage of this phenomenon, since the parts of the molecule which cause nonwetting are paraffin-type carbon chains joined to silicon which in turn bond strongly through oxygen bridges to the surface.

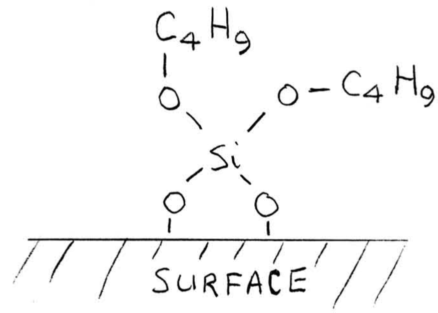
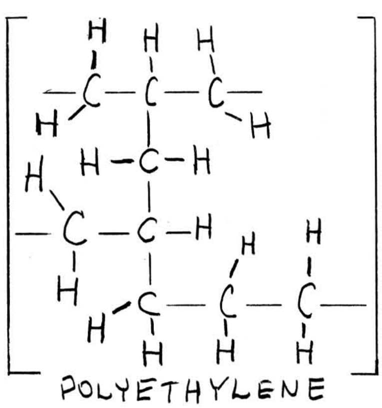


Figure II

There are also several newer organic materials which are abhesive. Teflon and the polyethylenes are being widely utilized. Each of these is a carbon structure with only one substituent on the carbon chain. Figure I indicates the structures.



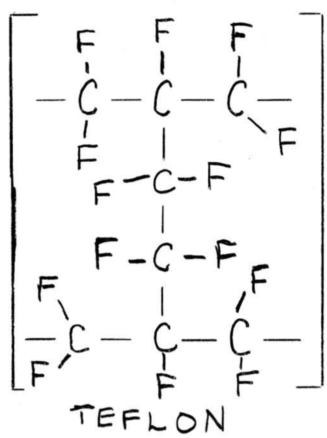


Figure III

Both structures, in a way, are similar to a paraffin wax in that they are not wetted by water. These materials have wide application since they have good structural strength and can be used at elevated temperatures.

C. Lubrication

Knowledge of surface properties has been recognized as an important factor in formulating good lubricants for boundary lubrication. These lubricants must minimize friction and galling at reasonable pressures. It has been found that materials which form a chemical compound with the metal surface enhance lubricant properties of oils and greases. It is thus necessary to have as an ingredient of the oil a compound which is capable of reacting with the metal surface.

It has been found that those metal surfaces which form compounds with difficulty could not be lubricated well. Titanium is an example of this type of metal.

The surface properties are equally important in the field of extreme pressure lubrication. It has been shown that many chlorinated lubricants for iron act by the formation of a ferrous chloride compound which has a low shear strength and is the actual lubricant. This points the way to methods of studying lubricants by the property of the surface itself. The study of metal-surface reaction appears to be an important requisite to the development of new extreme pressure lubricants.

III. Theoretical Considerations

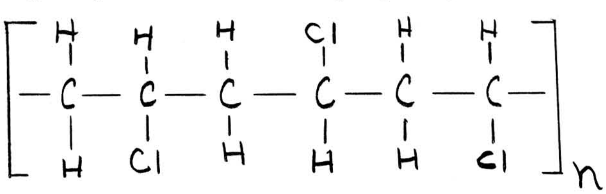
A. Theories of Adhesion and Abhesion

1. General

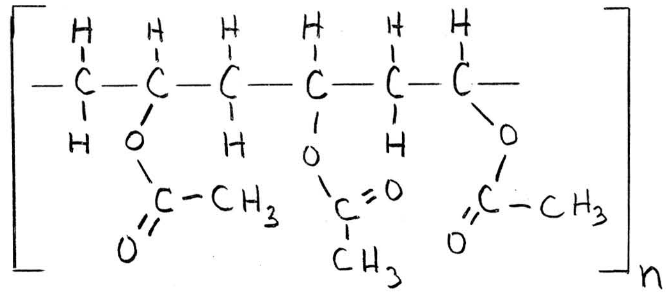
In years past, it has been the custom to abrade a surface in order to increase the chance for adhesion to occur. This has been done in the belief that adhesion is due to a mechanical interlocking of the adhesive in the substrate. Roughening a surface actually quite often reduces adhesion since it causes irregularities in the thickness of the adhesive.

