

Adherend Surface Preparation

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The importance of surface preparation of metals, to increase the strengths of adhesive joints made with them, is shown in Table I, by Muchnick.¹ Aluminum, stainless steel, and titanium sheets, as received, made significantly weaker joints with a vinyl-phenolic adhesive than did the same metals after being treated. Similar results were found with other adhesives.

All the treatments referred to in the table included degreasing with trichloroethylene. Treatments *A* and *B* were sulfuric acid-sodium chromate baths followed by washing in distilled water; treatment *C* included detergent washing followed by immersion in chromic oxide solution. These treatments were arrived at after considerable experimentation through which it was found that chromium ions were required for maximum joint strength with Al and Mg. With stainless steel and titanium, almost equal joint strengths were obtained with detergent treatments as with acid chromate.

Incidentally, the joints in Table I were of the single lap, tensile shear type. The best of them failed when the metal stretched and bent away from the adhesive. The adhesive bonds were as strong as the thin metal sheets.

Dannenberg,² in his paper on the blister method of measuring adhesion, also showed the effect of method of preparation on joint strength in stainless steel coated with Epon XA 200 (see Table II).

The superiority of sand blasting and sulfuric acid etching over the other treatments is attributed by Dannenberg to their more thorough removal of organic contamination. Similarly Muchnick noted that the treatments that gave maximum strength also permitted water droplets to spread or form very low contact angles on the metals. This is shown in Table I, where the strongest joints for each metal resulted from treatment that gave contact angles with water of 10 degrees or less. There is no doubt that mill oils and other organic contamination must be removed if maximum bond strength is to be

achieved. Even oils deposited by fingerprints can sometimes lower joint strength.

The last step in chemical treatments of metals for adhesive bonding usually is the removal of rinse water by drying. Complete removal of water from metals usually is not attained because the heats do not impart enough thermal energy to the adsorbed water molecules to vaporize them. Some idea of the adhesion energies of sorbed water on a metal oxide, is provided by the heats of immersion studies of Harkins and Boyd,³ from which Table III was taken.

Our experience with quartz⁴ confirms the presence of several adsorbed layers of water molecules in usual ambient conditions. A powdered quartz, with a surface area of 22 m.²/g., was equilibrated in air at 25°C. and 80% relative humidity. It was then transferred to a combustion furnace where it could be heated while dry nitrogen was sweeping out the liberated water vapor. The water was collected in an absorption cell which was weighed at intervals as heating proceeded. Thus it was found that on heating to 100°C., the equivalent of 2½ molecular layers of water was driven from the powder surface. Another layer had evaporated by the time the temperature reached 280°C.; the last layer required a temperature of over 1000°C. to completely remove it. Figure 1 shows the data from three such experiments. Some idea of the binding energies exerted by the quartz on the adsorbed water films can be gained from the temperatures to which the rock must be heated to drive off the water films.

If the adhesive is nonpolar and cannot dissolve the adsorbed water, the water can enter into the formation of hydrated oxides and carbonates on a metal surface. Furthermore, it can present a barrier to bonding. This was demonstrated at The Franklin Institute in a study of the bonding of asphalts to rocks. If the mineral surfaces were heated to over 300°F. before being coated with asphalt, the resulting coating could not be stripped

TABLE I
Test Results with Adhesive-Bonded Metal Joints (Vinyl-Phenolic Structural Adhesive)

Expt. No.	Metal	Treatment No.	No. specimens	θ , Av.	Av. shear strength, psi
1	Aluminum	As received	6	67	2442
2	Aluminum	Degreased	6	67	2741
3	Aluminum	A	6	0	5173
4	Al. panels dried in oven	A	6	78	3621
5	Stainless steel	B	12	10	7056
6	Stainless steel	As received	12	50-70	5215
7	Stainless steel	Degreased	12	67	6306
8	Titanium	As received	12	50-75	1356
9	Titanium	Degreased	12	61-71	3180
10	Titanium	B	3	10	6743
11	Magnesium	C	12	0	3842

away with hot water. But if the rocks were cold when coated, the joint could be destroyed with water.⁴

The usual structural adhesives are more polar than asphalt, and their bond to metals is not unduly weakened by the mono- or bimolecular layer of water left when a metal is dried. This layer of water, however, is an avid collector of airborne oily contamination. We have observed that Al, Mg, Ti, and stainless steel, when treated by good chemical formulations, and 17-7 PH stainless steel when vapor blasted, showed very low or zero contact angles with water immediately after treating. On standing in shop air for one hour, the contact angle rose to 25-50° and after several hours, to even higher values. Yet joints prepared after

