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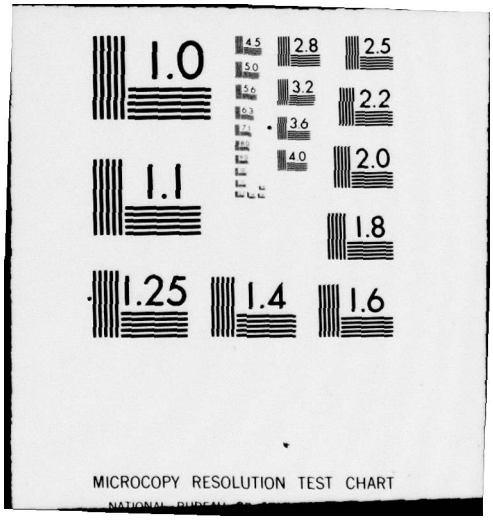
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# SURFACE TREATMENT FOR ALUMINUM BONDING

FINAL REPORT FOR THE PERIOD
July 28, 1978 through July 15, 1979



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CONTRACT NO. DAAK10-78-C-0274

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Dover, NJ 07801

T. Smith
Principal Investigator

OCTOBER 1979



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

At present the most widely used method for treating aluminum prior to bonding is the sulfochrom etch process (FPL, etch). Due to the carcinogenic nature of chromates, various companies and government agencies have been attempting to find new durable nonchromate-containing systems which can be used to treat aluminum prior to bonding.

The objective of this project was to discover a nonacid (nonchromate) surface treatment for Al 2024-T3 that would be both strong and durable. Initial

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studies[1] indicated that a simple degrease and water soak process (STAB(1)) would provide strong durable joints. However, further testing revealed this process to be hard to reproduce on a consistent basis. A second process (STAB (2)) was discovered that was equally as simple but was also difficult to reproduce. A third process, even more simple (STAB(3)) was discovered which did prove reproducible. This process eliminates the degrease step and involves no energy input (room temperature dip in super-concentrated sodium hydroxide). There are only three steps involved, a sodium hydroxide solution dip, a rinse and dry. This report gives the details of these three processes, the bond strength and endurance results and why each process did or did not work satisfactorily.

# FOREWORD

This final report covers work performed under Contract DAAK70-78-C-0274 from 7/18/78 through 7/15/79. The work was performed by the Polymer Reliability Group of the Rockwell International Science Center. The program was under the sponsorship of the U.S. Army Armament R&D Command at Picatinny Arsenal, Dover, New Jersey. Mr. Raymond Wegman was the program monitor.

Contractor personnel contributing to the program were Dr. Tennyson Smith, program manager and principle investigator; Messrs. R. P. Haak, G. W. Lindberg, L. R. Bivins and D. Collins.

OUTLINE

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# I. INTRODUCTION

At present the most widely used method for treating aluminum prior to bonding is the sulfochrom etch process (FPL, etch). Due to the carcinogenic nature of chromates, various companies and government agencies have been attempting to find new durable nonchromate-containing systems which can be used to treat aluminum prior to bonding.

The objective of this project was to discover a nonacid (nonchromate) surface treatment for Al 2024-T3 that would be both strong and durable. Initial studies[1] indicated that a simple degrease and water soak process (STAB(1)) would provide strong durable joints. However, further testing revealed this process to be hard to reproduce on a consistent basis. A second process (STAB(2)) was discovered that was equally as simple but was also difficult to reproduce. A third process, even more simple (STAB(3)) was discovered which did prove reproducible. This process eliminates the degrease step and involves no energy input (room temperature dip in super-concentrated sodium hydroxide). There are only three steps involved, a sodium hydroxide solution dip, a rinse and dry. This report gives the details of these three processes, the bond strength and endurance results and why each process did or did not work satisfactorily.

# II. TECHNICAL RESULTS

## 1. STAB(1)

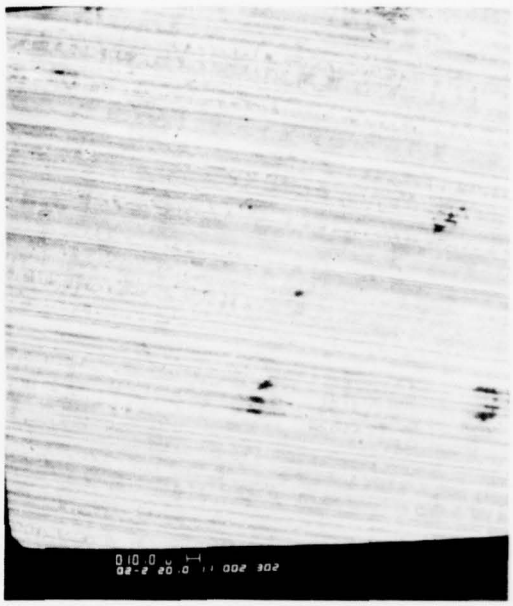
### 1.1 Experimental Procedure

STAB(1) involves a degrease step followed by a rinse and then exposure to 80°C stirred water for 10 min. It was originally discovered[1] that tap water would suffice for the hot water exposure. After checking the effect of cations and anions, it was decided that carbonate ions accounted for the improvement of tap water over deionized (D.I.) water. A number of solvents were tried for the degrease step. Ultrasonic degreasing in 9 parts solvent (Shell Sol. 140EC) plus 1 part concentrate (trade name "Gunk") proved best. If D.I. water was used, $K_2CO_3$ was added until the pH ~ 9.8 at room temperature.

### 1.2 Surface Characterization

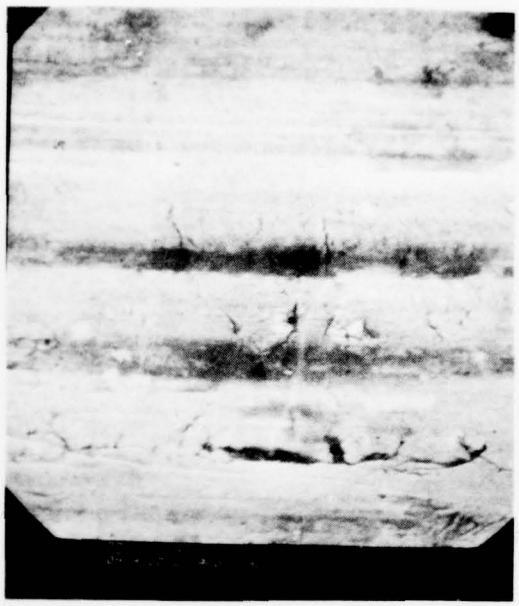
Figure 1 shows SEM micrographs of degreased Al 2024-T3 prior to STAB(1). The top pictures (a) are for unbent specimens, the bottom pictures (b) are for specimens that have been bent to fracture the surface. Figure 2 shows SEM micrographs of bent Al 2024-T3 after STAB(1). A very porous hydroxide is formed that appears to be ideal for mechanical interlocking with adhesive. The porous film is approximately 2000A thick. Although it is not obvious in Fig. 2, other micrographs reveal a second layer under the top layer.

Figure 3 shows an Auger Electron Spectrogram (AES) of an Al 2024-T3 sample after STAB(1) using tap water. The surface consists primarily of aluminum oxide or hydroxide with Na, N, Cl impurities from the water and Mg, Cu, Si and Fe alloy constituents. The major contaminant at the outer surface contains carbon. A similar spectrum after STAB(1) but with $K_2CO_3$ in D.I. water, is seen in Fig. 4. The carbon peak is much smaller and the impurities N, Na, Cl and alloy constituents Si, Cu and Fe are not present. Magnesium is present but at very low concentration. There is no evidence of potassium



x200

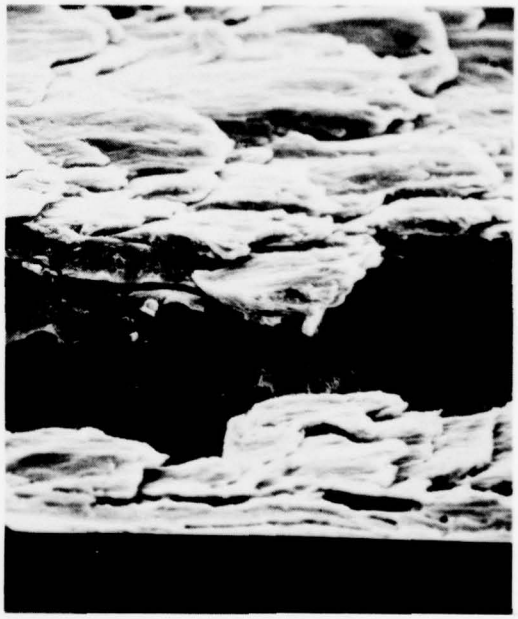
(a)



x4000

x200

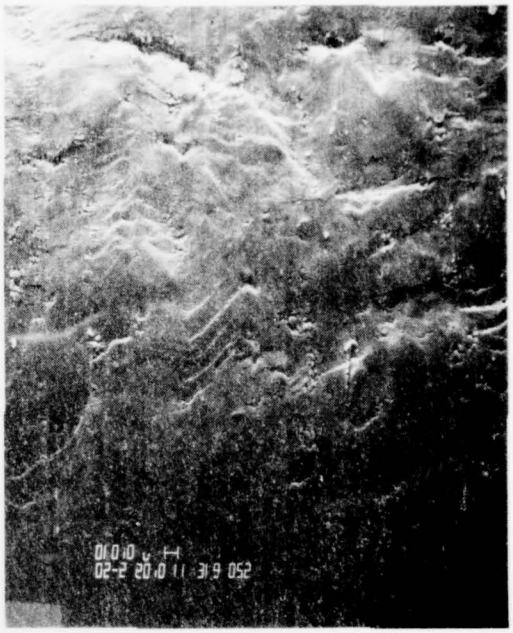
(b)



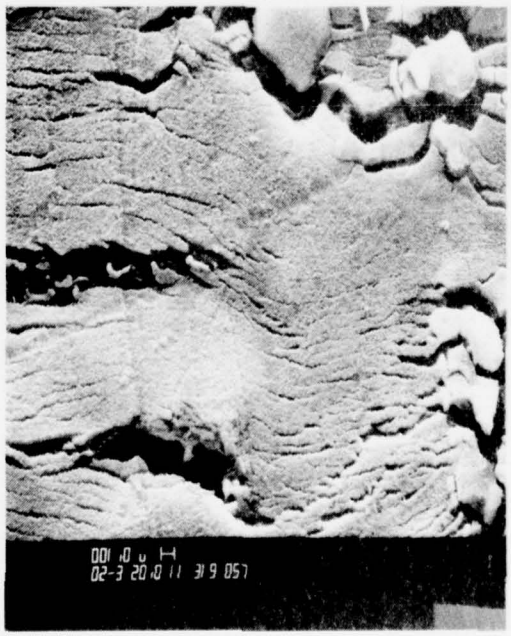
x1000

Fig. 1 SEM micrographs of degreased Al 2024-T3.
a) unbent
b) bent

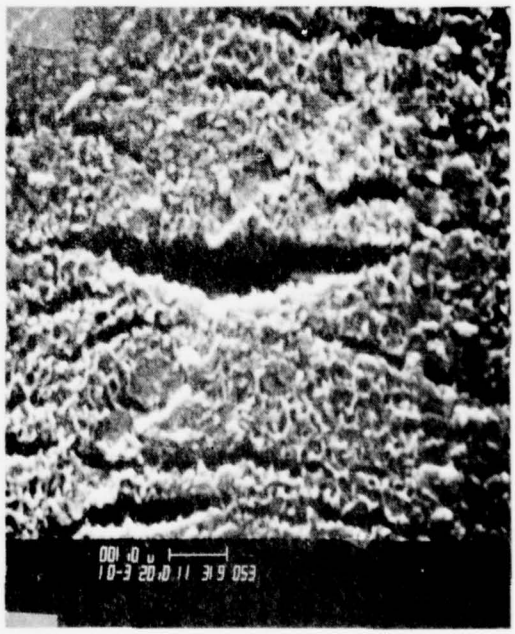
x20 (a)



x200 (b)



x2000 (c)



x10,000 (b)

Fig. 2 SEM micrographs of Al 2024-T3 after STAB(1).

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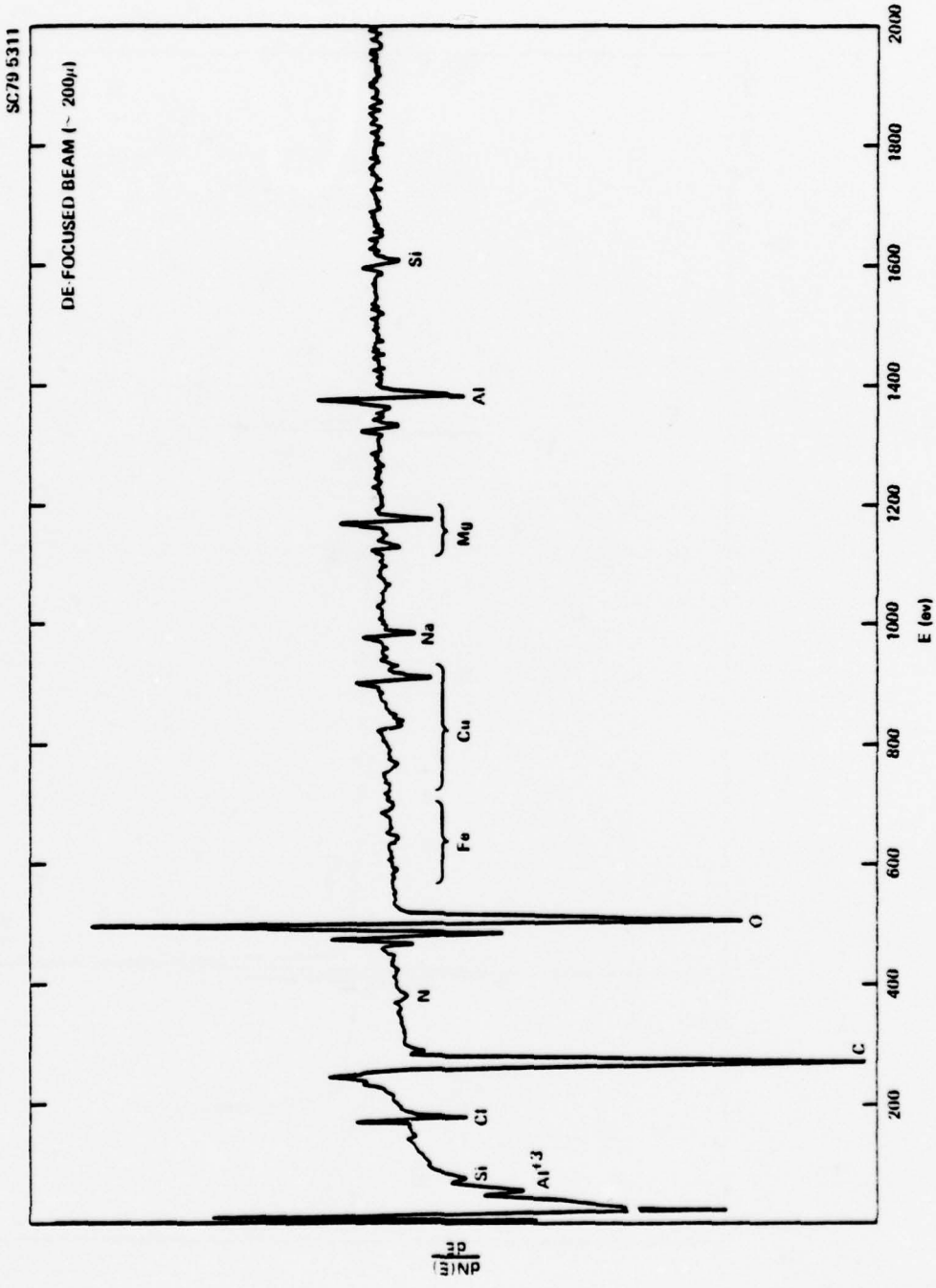


Fig. 3 AES of Al 2024-T3 after STAB(1) with tap water.

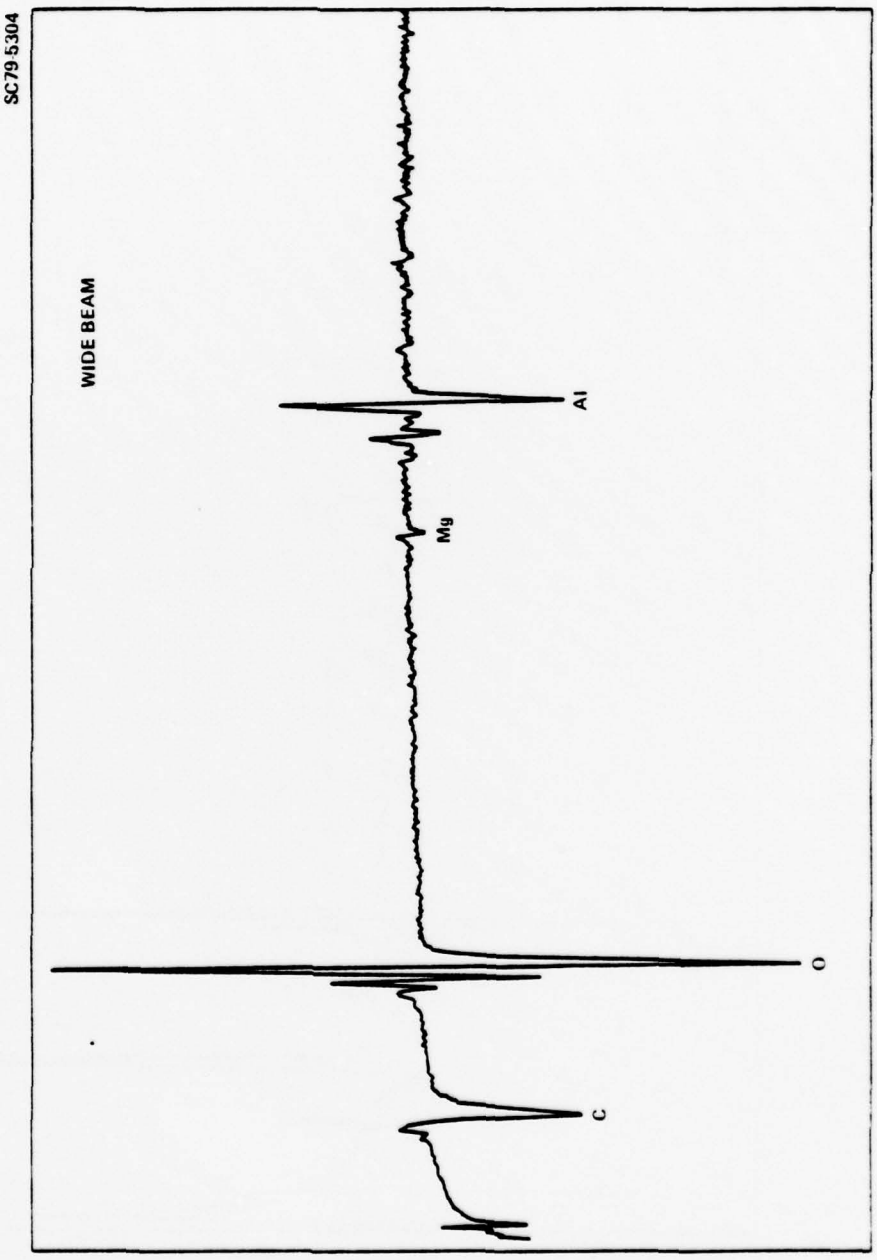


Fig. 4 AES of Al 2024-T3 after STAB(1) with $K_2CO_3$ in DI water.

which has a peak at 250 eV. For comparison Fig. 5 is the AES for degreased (ultrasonic, Gunk) Al 2024-T3, prior to STAB. This spectrum was taken after 1 min $Ar^+$ bombardment which removed an outer layer of carbon (i.e., the C peak was 7 times as large). Figure 6 reveals the effect of $Ar^+$ sputter-back etching on the degreased sample. After 4 min $Ar^+$ sputtering the 60 eV Al peak appears in addition to the 55 eV $Al^{+3}$ peak and the 1420 eV Al peak changes shape. These changes are due to the reduction of the $Al^{+3}$ by the electron beam.[2] Figure 7 is an AES after 40 min $Ar^+$ sputter, when most of the oxide had been removed.

Figures 8-11 are AES profiles of Al 2024-T3 after STAB(1) and before STAB(1). The APPH stands for Auger peak-to-peak height. The major difference between as-received (or degreased) and STAB(1) treated aluminum is that the electron beam can reduce the $Al^{+3}$ before STAB but cannot after. This is indicated by the increasing 60 eV neutral Al peak and decrease of oxygen during sputter etching, for the as-received and degreased samples but no 60 eV peak at all for the STAB(1) samples. This indicates much greater chemical stability of oxides formed after STAB as compared to the as-received oxide film. The lower stability of as-received or degreased aluminum makes it much more susceptible to corrosion under hydrothermal stress, as will be seen.

