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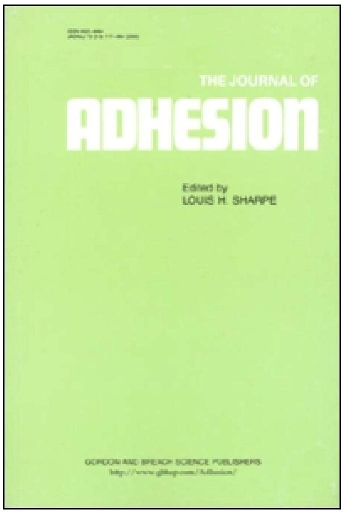

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Surface Preparation of Steel for Adhesive Bonding and Organic Coatings

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Note

Surface Preparation of Steel for Adhesive Bonding and Organic Coatings

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A new process for surface treatment of steel is described. Joints made with this new treatment show superior durability characteristics, as determined by the length of the time to failure when the joints are subjected to different levels of static stress and conditioned at moderately elevated temperature and high relative humidity. Polymer coated panels show superior resistance to salt spray and humidity. The results of electron diffraction and scanning electron microscope studies are given.

INTRODUCTION

The importance of surface treatment of a substrate for adhesive bonding or coating is well known. The purpose of surface treatment of metals is to remove mechanically weak surface layers of oils and corrosion products, usually oxides, and to generate or deposit a mechanically strong surface layer. The other important requisites for the surface treatment are that the newly generated or deposited surface layer should prevent or retard further corrosion of the substrate (hence be a continuous, nonporous film) and be chemically unreactive with the cured polymer system used for forming the joint or coating.

Corrosion of the substrate, especially stress corrosion, is one of the main reasons for the failure of a metallic joint. The Gibbs free energy change (ΔG°_{298}) for the reaction Fe/Fe_3O_4 is -242.4 Kcal/mole. Corrosion-resistant (CRES) steels resist corrosion even though the free energy of the reaction is negative. This passive behavior can be described in the words of Lange and Gerom [1]. "Passivity is a condition of the surface of a metal in which the rate of corrosion is very low in spite of a marked positive affinity." Schonbein and Faraday [2] were first to propose the term "passivity" and related this phenomenon to the presence of an oxide layer. Physical adsorption of molecular oxygen occurs rapidly. It has been shown by electron diffraction, in the work of Germer [3], MacRae [3-5], and Farnsworth [6], that some oxygen atoms are converted to ions by capturing electrons, and are then chemisorbed. A certain number of the atoms of the metal enter the plane approximately corresponding to the plane of the adsorbed oxygen atoms, thus forming a quite stable structure of oxygen ions (negative) and metal ions (positive).

In practice, the corrosion of metals is caused in the presence of water by an electrochemical reaction consisting of anodic (1) and cathodic (2) processes:

$$M + xH_2O \rightleftharpoons M^{n+}(xH_2O) + ne^- \qquad (1)$$

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

Lobanov and P'Yankova [7] have demonstrated clearly in polyethylene-to-steel joints that moisture and oxygen diffuse through polyethylene and that this is the cause of point corrosion. Interestingly enough the loss in joint strength was found to be independent of the initial joint strength. Various types of surface treatments, e.g., etching, phosphatizing and sand blasting did not prevent the drop in the joint strength in a medium with high activity of the water. The authors are of the opinion that it is more fruitful from a durability standpoint to try to prevent corrosion at the polymer-metal interface than to try to obtain coatings with maximum initial joint strength. This concept of preventing corrosion at the polymer-metal interface, to get a durable joint, has been clearly demonstrated on copper [8].