Numerous examples can be cited to substantiate the theory of specific adhesion, that is, that adhesion requires molecular and atomic interaction. R. W. Finholt and D. T. Hurd (7) studied the adhesion of copper couples as a function of the pretreatment given the samples prior to bonding. They found that a method of anodizing which produced a black oxide surface was best for forming strong bonds. These tests were performed by using an Instron tensile testing machine to measure the strength of the copper joints formed. This black oxide had a higher reactivity for the adhesive than other types of oxides or than a clean copper surface.

Chemically, glass has a reactive surface structure which consists almost wholly of hydroxyl (-OH) groups. Reaction with adhesive materials can occur through the formation of bonds involving these hydroxyl groups. The experimental data of F. Moser (8) verifies the predictions which would be made on the assumption that the adhesion depends on chemical reactivity. In this case, the bond strength of polyvinyl acetate and polyvinyl chloride are compared.



Polyvinyl chloride (PVC)



Polyvinyl acetate (PVAC)

On the basis of chemical considerations, one would expect a greater attraction between the hydroxyl group of the glass with an oxygen-containing compound such as polyvinyl acetate than with the chloride of polyvinyl chloride. Table II lists the bond strengths found for these materials and one mixture of these compounds. The bond obtained with a mixture containing 1/6 PVA is just about 1/6 as strong as that obtained with pure PVA which indicates that only 1/6 as many specific bonds are formed in this mixture.

Table II

Bond Strengths of PVC and PVAC

Adhesive	Bond Strength (psi)
Polyvinyl chloride (PVC)	0
5/6 PVC-1/6 PVAC	100
Polyvinyl acetate (PVAC)	550

The specific interaction theory of adhesion also applies to the case where no adhesion occurs. The decrease in the bond strength going from PVAC to PVC is an indication of this noninteraction or abhesion.

2. Surface Treatments

Proper surface treatments are necessary to remove any deleterious surface films and to produce the proper chemical composition for the desired bonding or nonbonding properties. In the field of adhesion several recent investigations have pointed up the advantages of proper treatment for good formation.

Muchnick (2) carried out a number of adhesive tests on aluminum, stainless steel, and titanium using a vinyl-phenolic adhesive FM-47 for which he determines the strength of metal to metal adhesive bonds. Comparison can be made of the improvement in bond strength due to the chemical treatment. Table III gives the results of these tests.

Table III

Shear Strengths of Several Metals With FM-47 Adhesive

Treatment	Shear Strengths (psi)		
	Aluminum	Stainless Steel	Titanium
As received	2442	5215	1356
Degreased	2741	6306	3180
Chemical Treatment	5173	7056	6743

In each case the chemical treatment radically improves the bond strength. It has been common industrial practice to merely degrease the metal before making the adhesive bond; however, it can be seen from the table that this treatment only slightly increases the ultimate adhesive strength. The increase is only 15 per cent in the case of aluminum. Quite marked increases in adhesive sheat strength are obtained by the proper chemical treatment as shown for all the three metals tested. The degreasing operation removes any organic or loosely adhering dirt. For proper bond formation, the correct surface structure must be produced by the chemical treatment.

The effect of surface films caused by chemical pretreatment can be further illustrated by the work of Murphy and Page (9) on the variation in bond strengths of a 1/6 polyvinyl acetate-5/6 polyvinyl chloride resin (designated VYHH) and an epoxy resin (Epon 1007) on aluminum pretreated in various ways. The aluminum samples were etched in a chromic acid solution and rinsed with water at a number of temperatures. It was found that those samples which were rinsed at a temperature below 160°C formed stronger bonds than the samples rinsed above 160°C. It has been established that Bayerite ($Al_2O_3 \cdot 3H_2O$) forms at the lower temperature, and boemite ($Al_2O_3 \cdot H_2O$) is formed at the higher temperature. Thus the crystal form and chemical constitution of the surface oxide layer are important to adhesive qualities. The extent to which each of these oxides adsorb adhesive molecules was also determined. The amounts adsorbed were found to correlate well with the bond strengths obtained over a range of surface film properties.

B. Theories of Lubrication

In general, surfaces may be lubricated by separating the surfaces with a thick film of a liquid lubricant, which has hydrodynamic properties that will reduce friction. However, for modern high speed equipment it is often necessary to rely on very thin films of lubricants to give the desired lubrication properties. These problems lie in the areas of boundary lubrication and of extreme pressure lubrication.

