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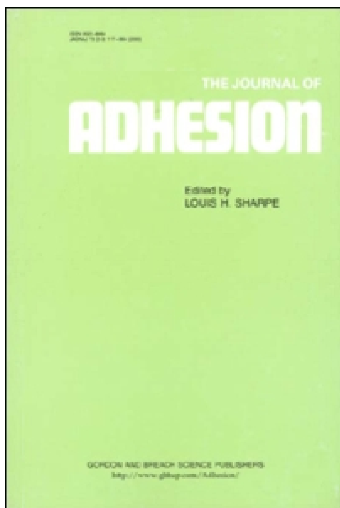

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Surface Preparation of Copper and Its Alloys for Adhesive Bonding and Organic Coatings

H. N. Vazirani[a]
[a] Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

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Note

Surface Preparation of Copper and Its Alloys for Adhesive Bonding and Organic Coatings

H. N. VAZIRANI, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974*

(Received April 10, 1969)

Two new surface treatments for copper are described, one based on oxidation with alkaline permanganate and the other on electrodeposition of chromium oxide from alkaline chromate bath. The nature and thickness of generated surface layers are discussed on the basis of scanning electron microscope, X-ray fluorescence, atomic absorption and electrolytic reduction results. Data on initial strengths and durability of joints made with different alloys and adhesives are given. It is shown that selective etching of zinc from low copper alloys, before surface treatment, improves initial joint strength and durability.

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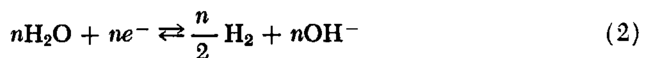
INTRODUCTION

There are numerous applications for bonding or coating of copper and its alloys. It is generally known to the people in the field that surface treatment before bonding or coating improves the initial strength and durability of the joints. Surface preparation is usually carried out in two steps. The first step is usually to remove oils and corrosion products, usually oxides. This first step usually leaves the surface of the metal very active and hence subject to corrosion. Corrosion, in general, is the loss of electrons by the metals in the presence of water by an electrochemical reaction consisting of anodic (1) and cathodic (2) processes.

$$M + xH_2O \rightleftarrows M^{n+}\ (xH_2O) + ne^- \quad (1)$$



$$nH_2O + ne^- \rightleftarrows \frac{n}{2} H_2 + nOH^- \quad (2)$$

Because of the unstable nature of the surface after the first step, it is necessary to generate or deposit a surface layer, usually oxide, which is uniform, non-porous and mechanically sound.

Oxide nuclei, as has been shown by Benard and Grouland [1], grow along the surface more rapidly than into the bulk until the oxide uniformly covers the entire surface. The growth of this thin film of an oxide is controlled in most cases by electron transfer from the metal to the oxide. Initial growth of the nucleus takes place relatively easily due to ease of transfer of electrons from the metal to the oxide as a result of the quantum mechanical tunnel effect described by Mott [2].

At the present time, two surface treatments commonly followed for preparing copper and its alloys for adhesion bonding are either vapor degreasing or solvent wiping alone or followed by oxidizing with Ebonol C, a proprietary material from