One of the common methods for surface treatment of CRES steels is vapor degreasing followed by immersion in 10-20% hydrochloric acid for a duration of five to fifteen minutes and rinsing the article free of hydrochloric acid. It has been shown with radioactive ions [9], that chloride is the most rapidly and tightly adsorbed of all the ions of strong inorganic acids. Kabanov and Leikis [10] consider that chloride ions stimulate stress cracking in austenitic steels, since the ions are adsorbed by the protective film and displace oxygen ions in it, producing $FeCl_2$ which dissolves in ambient moisture and forms pores in the protective film which act as stress raisers. In addition, hydrochloric acid causes severe corrosion in other steels. For this reason, sand or grit blasting is a usual procedure followed in the surface treatment of cold rolled steels. Sand or grit blasting suffers from the disadvantages that it is difficult to remove all the sand or grit from the surface layer of the substrate and, more serious, that the rough surface causes stress concentrations at or near the interface which result in early failure of a joint under stress.

One of the common methods for preparing steel for polymer coatings is to phosphate coat and follow with a chromate rinse.

This work was carried out to find a satisfactory method of surface treatment which would be applicable to most or all the steels.

EXPERIMENTAL

Five easily available and representative steels were chosen for this study.

1010—carbon steel, carburizing grade, has a carbon content or ~0.1% and a yield strength of ~46,000 PSI.

1095—carbon steel, hardening grade, has a carbon content of ~0.95% and a yield strength of ~96,000 PSI.

4340—ultra high strength steel, has the following composition:C 0.4%, Mn 0.85%, Si 0.2%, Cr 0.75%, Ni 1.80%, Mo %0.25, and a yield strength of ~270,000 PSI.

302—CRES steel, is an austenitic general purpose steel essentially non-magnetic and hardenable only by cold work. It has a composition of C 0.15%, Mn 2.0%, Si 1.0%, Cr 17-19%, Ni 8-10%, and a yield strength of 75,000 PSI.

410—CRES steel, is a martensitic, general purpose steel, magnetic and hardenable by thermal treatment. It has a composition of C 0.15%, Cr 11.5-13%, Mn 1.0%, Si 1.0% and a yield strength of ~40,000 PSI.

In this study, the chloride ion was avoided in the treatment solution and the acidity for chemical etching was provided by phosphoric acid.

Initial tensile shear strength [11] and durability [12] of the joints were taken as a measure of effectiveness of a particular surface treatment. Data given in all the tables, except one, are from joints made with a one-part, modified epoxy paste EC-2186 (3M Co., St. Paul, Minn.), cured one hour at 350°F. Table 6 shows the data obtained from a two-part epoxy adhesive system, Resiweld 7007 (H. B. Fuller Co., St. Paul, Minn.).

In the case of polymer coatings, standard Q-panels (0.032″ 1010 Steel) were used. The experimental study is divided into two sections:

1. Adhesive Bonding
2. Polymer Coating

Adhesive Bonding: The following general steps were followed for surface treatment of steels.

1. Vapor degrease
2. Alkaline clean in a solution of 3% each trisodium phosphate and sodium carbonate for five minutes at 180°F.
3. Rinse in deionized water.
4. Immerse in treating solution for two to ten minutes.
   The following treating solutions were used:
   a. 1:1:: Conc. $HCl:H_2O$ v/v
   b. 50g KI per l of 1:1:: Conc.$H_3PO_4:H_2O$ v/v
   c. 50g KI per l of 1:9:10::Conc.H_2SO_4:Conc.$H_3PO_4:H_2O$ v/v
   d. 50g KBr per l of 1:1:: Conc.$H_3P_4O:H_2O$ v/v
   e. 50g KBr per l of 1:9:10:: Conc.H_2SO_4:Conc.$H_3PO_4:H_2O$ v/v
5. Rinse in deionized water and dry at 70°-120°F.

The treatment in a solution of KI in phosphoric acid will be referred to as Iodophosphate treatment.

RESULTS AND DISCUSSION

In the case of cold-rolled steels, Iodophosphate treatment generates a continuous film of epsilon oxide as determined by electron diffraction, Fig. 1. Scanning electron microscope pictures of treated and untreated 1010 cold-rolled steel and 302 CRES Steel are given in Fig. 2-5.