Good boundary lubricants will reduce the coefficient of friction between sliding surfaces and reduce the amount of wear of the surfaces involved. The action of a good lubricant will lower the coefficient of friction from a value above 1 to values in the range of 0.05 to 0.15. The fatty acids, such as lauric acid, $C_{11}H_{23}COOH$, for example, will lower the coefficient of friction between cadmium surfaces from 0.5 when lubricated with paraffin oil to 0.05 when as little as 1 per cent lauric acid is added to the oil (10).

Table IV

Effect of Lauric Acid on Friction

Surface	Coefficient of Friction: Clean	Paraffin Oil	1% Lauric Acid in Oil	% Acid Reacted
Copper	1.4	0.3	0.08	4.6
Cadmium	0.5	0.45	0.05	9.3
Iron	1.0	0.3	0.2	trace
Aluminum	1.4	0.7	0.3	0.0

Metals which do not react with the fatty acids are not adequately lubricated as is evidenced by the minor reduction in friction made by the lubricant on iron and aluminum surfaces. These results suggest that the lubricating properties are obtained not from the action of the acid, but by the reaction of the metal soap formed by a reaction of the additive with the metal surface. The fact that both iron and aluminum are lubricated by the addition of cadmium laurate to the paraffin oil tends to bear out this hypothesis.

Surface reactions are also of importance in the area of extreme pressure lubrication. The high temperatures generated by the rubbing surfaces tend to break down the normal lubricating films. Effective lubrication is obtained with chlorine and sulfur containing organic materials. The chlorides work especially well on iron surfaces, where reaction can occur to form $FeCl_3$. This material has a laminar crystal structure which has low shear strength. Both MoS_2 and graphite also have a layer structure and are used as extreme pressure lubricants. Further study of compounds with the required laminar structure is needed for improved boundary and high temperature lubrication.

IV. Experimental Approaches

The current literature, as reviewed in the previous sections, points out the importance of specific surface interactions in the fields of abhesion, adhesion, and lubrication. In each of these cases, the desired property depends on the chemical reactivity of the surfaces of the materials.

A. Thermodynamic

The study of abhesive and adhesive qualities has usually been conducted by some measure of the surface activity. The formula which relates the readily measurable quantities to the energy of interaction is:

$$e_A = -\Delta H_W - \left(\gamma + T \frac{d\gamma}{dT} \right) \qquad \text{(a)}$$

where e_A is the energy of interaction (the unknown)
ΔH_W is the heat of reaction
γ is the surface tension of the liquid
$T \frac{d\gamma}{dT}$ is the temperature dependence of the surface tension

Since the interaction on an abhesive surface is quite small, the term ΔH_W although measurable, is quite small, so other types of measurements such as wettability are usually made to characterize these surfaces. As a method for determining the adhesive quality of a surface, this measurement is quite valuable since the value of ΔH_W is readily obtainable and relates directly to the number of chemical bonds formed between the adhesive and the surface and therefore to the probable overall bond strength of the adhesive.

B. Wettability

The measurement of the angle formed by a liquid with a substrate surface is also an indication of the amount of chemical interaction. Theoretically the work of adhesion, W_A, is related to this wetting or contact angle by the formula

$$W_A = \gamma_L (1 + \cos \theta) \qquad \text{(b)}$$

where γ is the surface tension of the liquid
θ is the angle formed by the interface between the liquid and the substrate

The value is quite often reported simply as the angle of contact, θ, which is sufficient if the systems being investigated are closely related and only comparative values are needed. This method is quite useful as a measure of organic contamination of a metal or glass surface where the angle is large. The measurement of the angle is also meaningful at the better wetting angles (i.e., below 10°) where it can most accurately be determined. The contact angle can be used in characterizing surfaces for adhesion and abhesion studies and is also useful as a measure of interaction of a surface with the organic materials used in paints.

In order to find the values of the energy (Eq. (a)) and work (Eq. (b)) of adhesion one needs to know the surface free energy of the liquid which is contacting the solid phase. This free energy per unit area is equal to the surface tension of the liquid, which can readily and precisely be determined. In addition to the above named applications, the difference in surface tension and wettability of various liquids is measured directly using a "Bartlett Cell" for determining the degree of adhesion of various paint formulations for the same substrate. The "Bartlett" apparatus measures the difference in affinity of two liquids by the displacement of one by the other. This type of measurement may also be used to assess the relative merits of solvent base adhesives for a particular adherend.

