

Durability of Bimetallic-Adhesive Laminate with Ethylene-Acid Copolymer Adhesives

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Synopsis

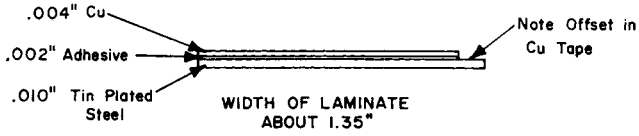
A broadband multicoaxial cable has been developed, based upon the use of ethylene copolymer thermoplastic adhesives to bond tin-plated steel to copper. The characteristics of the adhesive and the integrity of the bond formed between the dissimilar metals were of prime interest. The copolymers of ethylene examined as adhesives were ethylene-acrylic acid (EAA) and ethylene-methacrylic acid (EMAA). The influence of high humidity on the durability of bimetallic laminates of copper or aluminum with tin-plated steel and ethylene-acid copolymer adhesives has been studied. Infrared spectrometric and differential thermal analysis data had shown that a contributing cause to failure of bonds between EAA copolymers and copper is the solubilization of an underlying weak copper oxide layer under condition of the test. Electrolytic chromate-treated copper and immersion chromate-treated aluminum bonded to degreased tin-plated steel resulted in joints having comparable durability under stress and humid environments. These results reflect the durability of tin-tin bonded specimens. These materials engineering studies have shown that ethylene-acid copolymer adhesive, properly used and stabilized, can be employed with confidence in adhesive joints.

INTRODUCTION

Thermoplastic adhesive copolymers based upon an olefin and a carboxylic acid-containing monomer, such as an ethylene-acrylic acid copolymer (EAA), are being employed in new packaging concepts and in communication cable designs. In one application, the ethylene-acid copolymer adhesive has been employed to laminate copper to tin-plated steel for use in a new broadband coaxial cable (Fig. 1).¹ Considerable development effort has been expended to understand the structure-mechanical property relationship^{2,3} and the environmental behavior of the copolymer adhesives in contact with metal surfaces.⁴

An initial drop in peel strength is observed after exposure to humidity (Fig. 2) of degreased copper to tin-plated steel laminate followed by an increase on further aging, with a maximum occurring in 40 days at 70°C/95% relative humidity. It is believed that the reduction in peel strength of the copper to tin-plated steel laminates observed is caused by oxygen diffusing into the interphase region of the joint and forming a weaker copper oxide layer than existed previously.⁴ Assuming an environment-resistant copper surface layer were present, one would not anticipate the rapid loss in peel

THE COPPER-STEEL ADHESIVE LAMINATE



FORMED AND SOLDERED OUTER CONDUCTOR

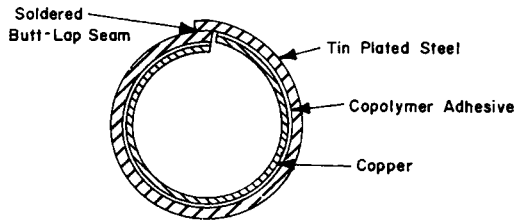


Fig. 1. Laminated coaxial outer conductor.

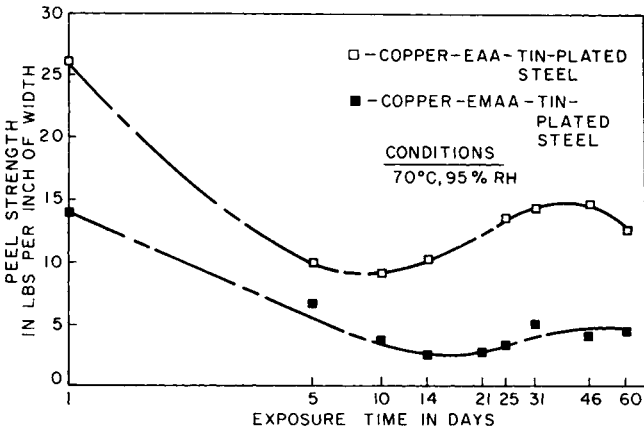


Fig. 2. Peel strength as a function of exposure time.

strength in a humid environment, and the behavior of the degreased copper to tin-plated steel laminate would resemble that of degreased aluminum to tin-plated steel (Fig. 3).