The initial carbon peak is about twice as high for STAB(1) with tap water as for STAB(1) with $CO_3^=$ or as-received. In each case (except STAB(1) with $CO_3^=$) the carbon is mostly removed within about 2 min. In the case of STAB(1) with $CO_3^=$ the Auger peak-to-peak height (APPH) has only slightly decreased after 5 min sputter. This may indicate some carbonate incorporation within the hydroxide for STAB(1) with $CO_3^=$.

The surface properties measured by ellipsometry ($\Delta$) photoelectron emission (PEE), surface potential difference (SPD) and water contact angle ($\theta_{H_2O}$), are rather erratic for STAB(1). This indicates that the hot water reaction with aluminum is very sensitive to the surface condition of the aluminum. This is consistent with the poor reproducibility of bond strength and endurance in the next section.

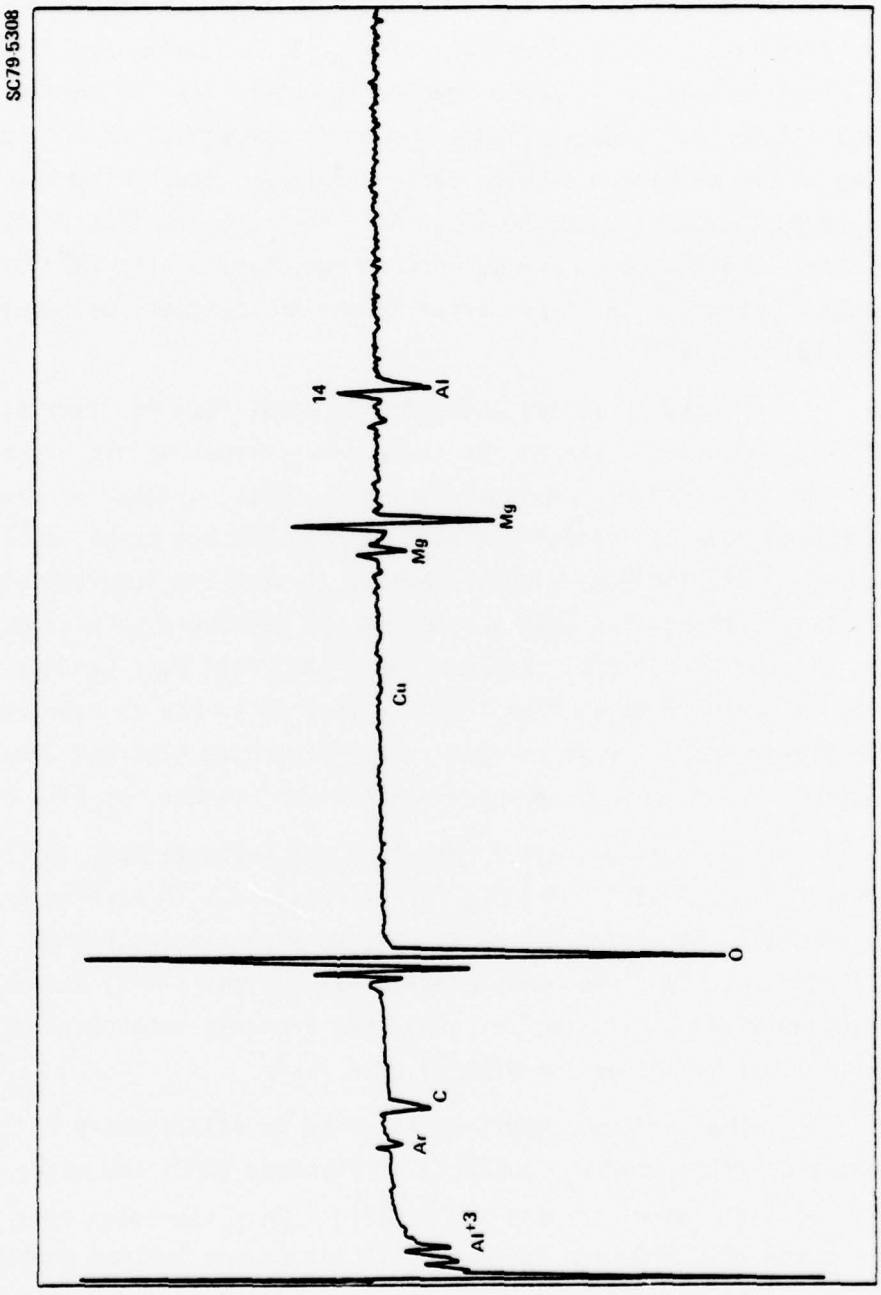


Fig. 5 AES of Al 2024-T3 after degrease only.

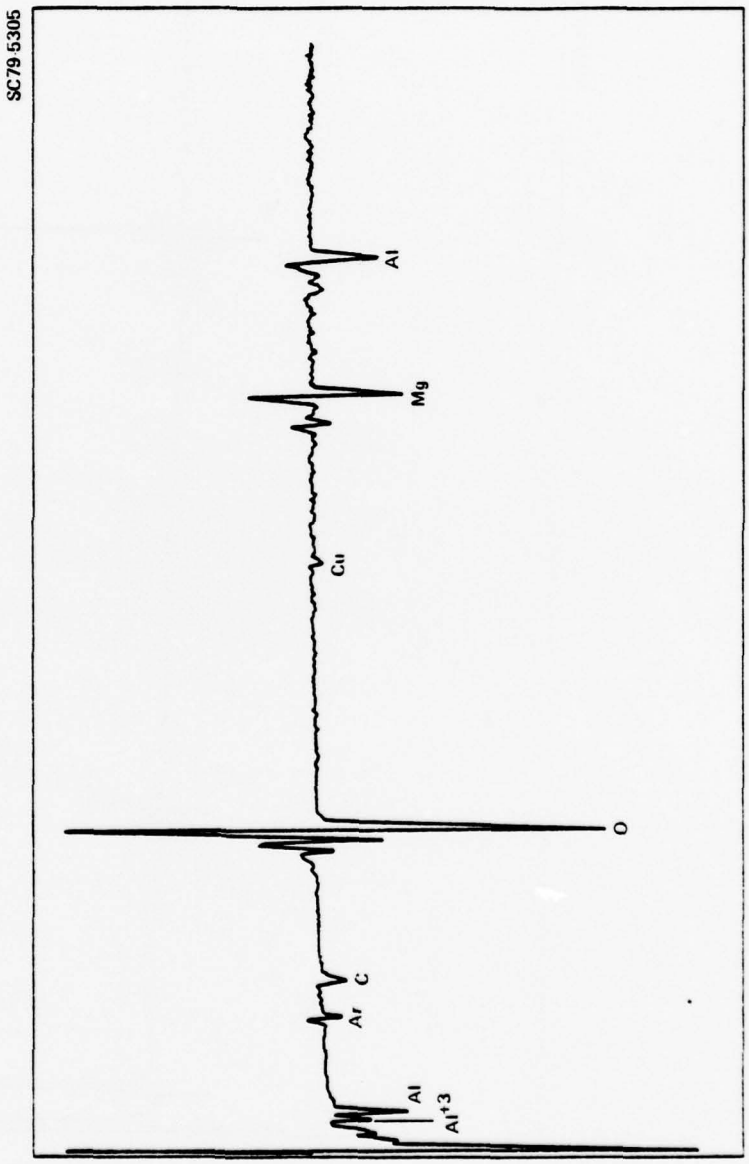


Fig. 6 AES of Al 2024-T3 after degrease only, plus 4 min. sputter etch.

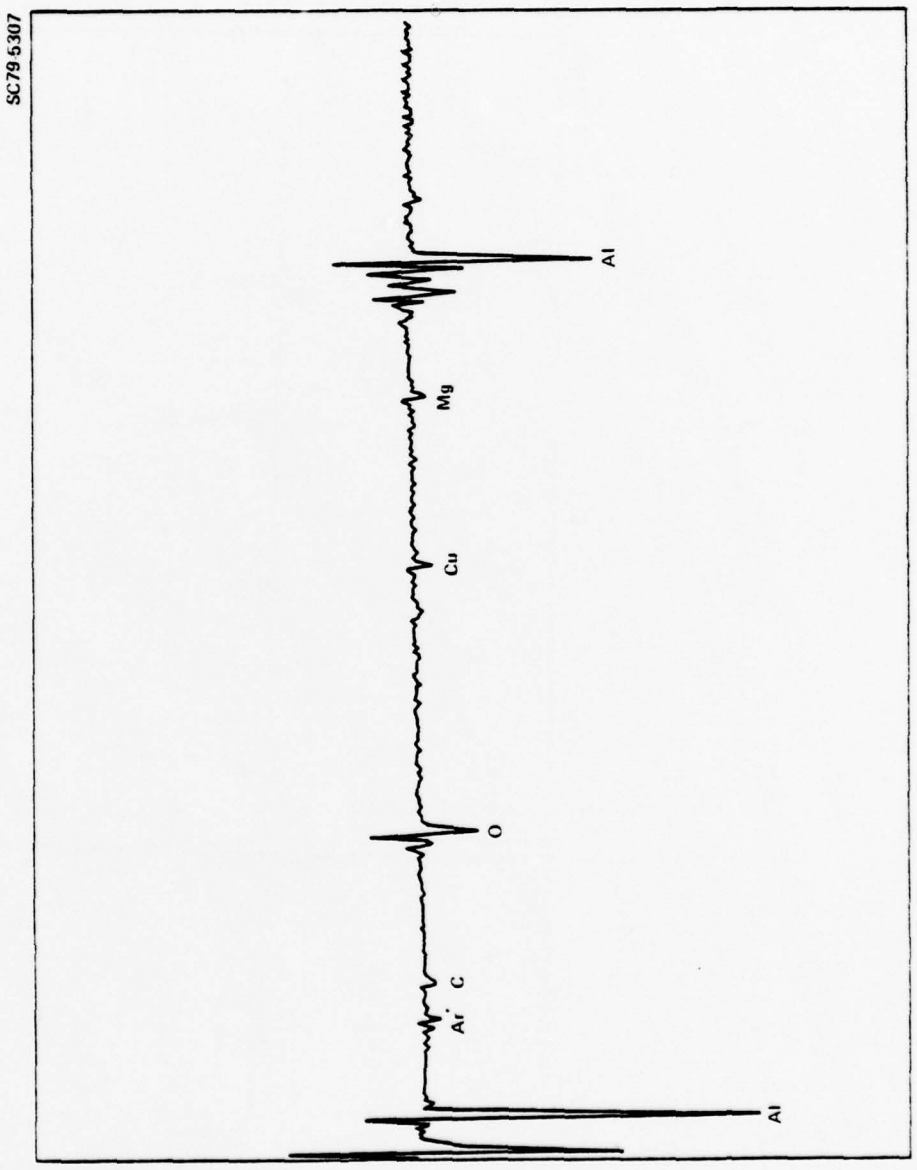


Fig. 7 AES of Al 2024-T3 after removal of the oxide by $Ar^+$ sputter.

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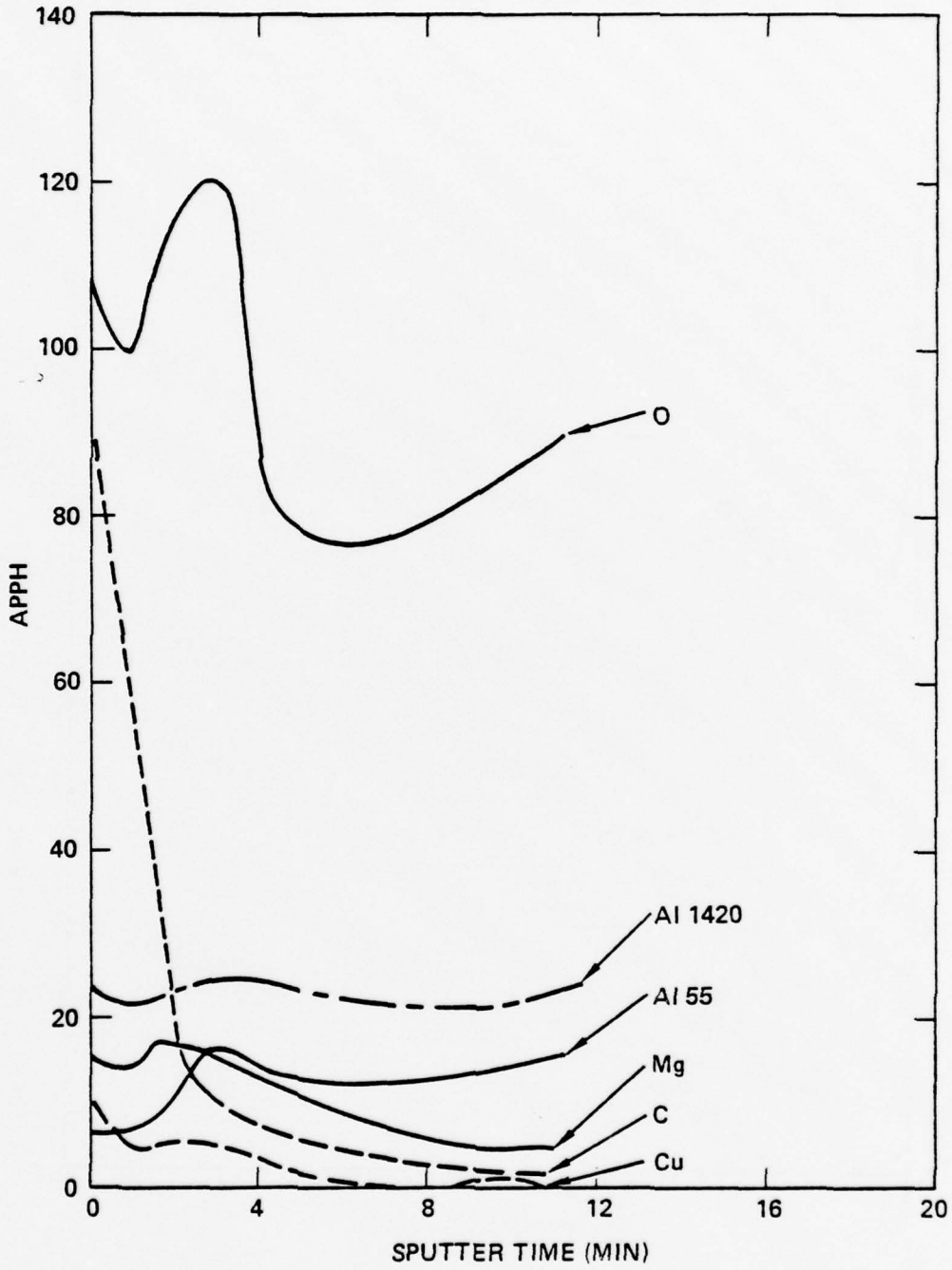



Fig. 8 AES sputter profile of Al 2024-T3 after STAB(1) with tap water.

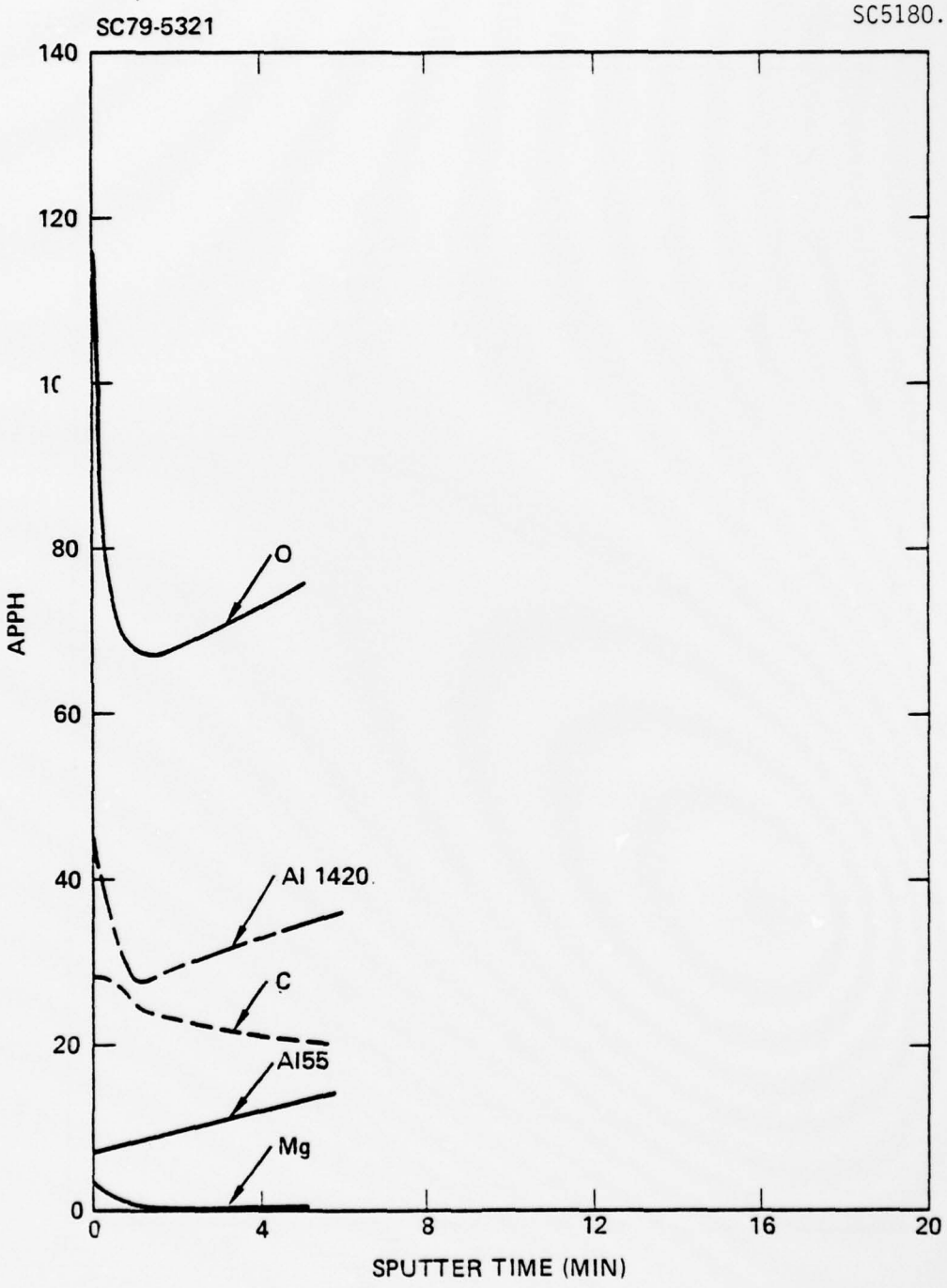



Fig. 9 AES sputter profile of Al 2024-T3 after STAB(1) with DI water and $K_2CO_3$.