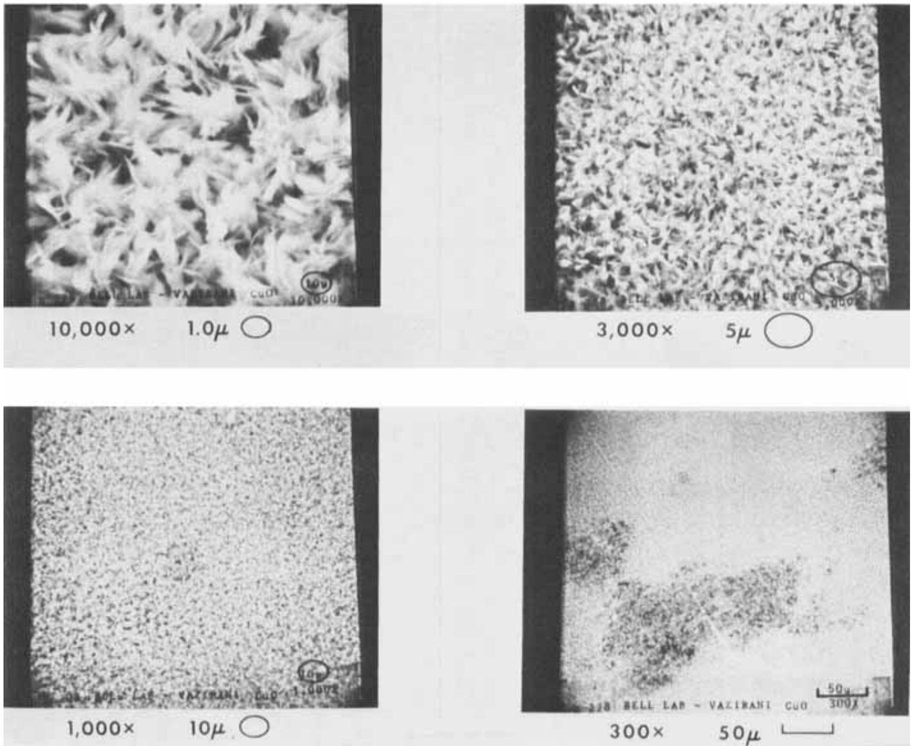


Figure 1. Scanning electron micrographs of Ebonol C treated copper at different magnifications.

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Enthone, Inc. The thickness of the oxide produced by this treatment is ~ 3,500 Å in three minutes and increases to ~ 11,000 Å in twenty minutes [3]. The thickness of the oxide produced varies with different alloys of copper. The total amount of oxide in terms of cuprous and cupric oxides is determined by a modified electrolytic method of Campbell and Thomas [4]. Figure 1 shows the scanning electron micrographs of copper which has been treated for three minutes in Ebonol C. As can be seen, the oxide is quite porous and a few microns thick, which is about 3-4 times the thickness of oxide as determined by the electrolytic reduction method. Production of thick oxide is only possible because of the solubility of oxidation products in the electrolyte and hence the porosity. Because of high surface area and porous structure of the surface layer, fairly high joint strengths are obtained under peel stress but not under shear stress, especially with structural adhesives. Other limitations of this method are that it should not be used for treating thin films of copper because of high relative dimensional change due to etching, and it should not be used on low copper alloys because it is not as effective.

Keeping the above limitations in mind, a study was carried out to find an oxidizing solution which would not corrode copper to any great extent but which would generate a thin, continuous, mechanically strong film of oxides ~ 500-1000 Å thick. Alkaline potassium permanganate was the first choice and it was tried.

It is shown in the results that there is a serious limitation for surface treatments which generate a copper oxide surface layer, when adhesive systems that are corrosive to copper are used. To overcome the problem of corrosion, a treatment that deposits a corrosion resistant film was tried.

EXPERIMENTAL

Unfortunately, the only way to evaluate different surface treatments is to make joints and to evaluate joint performance by mechanical means. Joint performance is dependent on, besides surface treatment of the adherends, the geometry of the joint, mechanical responses of the adhesive and adherends, rate of stress, rate of strain, temperature and some unknown factors. Therefore, it is absolutely necessary to run parallel tests of performance under the same conditions. Joints were tested for tensile shear [5] and T-peel strengths [6]. More importantly, joints were tested for durability by determining their time to failure when subjected to different levels of static stress in a moderately elevated temperature, high humidity environment. The time to failure is plotted against the stress level on a semilog graph. This graph can usually be extrapolated with fair accuracy. Joint strengths, nature of test, and substrate (its thickness and surface treatment) are given in the tables. In general, four treatments were evaluated.

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1. Vapor degrease with perchloroethylene.
2. Vapor degrease, acid etch in a mixture of conc.H_3PO_4: conc.HNO_3:H_2O:: 75:10:15 for about ½ minute, rinse, immerse in 18% Ebonol C for three minutes at 95°C and rinse with deionized water.
3. Vapor degrease, acid etch, rinse, immersion in an aqueous solution of 1% (by wt.) $KMnO_4$, 1% (by wt.) NaOH at 95°C for five minutes, rinse with deionized water.
4. Vapor degrease, acid etch, rinse, immerse as a cathode in a solution of 3% (by wt.) each of sodium chromate, carbonate and citrate and electrolyze at a current density of 20 amps./sq. ft. (~ 4 volts), for ½ minute using stainless steel as an anode, and rinse with deionized water. Current density can be varied within a range of 10-50 amps./sq. ft. (~ 3-6 volts). The time required for the surface treatment is short and self-limiting and therefore there is no upper limit as far as time is concerned.