This paper reports on the effect of stress and a humid environment on metal joints prepared with a number of ethylene-acid copolymer adhesives. In addition, the influence of surface treatments of copper and aluminum upon the durability of joints to tin-plated steel is reported.

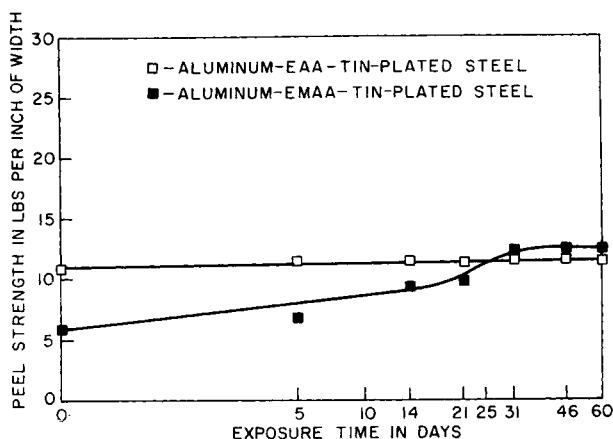


Fig. 3. Peel strength as a function of exposure time.

EXPERIMENTAL

The thermoplastic adhesives, Table I, were molded into 0.010-in. thick films using a 4-in. ram press at 40,000 lb ram pressure and 175°C. The adhesive film was then placed between the two metal surfaces which were overlapped 0.5-in. These metal coupons were 1 by 5 in. and 0.063-in. thick. Bond thickness was controlled by placing a 0.003-in. gold wire between the two metal surfaces along with the adhesive film. A bonding pressure of 20 psi was applied to the samples at 175°C for 15 min. After conditioning for 48 hr at room temperature, the samples were tested in tension at a deformation rate of 0.1 in./min. Various metal surface treatments were examined and are described below.

TABLE I
Properties of Ethylene-Acid Copolymers Used in this Study

Resin ^a	Weight-% acid	Melt index
EAA ^b	3.0	5.0
EAA	8.0	6.0
EAA	13.0	5.0
EMAA ^c	9.0	7.0

^a Supplied by the Dow Chemical Corp., Union Carbide Plastics Corp., and E. I. du Pont de Nemours & Co.

^b Ethylene-acrylic acid copolymer.

^c Ethylene-methacrylic acid copolymer.

Surface Treatment

Copper

Treatment A. Perchloroethylene vapor degreasing (1/2 min) and drying in a forced-air oven at 50°C. Samples were then stored in a vacuum desiccator and used within 48 hr.

Treatment B. A $\frac{1}{2}$ -min degreasing in perchloroethylene vapor was followed by a 5-min dip in 10% HNO_3 . This was followed by an electrolytic chromate treatment developed by Vazirani.⁵ Finally, the treated substrates were rinsed with distilled water and dried in a forced-air oven at 50°C. Samples were then stored in a vacuum desiccator and used within 48 hr.

Treatment C. A 30-sec immersion in the perchloroethylene vapor was followed with a 5-min dip in 10% HNO_3 and a 5-min etch in an acid solution consisting of 75% H_3PO_4 , 10% HNO_3 , and 15% H_2O . Finally, the