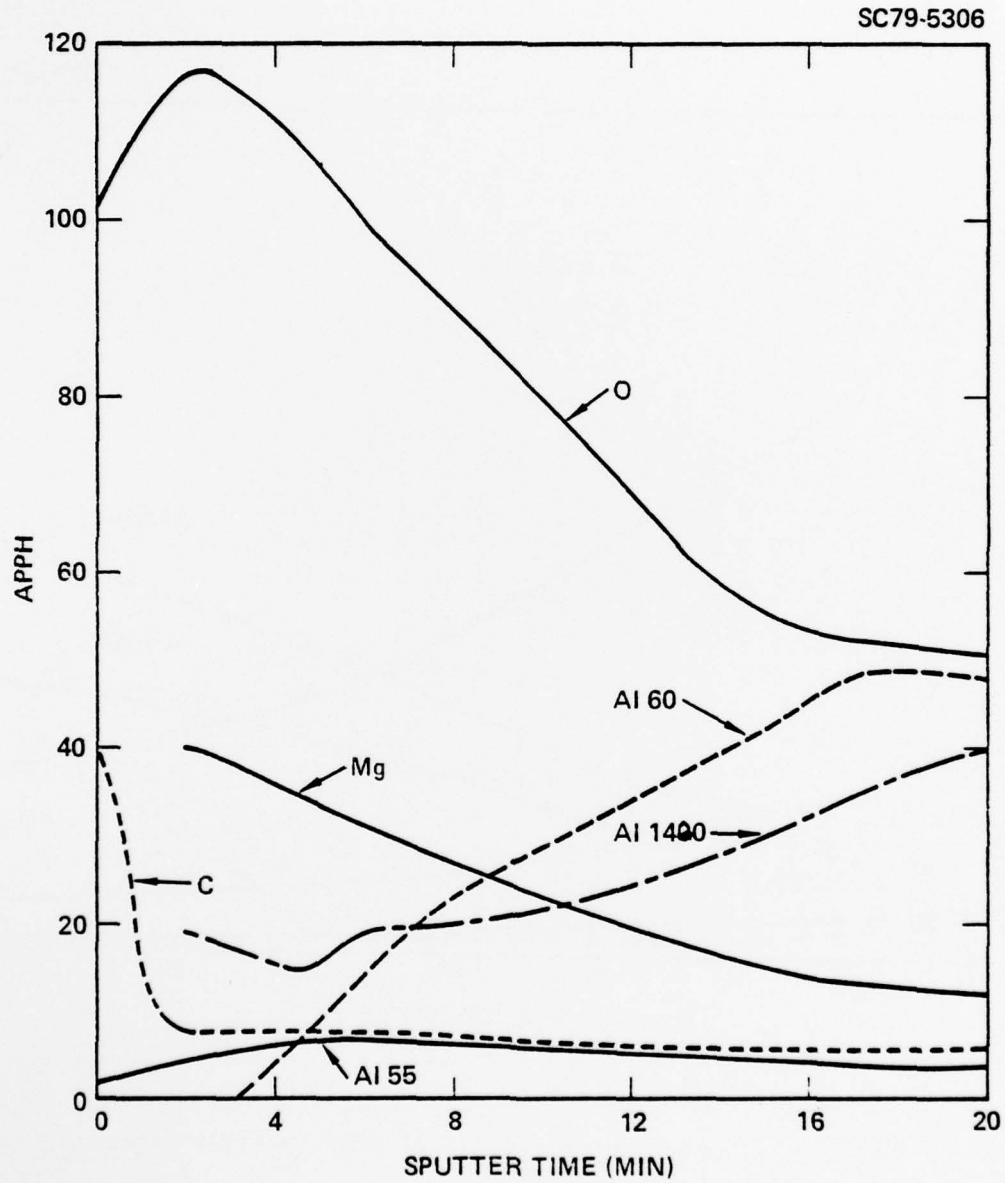



*Fig. 10 AES sputter profile of Al 2024-T3 as received.*

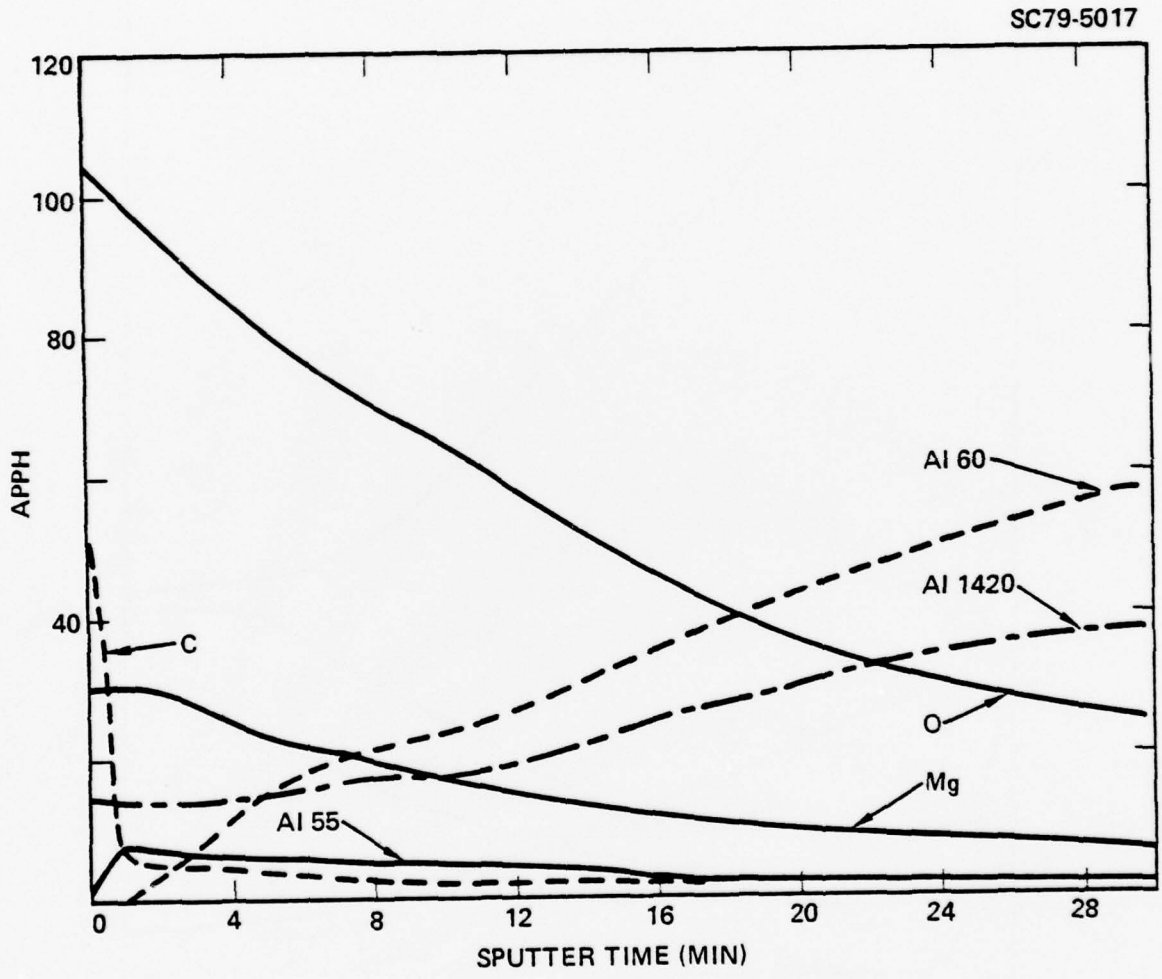



Fig. 11 AES sputter profile of Al 2024-T3 after degrease (ultrasonic gunk).

In order to get some idea of the changes that occur at the aluminum surface after STAB(1) but following the history that a wedge test specimen would experience, STAB(1) samples were exposed to lab air for about 30 min then placed in the curing oven for 180 min, to simulate primer and adhesive cure, then placed in the humidity chamber at 100% RH and 50°C (122°F) for 24 hrs, to simulate hydrothermal exposure. It is recognized that the aluminum surface will not experience the same conditions with and without adhesive present, but some indication of the effect of heat and moisture might be obtained.

An increase in the ellipsometric phase shift $\Delta$ is associated with a decrease in film thickness or decrease in film density. A decrease in PEE is associated with a decrease in electron attenuating properties of the hydroxide film and is therefore closely related to $\Delta$. Exposure to air immediately after STAB(1) causes $\Delta$ to increase, probably due to a decrease in film density as the film dries. Oven exposure probably causes film growth, decreasing $\Delta$ and PEE. Exposure to the humidity chamber appears to decrease film thickness or density from PEE and $\Delta$ up to 2000 min. Above 2000 min $\Delta$ decreases as the film grows since $\Delta$ is cyclic with film thickness.

The SPD and $\theta_{H_2O}$ values are partially correlated, since both are sensitive to the outer dipole layer. The water contact angle dramatically increases (5°-80°) during the oven heat then returns to the wettable condition upon exposure to the humidity chamber. The SPD is erratic but generally increases as $\theta_{H_2O}$ decreases.

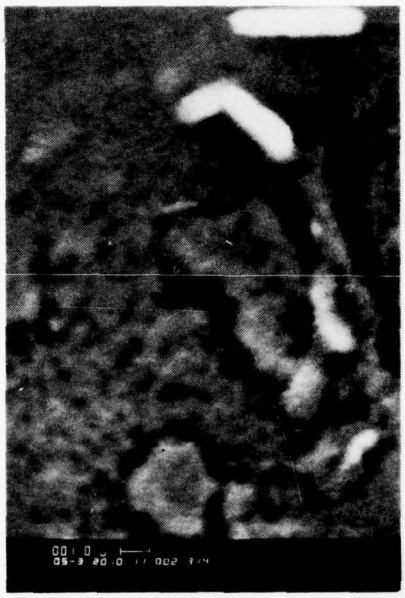
During the thermal and humidity history dramatic changes within the hydroxide film seem to occur, from the ellipsometric and PEE results. It is not known if these same changes or surface contamination cause the SPD and $\theta_{H_2O}$ results.

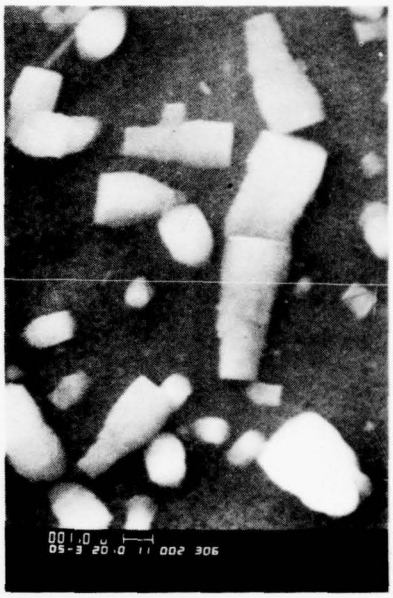
In order to discover relationships between physical and chemical properties of surface films and their subsequent application for adhesive bonds of high strength and durability, a number of surface properties have been measured. The process parameters are time in solution, temperature of solution,

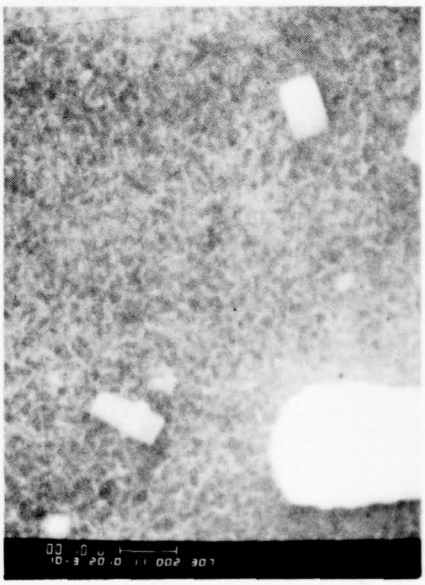
pH of solution, and ionic concentrations. The general strategy involved comparison of film properties that provide poor adhesive bond strength with those that provide good adhesive properties in order to determine the optimum surface conditions for strong bonds. The following results indicate that the approach is fruitful.

SEM pictures (Fig. 12) of aluminum exposed to 96°C deionized water and 50°C deionized water indicate that long exposures provide thick enough films to produce a well developed morphology in each case. The 96°C water produces boehmite with the orthorhombic plate-like structure, whereas the 50°C water produces bayerite with the monoclinic cone-like structure. The interesting feature is that beneath the well-formed crystallites is a uniform layer of pseudo boehmite or bayerite that appears very porous or foamy. This is more so with the 50°C (bayerite) than with the 96°C (boehmite) samples. In order to determine which of these crystalline structures is most advantageous for adhesive bonds, Fig. 13 shows a sharp decrease in lap shear bond strength ($\sigma$) at the temperature transition from bayerite to boehmite. Values of $\sigma = 4500 \pm 500$ psi correspond to the cohesive strength of the adhesive used and failure was observed to be cohesive in nature. Lower values of $\sigma$ correlate with interfacial or partial interfacial failure. All of the samples, represented in Fig. 13, were exposed for 10 minutes. The samples for Fig. 14 were exposed for different lengths of time at 80°C and the oxide film thickness was determined by ellipsometry after this exposure. Figure 14 shows that below about 1000A,* the film is stronger than the adhesive because these test specimens failed by cohesive failure. Beyond 1000A the bond strength decreases with film thickness.

*The discrepancy between film thicknesses from SEM and ellipsometry is due to the assumption that the films were nonporous. Therefore, the ellipsometric values are effective optical thickness values.







96° C water 46.7 hrs

50° C water 70 hrs

Fig. 12 SEM pictures of vapor deposited Al after exposure to 96° C water (left) for 46.7 hrs and 50° C water (right) for 70 hrs.

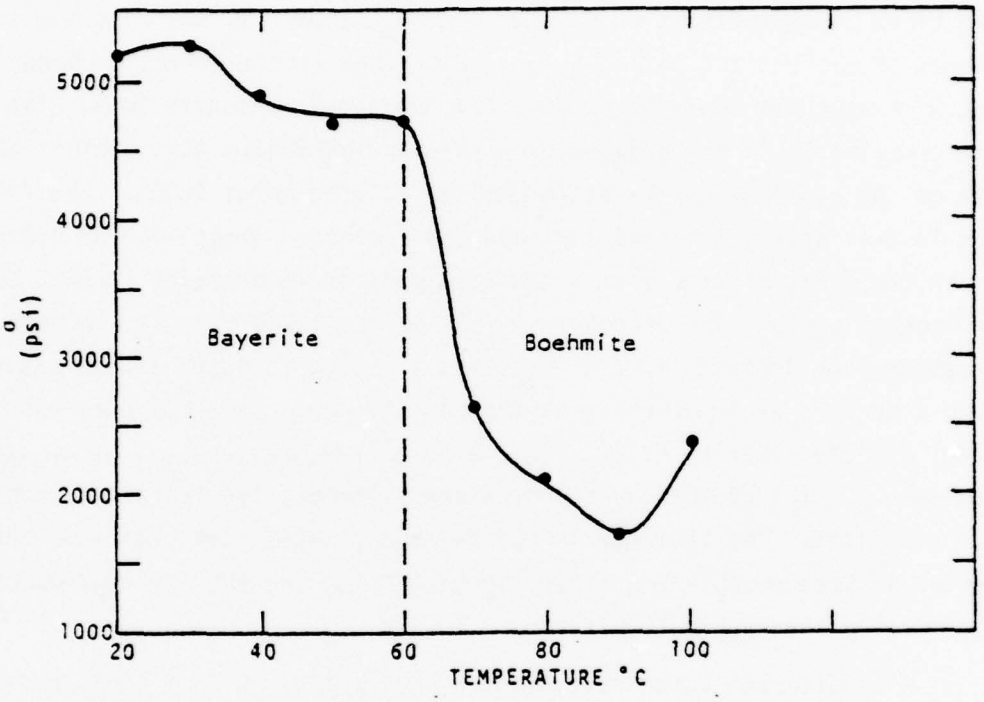



Fig. 13 Lap shear strength as a function of the crystalline form of the aluminum oxide layer on the adherend before bonding.

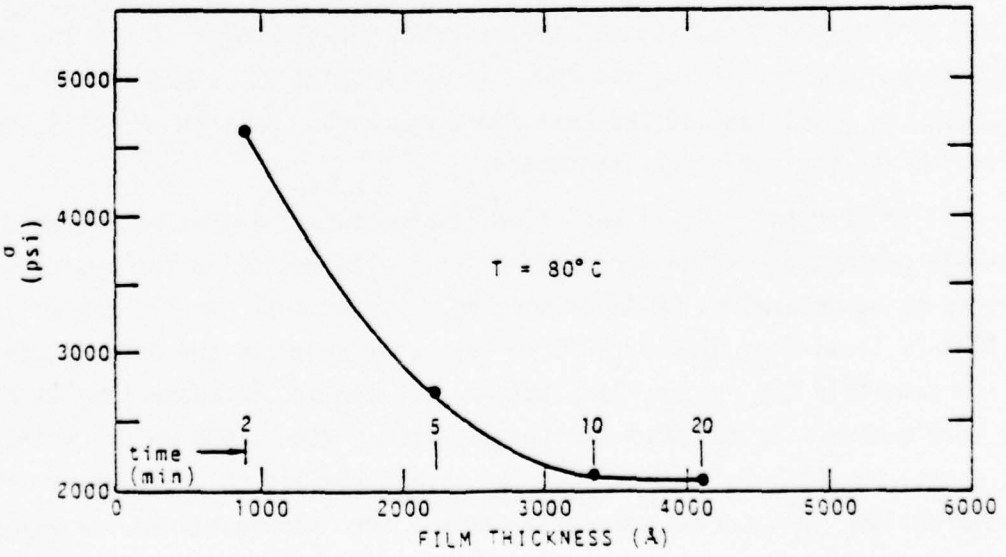



Fig. 14 Lap shear strength of adhesive bonds formed on aluminum surfaces with oxide layers of various thicknesses.

Figure 15 compares the surface properties of films formed by different times of exposure in D.I. water and tap water. It was observed that additions of cations and anions to D.I. water had little effect on bond strength, except for those compounds that contained carbonate ions. Tap water (which contains $CO_3^=$) and D.I. water with added carbonate ions inhibit the growth of the aluminum hydroxide (boehmite) film to about 1000A. The film formed in D.I. water is irridescent and transparent. About 500A of hydroxide forms in the first minute, with a corresponding sharp decrease in PEE, SPD and water contact angle. The decrease in PEE indicates the film is electron attenuating, the decrease in SPD indicates a change in outer dipole nature (toward a surface with molecules having negative ends pointing away from the surface) and the lowering of $\theta_{H_2O}$ toward zero indicates removal of organic contamination. All of these properties are different for tap water or carbonate solutions. The increase in PEE for a tap water soak indicates the formation of less attenuating or an emitting film, the SPD and $\theta H_2O$ decrease more gradually than for D.I. water.

A simple peel force test (Scotch tape pulled in 180° peel) and contact angles were performed to measure how they were modified by the pH of the carbonate solution used for the soak cycle. The aqueous carbonate solution ($2.5 \times 10^{-5}$ M $K_2CO_3$) had its pH adjusted with KOH and HCl. At low pH, $\theta_{H_2O}$ was high and the peel force was low. In the neutral and basic region (pH 5-10) $\theta_{H_2O}$ was low and the peel force was high. At high pH (>11), $\theta_{H_2O}$ increased and the peel force decreased.

At this point it is not known if the contact angles are related to inherent properties of the hydroxide or to contamination on the hydroxide. This is being determined by Auger spectroscopy and XPS. An XPS analysis of Al 7075-T6 treated by STAB at 80°C in tap water revealed the outer surface to be approximately 61% oxygen, 8% aluminum, 20% carbon, 7% magnesium, 3% silicon, and some sodium. In spite of the large carbon content, the water contact angle was low (15°) indicating that the carbon was not in the form of organic contamination. Sputtering partially through the film decreased the oxygen to

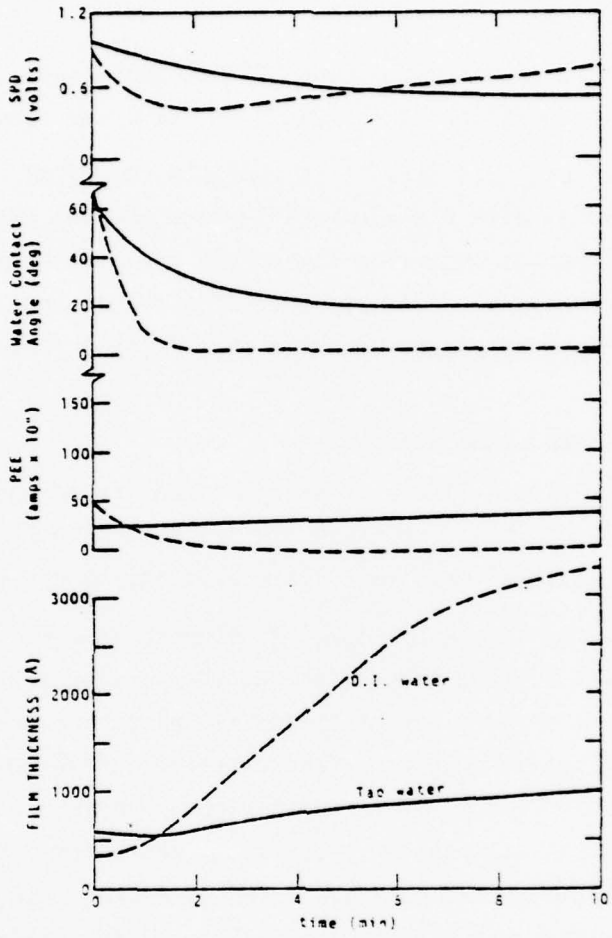



Fig. 15 Variation of various surface layer sensitive physical measurements as a function of time at which an aluminum surface is exposed to deionized water (D.I.) and ordinary tap water.

about 50%, increased aluminum to about 20% and decreased the carbon to zero. If carbonate is in the film, it is mainly in the outer atom layer.

From the data thus far, it is possible that STAB is effective because the reaction of water with the aluminum surface removes organic contamination and leaves a very porous hydroxide layer that can make an effective mechanical attachment to the adhesive. The presence of carbonate inhibits the growth of the weak porous layer of pseudo boehmite that forms in D.I. water.

## 1.3 Bond Strength and Endurance

In the original[1] STAB(1) research it was found that Al 2024-T3 and Al 7075-T6 gave strong bonds of ~34.4 MPa (~5 Ksi) with cohesive failure and wedge durability tests of 0.25 cm (0.10 ± 0.05 in)/24 hrs for 3M2214 adhesive.