Table 1—shows the results for joints made with 1010 steel. Among the data are the percent elongation before assembly failure. The importance of this parameter in defining joint strength is seen in Fig. 6. The figure shows plastic yield in the steel. Had yield not occurred in the metal outside the joint area the ultimate strength as measured by this test would have been considerably higher.

Tables 2 through 6—show the effectiveness of the Iodophosphate treatment on 1095, 4340, 302 and 410 steels as compared to presently used surface treatments.

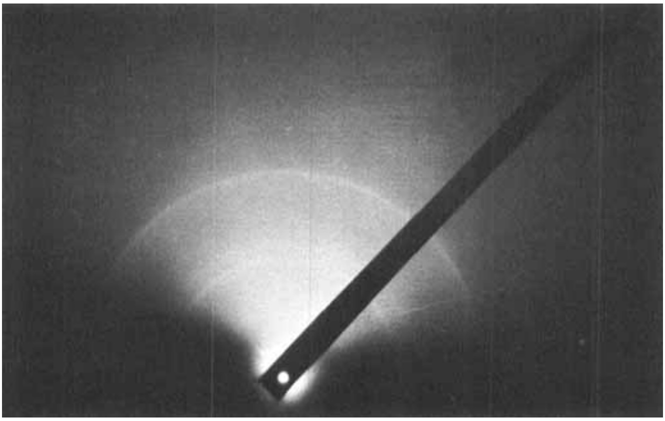

Figure 1. Electron diffraction pattern of the Iodophosphate treated 1010 Steel.
d – lines = 2.51 (inside)
2.24
1.93
1.47

Figure 2-5. Scanning electron microscope pictures.

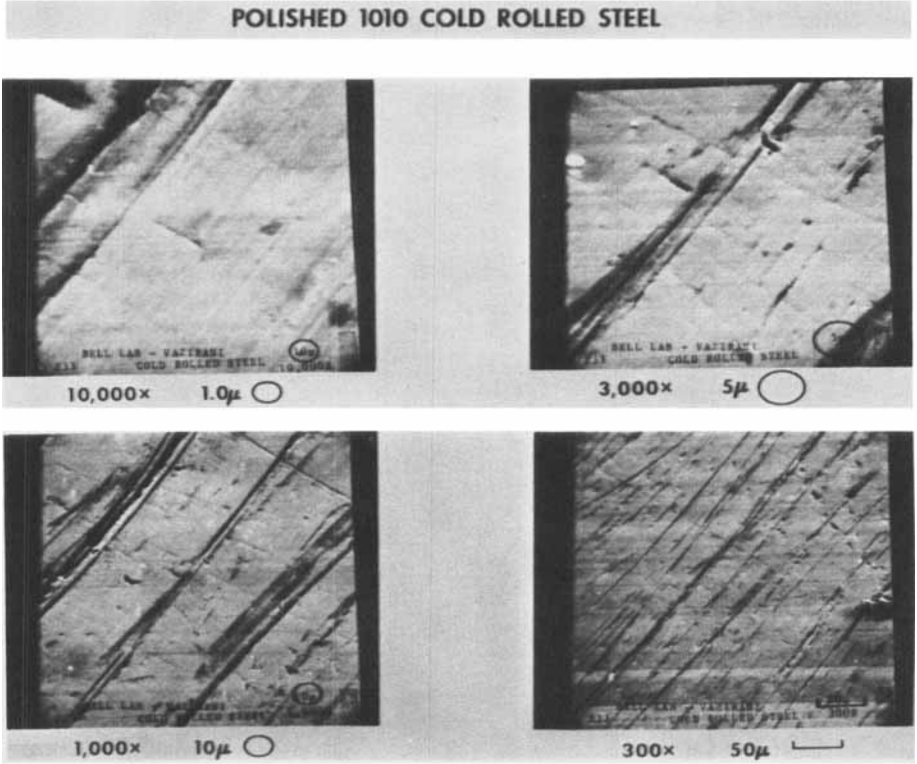

Figure 2—Polished 1010 steel.