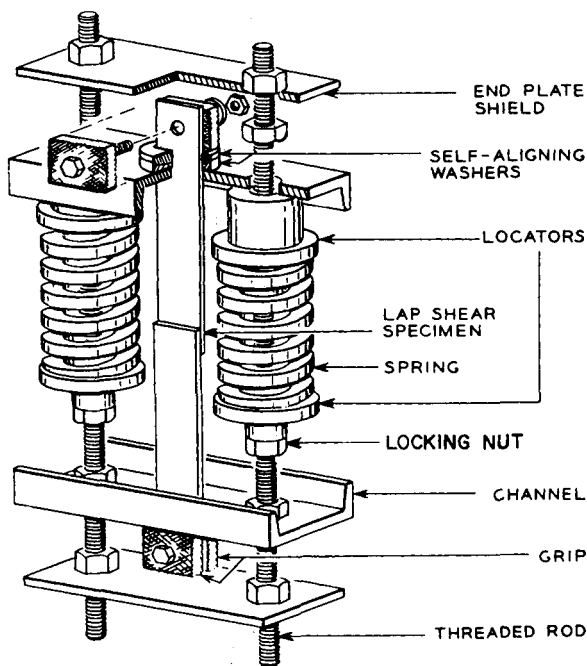


Fig. 4. Durability test apparatus.

treated substrates were rinsed with distilled water and dried in a forced-air oven at 50°C. Joints were prepared within 48 hr after storage in a vacuum desiccator.

Treatment D. Same as treatment C, but followed by the electrolytic chromate treatment described in treatment B.

Aluminum

A 30-sec dip in perchloroethylene vapor was followed by immersion in a 9% solution of Oakite 164 for 10 min at 82°C or 15 min at 70°C. Next, the metal samples were immersed in a sulfochromate solution of H_2O (30 parts by weight), H_2SO_4 (10 parts by weight), and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (1 part by weight). Finally, the treated substrates were rinsed in distilled water

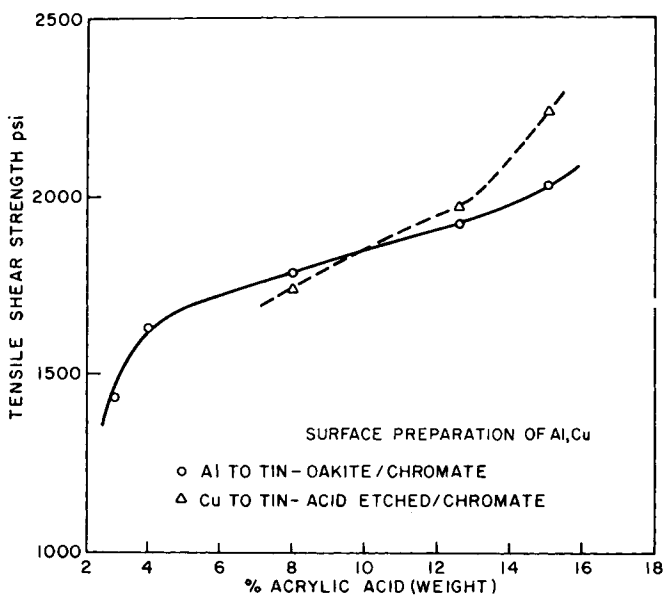


Fig. 5. Tensile shear strength of copper (aluminum)-ethylene-acrylic acid copolymer-tin-plated steel laminates.

(tap water rinse first), dried in a forced-air oven at 50°C, stored in a desiccator, and bonded within 24 hr.

Tin-Plated Steel

Tin-plated steel samples were prepared from cold rolled steel as follows: perchloroethylene vapor degreasing, rinsing in distilled water, mild acid etch in concentrated HCl, immersion in cyanide solution to neutralize surface acid, followed by a rinse in distilled water; copper was then electroplated upon the surface (0.00005-in. thick) followed by tin-plating (0.0001-in. thick).

The tin-plated steel was vapor degreased for 30 sec in perchloroethylene vapor prior to use.

Environmental Exposure Under Stress

Employing a mounting fixture⁸ shown in Figure 4, lap shear specimens were placed under constant stress (100 to 600 psi) in a humidity chamber at 27–50°C (2 cycles/day) and 95% relative humidity. The complete fixture is available from the General Machine Products Co., Trevese, Pa. 19047.