C. Adsorption

The three methods of investigating interface reactions mentioned above all depend on the reactivity of surface for the other phase. A direct measurement of the amount of adsorption, at constant temperature, is another way of determining the adhesive, abhesive and lubrication qualities of a surface. The studies carried by Murphy and Page point up this method in the abhesive field. Zisman and others have carried out studies on abhesive properties by adsorption and the method is now generally accepted in the lubrication area as being a prime tool in formulating new and better lubricants. The extent of the adsorption is also important in paint technology.

The adsorption can be detected in quite a large number of ways, both by chemical and physical means. Direct chemical analysis is probably the best known method, however, since very small quantities of adsorbing material are sometimes encountered, more sensitive techniques have to be applied. Radioisotopically labelled materials are now available in a variety of forms, and the measurement of the radioactivity of a sample before and after being exposed to adsorbing molecules can be made to determine the number of these molecules adsorbed under various conditions.

D. Contact Potential

Another way of investigating adsorption on metallic materials is by measuring the changes in work function of the sample after exposure to the materials under study. This contact or surface potential is very sensitive to surface changes and one may also get an insight into the orientation of adsorbing layers of active material. This technique is valuable in each of the fields of lubrication, adhesion and abhesion.

E. Electron and X-Ray Diffraction

The surface may be characterized by the crystal structure of the boundary layers. Both x-ray diffraction and electron diffraction of the surfaces before and after treatment are quite useful in defining the system under investigation. For a more complete understanding of the adhesive and abhesive properties of materials one must be able to reporduce the needed surface for the appropriate surface quality. Diffraction equipment in conjunction with the use of electron microscopy are powerful tools for the study of these surface properties.

V. Discussion

This report has covered some of the more recent publications and some of the methods for studying surface phenomenon in the fields of adhesion, abhesion and lubrication. Although much work has already been done in this field, it seems certain that by applying the knowledge gained through the use of the techniques of surface chemistry described above, better products may be made.

A. Tests of Adhesive Bonds

Thousands of publications have been written on adhesion and methods of testing adhesives. These tests have now been standardized and are recognized methods for studying adhesive joints and the adherence of coatings to substrates. These have not been covered in this report since the methods are available in the bulletins of the American Society for Testing Materials. The references to these methods are given on page 24 in the bibliography.

Many methods have been proposed for the study of adhesion for various systems which are not included in this paper. Most of these methods attempt to correlate the strength of adhesive joints with various physical properties of these systems. These are quite useful as tools for comparing joints after they have been made but do not lend themselves to an increased understanding of the interface reactions. Some of these methods deal with the measurement of the electrical properties of the adhesive system. Another method is the measurement and correlation of viscosity with the strength of adhesive joints. This present report deals mainly with the chemical aspects of surface reactions.

B. Internal Stresses

There are numerous other factors involved in adhesion besides the chemical reactivity. Some of these are:

1. The coefficient of the expansion of the adhesive compared with that of the substrate.

2. Thickness of the glue line.

3. The rugosity or the roughness of the substrate on which the adhesive is applied.

4. Time of molding or the extent of polymerization of the polymeric resin.

These factors must be taken into account in addition to the extent of chemical interaction between the adhesive and the metal or ceramic substrate.

1. Coefficient of Expansion

The coefficient of expansion of the adhesive or of a coating is quite important if any variation in temperature is expected in the life of the article under consideration. If the coefficients of expansion of the metal differ by a significant factor splitting will occur in either body or between them due to the differences in expansion.

2. Thickness of Glue line

The thickness of the adhesive is quite important since quite often thin films are much stronger than thick films of the same adhesive. Dietz (11) has investigated this phenomena and found that at the lowest ratio of bond thickness to bonded area bond strength was maximized. This is especially important in using conventional mechanical test pieces and devices, since the bonded area is usually quite small and therefore the glue line or bond thickness must be closely regulated to obtain significant results.

3. Roughness of Substrate Surface

Bikerman (12) has recently carried out some experiments which bear directly on the part played by rugosity in adhesion and in lubrication. In lubrication the roughness determines the thickness of lubricant which a bearing material can carry, since the rugosity determines the rate of drainage of the solid. In adhesion, the solids are pressed together squeezing out excess liquid. Therefore, the amount of liquid remaining between the solids depends on rugosity and the strength of the bond is thus directly proportional to the bond thickness.

4. Cure Time for the Adhesive

Adhesives are applied in a liquid form to the solids to be joined. These liquids may be made up of a fully polymerized resin dissolved in a solvent or emulsified in a liquid carrier or a semi-polymerized material which is cured by heat treatment or catalyzed reaction. For high polymers with which we are usually concerned, the adhesion increases with the degree of polymerization until a maximum is attained. Therefore it is important to know the optimum cure time for a given adhesive system.