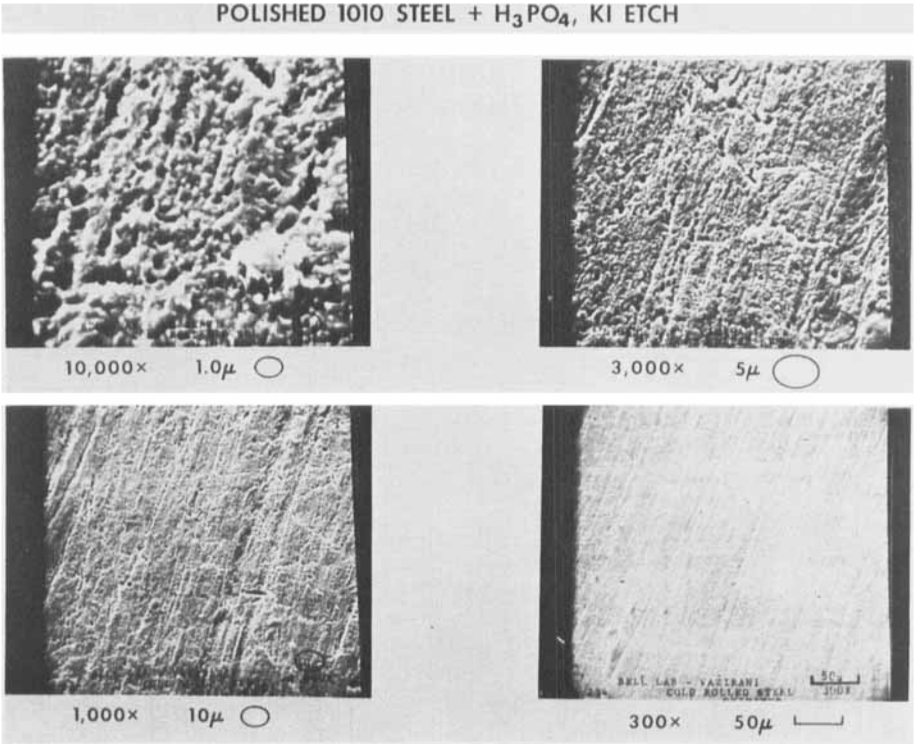

Figure 3—The Iodophosphate treated 1010.

Table 1. 0.063" 1010 Cold Rolled Steel and EC-2186

	1^a	2^b	3^c
Av. Tensile Shear, T_S, psi	5100^{5d}	6250^{5de}	6290^{6de}
Std. Deviation, σ, psi	441	67	81
Coefficient of Variance, c_v^f	8.64	1.07	1.29
Av. % elongation at assembly failure	0.0^{5d}	8.2^{5d}	7.0^{6d}
Av. Time to Failure, T_f^g, days	5^{3d}	18^d	12^{3d}
Av. Time to Failure, T_f^h, days	12^{3d}	39^{3d}	31^{3d}

[a] 1:1::conc. $HCl:H_2O$.
[b] 50g KI per l of 1:1::conc. $H_3PO_4:H_2O$ v/v at 185°F.
[c] 50g KI per l of 1:9:10::conc. H_2SO_4:conc. $H_3PO_4:H_2O$ v/v at 125°F.
[d] Superscript denotes number of joints tested.
[e] Three assemblies failed outside the joints
[f] $C_v = \frac{\sigma}{Ts} \times 100$
[g] Static stress of 4,000 psi, conditioned at 95°F/90% RH.
[h] Static stress of 3,000 psi, conditioned at 95°F/90% RH.