RESULTS AND DISCUSSION

Environmental Aging

The time to failure in humid and dry environments of stressed joints of copper (treatment A) to tin-plated steel is shown in Table II. Data on elec-

trolytic chromate-treated copper to tin-plated steel bimetallic joints are shown in Table III. It is apparent that surface treatment of copper is important. Thus, under a 100 psi stress, treatment A on copper does not result in durable joints with the adhesives at the two acid contents studied. In a dry environment, treated copper results in a more durable joint to tin-plated steel (Tables II and III) at four times the applied stress. The time to failure increases as the acid content of the ethylene-acrylic acid copolymer increases. Increasing the acid content results in an increased initial tensile shear strength. The increase in tensile shear strength reflects the improvement in cohesive strength of the ethylene-acid copolymer arising

TABLE II
Time to Failure under 100 psi Stress in Humid
and Dry Environments for Vapor-Degreased Copper
Bonded to Tin-Plated Steel

Adhesive	Avg. tensile shear strength at 23°C, psi	Environment	Time to failure, hr
EAA—8% acid	900 (660–1240)	27–50°C/95% RH ^a	2
		50°C/dry	2
EAA—13% acid	1250 (1160–1300)	27–50°C/95% RH	8
		50°C/dry	5

^a RH = Relative humidity.

TABLE III
Time to Failure under 400 psi Stress in a Dry
Environment (50°C) for Electrolytic Chromate-Treated
Copper Bonded to Tin-Plated Steel

Adhesive	Time to failure, hr	Avg. tensile shear strength, psi
EAA—3% acid	23	1440 (1330–1530)
EAA—8% acid	90	1780 (1680–1960)
EAA—13% acid	153	1920 (1800–2000)
EMAA—9% acid	11	1610 (1580–1620)

from increased hydrogen bonding of the acid groups which act as cross-links. It is interesting to note that ethylene-methacrylic acid copolymer (9% acid content) fails in a shorter period of time than an equivalent acid content ethylene-acrylic acid copolymer (8% acid content). In addition, although the methacrylic acid copolymer has a higher initial tensile shear strength than the 3% acid content acrylic acid copolymer, it fails sooner. This suggests that creep is one factor in determining the time to failure of these copolymers. (If a material creeps in the fixture it will result in a lower applied stress as related to the spring constant in Figure 4. Failure, when it occurs, will be at a fraction of the original applied stress reported in this work.) Other factors, such as a weaker boundary layer at the metal

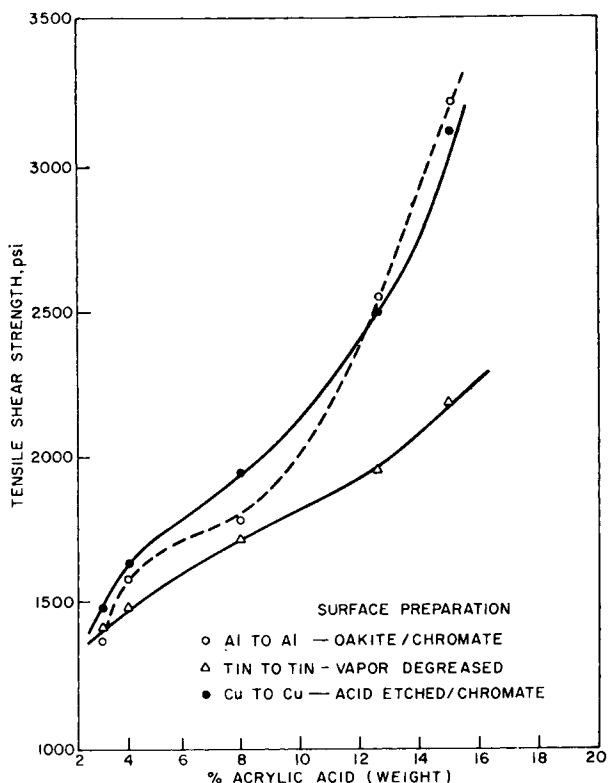


Fig. 6. Tensile shear strength of metal-ethylene-acrylic acid copolymer-metal laminate.