5. Physical Properties of Adhesive

The physical properties such as the flow of an adhesive in a system are very important. The adhesive or lubricant must be fluid enough to spread readily on the surfaces to be joined or the bearing to be lubricated. Spreading is affected by both the viscosity of the adhesive or lubricant and by the degree of wetting of the substrate.

Although each of these is important, the viscosity is quite often readily controllable so the degree of wetting is the determining factor in the ultimate strength of the bond. Adhesives are used either in the semipolymerized form or dissolved in a solvent. The viscosity can be controlled by the degree of polymerization of the resin, by the concentration of the solution or by the use of additives.

C. Wetting

The wetting of the surface is probably the most important single aspect in adhesion, abhesion and lubrication. The wetting angle has been specified as the property to be measured to determine the wettability of the surface. The wetting angle which will be specified by θ is directly related to the work of adhesion.

$$W_A = \gamma_S - \gamma_{LS} + \gamma_L$$

The work of adhesion is thus the difference between the surface tension of the solid minus the interfacial tension of the solid and liquid plus the free energy of the liquid. From this we arrive at the equation

$$W_A = \pi_e + \gamma_L (1 + \cos \theta)$$

where π_e is the difference between the surface tension of the solid before and after contact of the liquid or vapor, π_e can be determined from adsorption isotherms. Therefore, for a particular adhesive or lubricant the work of adhesion should be directly related to the angle θ which the liquid makes with the surface of the solid. The practice has grown up of using simply the angle for a particular system. This figure does not correctly characterize the interaction if the liquid or solid is different for the various systems under investigation. Muchnick and Moser both attempted to correlate this angle with the strength of the adhesive bond formed between a particular adhesive with various substrates. There was some good correlation within a particular adhesive system or within a particular metallic system. However, when the systems were mixed the angle did not give a true picture of the phenomenon under investigation. The values found would have been much more applicable if the surface tension γ_L and the adsorptive properties as given by π_e were also included to give a new value, W_A. Wetting can be assessed from the equation involving the work of adhesion along with the appropriate surface tensions. The strength of the bond might be lower than the inherent strength by such factors as rugosity and coefficient of expansion, discussed above. Since we are attempting to obtain the maximum strength possible, it is well to study these phenomena from the fundamental viewpoint. It would be well to decrease any losses by such things as incomplete wetting and to maximize the adhesion by making the system right for high adsorptive energies.

There is one experimental procedure which directly gives the interactions listed above and also takes into consideration the degree of completeness of wetting of a solid surface. The interaction can be measured by the degree of the heat of wetting of the solid by the adhesive or lubricant under consideration. The amount of heat produced by the interaction can be determined by using a microcalorimeter which uses small amounts of material and measures very small temperature changes. The temperature change has to be only on the order 10 for a reasonable reading to be obtained. The energy of adhesion is given by the equation

$$E_A = -\Delta H_W + \left(\gamma - \gamma \frac{d\gamma}{dT} \right)$$

which depends only on the calorimetrically determined heat plus a knowledge of the surface tension of the liquid under study. The one requirement of this system is that the reaction be quite rapid so that the heat is evolved over a sufficiently short period of time that it can be detected as a temperature change. Heats of wetting of numerous liquids have been determined with a variety of solid substrates. One may directly relate the heat as measured by this instrument to the heat given off per mole or reactants, if one also knows the area of solid which is interacting. This method is just coming into wide use in studying surface properties of different metallic materials and ceramics.

To carry out any of this type of experimentation, it is always well to first run adsorption experiments to determine the extent of coverage one gets at various concentrations of the active ingredient in the adhesive or the lubricant system. These experiments are quite simply run. One needs to only expose a known area of the solid material to a solution containing a known amount of the active chemical. At various times samples are taken of the liquid and the active material is quantitatively analyzed. From this information one can tell the amount of material adsorbed on the solid. The analyses may be carried out in a variety of ways including

1. by normal chemical means, by measurement for the functional group

2. by determining some physical property of the liquid such as conductivity or surface tension. (This method is quite useful since extremely small amounts of materials may be analyzed and accurately determined.)