In this program the tables give information about the surface treatment, the resultant surface properties and the bonding properties. The surface properties are $\Delta$ and $\psi$ for ellipsometry, which are related to optical thickness and refractive index, surface potential difference (SPD) which is related to the outer dipole layer, photoelectron emission (PEE) which is related to emitting and attenuation properties, and water contact angle ($\theta_{H_2O}$) which is extremely sensitive to organic contamination. In the bonding properties section of each table are reported 180° peel for Scotch tape, lap shear strength for EA9628, and results of the wedge test in terms of the initial crack extension and crack growth during the first hour and after 24 hours at 60°C and 100% RH. The purpose of each set of tests is recorded at the top of the tables and details are given at the bottom.

Boeing established 1.9 cm (0.75")/1 hr at 50°C (120°F), 100% RH as the maximum acceptable crack growth (see Fig. 15, Ref. 1). In view of the uncertainties associated with 1 hr exposure, data will be reported at 1 hr and 24 hr. For the exploratory work in this report, a more stringent test at 60°C (140°F), 100% RH, has been used.

Table (1) gives wedge test results for Hysol EA9628 and Al 2024-T3 with the FPL surface treatment for comparison with other treatments. The crack growth was acceptable (~0.76 cm (~0.3 in)/24 hr). Table (2) gives wedge test results for phosphoric acid anodize (PAA) for comparison. The crack growth is acceptable (~0.25 cm (~0.1 in)/24 hr).

Table 3 shows wedge test results to compare unprimed STAB(1) and EA9628 with FM73. The FM73 bonds are acceptable (consistent with previous work) but the EA9628 is not. A set of experiments was performed testing various solvents in the degrease step. Table 4 shows that after STAB(1) in tap water the contact angles were high, the peel force low, and the crack growth unacceptable for unprimed Al 2024-T3 and EA9628. An extra degrease in trichloroethylene (Table 5) improved $\theta_{H_2O}$, peel force and crack growth, but is still unacceptable. Other experiments to test effect of solvents (Tables 6-8) proved unsuccessful in reducing crack growth below the acceptance value of 1.9 cm (0.75 in)/24 hr, whereas priming the STAB(1) surface (Table 9) did. However, an error was made in the priming process, in that the primer was baked immediately after brush-on, rather than waiting 30 min. as required. As a consequence, failure was at the primer adhesive interface for initial fracture.

TABLE I

Investigator: Bivins  Alloy: 2024-T3  Adhesive: Hysol EA9628H

Purpose: To check the standard FPL treatment for comparison with other treatments.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | FPL | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-6-1 | G + Acetone | FPL Etched | 116.0 | 35.7 | +.45 | 8.5 | 3 | | | 3.30 (1.3) | 0.25 (0.1) | 0.51 (0.2) |
| 10-6-2 | G + Acetone | FPL Etched | 113.2 | 36.5 | +.45 | 10. | 2 | | | | | |
| 10-6-3 | G + Acetone | FPL Etched | 114.8 | 35.9 | +.45 | 8. | 2 | | | 3.56 (1.4) | 0.25 (0.1) | 0.76 (0.3) |
| 10-6-4 | G + Acetone | FPL Etched | 116.0 | 36.7 | +.52 | 10. | 2 | | | | | |
| 10-6-5 | G + Acetone | FPL Etched | 115.4 | 36.5 | +.5 | 10. | 2 | | | 3.30 (1.3) | 0.51 (0.2) | 0.76 (0.3) |
| 10-6-6 | G + Acetone | FPL Etched | 116.6 | 36.8 | +.45 | 12. | 2 | | | | | |

TABLE 2

Investigator: Bivins  Alloy: 2024-T3  Adhesive: Hysol EA9628H

Purpose: To check the phosphoric acid anodize treatment for comparison with other treatments.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | PAA | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-6-7 | G + 140 EC | PAA | 154.6 | 45.4 | -.2 | 0.10 | 2 | | | 2.64 (1.04) | 0.13 (0.05) | 0.38 (0.15) |
| 10-6-8 | G + 140 EC | PAA | 157.8 | 45.8 | -.1 | 0.09 | 2 | | | | | |
| 10-6-9 | G + 140 EC | PAA | 157.4 | 45.8 | -.1 | 0.08 | 3 | | | 3.30 (1.3) | 2.25 (0.1) | 0.51 (0.2) |
| 10-6-10 | G + 140 EC | PAA | 166.0 | 45.7 | -.1 | 0.08 | 3 | | | | | |
| 10-6-11 | G + 140 EC | PAA | 155.2 | 44.5 | -.15 | 0.08 | 2 | | | 4.32 (1.7) | 0 | 0.13 (0.05) |
| 10-6-12 | G + 140 EC | PAA | 161.4 | 46.9 | -.15 | 0.08 | 3 | | | | | |

TABLE 3

Investigator: Bivins

Alloy: 2024-T3

Adhesive: FM73
Hysol EA9628H used for samples 17 and 18.

Purpose: To check FM73 vs. EA9628H for STAB

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta H_2O$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 4-13 | G + C | (1) | | | | | 6 | | | 6.85 (2.7) | 1.12 (0.4) | 1.27 (0.5) |
| 4-14 | G + C | (1) | | | | | 4 | | | | | |
| 4-15 | G + C | (1) | | | | | 4 | | | 3.30 (1.3) | 0.76 (0.3) | 1.02 (0.4) |
| 4-16 | G + C | (1) | | | | | 4 | | | | | |
| 4-17 | G + C | (1) | | | | | 4 | Hysol EA9628 | | 3.05 (1.2) | 1.02 (0.4) | 2.54 (1.0) |
| 4-18 | G + C | (1) | | | | | | | | | | |

Remarks: "G + C" - one part gunk, nine parts original Chevron solvent, 10 min., U.S. hardspray rinse with $DiH_2O$, "STD" fresh batch $DiH_2O$ - stir until pH = 5, then add $K_2CO_3$ until 9.8 pH - start heating to 80°C - STAB for 10 min., fast stir, pull from STAB bath - hard spray group then individually spray $DiH_2O$ - setup to drain until all are rinsed - dry $N_2$ gas stream - stand up againg 5-10 min. - check $\theta H_2O$ - pH meter calib. checked at end of day - pH 10 std. was found to read 9.5 (subtract .5 pH from 9.8 pH), this means that the pH was actually 9.3.

TABLE 4

Investigator: G.L. Alloy: 2024-T3 Adhesive: Hysol EA9628H

Purpose: To test tap water STAB(1) after standard degrease. These samples to be compared to tap water STAB after extra degrease. (next table).

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1 | G + 140 EC | (1) | 66.6 | 37.0 | .25 | .44 | 52 | 510 | | 2.54 (1.0) | 2.16 (0.85) | 5.33 (2.1) |
| 2 | G + 140 EC | (1) | 58.8 | 42.0 | .14 | .7 | 52 | 523 | | 2.29 (0.9) | 1.52 (0.6) | 6.36 (2.5) |
| 3 | G + 140 EC | (1) | 56.4 | 35.6 | .18 | .6 | 43 | 510 | | 2.92 (1.15) | 4.32 (1.7) | 8.13 (3.2) |
| 4 | G + 140 EC | (1) | 68.0 | 39.4 | .24 | .33 | 62 | 542 | | 2.54 (1.0) | 1.78 (0.7) | 5.33 (2.1) |
| 5 | G + 140 EC | (1) | 63.6 | 34.3 | .16 | .6 | 54 | 510 | | 1.78 (0.7) | 1.65 (0.65) | 5.59 (2.2) |
| 6 | G + 140 EC | (1) | 57.4 | 39.3 | .25 | .36 | 62 | 510 | | 2.54 (1.0) | 0.20 (0.08) | 9.40 (3.7) |

Remarks: "Gunk" degrease was ultrasonic for 10 min in 1 part Gunk, 9 parts Shell SOL. 140 EC solvent, then rinsed in flowing D.I. $H_2O$ and dried in flowing $N_2$.
Approximate psi for Hysol cure = 20 psi
The samples were bonded to PAA samples.

TABLE 5

Investigator: GI  Alloy: 2024-T3  Adhesive: Hysol EA9628II

Purpose: To test tap water STAB after standard degrease but with extra trichloroethylene degrease.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLL (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 7 | G + Trichlor | (1) | 54.0 | 37.3 | .1 | .7 | 26 | 638 | | 2.79 (1.1) | 1.27 (0.5) | 5.33 (2.1) |
| 8 | G + Trichlor | (1) | 54.6 | 34.3 | .1 | .6 | 25 | 654 | | 2.29 (0.9) | 0.76 (0.3) | 4.57 (1.8) |
| 9 | G + Trichlor | (1) | 60.0 | 34.3 | .1 | .7 | 32 | 735 | | 2.54 (1.0) | 0.25 (0.1) | 4.57 (1.8) |
| 10 | G + Trichlor | (1) | 60.8 | 34.3 | .09 | .64 | 18 | 702 | | 2.79 (1.1) | 0.13 (0.05) | 2.54 (1.0) |
| 11 | G + Trichlor | (1) | 65.2 | 36.3 | .11 | .41 | 30 | 606 | | 3.05 (1.2) | 0.51 (0.2) | 3.81 (1.5) |
| 12 | G + Trichlor | (1) | 53.0 | 38.4 | .1 | .74 | 30 | 622 | | 2.29 (0.9) | 0.51 (0.2) | 3.56 (1.4) |

Remarks: "Gunk degrease was ultrasonic for 10 min in 1 part Gunk, 9 parts Shell SOL. 140. solvent, then rinsed in flowing D.I. $H_2O$ and dried in flowing $N_2$.
(I) STAB, D.I. $H_2O$, pH = 9.8 using $K_2CO_3$, at 80°C for 10 min, stirred, then rinsed in flow D.I. $H_2O$ and dried in flowing $N_2$.
"extra" - ultrasonic trichloroethylene, rinse in methanol and dry in flow $N_2$.
The samples were bonded tfo PAA samples.
Approximate psi for Hysol cure = 20 psi.

TABLE 6

Investigator: Bivins  Alloy: 2024-T3  Adhesive: Hysol EA9628H

Purpose: Test the effect of different solvents on the bond strength. This test used Shell SOL. 140.EC

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1 | G + S | (1) | | | | | 6 | | | 3.3 (1.3) | 3.0 (1.2) | 4.3 (1.7) |
| 2 | G + S | (1) | | | | | 9 | | | | | |
| 3 | G + S | (1) | | | | | 7 | | | 3.0 (1.2) | 0.3 (0.1) | 2.8 (1.1) |
| 4 | G + S | (1) | | | | | 6 | | | | | |
| 5 | G + S | (1) | | | | | 11 | | | 3.3 (1.3) | 1.3 (0.5) | 3.8 (1.5) |
| 6 | G + S | (1) | | | | | 13 | | | | | |

Remarks: "G + S" = 1 part Gunk, 9 parts Shell SOL. 140. C, 10 min u.s., hard spray rinse, D.I. $H_2O$.
(1) - D.I. $H_2O$, pH = 9.8 using $K_2CO_3$, at 80°C for 10 min, stirred (fast as you can go - higher), hard spray rinse D.I. $H_2O$, dry in flowing $N_2$.

Note: Waited at room temperature, no humidity, for 1 hour after placing wedge, got approximately .1 inch crack growth before putting in humidity chamber.

TABLE 7

Investigator: Bivins  Alloy: 2024-T3  Adhesive: Hysol EA9628H

Purpose: Test the effects of different solvents on the bond strength.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (y/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 7 | G + C | (1) | | | | | 8 | | | 3.30 (1.3) | 1.02 (0.4) | 3.86 (1.52) |
| 8 | G + C | (1) | | | | | 5 | | | | | |
| 9 | G + C | (1) | | | | | 4 | | | 3.81 (1.5) | 0.25 (0.1) | 2.79 (1.1) |
| 10 | G + C | (1) | | | | | 6 | | | | | |
| 11 | G + C | (1) | | | | | 3 | | | 3.18 (1.25) | 0.76 (0.3) | 3.05 (1.2) |
| 12 | G + C | (1) | | | | | 3.5 | | | | | |

Remarks: "G + C" - 1 part Gunk, 9 parts Chevron solvent, 10 min u.s. hard spray rinse with D.I. $H_2O$
(1) - D.I. $H_2O$, pH = 4.8 using $K_2CO_3$, at 80°C for 10 min, stirred fast, hard spray rinse with D.I. $H_2O$, dry in flowing $N_2$.

Note: Waited at room temperature, no moisture, for 1 hour after placing wedge - got approximately .1 in. crack growth, before placing in humidity chamber.

TABLE 8

Investigator: Bivins  Alloy: 7075-T6  Adhesive: Hysol EA9628H

Purpose: Testing various degreasing treatments, Gunk and Kerosene and Gunk and Shell SOL.140.EC

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1 | G + K | (1) | | | | | 14 | | | 3.81 (1.5) | 0.25 (0.1) | 5.08 (2.0) |
| 2 | G + K | (1) | | | | | 8 | | | | | |
| 3 | G + S | (1) | | | | | 4 | | | 6.35 (2.5) | 0.76 (0.3) | 4.06 (1.6) |
| 4 | G + S | (1) | | | | | 6 | | | | | |

Remarks: "G + K" - 1 part Gunk, 9 parts Kerosene, 10 min u.s., hard spray rinse, $H_2O$.
"G + S" - 1 part Gunk, 9 parts Shell SOL. 140. EC, 10 min u.s., hard spray rinse, dry in flowing $N_2$.

Note: Each "pair" of samples used a "fresh" STAB solv.
(1) = D.I. $H_2O$, pH = 9.8 using $K_2CO_3$, at 80°C for 10 min., stirred fast with big bar, hard spray rinse D.I. $H_2O$, dried in flowing $N_2$.

TABLE 9

Investigator: Bivins

Alloy: 2024-T3

Adhesive: EA9628H
Primer: EA9210H

Purpose: Test EA9628H adhesive with EA9210H primer on PAA and STD STAB samples
Wrong procedure on application of the primer.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | STAB | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-11-1 | G + Kerosene | 10 min 9.3pH | 102. | 46.6 | +.12 | -.05 | 2° | | | 5.59 (2.2) | 0.35 (0.12) | 1.27 (0.5) |
| 11-2 | G + Kerosene | P.A.A. | | | | | | | | | | |
| 11-3 | G + Kerosene | 10 min 9.3 | 104.8 | 46.1 | +.04 | -.05 | 4° | | | 6.75 (2.7) | 0.25 (0.1) | 0.82 (0.32) |
| 11-4 | G + Kerosene | P.A.A. | | | | | | | | | | |
| 11-5 | G + Kerosene | 10 min 9.3pH | 106. | 38.1 | -.01 | -.06 | 2° | | | 6.73 (2.65) | 0.51 (0.2) | 1.02 (0.4) |

Remarks: Std Gunk 1 part, 9 parts kerosene u.s. 10 min rinse w/spray
P.A.A. - Gunk - kero, 10 min - 10 volts - dry w/jet $N_2$ gas.
Primer: should be brushed on tabs, air dry 30 min, bake 150°C for 30 min, flo thru oven
In this test, the 30 min wait was omitted.

TABLE 10

Date: 12-18-78 Investigator: I. Smith Alloy: Al 2024-T3 Adhesive: FM 73

Purpose: Check STAB(1) but with no rinse after water treatment. Use tap water for samples 1-6, D.I. water + $K_2CO_3$ for samples 7-12

| | Surface Treatment | | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Degrease | STAB(1) | | | | | | | Peel | Lap | Wedge Crack Growth/cm(in) | | |
| Sample No. | Ultrasonic G (min) | Time (min) | Temp (°C) | Δ (deg) | Ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Force (g/cm) | Shear (ksi) | (Initial) | (1 hr) | (24 Hr) |
| 12-18-78- | | | | | | | | | | | | | |
| 1 | 10 | 10 | 80 | 64 | 59 | 0.34 | 0.30 | 60 | | | 4.06 (1.6) | 0.51 (0.2) | 2.29 (0.9) |
| 2 | | Tap Water | | 24 | 58 | 0.33 | 0.30 | 45 | | | 3.81 (1.5) | 0.51 (0.2) | 2.79 (1.1) |
| 3 | | | | 64 | 39 | 0.26 | 0.30 | 42 | | | 3.81 (1.5) | 0.51 (0.2) | 2.03 (0.8) |
| 4 | | | | 286 | 33 | 0.26 | 0.20 | 52 | | | | | |
| 5 | | | | 290 | 37 | 0.40 | 0.15 | 55 | | | | | |
| 6 | | | | 314 | 67 | 0.40 | 0.18 | 50 | | | | | |
| 7 | | $K_2CO_3$ | | 306 | 21 | 0.40 | 0.12 | 50 | | | 5.89 (2.2) | 0.76 (0.3) | 2.29 (0.9) |
| 8 | | pH 9.8 | | 326 | 25 | 0.47 | 0.12 | 50 | | | 5.89 (2.2) | 0.51 (0.2) | 1.52 (0.6) |
| 9 | | | | 326 | 28 | 0.39 | 0.22 | 60 | | | 5.33 (2.1) | 0.51 (0.2) | 2.03 (0.8) |
| 10 | | | | 326 | 28 | 0.41 | 0.17 | 53 | | | | | |
| 11 | | | | 296 | 21 | 0.41 | 0.20 | 63 | | | | | |
| 12 | | | | 328 | 26 | 0.38 | 0.20 | 53 | | | | | |

Remarks: Stirred tap water, 10 min, no rinse, cold tap water pH~8.3
Cure Temp. 325° by mistake
Roll groove texture parallel to sample axis, all others have been perpendicular
Mate: 1-4, 2-5, 3-6, 7-10, 8-11, 9-12

TABLE 11

Date: 12-19-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: FM 73

Purpose: Check STAB(1) but with no rinse after water treatment

| Sample No. | Surface Treatment: Degrease Ultrasonic G (min) | Surface Treatment: STAB(1) $K_2CO_3$ (min) | Surface Properties: Δ (deg) | Ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-19-78- | | | | | | | | | | | | |
| 1 | 10 | 11 | 276 | 13 | 0.20 | 0.09 | 30 | | | 4.83 (1.9) | 0.51 (0.2) | 8.89 (3.5) |
| 2 | ↓ | ↓ | 78 | 10 | 0.18 | 0.14 | 30 | | | 4.06 (1.6) | 0.76 (0.3) | 3.81 (1.5) |
| 3 | | | 276 | 36 | 0.18 | 0.13 | 20 | | | 4.06 (1.6) | - | 3.30 (1.3) |
| 4 | | | 320 | 21 | 0.24 | 0.15 | 30 | | | 4.83 (1.9) | 1.27 (0.5) | 8.89 (3.5) |
| 5 | | | 340 | 21 | 0.24 | 0.13 | 35 | | | 4.32 (1.7) | 1.52 (0.6) | 8.89 (3.5) |
| 6 | | | 328 | 30 | 0.22 | 0.14 | 30 | | | 4.06 (1.6) | - | 7.62 (3.0) |
| 7 | | | 322 | 19 | 0.19 | 0.06 | 30 | | | | | |
| 8 | | | 306 | 23 | 0.12 | 0.16 | 30 | | | | | |
| 9 | | | 336 | 23 | 0.17 | 0.12 | 35 | | | | | |
| 10 | | | 302 | 56 | 0.16 | 0.17 | 20 | | | | | |
| 11 | | | 288 | 51 | 0.16 | 0.17 | 20 | | | | | |
| 12 | | | 264 | 42 | 0.18 | 0.14 | 20 | | | | | |

Remarks: D.I. water + $K_2CO_3$ to pH = 9.9, Temp. 80°C
Did not rinse after water soak
Mate: 1-7, 2-8, 3-9, 4-10, 5-11, 6-12

TABLE 12

Date: 12-21-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(1) but with different degrease step
Degrease by 20 min in MICRO only (1-6)
Degrease by 20 min in MICRO + 10 min ultrasonic in MICRO (7-12)

| | Surface Treatment | | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Degrease | | STAB(1) | | | | | | Peel | Lap | Wedge Crack Growth/cm(in) | | |
| Sample No. | MICRO + U.S. | | $K_2CO_3$ | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Force (g/cm) | Shear (Ksi) | (Initial) | (1 hr) | (24 Hr) |
| 12-21-78 | | | | | | | | | | | | | |
| 1 | 20 | 0 | D.I. water | 10 | 37 | 0.24 | 0.04 | 25 | | | 3.81 (1.5) | 0.51 (0.2) | 3.30 (1.3) |
| 2 | 20 | 0 | pH 9.8 | 18 | 27 | 0.22 | 0.08 | 20 | | | 3.81 (1.5) | - | 3.05 (1.2) |
| 3 | 20 | 0 | ↓ | 10 | 29 | 0.18 | 0.06 | 15 | | | 3.81 (1.5) | - | 3.30 (1.3) |
| 4 | 20 | 0 | ↓ | 26 | 36 | 0.18 | 0.06 | 12 | | | | | |
| 5 | 20 | 0 | ↓ | -8 | 37 | 0.32 | 0.06 | 10 | | | | | |
| 6 | 20 | 0 | ↓ | 6 | 20 | 0.23 | 0.12 | 12 | | | | | |
| 7 | 20 | 10 | ↓ | -4 | 43 | 0.11 | 0.02 | 0 | | | 3.30 (1.3) | 0.05 (0.02) | 0.76 (0.3) |
| 8 | 20 | 10 | ↓ | 34 | 41 | 0.10 | 0.02 | 0 | | | 3.05 (1.2) | 0.08 (0.03) | 0.76 (0.3) |
| 9 | 20 | 10 | ↓ | 96 | 47 | 0.08 | 0.06 | 0 | | | 3.56 (1.4) | 0.10 (0.04) | 0.76 (0.3) |
| 10 | 20 | 10 | ↓ | 78 | 32 | 0.09 | 0.05 | 0 | | | | | |
| 11 | 20 | 10 | ↓ | 14 | 40 | 0.10 | 0.04 | 0 | | | | | |
| 12 | 20 | 10 | ↓ | 40 | 33 | 0.18 | 0.05 | 0 | | | | | |

Remarks: D.I. water + $K_2CO_3$ to pH = 9.8, Temp. = 80°C

Table 10 and 11 show results for STAB(1) but neglecting the final rinse after the hot water soak. Regardless of the use of tap water or D.I. water + $K_2CO_3$ the crack growth was unsatisfactory, at least with FM73 and no primer. In Table 12, two degreasing steps were tested prior to STAB(1) with carbonate. With ultrasonic cleaning and with Hysol 9628 and 9210 primer successful results were obtained (i.e., 0.76 cm (0.3 in)/24 hr).