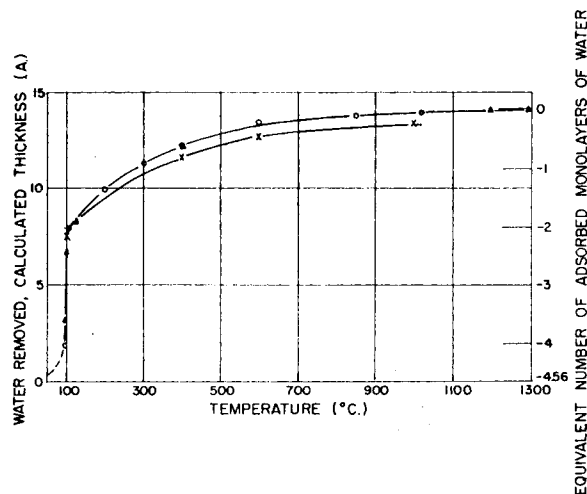


Fig. 1. Experimental data: (O) run No. 1, (▲) run No. 2, and (X) run No. 3.

TABLE II
Effect of Preparation of Stainless Steel

Method of preparation	Work of detachment, cm.-g./cm. ²
Vapor degreasing	113
Alkaline wash ^a	99
H ₂ SO ₄ etch ^a	436
HF brightness ^a	221
Sand blasting	659

^a This treatment was in addition to the treatments listed in Table II.

these exposures were not weaker than those bonded immediately after drying.⁵

The contact angle of a drop of water on a hydrophilic surface (1), containing hydrophobic particles (2), has been shown by Philippoff⁶ to vary as follows:

$$X = (1 - \cos \theta_M) / (1 - \cos \theta_2)$$

where X is the fraction of the total area occupied by (2), θ_2 is the contact angle to a complete film of (2) and θ_M is the contact angle to the composite surface. This relationship which was derived by Philippoff is illustrated in Figure 2 for a composite glass-Lucite surface. It suggests that after a metal surface is treated to be hydrophilic, and organics adsorb in patches on it, the contact angle may rise to 20° or more even when 90% of the surface area is free of contamination. It appears that suitable bonding can occur when so much of the metal is clean.

Since, however, a clean metal surface can become highly contaminated through several hours of exposure to shop air, a customary procedure is to prime the surfaces immediately after they are cleaned. If this is done and the parts are stored for any length of time before bonding, it may be necessary to wrap them in a moisture-proof barrier material, since water, if absorbed from humid air by the primer, can cause a lowering of subsequent joint strengths.

TABLE III
Energies of Adhesion at 25°C.

Liquid	Energy of Adhesion, ergs/cm. ²	
	TiO ₂	Graphite
H ₂ O	520	265
C ₂ H ₅ OH	500	250
C ₄ H ₇ OH	350	
C ₆ H ₆	150	225

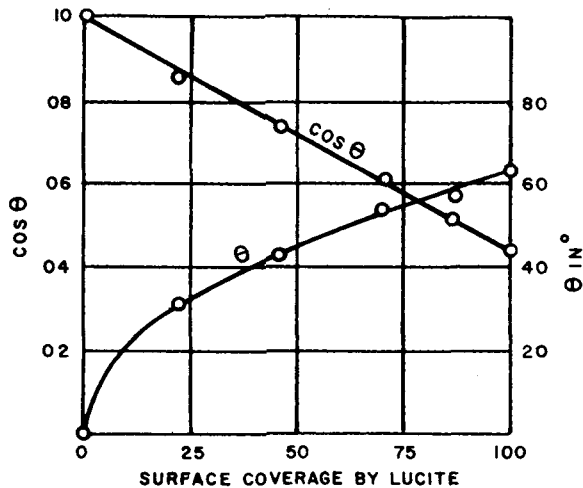


Fig. 2. Composite surfaces—contact angle and coverage (courtesy of *Mining Engineering*⁶).

While a metal surface is being rinsed, the combination of heat and moisture promotes the formation of oxides. Murphy and Page⁷ found with aluminum immersed in water that bayerite ($\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is formed at temperatures below 160°F., whereas boehmite ($\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is formed above this temperature.