Experimental joints:
Substrates used:

1. 0.032″ soft copper
2. 0.063″ half hard copper

3. 0.063″ soft red brass (85% Cu, 15% Zn)
4. 0.063″ cartridge brass (70% Cu, 30% Zn)
5. 0.063″ Muntz metal (60% Cu, 40% Zn)
6. 0.063″ nickel silver (65% Cu, 18% Ni, 17% Zn)

Adhesives used:

1. EC 2216: Two-part epoxy, room temperature cured. (3M Co.)
2. EC 2214: One-part epoxy, cured at 250°F for 40 minutes. (3M Co.)
3. EC 2186: One-part epoxy, cured at 350° for 1½ hrs. (3M Co.)
4. Epon 828: Epoxy resin (Shell), Curing Agent A (7 pbw) (diethylamino propylamine)
5. Plastilock 601 nitrile-phenolic tape, cured at 375°F for ½ hr. under 200 psi (B. F. Goodrich).
6. 3% and 7.5% acrylic acid-ethylene copolymer (Dow Chemical, Zetabond)
7. Surlyn 1650 (duPont's ionomer).

Chemicals used:

All chemicals used were reagent grade. Sodium chromate, sodium hydroxide and sodium carbonate were products of Allied Chemical, Morristown, New Jersey. Potassium permanganate and sodium citrate were products of J. T. Baker Chemical Co., Phillipsburg, N. J.

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RESULTS AND DISCUSSION

Alkaline permanganate was found to be an effective surface treatment for copper and its alloys. The solution is effective over a wide range of concentrations of sodium hydroxide and potassium permanganate and temperature. The thickness of the oxides generated depends on the concentration, time and temperature. An effective and economical solution is aqueous 1% (by wt.) sodium hydroxide and 1% (by wt.) potassium permanganate. The treatment is carried out at ~ 95°C for about five minutes. The thickness of oxide produced is ~ 500-700 Å. The advantage of this method of oxidation is that the oxide produced is essentially uniform, non-porous and self-limiting in thickness. Figure 2 shows scanning electron micrographs of the oxide. Comparing these pictures with those of polished copper, Fig. 3, it can be estimated that the oxide is indeed ~ 500 Å thick.

The relationship of thickness and nature of oxide with time, temperature and concentration for the alkaline permanganate surface treatment is shown in Table 1.

Adhesives which corrode copper affect the life of the joints. Some such systems are RTV silicones that give off acetic acid during vulcanization (Fig. 4), ethylene-acrylic acid copolymers and certain curing agents for epoxies. Ethylene-acrylic acid copolymers, under certain conditions, actually form a copper salt. The copper salt can be characterized by etching the copper from the joint with ammonium persulphate and running differential infrared spectroscopy on the polymer.