One of the factors which has not been mentioned to this time is the orientation of the functional groups of the active material with that of the metal substrate. For maximum adsorption or reaction between materials the materials must be oriented so that the reactive groups are able to react with the substrate. One method of determining this is by the degree of adsorption experiments and also the magnitude of the heat given off when the two materials interact using a microcalorimeter.

D. Interface Structure

To provide further valuable information on interface structure, electron diffraction patterns of the substrate before and after exposure to the active materials may be used. This method does not always work since the diffraction depends on the degree of crystallinity which is obtained and the ability to determine what crystal structure is involved. In some cases the coatings are amorphous instead of being crystalline and then very little or nothing can be said about the interaction occurring. However, where applicable, this method is quite useful in determining the extent of interaction of various materials. In the field of extreme pressure lubrication quite often electron diffraction determines whether the correct type of laminar structure is obtained when the gas or liquid or solid lubricant reacts with the bearing or metal surface. This does not always give a complete picture but it gives the very good indication of the reaction occurring. For instance in the case of graphite lubrication, the laminar structure is present. However, lubrication only occurs if there is a small amount of water vapor present so that the laminar flakes of the carbon can be distorted easily.

VI. Conclusions and Recommendations

Improvements in the practical problems involving adhesion, abhesion and lubrication are amenable to laboratory techniques. The interface reactions of liquids and gases with solid materials are important to the proper functioning of adhesives or lubricants. Surface interactions are due to the chemical and physical reactivity of the materials in contact. For adhesion to occur the reactivity should be maximized; to prevent adhesion reactivity should be minimized. In studying lubrication one must also determine the effect of the compound formation on the lubricating properties of the system.

The experimental measurements which appear applicable to a study of these phenomena are:

1. The extent of adsorption of the liquid or gas onto the solid.

2. The work of adsorption as determined by the wetting characteristics.

3. The energy of adsorption which is evaluated by calorimetric heats of wetting.

A program should be set up to study the interaction of adhesive and lubricating materials with a number of common metals which are widely used within the company. A study is now under way on the reactions of copper with a polymeric material, polyvinyl stearate. Other metals which should be investigated are stainless steels, titanium, and aluminum.

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Books of General Interest

Survey of Adhesives and Adhesion
Rinker and Kline
NACA - PB106026 (OTS)

The article explains some of the background concerned in the field of adhesion.

Adhesives Handbook Part I - Engineering Principles
NAVORD Report 2272
PB120812 (OTS)

This book covers the testing procedures and the design parameters for preparing adhesive joints for testing purposes.

Adhesives Handbook Part II - Engineering Data
NAVORD Report 2273
PB120813 (OTS)

This report is a compendium of typical data and information on proprietary adhesives and has listed some specific application involving various adhesive-adherent systems.

Adhesives
Coss, W. E. and Zavist, A. F.
G.E. R53SL107

A list of various commercial adhesives and some of the principles of adhesion are given.

Adhesion and Adhesives
DeBruyne, N.A. and Houwink, R.
Elsevier Publishing Co., N. Y. 1951

The book contains a good general coverage of the field of adhesion from a practical as well as a theoretical viewpoint. It also contains several hundred references prior to 1951.

Adhesion and Adhesives
Clark, Rutzler, Savage Editors
John Wiley and Sons, N. Y., 1954

The papers collected in this volume are from a symposium held in 1952. There are 14 articles on the fundamentals and 30 on various practical applications and testing methods of adhesives.

The Technology of Adhesives
Delmonte, J.
Reinhold Publishing Corp., N. Y., 1947

The practical aspects of synthetic and natural adhesives are treated. Numerous references to patents and production methods are given.

The Friction and Lubrication of Solids
Bowden and Tabor
Clarendon Press, Oxford (1954)

A comprehensive treatment of the lubrication field is given and some of the theoretical aspects are reviewed by the authors, who are two of the foremost authorities from a theoretical viewpoint.

The Physical Chemistry of Surface Films
Harkins, W. D.
Reinhold Publishing Corp., N. Y. (1952)

The general field of interface properties are covered mainly from the 700 publications of W. D. Harkins. The abhesive and adhesive nature of surfaces are treated from a theoretical viewpoint.

Colloid Science
McBain, J. W.
D. C. Heath and Co., Boston, (1950)

A general book on the nature of surfaces from a study of colloidal properties.

Colloid Chemistry
Hartman, R. J.

Another general book with chapters on adsorption and monomolecular films, which information is useful in adhesion and abhesive studies.