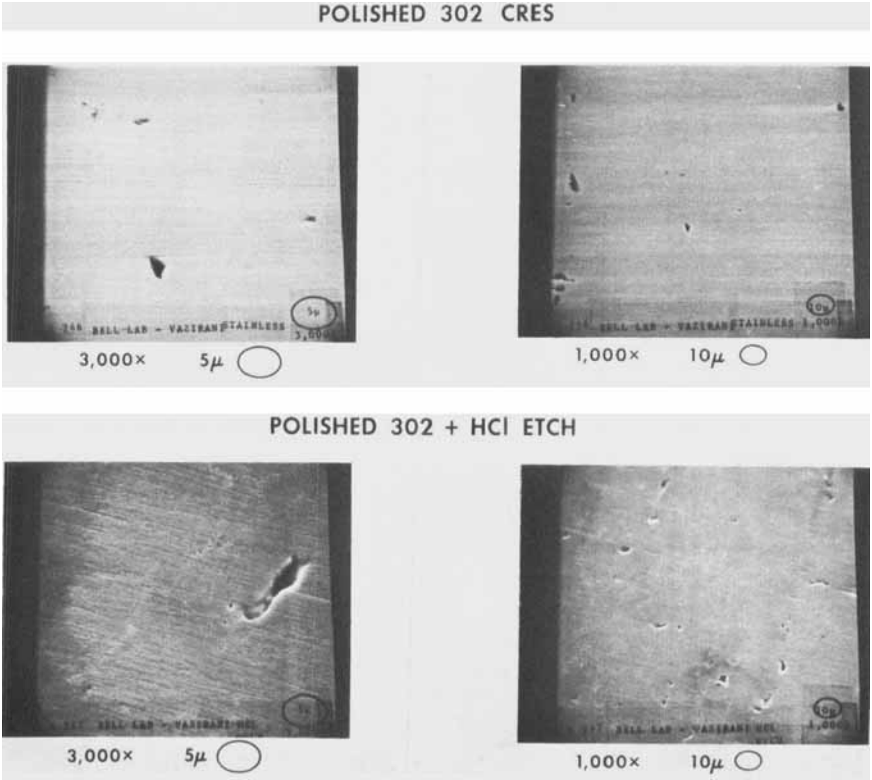

Figure 4—Top—polished 302 steel.
Bottom—HCl etched 302 steel.

Table 2. 0.063" 1095 Cold Rolled Steel and EC-2186

	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]
Av. Tensile Shear,[g] T_s, psi	8450^{5g}	8300^{5g}	8200^{5g}	6430^{5g}	6100^{5g}	6630^{5g}
Std. Deviation, σ	347	660	522	557	777	757
C_V	4.11	7.95	6.37	8.66	12.74	11.42
$T_f{}^h$, days	9^{3g}	23^{3g}	22^{3g}	3^{3g}	1^{3g}	1^{3g}
$T_f{}^i$, days	37^{3g}	38^{3g}	48^{3g}	17^{3g}	11^{3g}	12^{3g}

[a] Sand blasted.
[b] 1:1::10% KI:conc. H_3PO_4 at 140°F.
[c] 1:1::10% KIconc. H_3PO_4 at 180°F.
[d] 50:49:1::10% KI:conc. H_3PO_4:conc. H_2SO_4 at 180°F.
[e] 50:49:1::H_2O:conc. H_3PO_4:conc. H_2SO_4 at 180°F.
[f] 1:1::conc. HCl:H_2O.
[g] Superscript denotes number of joints tested.
[h] Static stress of 5,000 PSI, conditioned at 95°F/90% RH.
[i] Static stress of 4,000 PSI, conditioned at 95°F/90% RH.