## 1.4 Post Fracture Analysis

To examine the interface after the wedge test humidity exposure, the couples were split apart and about 0.5 cm of the 11.24 cm (6 inch) specimen was cut out without disturbing the surface to be examined. The surface to be examined was the region of debond during crack growth in the humidity chamber. The cut out piece was then bent until it failed, mounted and gold deposited for SEM.

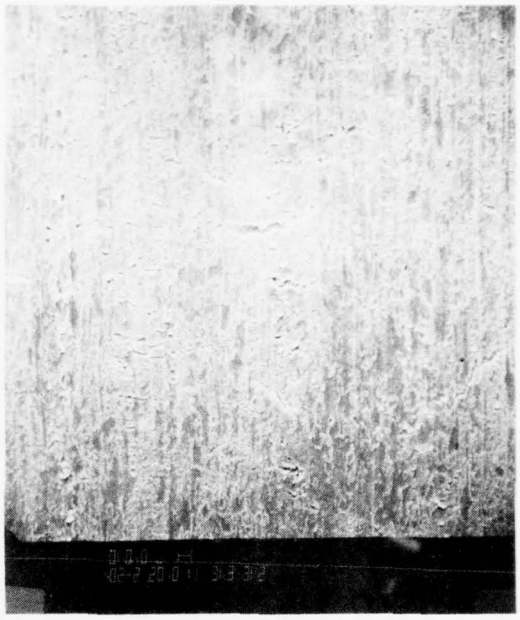
Table 13 lists micrographs from good (~0.76 cm (0.3 in)/24 hr), medium (~1.78 cm (0.7 in)/24 hr) and bad (3.81 cm (1.2 in)/24 hr) wedge tests. In Figs. 16, 17 and 18 the lower series of numbers on each micrograph identifies the magnification (e.g., 02-1 in Fig. 16a is X20), the specimen number (second to last series of 3 numbers) and picture number (last series of three numbers). In Fig. 16a the magnification is X20, the specimen number is 312 and the picture number is 067.

TABLE 13

Key To Micrographs In Figs. 16, 17 and 18

| Specimen No. | Bond Type | Interface Mate | Degrease | Treatment | Crack Growth cm(in)/24 hr |
|---|---|---|---|---|---|
| 312 | Good | Metal | US-MICRO | STAB(1) | 0.76 (0.3) |
| 313 | Good | Adhesive | US-MICRO | " | 0.76 (0.3) |
| 316 | Medium | Adhesive | US - G | " | 1.79 (0.7) |
| 314 | Medium | Metal | STAB(3) | " | 1.78 (0.7) |
| 311 | Bad | Adhesive | MICRO | " | 3.05 (1.2) |


e

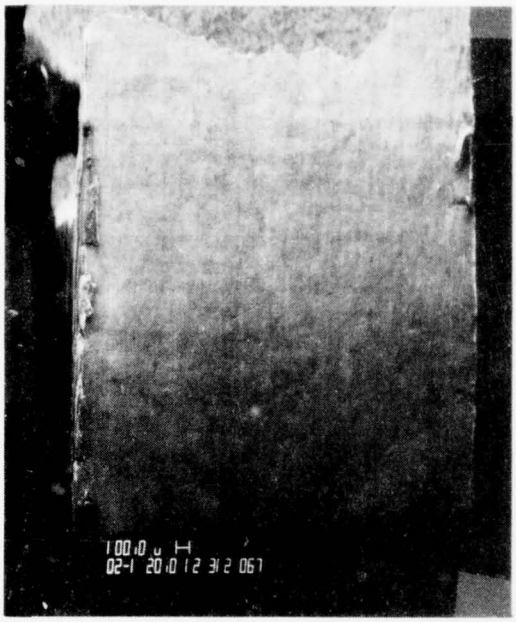


f

g

h

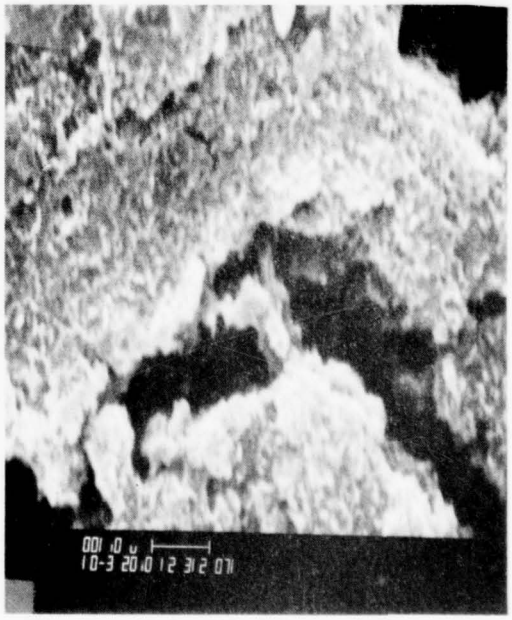
Fig. 16 continued



a

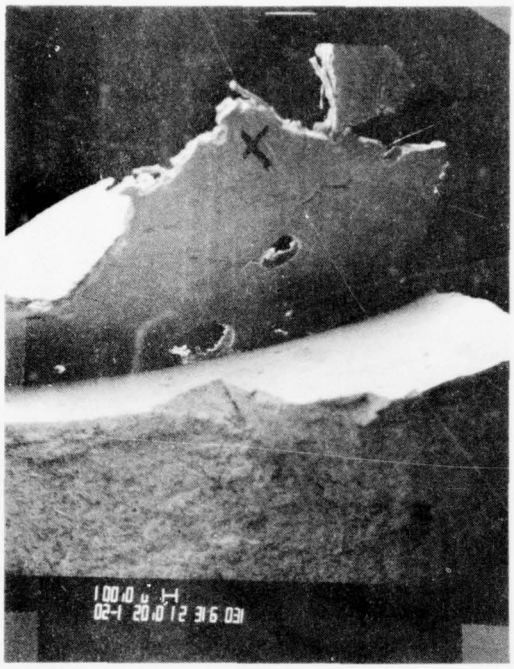
b

c

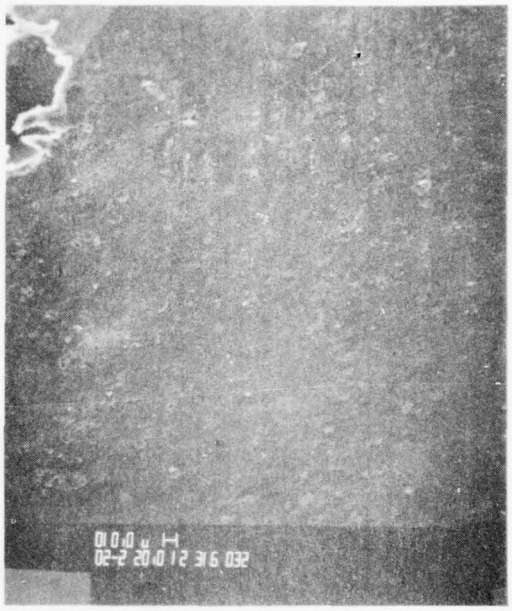


d

Fig. 16 SEM pictures of the debond region of a good wedge test joint (STAB(1)).

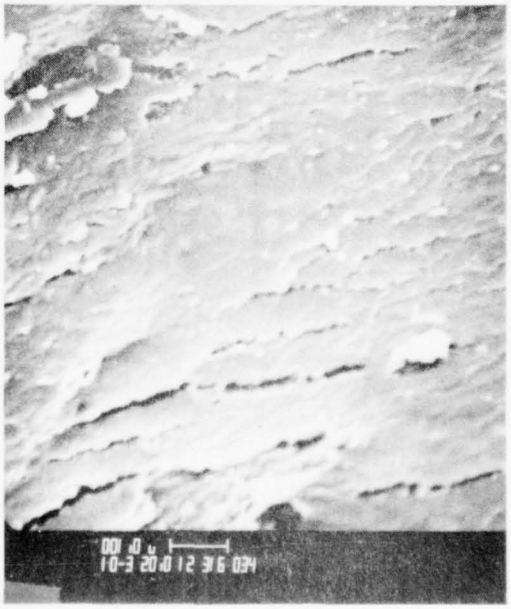



a



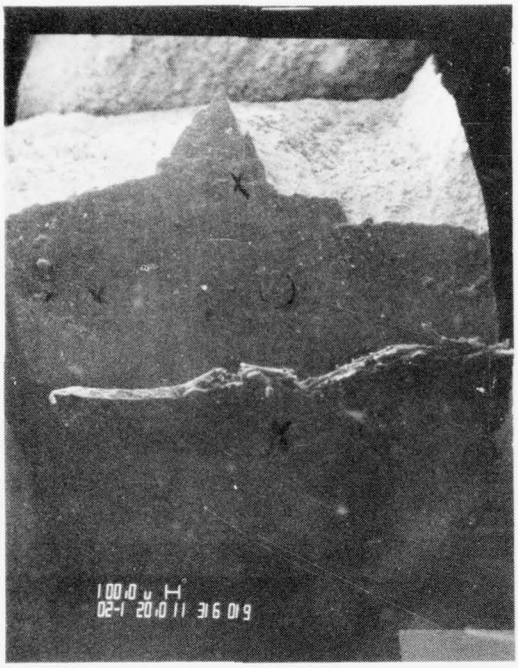

b


c




d

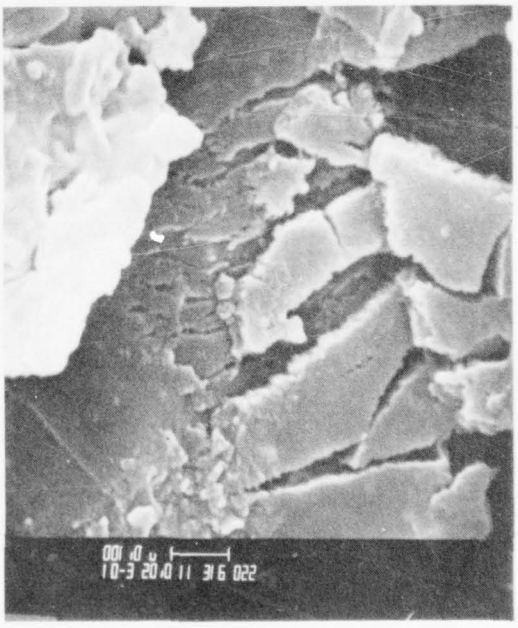
Fig. 17 SEM pictures of debond region of a medium wedge test joint (STAB(1)).




e


f

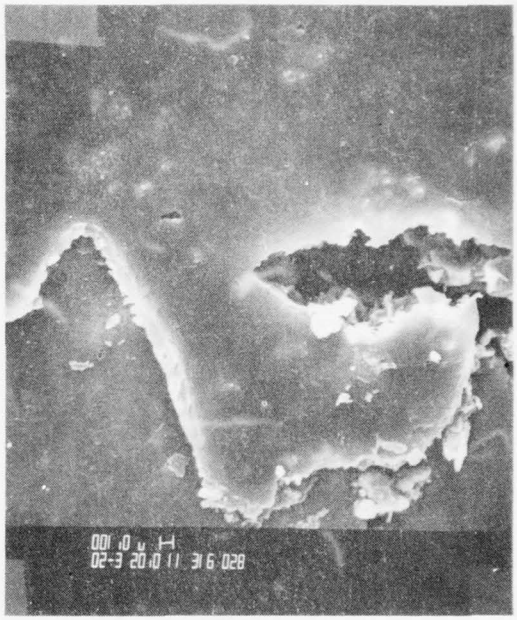

g



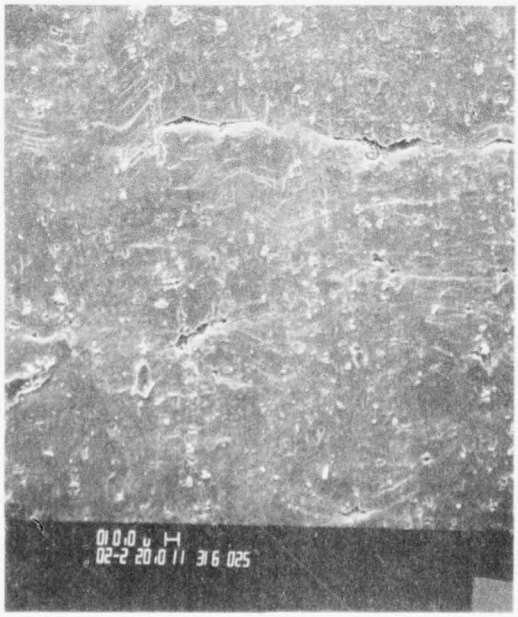

h

Fig. 17 continued

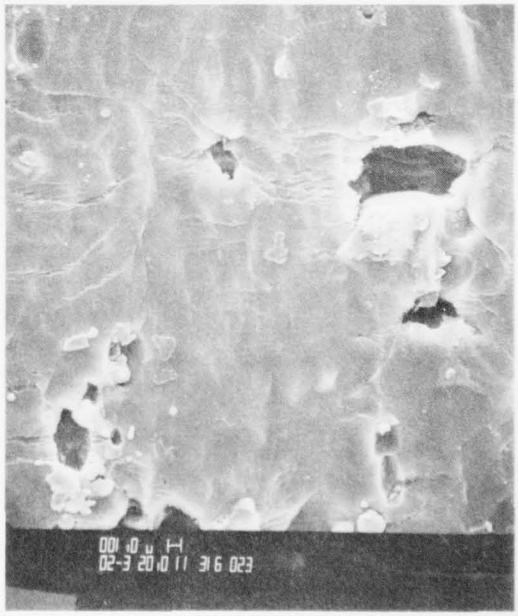
i



j

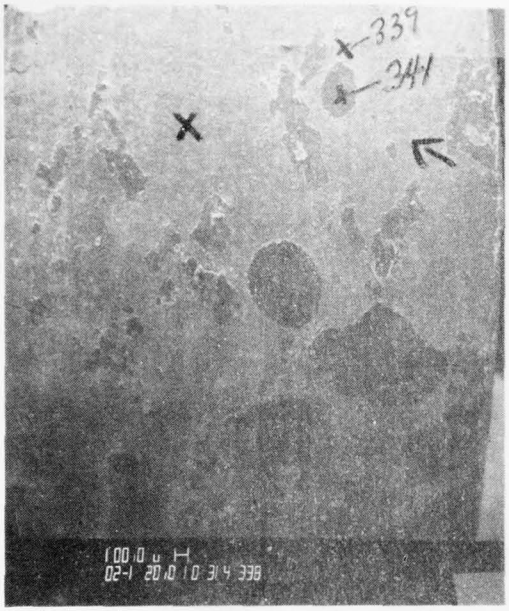


k



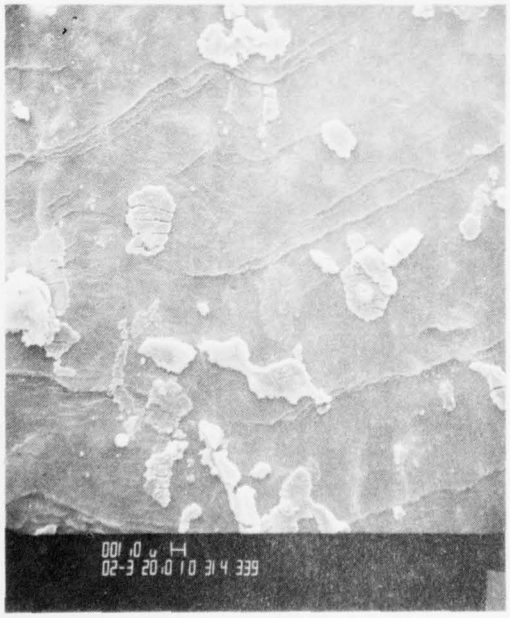
l

Fig. 17 continued

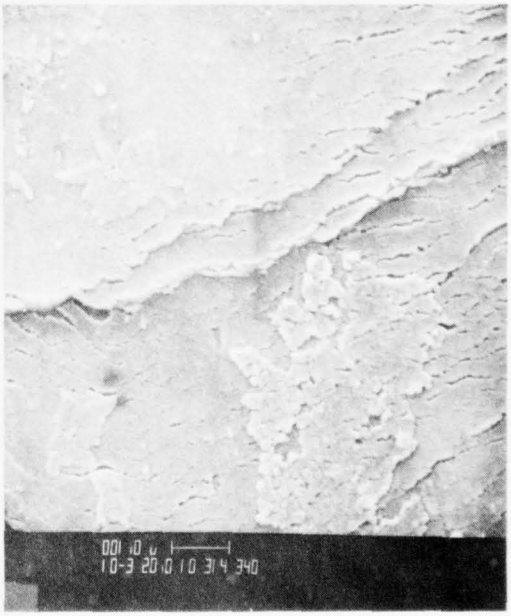



a

b



c



d

Fig. 18 SEM pictures of debond region for a medium wedge test joint (STAB(1)).

The top numbers in each picture identify the distance in microns between white lines. The first column in Table 13 identifies the specimen number. Table 13 lists the type of bond (good, medium or bad) with respect to the wedge test, as well as the degrease treatment and STAB treatment.

The SEM pictures reveal four surfaces, the metal (with its hydroxide) that has debonded during the wedge test, the metal that did not debond during the wedge test but did debond upon bending of the cut out piece, and the mating adhesive to these surfaces.

Figures 16a-d are SEM pictures of the metal debond region of a wedge test that was good (~1.78 cm (0.3 in)/24 hr) after STAB(1). Figure 16a is X10, b is X200, c is X2000 and d is X10,000. The hydroxide film is seen to be layered and is fractured due to bending of the cut out piece. The X10,000 picture (d) reveals the cellular porous structure of the hydroxide, and when compared to Fig. 2, appears to have failed in the primer-hydroxide interface. Figures 16e-h show the metal surface that did not debond during the wedge test but fractured during metal bending. Again the failure is at the hydroxide-primer interface, the layered film is observed but in this case it is obvious that failure had occurred in the primer, leaving primer embedded within the hydroxide.