After Alclad 2024-T3 aluminum alloy, 0.064 gage, was degreased and treated with acid chromate, specimens were rinsed for 10 min. at various temperatures, dried, and bonded in lap shear joints, with Shell Epon VIII adhesive. When tested in tension, strengths and types of breaks were as given in Table IV.

We also found⁵ better bond strength when rinsing temperatures for aluminum are kept around 155°F.

Austin and Brand⁸ coated steel, aluminum, and two magnesium alloys with a number of lacquers and varnishes, subjected them to accelerated weathering and mechanically stripped off the coatings. Both the stripped coating and the panels were then examined by electron diffraction. While there were some differences due to the various coating materials, weathering strikingly weakened

TABLE IV
Strengths and Types of Breaks

Rinse water temp., °F.	Bond strength, psi	Type of break
70	2850	50% cohesive
120	3100	75% cohesive
150	3400	100% cohesive
175	1750	100% adhesive
200	2500	95% adhesive

the joints, and most of the weathered joints when stripped parted cohesively within the oxides. In this work oxides formed on accelerated weathering much faster than they would in an adhesive joint, because the coatings were only 1 mil thick. Nevertheless, oxides must be dealt with in adhesive bonding.

In a paper by Perry, Chreitzberg, Silver and Matthews¹⁶ some cases of corrosion of metals by phenolics, rubbers, vinyls, halocarbons, cellulose, and polyester laminates were reported. They suggest that "the evaluation of the corrosivities of plastics and rubbers may be based on the following criteria: (1) The concentrations and conductances of ions existing within the material. (2) The permeability of the material to water and electrolytes. (3) The ability of the ions to form soluble salts at the anode." While corrosion of metal adherends by adhesives is not generally observed, it can happen, particularly under tropical conditions.

Now, to reverse the attack, it is known that at elevated temperatures in the presence of air, stainless steel will char certain adhesives, causing them to fail. Black and Blomquist⁹ exposed stainless steel and aluminum joints containing various adhesives to 550°F. in the presence of air for 50 and 100 hr. The phenolic-type resins in particular stood up reasonably well on aluminum but lost practically all their strength on stainless steel. On the other hand, a nylon-epoxy type and a butadiene-acrylonitrile type rich in butadiene survived very well.

The attack was attributed to solid phase oxidation-reduction reactions in the oxides on the steel surface, which permitted the iron atoms to catalyze the oxidation of the resins. When zinc and cerium naphthenates were applied to the steel surface before bonding, shear strengths of the FPL-878 adhesive were much better retained during heat aging.

It appears from the foregoing instances that some metals might well be electroplated or otherwise treated to mitigate the formation of oxides or the attack of metal ions on an adhesive. In connection with this sort of thinking, some ideas regarding the mechanisms of adhesion may be pertinent. In an earlier paper⁵ the author discussed the possibility that a somewhat polar adhesive adheres to stainless steel and titanium by interaction of its excess electrons with the incomplete d -shells in these transition elements. In his study of electrical charge transfer in adhesion, Skinner¹⁰

discussed the contributions of electrical charge transfer to tensile strengths of bonds. Charge densities of 10^{21} electrons/cm.² of adhesive interface are thought possible; from classical electrostatic theory they could contribute as much as 600 psi to the tensile strength of the joint. If this strength factor is to be gained, however, the adhesive and the metal must be matched so that the gap between their electronic potentials is small.

Other guide lines for the selection of finishes on adherends can be seen in the work of Taylor and Rutzler.¹¹ They made molecular models of polymers, and tried to fit them onto scale drawings of Ti and Fe metal surfaces, and Ti-O-Fe-O and Fe₂O₃. They found that a large proportion of the presumed active groups in a polymer molecule could not be brought close enough to the active sites in the adherend and that much potential bond strength is lost because of this uncongeniality. They suggest that the role of TiO₂ formed on aluminum or steel adherends, to promote adhesion to polyethylene, may be to supply many more active sites. The paper contains much other information of a similar nature.

The same investigators¹² studied the effects of primary and secondary roughness of an adherend, and in general found lower tensile values with the rougher substrates. They point out that a polymer's molecules must conform to a surface if it is to bond well, and this is hindered by roughnesses of a molecular order. They also noted striking gains in the strength of adhesion of polyethylene to a cold-rolled steel and a stainless steel, after they had been oxidized in hot air (310°C.) for 15 min. They believe that the cause of this gain is the reduction of primary roughness resulting from converting the surface to an oxide layer.