TABLE IV
Time to Failure under Stress for Electrolytic Chromate-Treated Copper Bonded to Tin-Plated Steel with Ethylene-Acid Copolymer Adhesives

Adhesive ^b	Time to failure, hr					
	700 psi	600 psi	500 psi	400 psi	300 psi	200 psi
EAA—3% acid	—	1.5	3	5	—	21
EAA—8% acid	1	—	14	80	—	>720 ^a
EAA—13% acid	—	4	20	>720 ^a	—	>720 ^a
EMAA—9% acid	—	4	4	9	—	115

^a No failures.

^b Environment: 27–50°C (2 cycles/24 hr)/95% relative humidity.

substrate by the methacrylic compared to the acrylic acid copolymer, can also account for these variations in time to failure.

Moisture markedly influences the ability of a bimetallic joint to sustain stress.⁶ The times to failure under stress in a humid environment of surface-treated copper and aluminum substrates each bonded to vapor-degreased tin-plated steel with EAA and EMMA adhesives are found in

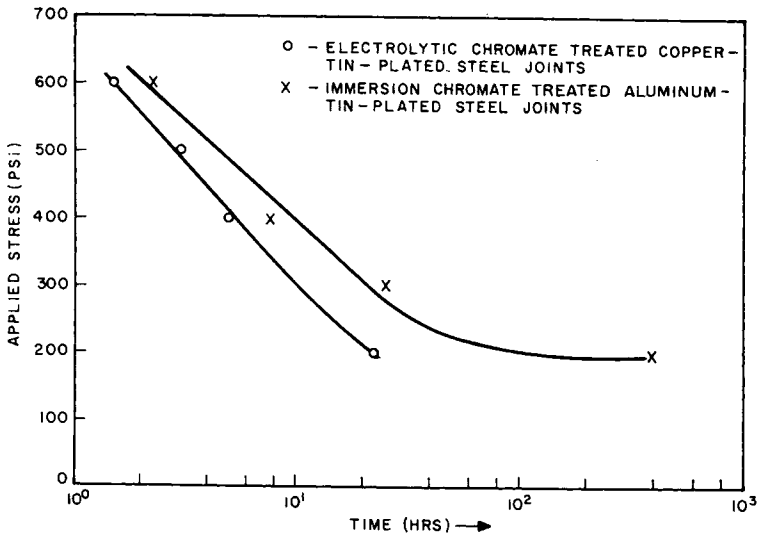


Fig. 7. Time of failure vs. stress for EAA (3% acid) at 27-50°C/95% relative humidity.