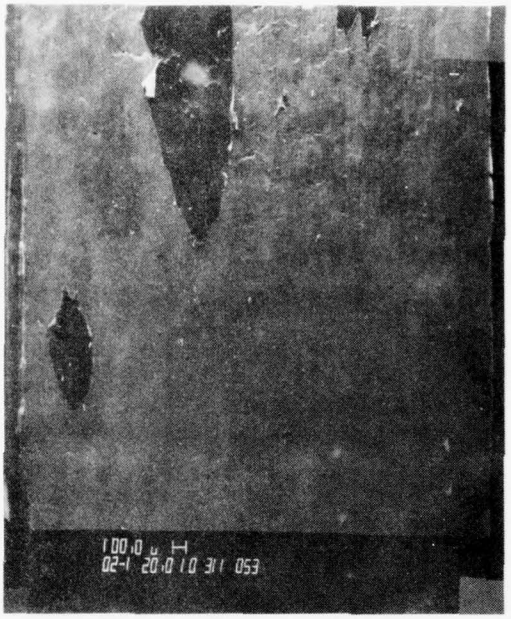
Figure 17a-g is of the debond region of a joint after STAB(1) which was medium with regard to the wedge test (~0.7 in/24 hr). Figure 17a is a low magnification showing the adhesive peeled away from the metal during metal bending. The holes in the adhesive layer were caused by gas bubbles that are found in nearly every hexagonal cell outlined by the nylon scrim. If the bubbles are excessively large, the thin adhesive (or primer) layer tears away from the adhesive layer and remains on the adherend and a hole is left in the adhesive film. Figures 17b, c and d reveal the mating adhesive surface, in the region marked by an X in Fig. 17a. The adhesive appears rather smooth and untorn but Fig. 17d indicates a thin (2000A-3000A) layer has been transferred from the metal. The picture numbers identify the regions in Fig. 17e where they were taken. For example, Figs. 17f, g and h show increasing magnifica-

tion of region 20 at the left of Fig. 17e. The main feature is the layers of hydroxide along with large particles of adhesive. Failure appears to be primarily in the hydroxide lamalae. Figure 17i reveals a small piece of primer (circled in Fig. 17e). A larger magnification of part of the primer particle is seen in Fig. 17j, it is very smooth on top and indicates delamination at the primer-adhesive interface. Figures 17k and l are larger magnifications of the region around the primer, i.e, hydroxide that has appeared to have failed between lamalae. Note that the surface structure does not appear as in Figs. 2c and d.

Figure 18 shows the debond region of the metal for another medium wedge test. Debonding has occurred at the metal-primer interface. Patches of primer are left where bubbles had formed leaving a smooth polymer surface (Fig. 18b). Figure 18b is of the primer surface and Figs. 18c and d are of the hydroxide surface. The layers of hydroxide can be seen and failure again appears to be between lamalae.

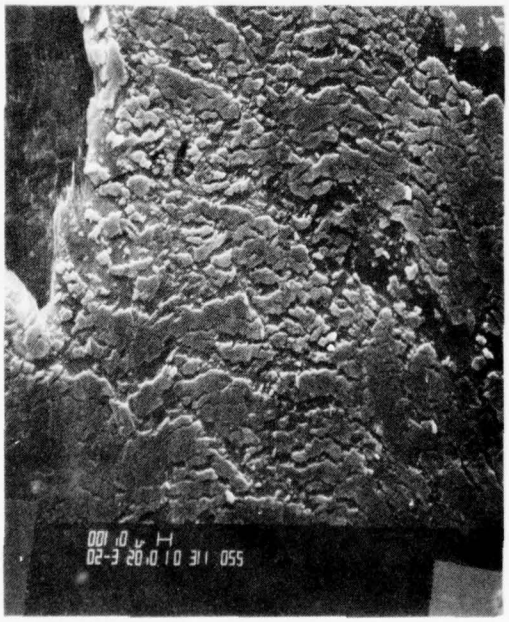
Figure 19 is for a wedge test that was bad (~3.0 cm (1.2 in)/24 hr). In Fig. 19a large pieces of primer remain on the surface in the debond region. They seem too big to be formed by bubbles but are probably due to poor contact between the primer and adhesive. Figures 19c and d are larger magnifications of the region 55 in Fig. 19b. The peeled back piece of primer (region 59) in Fig. 19b and the enlargement of this region in Fig. 19h reveal failure between lamalae in the hydroxide film, a layer of hydroxide has been transferred to the primer. Figures 19e shows a region of the debonded adhesive. Although the roll pattern from the metal is on the adhesive, Fig. 19f (a larger magnification of 19c) shows that failure occurred cohesively in this region. Figure 19g is a larger magnification of the primer surface.

Apparently STAB(1) forms a layered structure of hydroxide with a very porous outer layer in which the primer becomes mechanically attached. In some cases separation between these layers causes crack growth under hydrothermal stress.

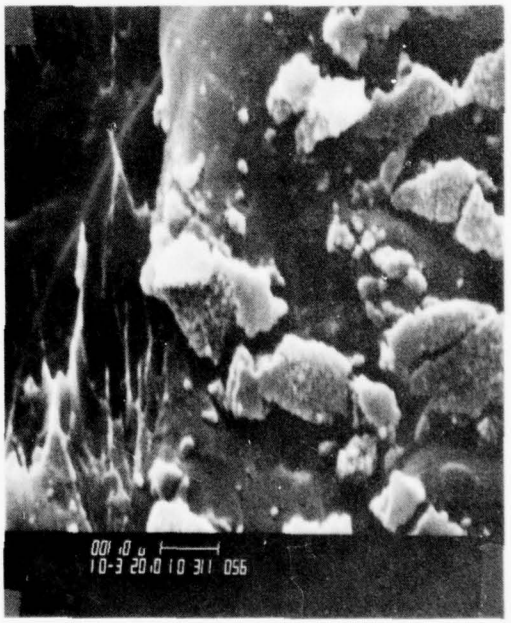



a


b



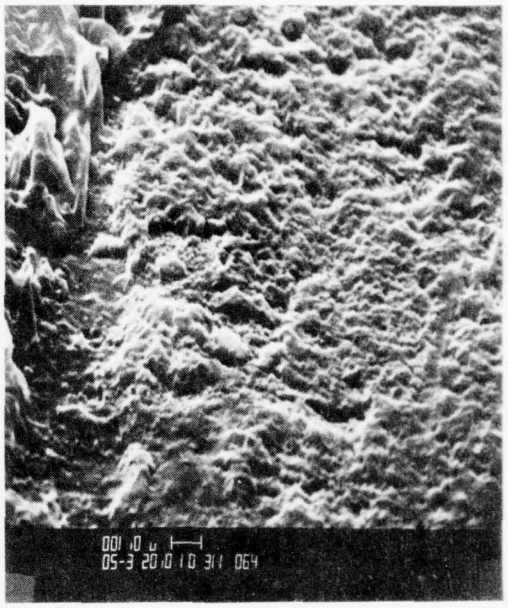

c



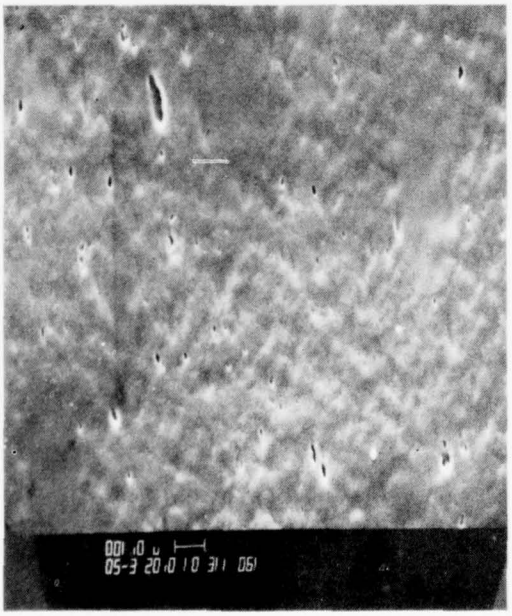

d

Fig. 19 SEM pictures for debond region in a bad wedge test joint (STAB(1)).

e



f



g

h

Fig. 19 continued

## 2. STAB(2)

During the study of the effect of various degreasing steps for STAB(1), it was discovered that a commercial cleaner "MICRO"* appeared to give considerable improvement in bond durability. Because of the simplicity of this treatment an effort was expended to explore it in more detail.

### 2.1 Experimental

STAB(2) involves a degrease followed by room temperature soak in a solution of 60 ml of MICRO in 1 liter of water. This solution has a pH of about 9.8 as for STAB(1).

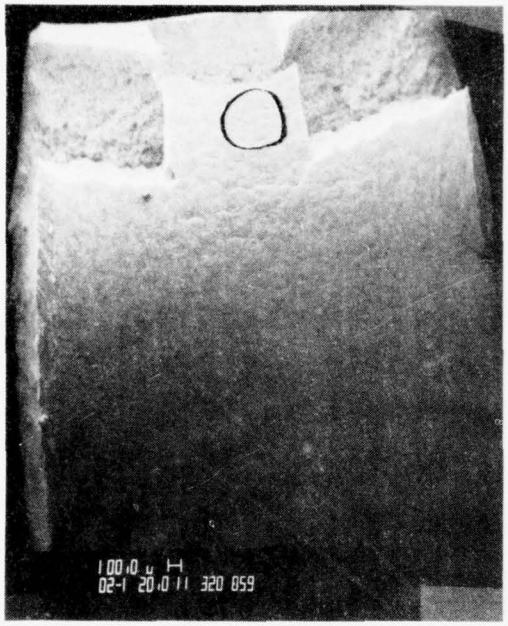
### 2.2 Surface Characterization

Figure 20 shows SEM pictures of Al 2024-T3 after STAB(2). A hydroxide film a few thousand angstroms thick is formed but the outer surface does not have the porous open structure as for STAB(1) (Fig. 2). Figure 21 is an AES and Fig. 22 shows a sputter profile of Al 2024-T3 after STAB(2). As for STAB(1) the film is stable in the electron beam, no Al 60 eV appears. The initial carbon peak is large, but is removed in less than a minute of $Ar^+$ sputtering. Note that the oxygen peak increases as the carbon is removed because the oxide is covered by the organic contamination.

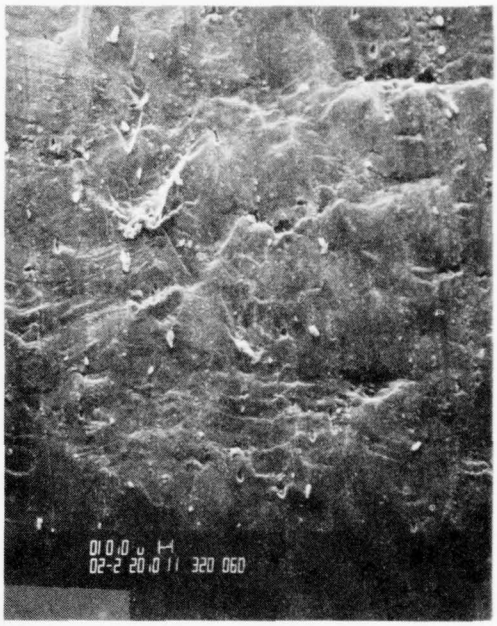
Figures 23a and b show changes in the surface properties as measured by ellipsometry and photoemission. Just as the chemistry and morphology differ between STAB(1) and STAB(2), so does the surface property profile during thermal, humidity history. The only similarity is that $\theta_{H_2O}$ (in Fig. 23c) increases during oven exposure and decreases during humidity exposure.

The effect of time in MICRO (STAB(2) Table 12), and the effect of ultraviolet light exposure after STAB(2), have been studied to elucidate

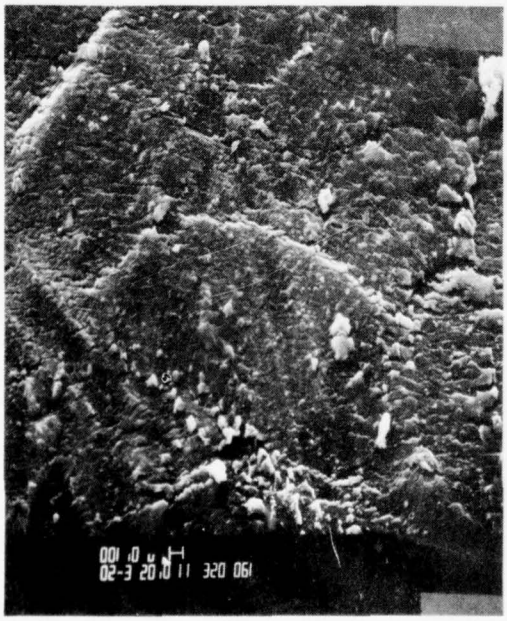
*"MICRO" is a trade name for a detergent cleaning solution containing amonium hydroxide. International Products Corp., P.O. Box 118, Trenton 1, NJ.



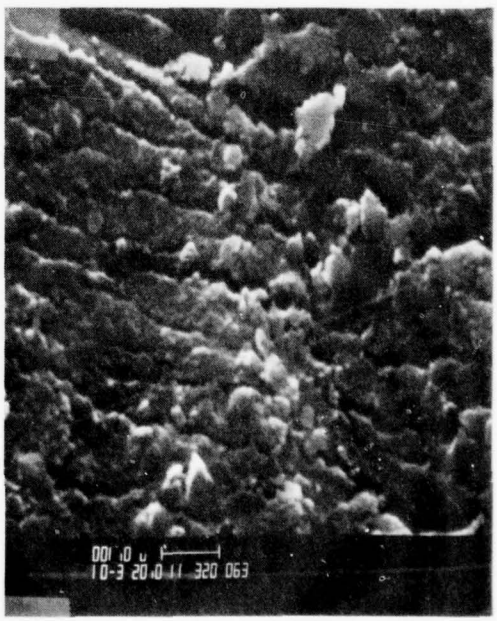

a




b




c




d

Fig. 20 SEM pictures of Al 2024-T3 after STAB(2).

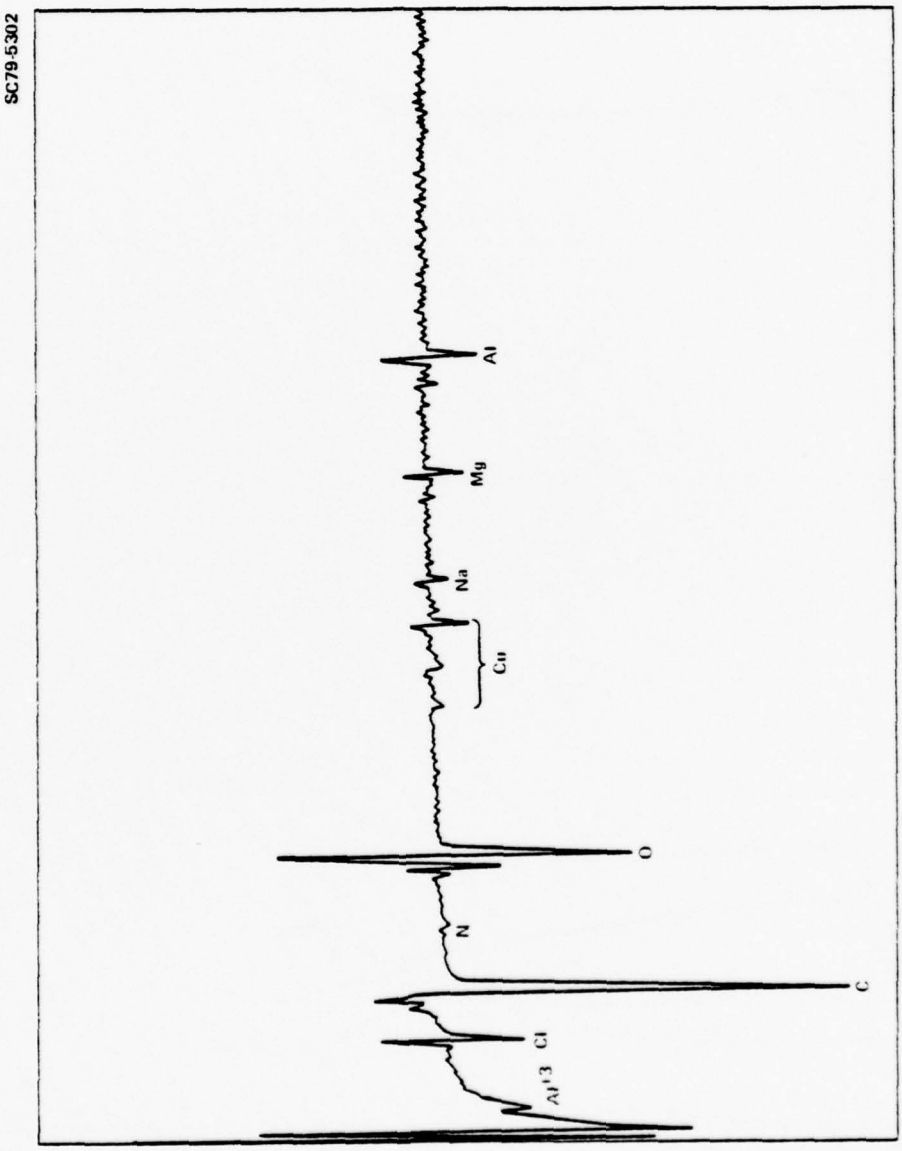



Fig. 21 AES of Al 2024-T3 after STAB(2).

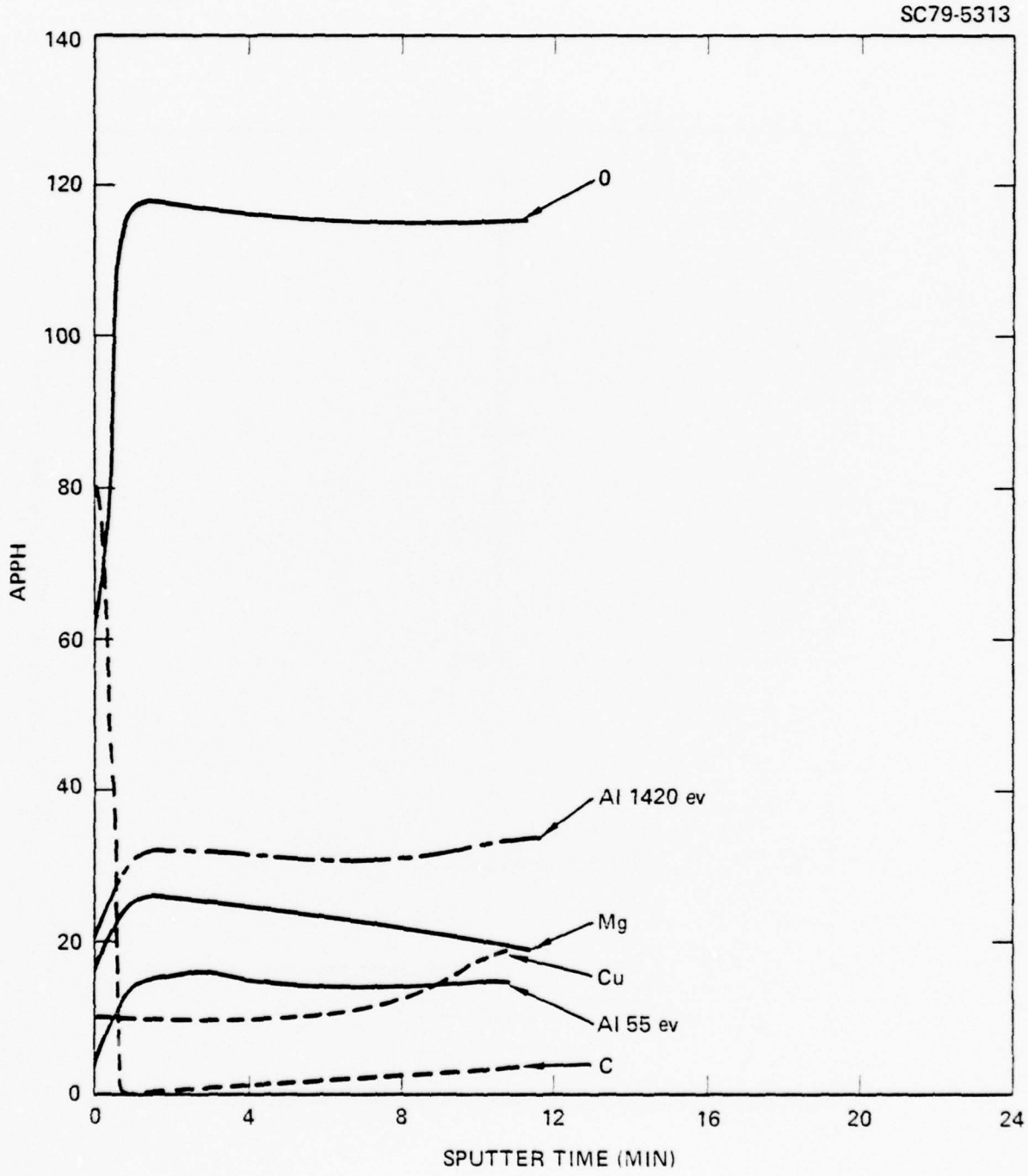



Fig. 22 AES sputter profile of Al 2024-T3 after STAB(2).