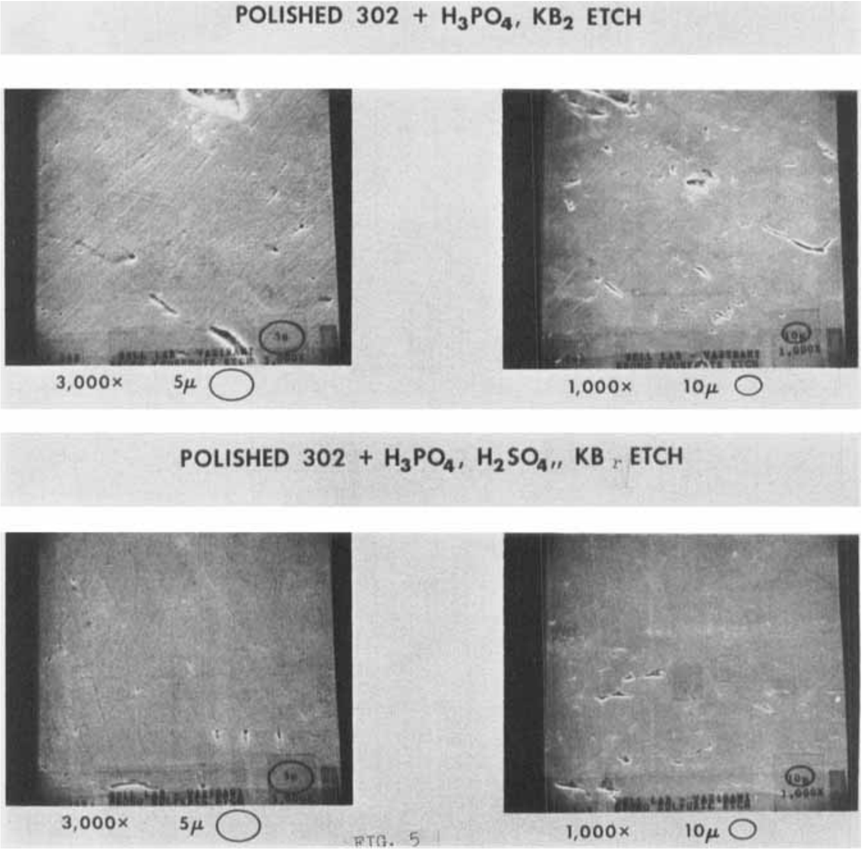

Figure 5—Top—Acid etch in 50g KBr per l of 1:1::Conc. H_3PO_4:H_2O v/v. Bottom—Acid etch in 50g per l of 1:9:10:: Conc. H_2SO_4: Conc.H_3PO_4:H_2O v/v.

Table 3. 0.063" 4340 High Strength Steel and EC-2186

	1^a	2^b	3^c
Av. Tensile Shear, T_s, psi	6690^{5f}	7510^5	7340^5
Std. Deviation	421	117	285
C_v	6.3	1.56	3.89
T_f^d, days	6^3	21^3	24^3
T_f^e, days	12^3	57^3	65^3

[a] Sand blasted.
[b] 1:1::conc. HCl:H_2O
[c] 50g KI per l of 1:1::conc. H_3PO_4:H_2O
[d] Static stress of 5,000 psi, conditioned at 95°F/90% RH.
[e] Static stress of 4,000 psi, conditioned at 95°F/90% RH.
[f] Superscript denotes number of joints tested:

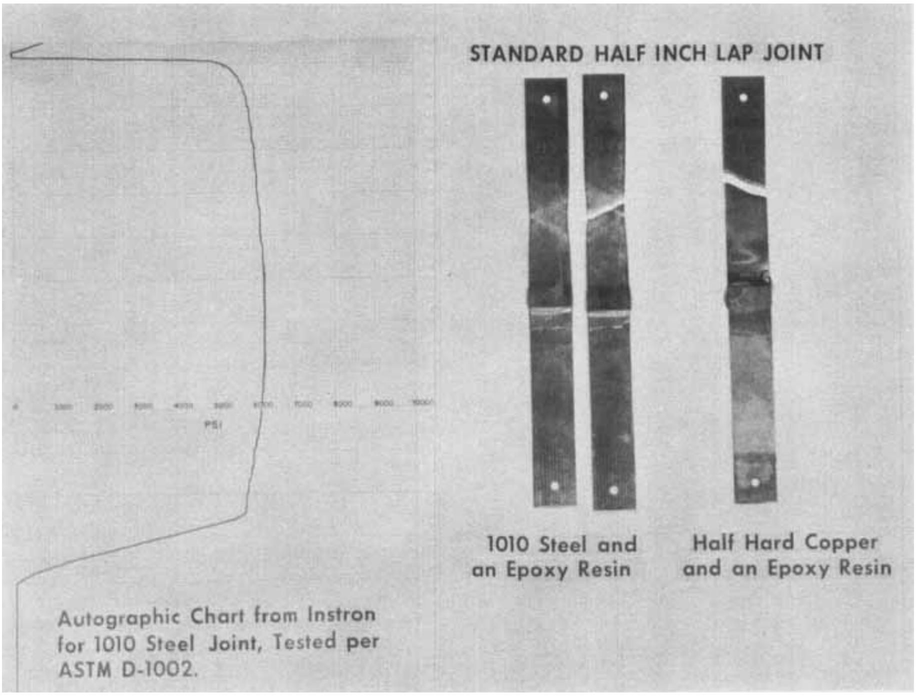

Figure 6—Instron autographic chart showing plastic yield in metal, when tested for tensile shear strength.

Table 4. 0.063" 302 CRES Steel and EC-2186

	1^a	2^b	3^c
Av. Tensile Shear, T_s, psi	7210^{6e}	7460^6	7260^6
Std. Deviation	485	395	440
C_V	6.73	3.95	6.06
$T_f{}^d$, days	28^3	33^3	54^3

[a] 1:1::conc. $HCl:H_2O$
[b] 50g KBr per l of 1:1::conc. $H_3PO_4:H_2O$ at 205°F.
[c] 50g KBr per l of 1:9:10::conc. H_2SO_4:conc. $H_3PO_4:H_2O$ at 205°F.
[d] Static stress of 3,500 psi, conditioned at 95°F/90% RH.
[e] *Superscript denotes number of joints tested.*

Table 5. 0.063" 410 CRES Steel and EC-2186

	1[a]	2[b]
Av. Tensile Shear, T_s, psi	6310^{5c}	6490^{5}
Std. Deviation	427	315
C_V	6.78	4.86
T_f^d, days	2^{3c}	9^{3c}
T_f^e, days	50^{3c}	59^{3c}

[a] 1:1::conc. $HCl:H_2O$
[b] 50g KI per l of 1:1::conc. $H_3PO_4:H_2O$ at 185°F.
[c] Superscript denotes number of joints tested.
[d] Static stress of 5,000 psi, conditioned at 95°F/90% RH.
[e] Static stress of 4,000 psi, conditioned at 95°F/90% RH.

Table 6. 0.063" 1010 Steel and Resiweld 7007

	1[a]	2[b]	3[c]	4[d]
Av. Tensile Shear, T_s, psi	2900^{6f}	2910^{6}	4260^{6}	4470^{6}
Std. Deviation	464	332	333	181
C_V	15.97	11.41	7.82	4.05
Av. Time to Failure, T_f^e, days	20^{6}	28^{6}	101^{6}	170^{6}

[a] As received
[b] Vapor degrease
[c] Grit blasted
[d] Iodophosphate
[e] Static stress of 1,500 psi, conditioned at 95°F/90% RH.
[f] Superscript denotes number of joints tested.

Table 7. Salt Spray[d] and Humidity Resistance of an Organic Coating System on 1010 Steel

Salt Spray Exposure	*Set I*[a]	*Set II*[b]	*Set III*[c]
24 hrs.	Loose film	O.K.	O.K.
100 hrs.	Loose film	Loose film	O.K.
500 hrs.			O.K.
1200 hrs.			O.K.
3000 hrs.			O.K.
Humidity resistance[e] 500 hrs.	Loose film	Loose film	O.K.

[a] Vapor degreased
[b] Vapor degreased + Phosphate coating and Chromate Wash.
[c] Vapor degreased + Iodophosphate.
[d] Per ASTM B117
[e] AT&T cycling.