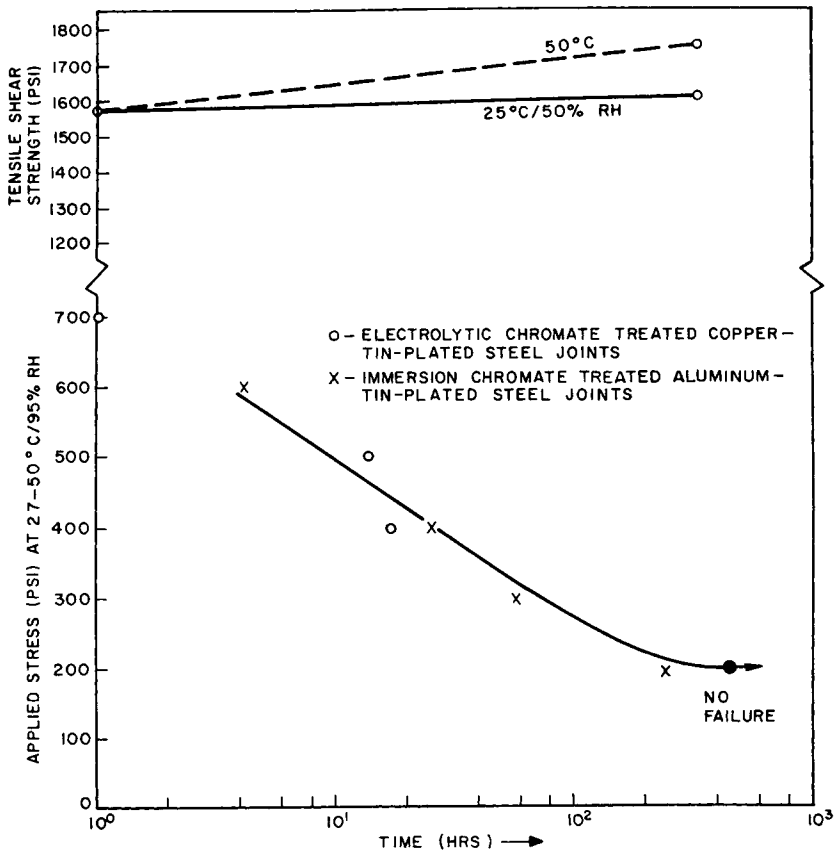


Fig. 8. Aging of EAA (8% acid).

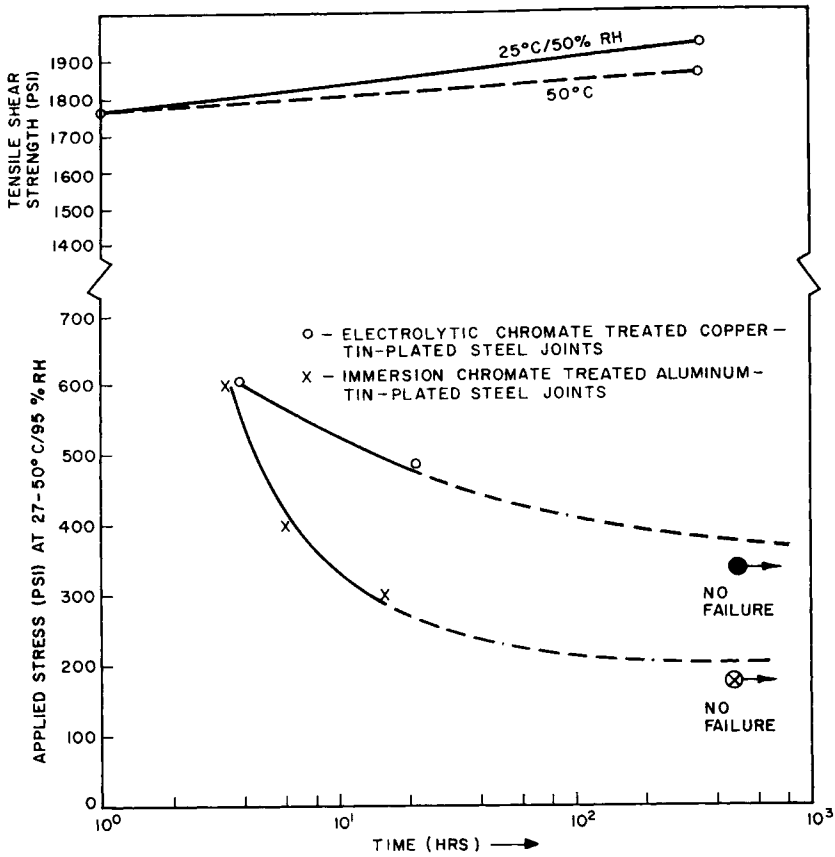


Fig. 9. Aging of EAA (13% acid).

Tables IV and V. If durability is defined as no failures at the lowest applied stress levels during the test period, the only thermoplastic adhesive showing durability would be the 8 and 13% acid content EAA.