Surface Chemistry for Industrial Research
Bikerman, J. J.
Academic Press Inc., N. Y. (1948)

A good book on the general subject of surface properties. It includes extensive methods for investigating the surface chemistry of liquids and solids.

The Physics and Chemistry of Surfaces
Adam, N. K.
Oxford University Press, London (1941)

This book is a good general text of the entire field of surface properties and their measurement.

Articles

Adhesion

The Reaction of Organic Resins with Surface Films on Aluminum
Murphy, J. F. and Page H. A.
Paper 4

The degree of chemical interaction (adsorption) is correlated with the strength of adhesive joint formation.

Polymeric Adhesives for Glass
Moser, F.
Plastic Technology 2, 799-803, 5 (1956)

The adhesive strength of numerous organic resins is obtained for glass and compared to the wettability of the surface.

Adhesive Bonding of Metals
Muchnick, S. N.
Mechanical Engineering, 78, 19-22 (1956)

The strengths of adhesive-bonded metal joints are made to approach the cohesive strength of the bonding agent when the metal surfaces are treated properly.

Adhesive Bonding Properties of Various Metals as Affected by Chemical and Anodizing Treatments of the Surfaces
Eickner, H. W.
U. S. Dept. of Agriculture, Forest Service, Forest Products Lab.
Report 1842 (1954)

The metals under discussion are magnesium, aluminum, steel and titanium.

Comparative Strengths of Some Adhesive-Adherend Systems
DeLolles, et al.
PB97148

Adhesive strengths of couples of steel, aluminum alloys, paper, rubber, wood and glass were determined with polyvinyl acetate, neoprene, cellulose nitrate, and several natural resins.

Survey of Adhesives and Adhesion
Rinker and Kline
NACA (1945)

The survey includes 20 pages of references to articles on adhesion prior to 1945.

Development of Room Temperature-Curing Structural Adhesives for Metals
Bjorkston, Lappala, Yaeger, and Roth
WADC - PB111764

One of the formulation made by this group had good pot life and gave a fairly high strength bond.

Investigation of Adhesives: Metal to Metal Bonding
Furrer, J. F. and Merlark, W. A.
Army Chemical Center, Md. PB111445 (OTS) (1953)

An adhesive was found which was equal to or better than a solder joint for a bomb-fin assembly.

The Adhesion of Various Materials to Copper Oxide Surfaces
Finholt, R. W. and Hurd, D. T.
G.E. RL559 (1951)

An anodized surface treatment of copper increases the adhesive strength of copper with a vanity of adhesives.

Room Temperature Curing Metal-to-Metal Adhesives
Smith, A. E., Elliott, P. M., and Robinson, H. W.
AF Tech. Report 6514, PB108755

Numerous formulations were tested for the strength of adhesive joints formed.

The Bonding of Metal Foils to Plastics for Use in Printed Circuits
Mansfield, H. G. and Robertson, J. M.
PB104455

Directions are given for forming the bond between copper and the plastic base.

Dissimilar Material Bonding with Certain Adhesives
Brandon, R. E.
G.E. R51GL89

The epoxy resins were found to be the superior material considering cost and physical factors.

Abhesion

The Spreading of Liquids on Low Energy Surfaces

I. Polytetrafluorethylene
Zisman, W. A. and Fox, H. W.
J. Colloid Science 5, 514 (1950)

II. Modified Tetrafluorethylene Polymers
Zisman, W. A. and Fox, H. W.
J. Colloid Science, 7, 109 (1952)

III. Hydrocarbon Surfaces
Zisman, W. A. and Fox, H. W.
J. Colloid Science 7, 482 (1952)

IV. Monolayer Coatings on Platinum
Zisman, W. A. and Shafrin, E. G.
J. Colloid Science 7, 166 (1952)

V. Perfluorodecanoic Acid Monolayers
Zisman, W. A. and Schulnan, F.
J. Colloid Science 7, 465 (1952)

VI. Branched Chains, Aromatic Surfaces and Thin Liquid Films
Zisman, W. A. and Fox, H. W.
J. Colloid Science 8, 194 (1953)

This series of papers covers quite completely most of the basic work in abhesive surfaces.

Fundamental Studies of the Adhesion of Ice to Solids
Berghausen, P. E.; Good, R. J.; Kraus, G.; Podolsky, B.; Soller, W.
WADC Report 55-44, PB121047

A theoretical and experimental treatment of the chemical interaction of water with adhesive and abhesive surfaces.