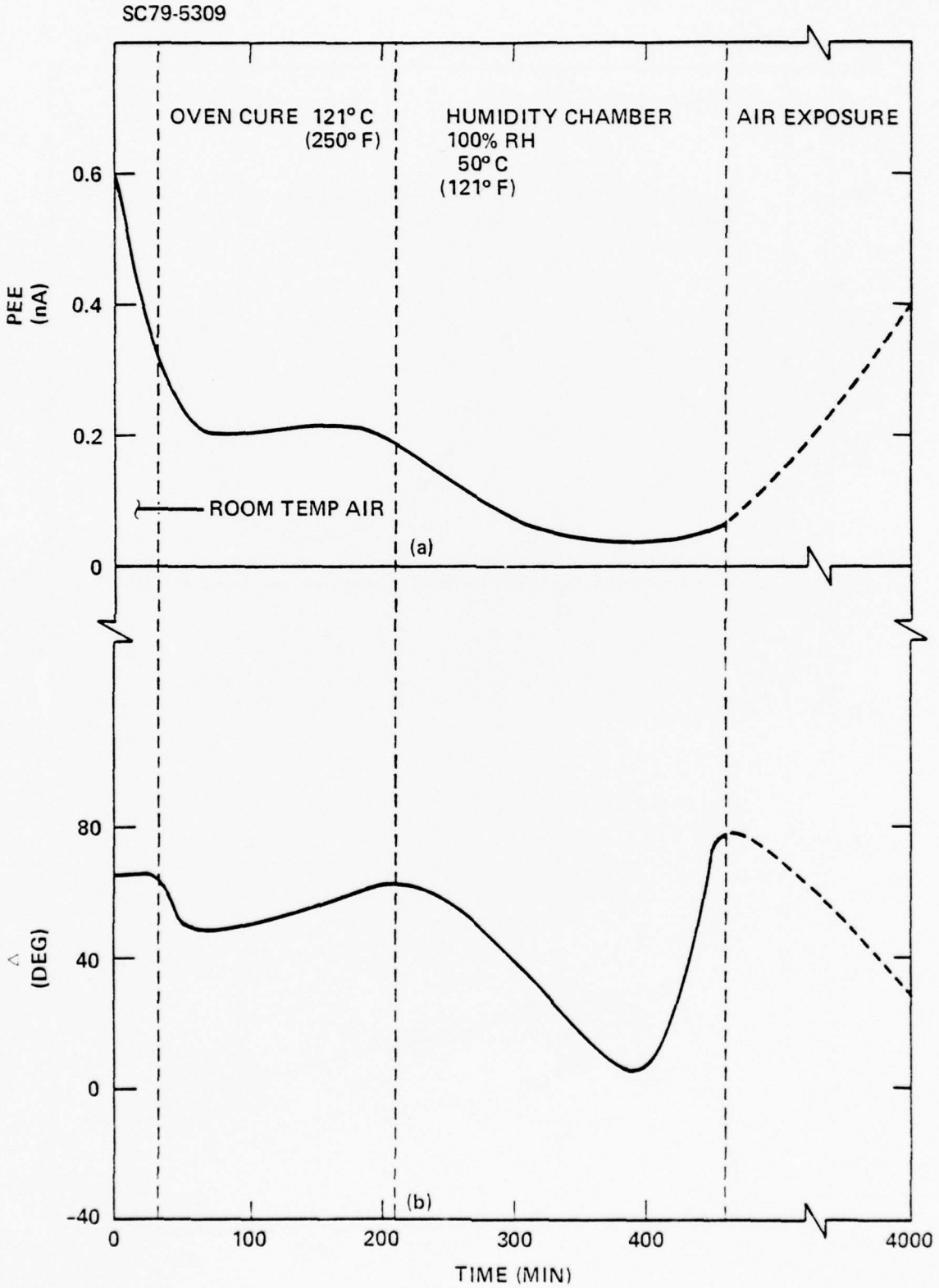



Fig. 23 a,b Changes in surface properties of Al 2024-T3 after STAB(2). The time history coincides with that for wedge test specimens.

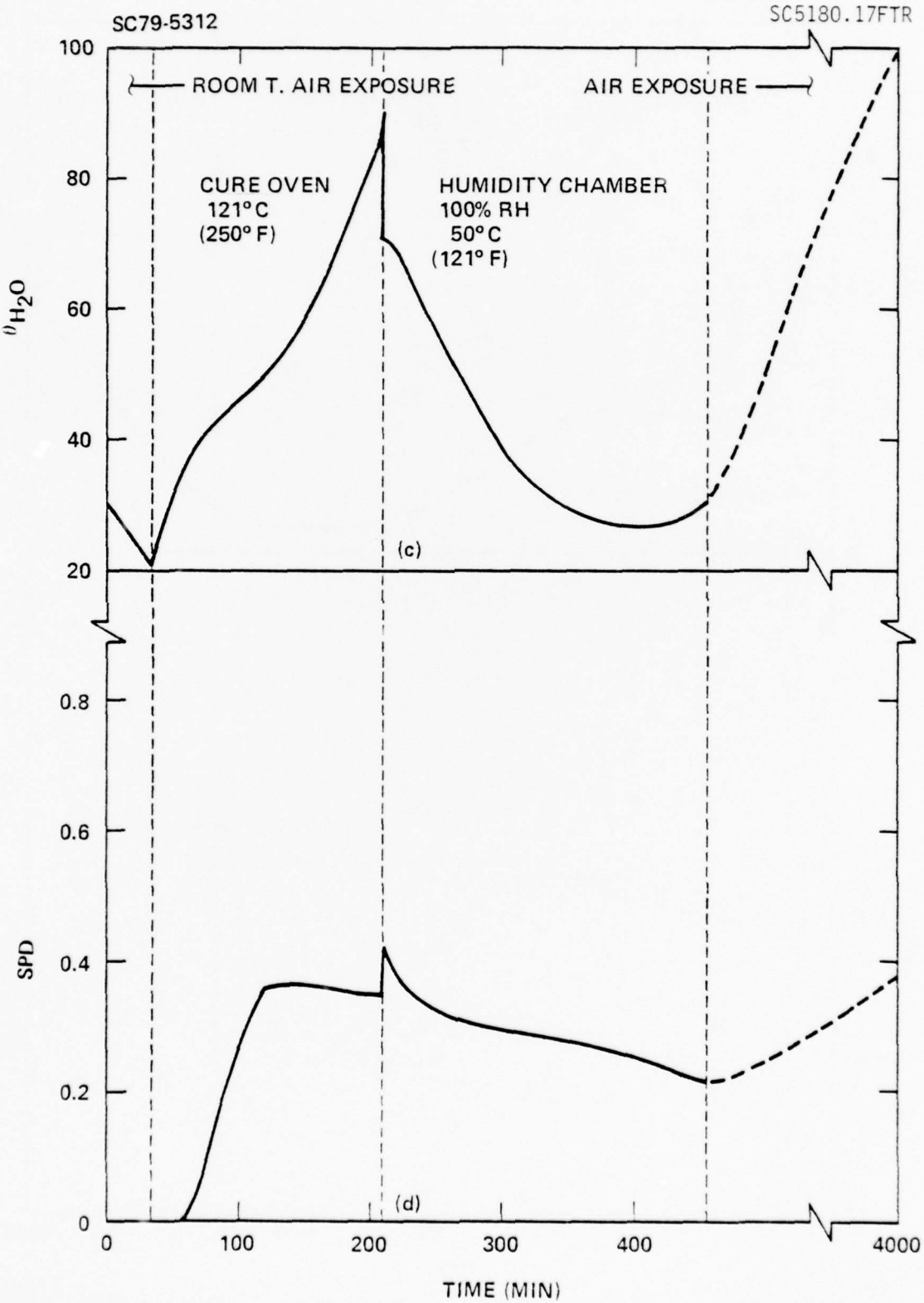



Fig. 23 c,d Changes in surface properties of Al 2024-T3 after STAB(2). The time history coincides with that for wedge test specimens.

surface chemical changes. Table 14 gives surface property values for samples that were exposed to MICRO solution with (samples 26 to 30) and without (samples 24,25) a degrease step. The samples were treated for the various lengths of time, removed rinsed and dried, surface properties measured, then re-exposed for the next time period. The results of Table 14 are plotted in Figs. 24, 25, and 26 as SPD, PEE and $\theta_{H_2O}$ vs. log time. In Fig. 24 the SPD starts at about 0.7 volts for as-received samples then decreases to a minimum (~0.1 volts) at about 200-300 min and then increases to about 0.3 volts.

As seen in Fig. 25 the PEE current increases with MICRO exposure time. The degreased samples reproduce each other in a peculiar time dependence, but generally increases from about $0.2 \times 10^{-9}$ amps for as-received to ~$1.1 \times 10^{-9}$ amps after 1700 min of MICRO exposure. Figure 25 reveals that the water contact angle is not much affected between 0 and 300 min, for the no degreased samples but then decreases to about zero. The degreased samples decrease monotonically to zero between 0 and 1700 min. Figure 27 shows the effect of time in MICRO and degrease steps on Wedge Test durability. There is a definite improvement with time in MICRO, for no degrease, but the degrease makes a drastic improvement.

The effect of UV radiation on the surface properties of as-received, degreased, and degrease + 30 min MICRO exposure is seen in Figs. 28, 29 and 30. There is no effect of UV on SPD (Fig. 28). The PEE current drops dramatically from about $0.4 \times 10^{-9}$ amps to about $0.1 \times 10^{-9}$ amps after 1 min UV exposure, then remains constant, for as-received or degreased samples. If the sample was degreased then exposed to MICRO solution 30 min, PEE drops more slowly to about $0.15 \times 10^{-9}$ amps in 24 min. The contact angle is rather low (~20°) for as-received material and increases dramatically (~65°) upon degreasing. This indicates that degreasing generally leaves at least a monolayer of organic contaminant on a surface. UV exposure slowly decreases $\theta_{H_2O}$ to <10° in 24 min. In spite of the changes in surface properties, Table 16 indicates little, if any, effect on Wedge Test durability.

TABLE 14

Effect of MICRO Exposure on Surface Properties
(All measurements after removal from MICRO, rinse and dry)

| Sample | History | MICRO Exposure Time (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ |
|---|---|---|---|---|---|---|---|
| 24 | As-received | 0 | 40 | 37 | 0.73 | 0.11 | 58 |
| | In MICRO | 47 | 35 | 34 | 0.29 | 0.17 | 68 |
| | | 80 | 24 | 26 | 0.26 | 0.22 | 78 |
| | | 201 | -32 | 21 | 0.15 | 0.27 | 63 |
| | | 311 | -20 | 24 | 0.17 | 0.30 | 79 |
| | | 1211 | -4 | 26 | 0.23 | 0.45 | 20 |
| 25 | As-received | 0 | 68 | 44 | 0.70 | 0.20 | 67 |
| | In MICRO | 26 | 52 | 32 | 0.34 | 0.28 | 80 |
| | | 78 | 36 | 27 | 0.13 | 0.70 | 70 |
| | | 173 | 18 | 35 | 0.12 | 0.65 | 51 |
| | | 228 | -14 | 24 | 0.10 | 0.65 | 52 |
| | | 1728 | -40 | 11 | 0.28 | 1.1 | 0 |
| 26 | As-received | 0 | 70 | 39 | 0.64 | 0.18 | 93 |
| | 5 Min in Solvent | 26 | -80 | 23 | 0.20 | 0.48 | 68 |
| | + MICRO Soak | 78 | 66 | 21 | 0.13 | 0.35 | 48 |
| | | 173 | 52 | 48 | 9.13 | 9.75 | 60 |
| | | 228 | -4 | 39 | 0.09 | 1.1 | 52 |
| | | 1728 | -52 | 13 | 0.32 | 0.8 | 0 |
| 30 | As-received | 0 | 68 | 40 | 0.65 | 0.20 | 85 |
| | 5 min ultrasonic | 26 | -80 | 40 | 0.65 | 0.20 | 85 |
| | | 78 | -124 | 22 | 0.04 | 0.26 | 58 |
| | | 173 | -122 | 62 | 0.06 | 0.75 | 43 |
| | | 228 | -24 | 40 | 0.02 | 1.0 | 52 |
| | | 1728 | -50 | 6 | 0.25 | 0.08 | 0 |

TABLE 15

The Effect of UV Radiation on Surface Properties

| Sample | History | UV Exposure Time (min) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) |
|---|---|---|---|---|---|
| 13 | As-received | 0 | 0.70 | 0.35 | 24 |
| | UV Exposure | 1 | " | 0.22 | 56 |
| | | 2 | " | 0.13 | 48 |
| | | 5 | " | 0.06 | 53 |
| | | 10 | " | 0.02 | 38 |
| 1 | As-received | 0 | 0.70 | - | 24 |
| | Ultrasonic - | 0 | 0.64 | 0.70 | 68 |
| | Solvent, 5 min | 1 | | 0.20 | 61 |
| | | 2 | | 0.15 | 61 |
| | | 3 | | 0.13 | 65 |
| | | 5 | | 0.10 | 55 |
| | | 10 | 0.67 | 0.10 | 32 |
| | | 15 | | 0.08 | 30 |
| | | 25 | 0.67 | 0.13 | 20 |
| 14 | Ultrasonic - | 0 | | 0.4 | 65 |
| | Solvent, 5 Min | 1 | | 0.17 | 65 |
| | | 2 | | 0.09 | 60 |
| | | 5 | | 0.04 | 60 |
| | | 10 | | 0.05 | 60 |
| 15 | Ultrasonic - | 0 | | 0.40 | 74 |
| | Solvent, 5 Min | 1 | | 0.11 | 64 |
| | | 2 | | 0.09 | 55 |
| | | 5 | | 0.05 | 53 |
| | | 10 | | 0.04 | 42 |
| 16 | Ultrasonic - | 0 | 0.23 | >0.50 | |
| | Solvent, 5 Min | 2 | | 0.30 | 82 |
| | + 30 Min MICRO | 4 | | 0.22 | 67 |
| | | 6 | | 0.19 | 60 |
| | | 10 | | 0.17 | 28 |
| | | 23 | | 0.15 | 12 |

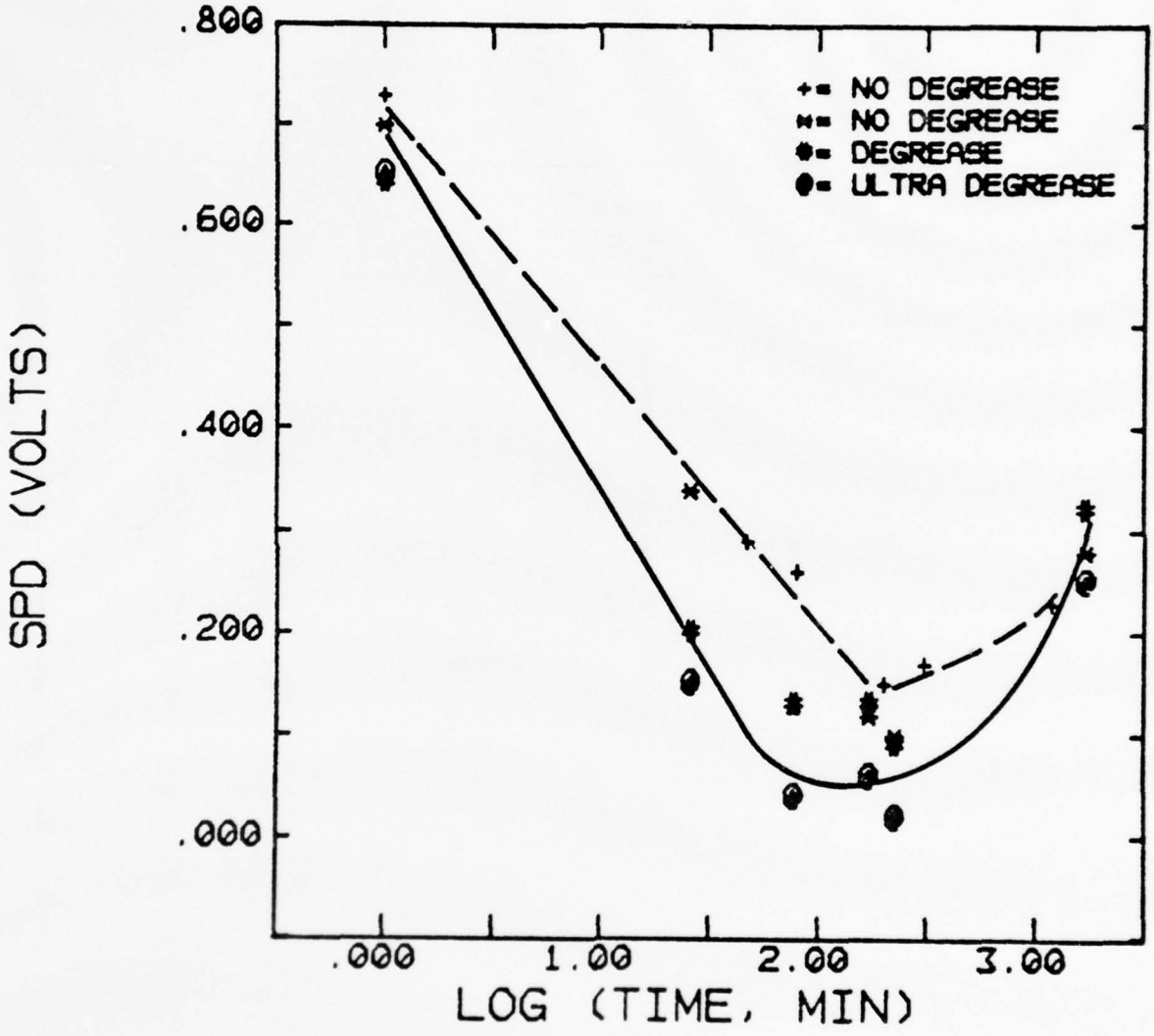



Fig. 24 Effect of micro exposure on SPD.

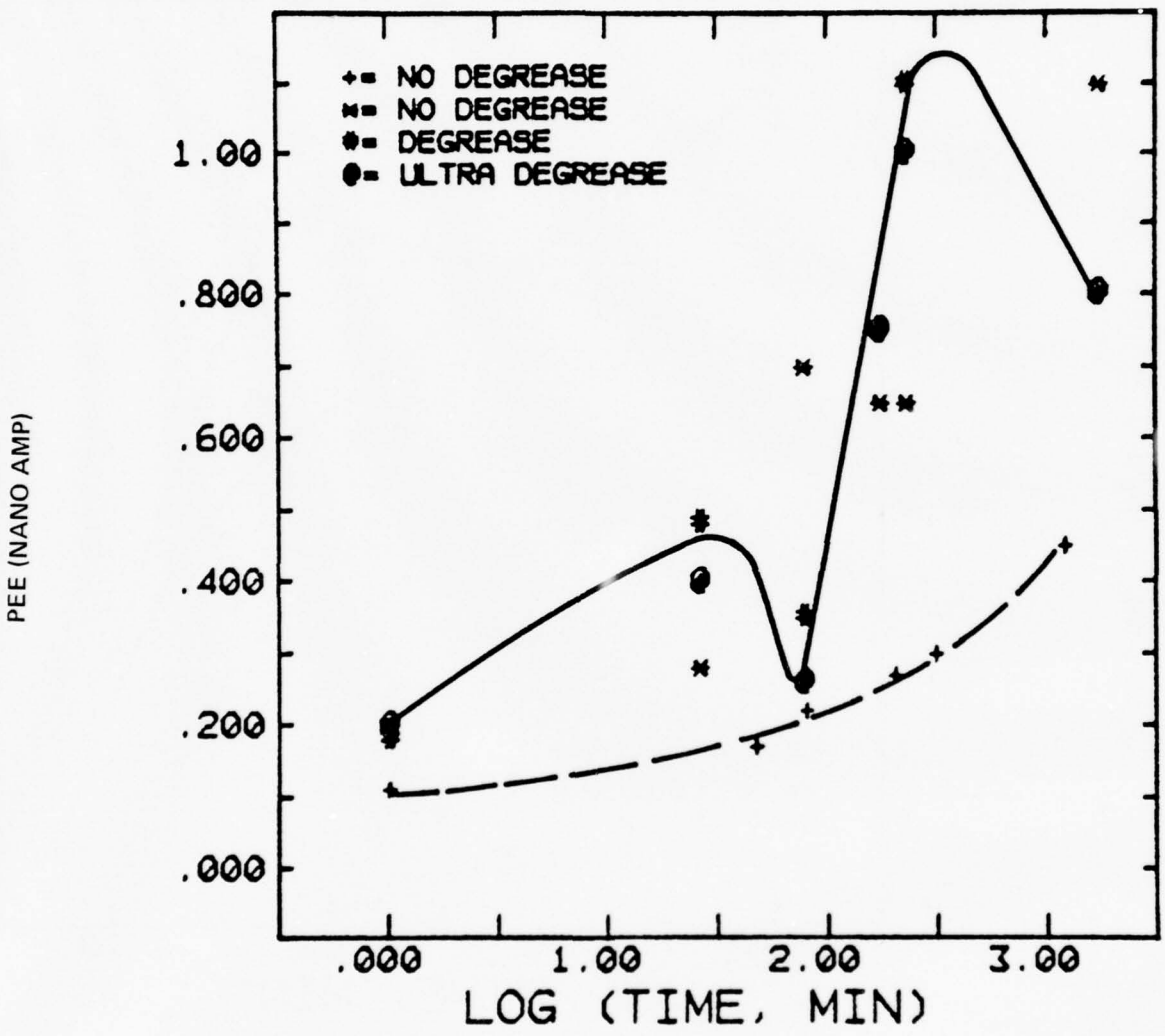



Fig. 25 Effect of micro exposure on PEE.