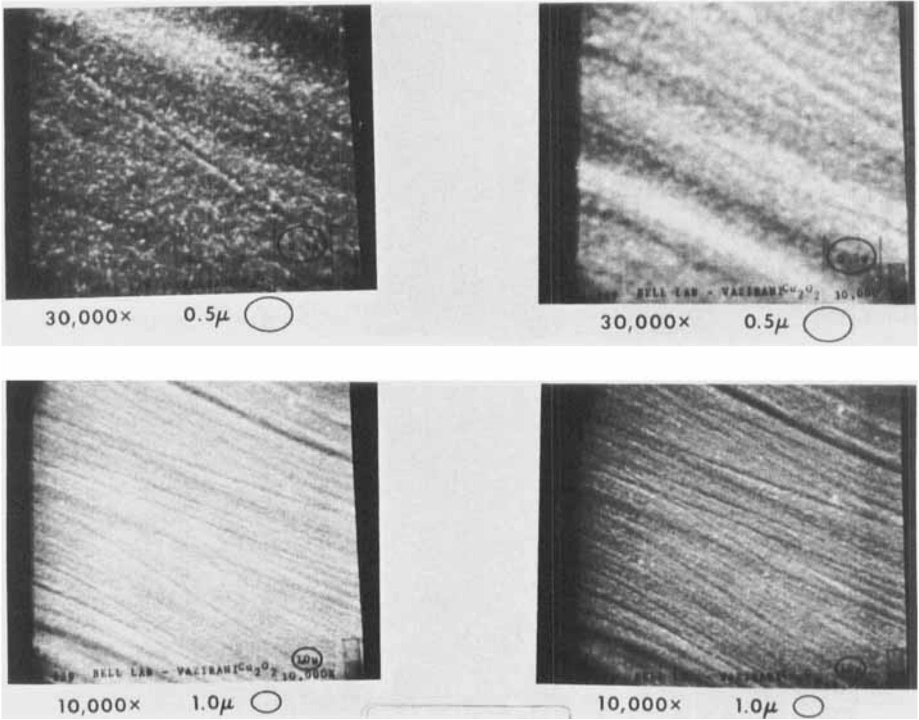

Figure 2. Scanning electron micrographs of alkaline $KMnO_4$ treated copper.

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Table 1. Thickness of Oxides as Determined by Reduction

Time, Min.	$KMnO_4$%	NaOH%	Cu_2O Å	CuO Å
		Solution at 77°F		
0	—	—	50	—
10	5	5	130	130
		Solution at 180°F		
5	1	1	140	110
10	1	1	140	160
3	10	10	240	410
6	10	10	250	540
		Solution at 200°F		
5	1	1	220	240
10	1	1	310	490

POLISHED COPPER

10,000× 1.0μ ○ | 3,000× 5μ ○

1,000× 10μ ○ | 300× 50μ

Figure 3. Scanning electron micrographs of polished copper.

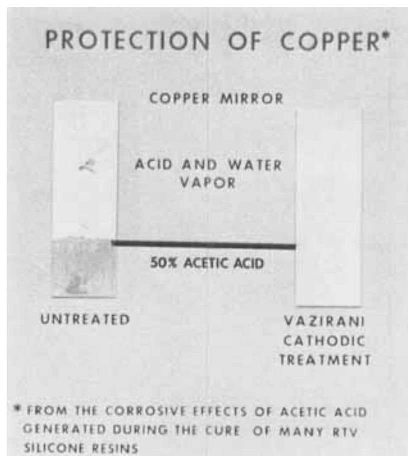

Figure 4. Corrosion of copper due to acetic acid. A simulation of conditions when acetic acid evolving RTV silicone resins are used in copper assembly.

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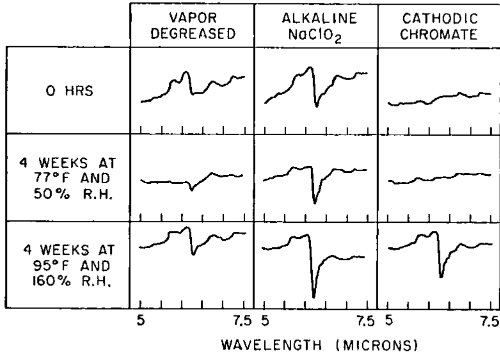

Figure 5. Differential infrared spectra showing the absorption at ~6.25 microns of a copper salt of EAA copolymer. The films of polymer were obtained by dissolving the copper with ammonium persulphate solution, from joints conditioned at different temperatures and relative humidity.