Heats of Immersional Wetting of Rutile and Graphon in Organic Liquids
Healey, F. H.; Chessick, J. J.; and Zettlemoyer, A. C.
J. Physical Chemistry 58, 887 (1954)

Thermochemistry is applied to adhesive and abhesive surfaces.

Competitive Adsorption from Solution between Hydrophilic and Hydrophobic Molecules and Ions
Zisman, W. A., and Shafrin, E. G.
J. Colloid Science 4, 571 (1949)

Adhesion and Adhesives
DeBruyne, N. A. and Houwink, R
Elsevier Publishing Co., N. Y. (1951)

The book contains a good general coverage of the field of adhesion from a practical as well as a theoretical viewpoint. It also contains several hundred references prior to 1951.

Lubrication

A Study of Boundary Lubricant Films by Electron Diffraction
Menter, J. W.
Physics of Lubrication, British Journal of Applied Physics, Suppl. 1, 52-4 (1951)

Lubrication occurs only when the lubricant is present as a solid film of oriented molecules.

Fundamental Studies of the Combination of Bearing Metals
Migagana, Y, and Soda, N.
Report of Inst. of Science and Technology, Univ. of Tokyo, 2, 23-30 (1948)

Couples of copper, nickel and soft iron were investigated when aliphatic acids were used as lubricants.

Graphite Lubrication
Savage, R. H.
J. Applied Physics, 19, 1-10 (1948)

Graphite, although it has the laminar lubricating structure, must also have an adsorbed film of a material like water to be truly lubricating.

Adsorption and Lubrication at Crystal Surfaces
Hutchinson, E. H.
Transactions of the Faraday Society, 43, 443 (1947)

The heats of immersion and adsorption on a crystalline material, sodium fluoride, are given for some aliphatic lubricating materials.

The Adsorption of Long Chain Polar Compounds from Solution on Metal Surface
Greenhill, E. B.
Trans, Faraday Society, 45, 625 (1949)

The adsorption of aliphatic compounds on various metal surfaces are correlated with lubricant properties.

The Lubrication of Metal Surfaces by Mono and Multi-Molecular Layers
Greenhill, E. G.
Trans. Faraday Society, 45, 631 (1949)

The temperature dependence of lubricating films was determined.

Physical and Chemical Adsorption of Long Chain Compounds on Metals
Bowden, E. P. and Moore, A. C.
Research (London), 2, 585 (1949), Chemical Abstracts, 44, 3766c.

Adsorption was studied by radioactive techniques on zinc, cadmium, copper, platinum, and gold metal surfaces.

Metallic Friction and Lubrication by Laminar Solids
Koenigsberg, E., and Johnson, V. R.
Mechanical Engineering, 77, 141 (1955)

This is a review of current theories.

ASTM Tests

Cleavage Strength of Metal-to-Metal Adhesives
ASTM Standards, Part 7, p. 1156 (1956)
D1062-51

Standard shape metal pieces are tested. It is especially good for comparing metal pretreatments.

Strength of Adhesives on Flexural Loading
ASTM Standards, Part 7, p. 1195 (1956)
D1184-55

This test is best for laminated structures and those adhesives which are non-rigid.

Strength Properties of Adhesives in Shear by Compression Loading
ASTM Standards, Part 7, p. 1203 (1956)
D905-49

This method is primarily designed for evaluating adhesives for wood.

Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)
ASTM Standards, Part 7, p. 1207 (1956)
D1002-53T

This is for comparative shear strengths on metal joints.

Tensile Properties of Adhesives
ASTM Standards, Part 7, p. 1215 (1956)
D897-49

This test is for standard shape specimens and defined pretreatment and temperature.

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TITLE
Surface Chemistry of Adhesion, Abhesion and Lubrication

ABSTRACT
This report discusses the dependence of adhesion, abhesion, and lubrication on the surface properties and the chemical interactions of adsorbing molecules on solid substrates. Some of the more recent literature has been surveyed in order to determine the status of knowledge in these fields and to determine what experimental techniques are available to study these phenomena. Annotated bibliography— appended

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CONCLUSIONS
Properly designed laboratory investigations can assist materially in the solution of practical problems of adhesion, abhesion, and lubrication. In these three fields surfaces and interfaces may be characterized by certain experimental techniques. Available experimental measurements applicable to many interface problems include:

1. The extent of adsorption of liquids and gases on solids.

2. The work of adhesion of liquids to solids.

3. The energy of adsorption or wetting as determined by calorimetric methods.

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