In connection with the formation of surfaces with a low order of roughness, the discussion in Adamson¹³ of the Beilby layer is of interest. It is pointed out that polishing (with a soft material), unlike grinding (abrasive material) or electro-polishing, may convert a crystalline surface into an amorphous one. Examples cited included gold and nickel. The amorphous layer is unstable and on aging or heating tends to revert. What effect this will have on the matching of polymer molecules to the metal, and on subsequent stability of bond, is an interesting question.

Surface roughness from another point of view is discussed by de Bruyne.¹⁴ Using Cassie's equation,¹⁵ he calculated from the contact angles of water drops on smooth and mat polyethylene

sheets the per cent of air trapped under the water drops on the mat surface. It was 53%. He then made joints of the mat polyethylene with an epoxy resin by (a) merely coating the polyethylene, (b) rubbing the resin into it, and (c) applying the resin to the polyethylene at 2 mm. atmospheric pressure. Mean joint strengths were 92, 140, and 240 lb.

While this appears to be an extreme case of air entrapment, enhanced by poor wetting, at least the resin was reasonably fluid. With structural adhesives in the form of solid films, one wonders how much air is trapped, and whether it all will dissolve in the resin and/or escape during hot pressing of the assembly.

De Bruyne also discusses the shape of pits in the adherend, and their capability of being filled by adhesive flow. He points out, among other things, the effect of the angle of slope of the pore wall, ϕ , in conical pits. He states that when the liquid contact angle, θ , plus the slope angle, ϕ , add up to less than 180°, the liquid pressure will be negative, and it will not penetrate the pit (unless forced to by external pressure).

One other point regarding surface roughness needs to be brought out. At Wright Air Development Center a mild, nonetching treatment for stainless steel was developed that gave about as good joint strengths as a very concentrated acid etching bath. However the peel strengths with the mild treat were only about one-third as good as for the etching treat. De Bruyne reports that when a pickled Alclad sheet is used, cohesion failure occurs in the glue and the peel strength is at least 10 times greater than with unpickled sheet. He provides a theory for this, which leads one to the conclusion that for peel strength in adhesive joints made from thin metals, the metal had better be somewhat rough.

The phenomena of syneresis, diffusion, or porosity in connection with structural adhesive joints were not discussed because they are more important with nonmetallic adherends, such as resin-bound powders or fibers, plastic sheets, or paper or leather products.

It is concluded that with metal adherends, proper surface preparation and quality control is likely to be necessary to: (a) remove oil, dirt, and dust; (b) control adsorbed water; (c) control oxide formation or get favorable oxides; (d) deposit chromium atoms or TiO₂ to promote adhesion; (e) poison iron or other surface atoms which catalyze polymer breakdown; (f) protect the adherend from

the adhesive and vice versa; (g) match the adherend crystal structure to the adhesive molecular structure; and (h) control surface roughness.

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Synopsis

If an adhesive joint is to be strong and permanent its adherend surfaces must be treated at least to remove oil, dirt, and dust. In addition, control of surface roughness, oxide formations, and sometimes adsorbed water is required. Deposition of chromium atoms or TiO_2 is indicated for electron donor metals surfaces, and treatments may be useful to protect the adhesive from the adherend or vice versa, or to make their structures more congenial.

Résumé

Si un joint adhésif doit être fort et permanent, ses surfaces adhérentes doivent être traitées au moins pour en retirer l'huile, la crasse et la poussière. De plus, il est nécessaire de contrôler la rugosité des surfaces, la formation d'oxyde et parfois l'adsorption d'eau. Un dépôt d'atome de chrome ou de TiO_2 est indiqué pour des surfaces métalliques donneuses d'électrons et il peut être utile d'effectuer des traitements pour protéger le joint adhésif des surfaces adhérentes ou inversement, ou de rendre leurs structures plus appropriées.

Zusammenfassung

Zur Erreichung einer festen und dauerhaften Klebeverbindung müssen die zu verklebenden Oberflächen wenigstens von Öl, Schmutz und Staub befreit werden. Zusätzlich ist eine Kontrolle der Oberflächenrauigkeit, Oxydbildung und manchmal der Wasseradsorption erforderlich. Für Elektronendonormetalloberflächen ist eine Abscheidung von Chromatomen oder TiO_2 angezeigt und Behandlungsverfahren zum Schutze der adhärenierenden Stoffe gegeneinander oder zur besseren Angleichung ihrer Struktur aneinander können sich als nützlich erweisen.