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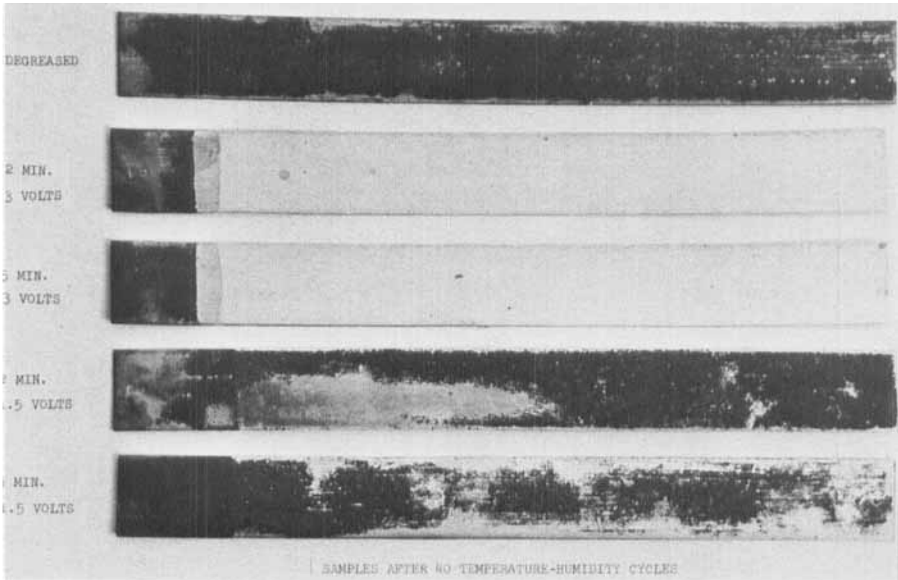

Figure 6. Corrosion resistance of cathodic chromate treatment due to high humidity and elevated temperatures (40 AT&T Cycles).
Top to bottom
1. **Degreased copper**
2. **Two minutes at 10 amps/sq. ft.**
3. **Five minutes at 10 amps/sq. ft.**
4. **Two minutes at 1 amp/sq. ft.**
5. **Five minutes at 1 amp/sq. ft.**

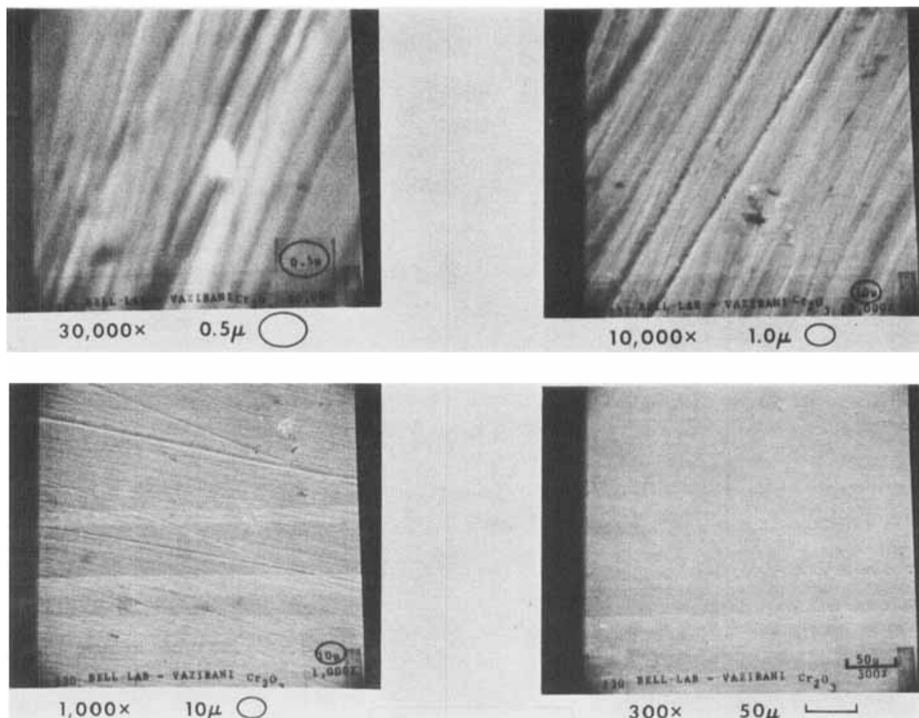

Figure 7. Scanning electron micrographs of cathodic chromate treated copper.

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Figure 5 shows infrared spectra of ethylene-3% acrylic acid copolymer which was bonded to copper.