There are differences in the aging of treated aluminum and copper joints to tin-plated steel. The tensile shear strengths of treated aluminum and copper joints to tin-plated steel are similar (Fig. 5) and appear to reflect the

TABLE V
Time to Failure under Stress for Immersion Chromate-Treated Aluminum Bonded to Tin-Plated Steel with Ethylene-Acid Copolymer Adhesives

Adhesive ^a	Time to Failure, hr.			
	600 psi	400 psi	300 psi	200 psi
EAA—3% acid	2	9	25	390
EAA—8% acid	4	26	59	460
EAA—13% acid	3	6	16	>720 ^b
EMAA—9% acid	2	4	18	54

^a Environment: 27–50°C (2 cycles/24 hr)/95% relative humidity.

^b No failures.

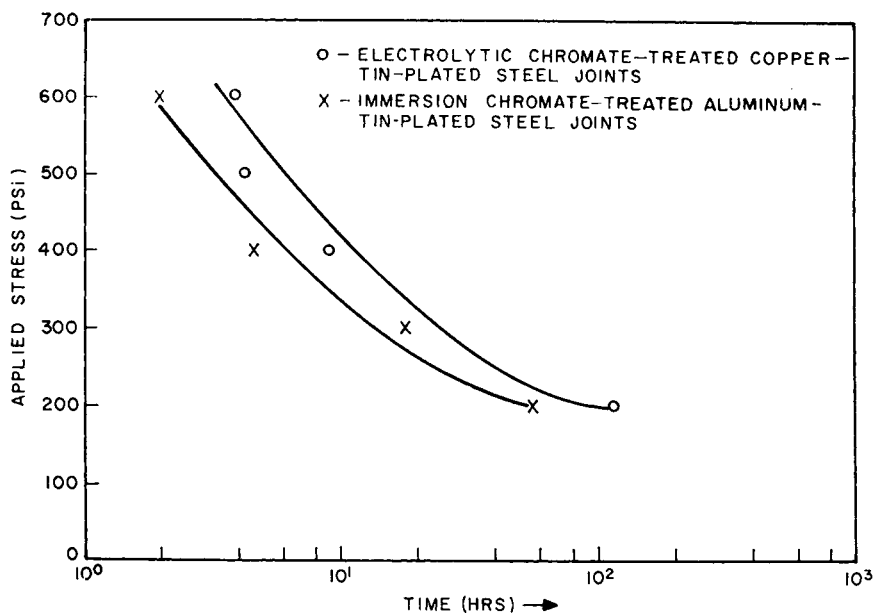


Fig. 10. Time to failure vs. stress for EMAA (9% acid) at 27–50°C/95% relative humidity.

tin-tin joint strength (Fig. 6) in all ethylene-acid copolymer adhesives examined. However, examination of Figures 7–9 shows that at low levels of acid content in EAA (3%), the aluminum to tin-plated steel joints are more durable than the copper to tin-plated steel. With the 8% acid content EAA, there does not appear to be a significant difference in the durability of the copper and aluminum bimetallic joints to tin-plated steel during the test period (Fig. 8). However, the 13% EAA copolymer shows a large improvement in durability (Fig. 9) of the copper to tin-plated steel joint over the aluminum to tin-plated steel joint. From Table IV and Table V it would appear that EMAA at 9% (Fig. 10) forms a more durable joint with copper than with aluminum. The considerable differences observed in durability for the 3% acid content EAA in contact with aluminum and copper might reflect a weaker boundary layer at the interface of this copolymer with copper than with aluminum.⁷

The tensile shear strength of unstressed electrolytic chromate-treated copper to tin-plated steel joints after aging at low humidity are shown in the upper part of Figures 8 and 9. After 360 hr of exposure to 25°C and 50°C, the strength of the laminate increases slightly. This slight increase in strength contrasts with failure of the stressed joint in a humid environment at a fraction of the initial shear strength shown in the lower section of the figures and also in Tables III and IV, 400 psi.