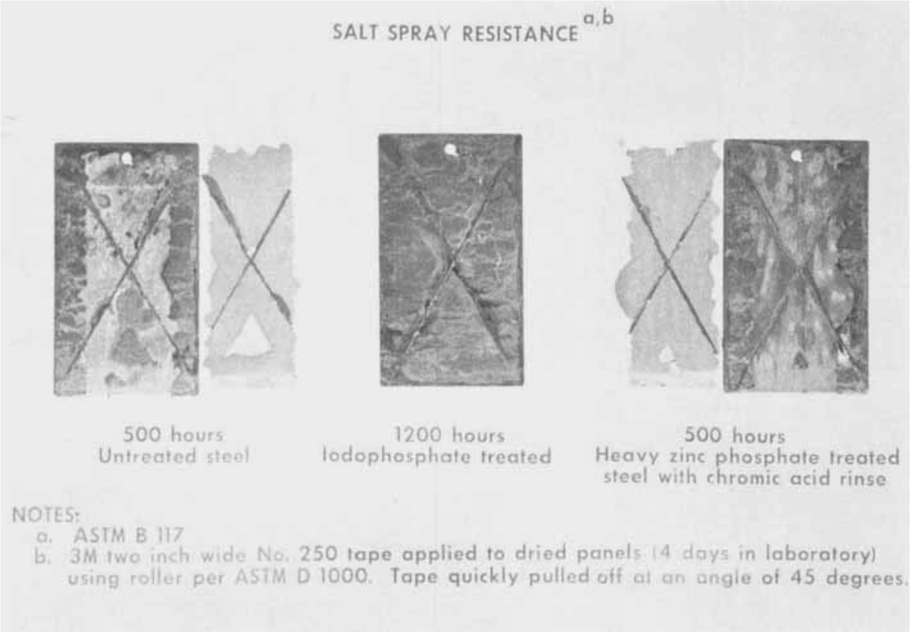

Figure 7—Q-panels which have been exposed to salt spray.

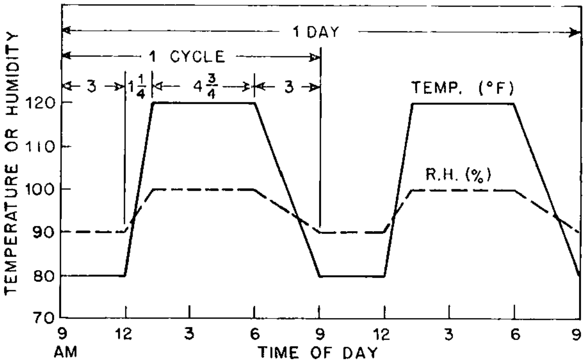

Figure 8—AT&T humidity-temperature cycle.

Polymer Coatings: The importance of durability of the polymer-coated steel cannot be overemphasized since more steel is coated with polymeric protective coatings than any other metal.

For the purpose of salt spray and humidity resistance studies, Q-panels were prepared in the following way:

a. 0.0005″ P-289 primer, baked five mintues at 300°F
b. 0.005 top coat of vinyl-organosol U-127, baked at 360°F for ½ hour.

Both the primer and organosol were products of J. L. Armitage Co., Newark, N. J.

The results of salt spray and humidity resistance (AT&TCo cycle) are given in Table 7. Figure 7 shows the panels which have been tested for salt spray resistance. The figure clearly demonstrates the superiority of the Iodophosphate treatment. (see previous page)

CONCLUSIONS

A new surface treatment, based on the oxidation of steel to produce a continuous epsilon-Fe_2O_3, gives strong and durable adhesive joints and improves the salt spray and humidity resistance of polymer coated steels.

The following procedure is recommended for the surface treatment of steels.

1. Vapor degrease
2. Alkaline clean
3. Rinse.
4. Immerse in a solution of 50g KI per l of 1:1:: Conc.H_3PO_4:H_2O for two to ten minutes at 200°±20°F.
5. Rinse in deionized water and dry at 60°-160°F.

KBr should be used instead of KI for CRES steels. 1-5% (by vol.) Con.H_2SO_4 may be added to the treating solution in case of difficult-to-etch CRES steels to ensure the removal of the existing surface layer.

This method can be adapted to spraying techniques for a commercial operation.

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