To overcome the problem of corrosion, a novel process was developed in which the copper is made cathodic in an aqueous solution of sodium chromate, carbonate and citrate. This deposits a very thin continuous layer of chromium oxide. Kolthoff and Shams El Din [7] carried out reduction of hexavalent chromium on a platinum electrode and found a monomolecular film of Cr^{+3} which prevented further reduction of Cr^{+6}. The film formed was insoluble in HNO_3 up to 5*N* and HCl up to 1*N*. They also suggested that deficiency in hydrogen ions is a favorable condition for film formation. X-ray fluorescence and atomic absorption analysis suggest that chromium is present to the extent of ~ 1.0 microgram per sq. cm. of nominal surface area. This corresponds to a film about 25 Å thick. This film is resistant to corrosion (Fig. 4-6). For any coating to be resistant to corrosion, it has to be continuous and non-porous. Scanning electron micrographs are given in Fig. 7. Resolution of the SEM is ~ 100 Å and therefore the pictures do not look any different from the pictures of untreated copper. The photographs show that nothing thicker than 100 Å is deposited. This is evidence that the film is probably fairly continuous.

The concentration of $KMnO_4$ is not as critical as the concentration of NaOH (Table 2). About 1% by wt. NaOH seems to give stronger joints than the higher concentrations. The last column gives the percent elongation in the assembly before it fails. The joint strength, as tested, would have been considerably higher, depending on the percent yield, if the yield did not take place.

Table 3 shows that the alkaline $KMnO_4$ treatment gives higher initial joint strengths. More importantly, the reliability of these joints is much greater as is evidenced by the lower standard deviation in joint strengths obtained from alkaline permanganate treated copper.

The effectiveness of alkaline $KMnO_4$ treatment on beryllium copper as evidenced by initial joint strengths and lower standard deviation is shown in Table 4.

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Table 2. Effect of Solution Composition on Initial Joint Strengths (0.063" Soft Red Brass Bonded with EC 2186)

No.	$KMnO_4$%	NaOH%	Av. Tensile Shear Strength[a] psi	% Elongation Before Joint Failure
1	1	1	3000	4.5
2	1	10	2910	3.9
3	5	1	2970	4.4
4	5	10	2740	3.0
5	10	1	2970	4.2
6	10	10	2790	3.2
Ebnol C			2870	3.6
Acid etch only			2870	3.6

[a] Average of six joints.
One half minute acid etch in 75:10:15::Conc.H_3PO_4:Conc.HNO_3:H_2O mixture was carried out prior to surface treatments.

Table 3. Alkaline Permanganate Compared to Ebanol C Treatment (0.063" Half-Hard Copper Bonded with EC 2214)

	Ebonol C	Alk. $KMnO_4$
Av. Tensile Shear Strength, T_S, psi	4840^{6a}	5360^{6}
Std. deviation, σ	195	67
C_V[b]	4.03	1.25
Time to Failure,[c] days	$>40^{d}$	$>45^{6}$

[a] Superscript denotes the number of joints tested.
[b] $C_V = \frac{\sigma}{T_s} \times 100$.
[c] Under static stress of 3,000 psi, conditioned at 95°F/90% R.H.
[d] One out of six joints failed. The test was discontinued after 45 days.

Table 4. Alkaline Permanganate Compared to Ebonol C Treatment (0.063" Beryllium Copper Bonded with EC 2186)

	Ebonol C	*Alk. $KMnO_4$*
Av. Tensile Shear Strength, psi	6680[a]	7010[a]
Std. Deviation	740	530
C_V	11.1	7.46
Time to Failure,[b] days	83[a]	109[a]

[a] Average of six joints.
[b] Under static stress of 4,000 psi, conditioned at 95°F/90% R.H.

Table 5. Effect of Various Treatments on Initial Joint Strength and Durability (0.063" Muntz Metal Bonded with Epon 828 and Curing Agent A)

	1[a]	2[b]	3[c]	4[d]
Av. Tensile Shear Strength, psi	1790	2480	2330	1900
Time to Failure,[e] days	2	>125[f]	>125[f]	>48[g]

[a] Vapor degreased.
[b] Vap. degr. + acid etch + cathodic chromate.
[c] Vap. degr. + acid etch + alk. $KMnO_4$.
[d] Vap. degr. + acid etch + Ebonol C.
[e] Conditioned at 95°F/90% R.H. under a static stress of 800 psi.
[f] Test discontinued after 125 days.
[g] Four out of six joints failed. Averages are for six specimens.