Copper Surface Treatment

Copper, as received, will exhibit surface contamination variability. Treated copper surface prepared by methods B or C appears to be less

sensitive to attack by the ethylene-acid copolymer adhesives than the oxide surface originally present.

The results obtained with copper-copper joints prepared in 1967 and similar joints prepared in 1968 are shown in Table VI. Both copper specimens ($1/2$ hard) exhibited the same Rockwell Hardness (F scale 80), although they were received from different sources. Examination of the data in Tables VI and VII reveals that the tensile shear strengths observed for 1967 copper are superior to those for 1968 copper. Copper coupons from 1967 were available and were used to check the results. The joint strength data obtained earlier were reproducible. The tin-tin joint strengths also were found to be reproducible, although the tin-plated steel specimens were plated a year apart. Hence, the adhesives are not at fault. For 1968 copper in Table VI, treatment D (electrolytic chromate in combination with an acid etch) exhibits improvement in tensile shear strength

TABLE VI
Tensile Shear Strength of Copper-Copper as Influenced by Copper Source

EAA adhesive, % acrylic acid	Surface treatment of copper	Avg. tensile shear strength, psi
1967		
8%	B	1930 (1830-2060)
	C	1800 (1640-1920)
13%	B	2480 (2100-2750)
	C	1950 (1900-2020)
1968		
8%	B	1675 (1600-1820)
	C	1600 (1400-1770)
	D	1770 (1620-1870)
13%	B	2080 (1960-2180)
	C	1960 (1640-2200)
	D	2350 (2040-2680)

TABLE VII
Tensile Shear Strength of Bimetallic Laminates
of Electrolytic Chromate-Treated Copper to Tin-Plated Steel

Adhesive	Metal	Avg. tensile shear strength, psi
EAA-8% acid	copper-tin (1967)	1780 (1680-1960)
EAA-13% acid	copper-tin (1967)	1920 (1800-2000)
EAA-8% acid	copper-tin (1968)	1580 (1400-1680)
EAA-13% acid	copper-tin (1968)	1720 (1620-1860)
EAA-8% acid	tin-tin (1967)	1715 (1620-1820)
EAA-13% acid	tin-tin (1967)	1840 (1740-1940)
EAA-8% acid	tin-tin (1968)	1670 (1540-1800)
EAA-13% acid	tin-tin (1968)	1830 (1700-1960)

over acid etch alone and is superior to electrolytic chromate in combination with a nitric acid pretreatment (treatment B).

The results obtained in evaluating the durability of 1968 surface-treated copper are shown in Table VIII. The data generally indicate that acid etch of copper alone (treatment C) is not sufficient for durability of a bi-metallic joint unless it is combined with an electrolytic chromate treatment⁵ (treatment D). Also, there does not appear to be any significant difference observed during the test period to indicate the superiority of treatment B or D for copper.

TABLE VIII
Time to Failure under Stress for Surface-Prepared Copper (1968)
Bonded to Tin-Plated Steel with Ethylene-Acid Copolymer Adhesives

Copper treatment	Adhesive	Time to failure, hr	
		400 psi	200 psi
B	EAA—8% acid	41	>700
B	EAA—13% acid	115	—
C	EAA—8% acid	37	360
C	EAA—13% acid	63	240
D	EAA—8% acid	48	>700
D	EAA—13% acid	130	>700

The variability in joint strength with 1968 copper specimens suggests an incomplete surface pretreatment. The weak oxide scale on this copper could be thicker and would then require a more severe chemical pretreatment prior to joint preparation.

CONCLUSION

Copper, as received, has a weak oxide surface, and bonds formed with ethylene-acid copolymers have low initial strength and poor aging characteristics in humid environments and under stress.

Electrolytic chromate-treated copper and immersion chromate-treated aluminum bonded to degreased tin-plated steel results in joints having comparable durability under stress and in humid environments. These results reflect the durability of tin-tin bonded specimens.

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