Table 6. Selective Alkali Etching of Zinc (0.063" Cartridge Brass Bonded with Plastilock 601 Tape)

	Ebonol C		*Alk. $KMnO_4$*		*Cathodic Chromate*	
	Acid Etch[c]	*Alk. Etch*[d]	*Acid Etch*	*Alk. Etch*	*Acid Etch*	*Alk. Etch*
Av. Tensile Shear Strength, psi	2220	2010	510	2120	2560	2800
Std. Deviation, σ	446	73	128	139	239	120
Time to Failure,[a] days	<1	<1	—	30	1	17
Time to Failure,[b] days	41	>180[e]	—	>180[e]	36	>180[e]

[a] Conditioned at 95°F/90% RH under static stress of 1,250 psi.
[b] Conditioned at 95°F/90% RH under static stress of 1,000 psi.
[c] Acid etch—one half minute in a mixture of conc.H_3PO_4:conc.HNO_3:H_2O::75:10:15.
[d] Alk. etch—five minutes in 10% by wt. aqueous solution of NaOH at 200°F.
[e] Test discontinued after 180 days.

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The suitability of the cathodic chromate surface treatment for bonding with epoxy resins is shown in Table 5. It is also evident from the table that durability of the joints, as tested, is higher for both alkaline permanganate and cathodic chromate treatments.

The initial strength and durability of joints is increased considerably when a zinc-containing, low copper alloy is first immersed in hot sodium hydroxide to selectively etch out the zinc. This selective etching of zinc enhances the effectiveness of the surface treatments (Tables 6-8).

Table 9 shows T-peel strength increasing with time. This is probably due to morphological changes in the polymer. This increase in joint strength with time was noticed throughout the work done with EAA. The table also shows the effectiveness of cathodic chromate treatment in improving joint strengths.

The superiority of the cathodic chromate surface treatment is shown again in Table 10. Cyclic temperature and humidity conditions of the AT&T Cycle are considered quite severe and it is quite often used as an accelerated method of testing the life of joints.

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Table 7. Selective Alkali Etching of Zinc (0.063" Cartridge Brass Bonded with EC 2186)

	Alk. $KMnO_4$	
	Acid Etch[b]	Alk. Etch[c]
Av. Tensile Shear Strength, psi	6370	6500
Std. Deviation	360	398
C_V	5.65	6.08
Time to Failure,[a] days	54	56

[a] Conditioned at 95%/90% RH under static stress of 4,000 psi. Average of six specimens tested.
[b] Acid etch—one half minute in a mixture of conc.H_3PO_4:conc.HNO_3:H_2O::75:10:15.
[c] Alk. etch—five minutes in 10% by wt. aqueous solution of NaOH at 200°F.

Table 8. Selective Alkali Etching of Zinc (0.063" Nickel Silver Bonded with EC 2214)

	1[a]	2[b]	3[c]	4[d]
Av. Tensile Shear Strength, psi	3580	4680	5420	5520
Std. Deviation	180	720	315	291
C_V	5.03	15.4	5.82	5.23
Time to Failure,[e] days	—	<1	31	42
Tibe to Failure,[f] days	<1	<1	42	97

[a] Vapor degrease.
[b] Vap. degr. + acid etch + cathodic chromate.
[c] Vap. degr. + alk. etch + cathodic chromate.
[d] Vap. degr. + alk. etch + alk. $KMnO_4$.
[e] Conditioned at 95°F/90% RH at static stress of 4,000 psi.
[f] Conditioned at 95°F/90% RH at static stress of 3,500 psi.

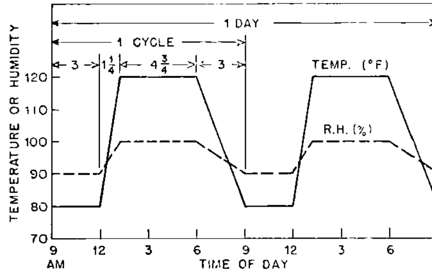

Figure 8. AT&T humidity and temperature cycle.

Table 9. T-Peel Strength as Function of Surface Treatment and Time after Bonding (0.032" Soft Copper Bonded with 7.5% EAA Copolymer)

T-Peel Strength, lb/in. width	*1*[a]	*2*[b]	*3*[c]
3 hrs. after bonding	2.2	9.3	14.4
24 hrs. after bonding	3.0	12.9	24.3
100 hrs. after bonding	14.0	17.5	28.0

[a] Vapor degrease.
[b] Vap. degr. + acid etch.
[c] Vap. degr. + acid etch + cathodic chromate.

Table 10. Effect of Surface Treatments and Conditioning on T-Peel Strength (0.032" Soft Copper Bonded with 7.5% EAA and Surlyn)

T-Peel Strength, lb/in. width	*1*[a]		*2*[b]		*3*[c]		*4*[d]	
	EAA	*Surlyn*	*EAA*	*Surlyn*	*EAA*	*Surlyn*	*EAA*	*Surlyn*
½ hr. after bonding	4.8	2.4	11.6	1.0	18.5	13.5	25.0	13.5
100 hrs. after bonding	7.4	5.0	22.5	15.0	22.0	12.0	32.0	11.4
100 hrs. at 160°F/95% RH	1.0	0.0	7.4	0.7	0.5	0.2	18.5	10.6
After 30 AT&T Cycles	0.7	1.7	14.0	0.3	9.0	2.7	29.5	10.8

[a] Vapor degreased.
[b] Vap. degr. + acid etch.
[c] Vap. degr. + acid etch + alk. $KMnO_4$.
[d] Vap. degr. + acid etch + cathodic chromate.

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That the cathodic chromate surface treatment is better than the commonly used methods of treatment for bonding EAA to copper is shown in Table 11.

CONCLUSIONS

Two new methods described in this paper have been shown to be superior to existing surface treatment methods for copper and several of its alloys. The following is a brief description.

Method 1: This is an immersion method. The immersion time is between 3-10 minutes and the concentration of potassium permanganate and sodium hydroxide form 1-10%. The temperature range of this treatment is also wide, from ~ 70°F to 210°F. Surface oxides are removed by ½ minute immersion in a mixture of conc.H_3PO_4:conc.HNO_3:H_2O::75:10:15 prior to immersion in alkaline permanganate. Selective etching in hot sodium hydroxide, in cases of low copper alloys, prior to surface treatment improves the bonds made with adhesives. A recommended procedure for surface treatment of copper and its alloys is the following:

1. Vapor degrease, if grossly oily.
2. ½ minute acid etch in conc.H_3PO_4:conc.HNO_3:H_2O::75:10:15.
3. Rinse with water.
4. Immerse in 20% NaOH at 200°F for five minutes (in case of low copper alloy).
5. Rinse.
6. Immerse in a solution of 1% each permanganate and sodium hydroxide at 200°F for five minutes.
7. Rinse.

Method 2: This is an electrochemical method. The alloy to be treated is made the cathode, using stainless steel as an anode, in a solution of 3% each sodium

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Table 11. Effect of Surface Treatments and Conditioning on T-Peel Strength (0.032" Soft Copper Bonded with 7.5% EAA)

T-Peel Strength, lb/in. width	1[a]	2[b]	3[c]	4[d]	5[e]
3 hrs. after bonding	15.5	15.0	15.0	9.5	34.5
24 hrs. after bonding	23.0	20.0	19.0	9.0	31.5
125 days after bonding	29.2	29.0	31.5	24.0	—
215 days after bonding	33.0	34.0	32.5	31.0	—
15 days at 160°F/95% RH	1.0	18.0	16.5	2.0	3.5

[a] Vap. degr. + acid etch + alkaline $KMnO_4$.
[b] Vap. degr. + acid etch + cathodic chromate, 10 amps/sq. ft.
[c] Vap. degr. + acid etch + cathodic chromate, 50 amps/sq. ft.
[d] Vap. degr. + acid etch + Ebonol C.
[e] Vap. degr. + acid etch + alk. $NaClO_2$.

chromate, citrate and carbonate, at a current density of 10-50 amps/sq. ft. A recommended procedure:

Steps 1-5 same as in method 1

6. Cathodic treatment for one minute at 10 amps/sq. ft. This method is particularly suitable when the adhesive is slightly corrosive to copper. This method can be designed for a continuous process.

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