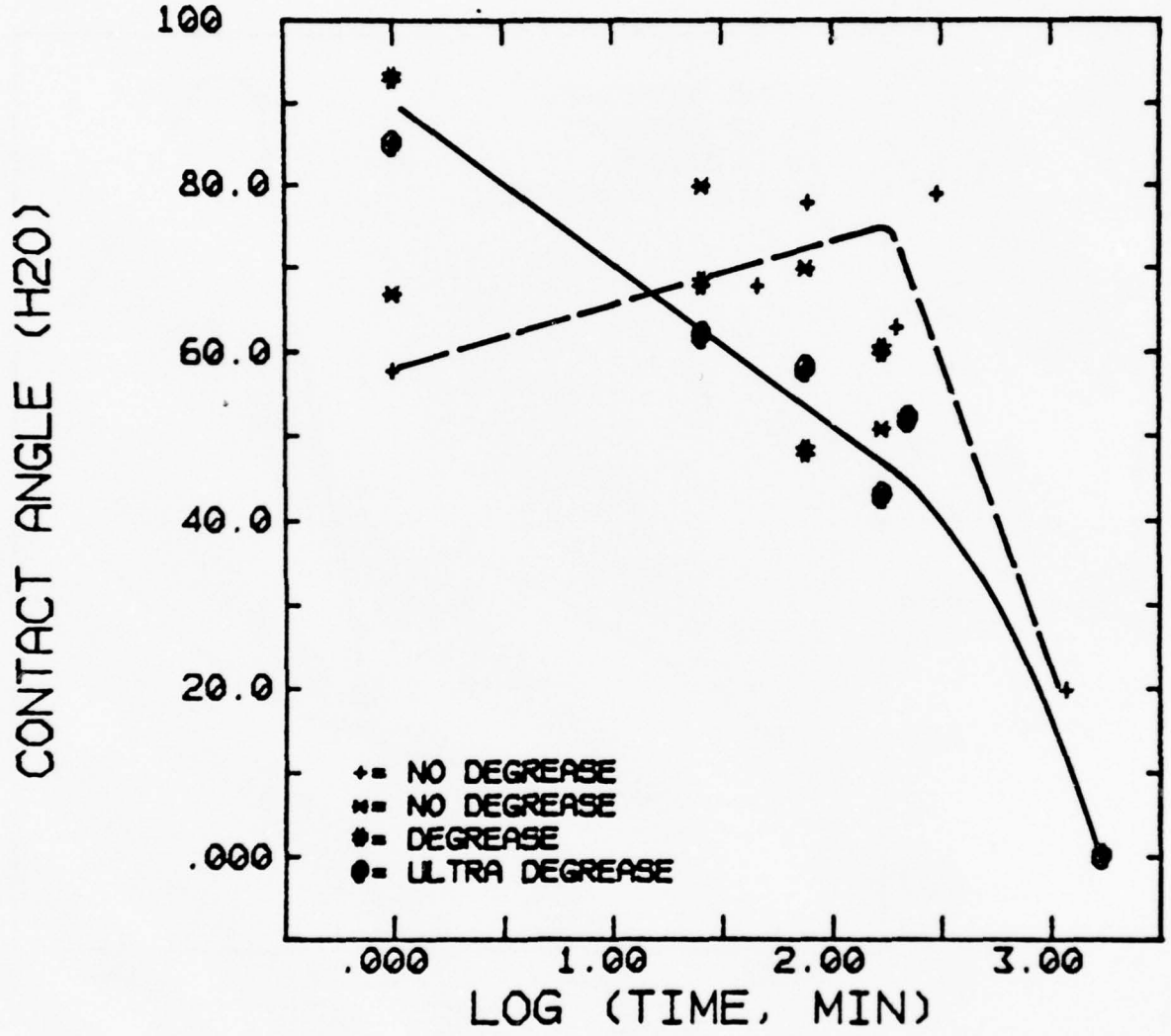



Fig. 26 Effect of micro exposure on contact angle.

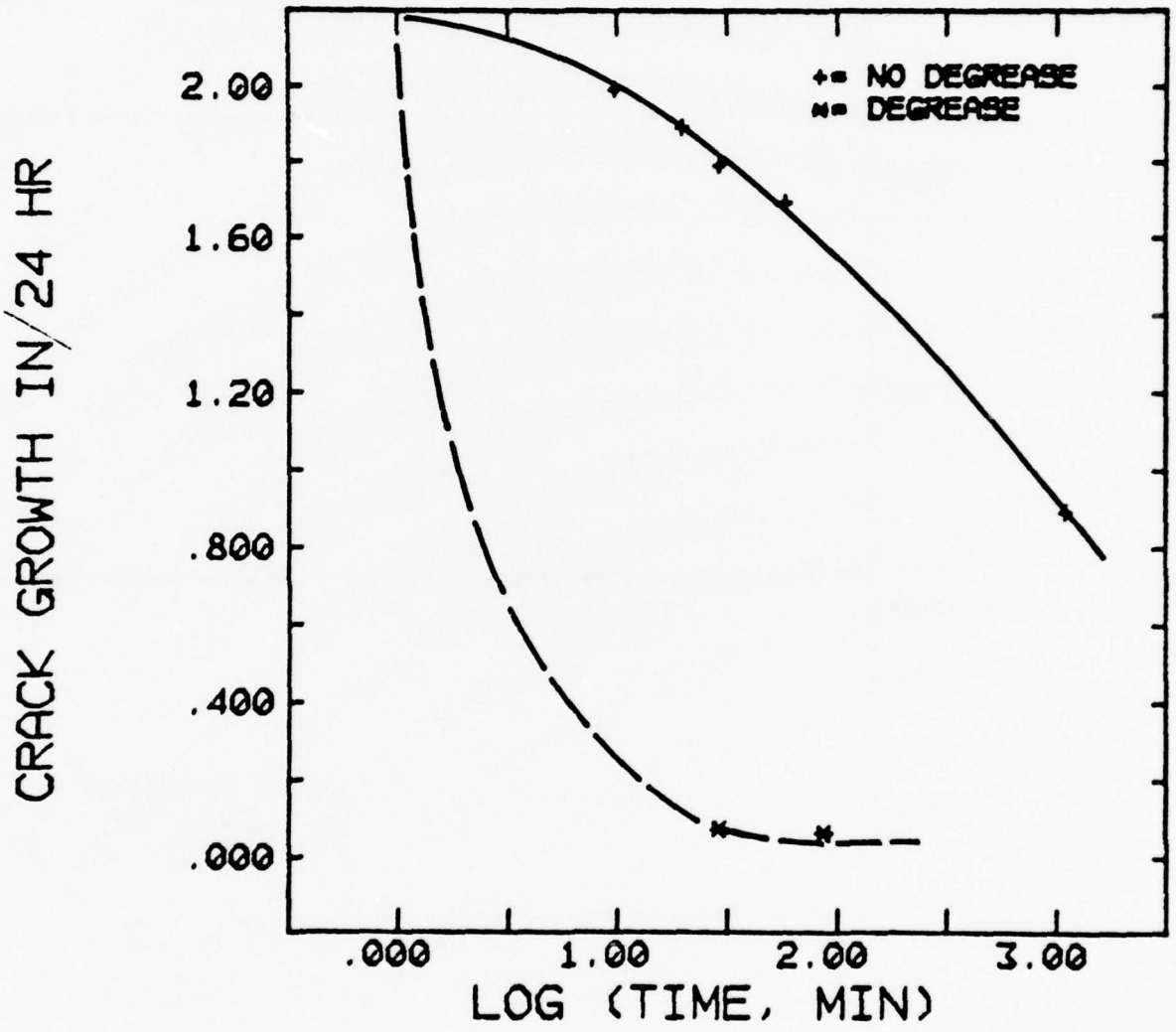



Fig. 27 Effect of time in micro on wedge test durability.

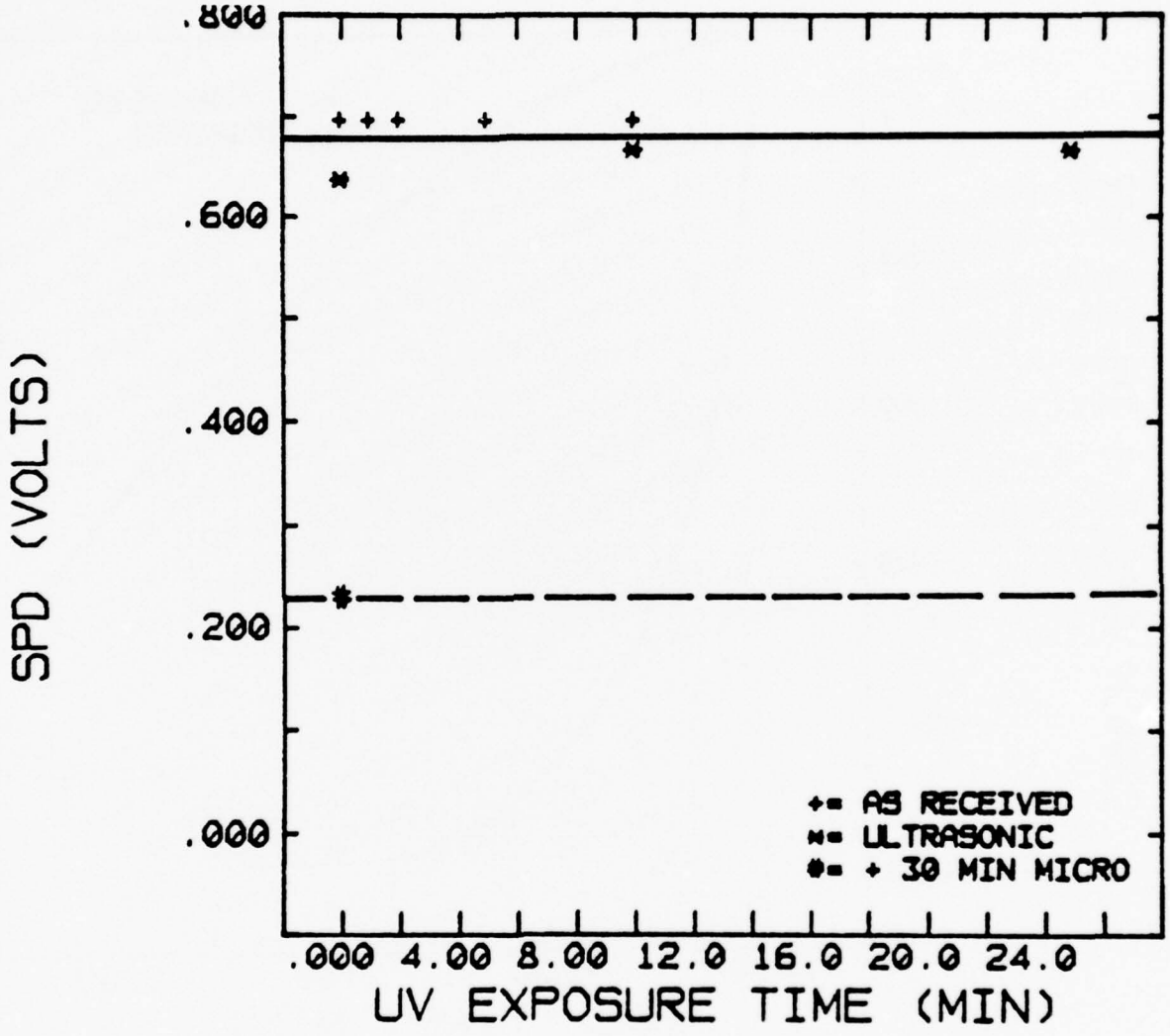



Fig. 28 Effect of UV radiation on SPD.

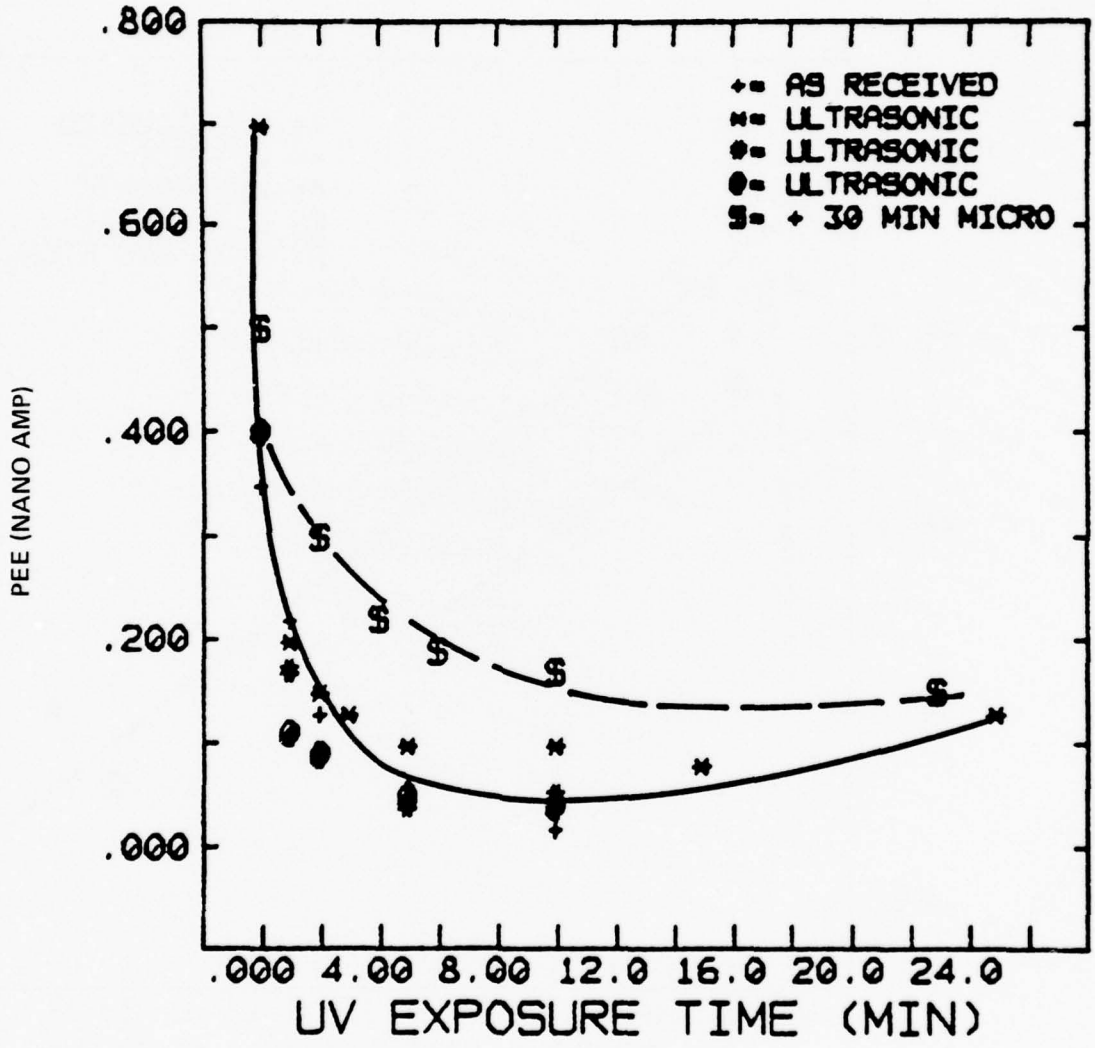



Fig. 29 Effect of UV radiation on PEE.

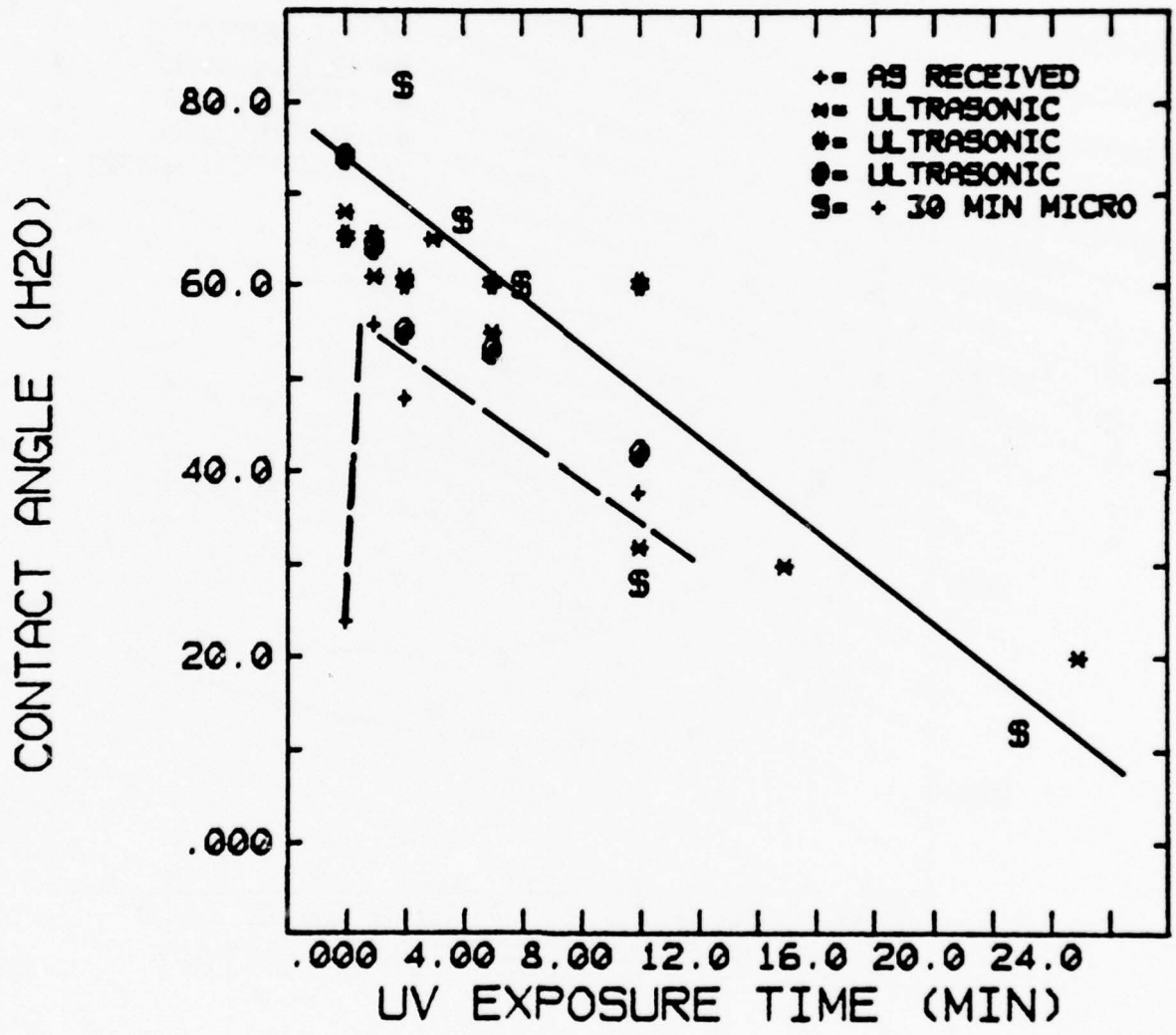



Fig. 30 Effect of UV radiation on contact angle.

## 2.3 Bond Strength Endurance

Figure 31 shows the effect of time in MICRO solution on the growth of a crack as deduced from the Boeing wedge test procedure for FM73 adhesive. The curve at the top of Fig. 31 indicates that this crack extension is independent of the time of degreasing in commercial solvents. On the other hand, the time of exposure of MICRO decreases the crack growth from the unacceptable range to the region considered by Bethune to be acceptable. There seems to be a close correlation between crack growth and water contact angle, but further work has not substantiated this. Table 16 reveals that 10 min in MICRO solution gives much better crack growth than for untreated samples (~3.05 cm (1.2 in)/24 hr vs. ~8.89 (3.5 in)/24 hr in Fig. 31 with FM73) but is unacceptable for Hysol. A 20 min STAB(2) soak (Table 17) greatly improved crack growth in spite of high contact angles and low peel forces and a 30 min STAB(2) (Table 18) improved crack growth even more. It should be noted in Tables 16-18 the initial crack length was too high (i.e., ~5.08 cm (2 in) vs. the normal 3.81 cm (1.5 in) indicating lower peel strength and therefore lower stress at the crack tip during humidity exposure. This is evidenced in Table 19, for which the initial crack decreased to about 4.31 in (1.7 in) with resultant increase in crack growth to about 3.30 cm (1.3 in)/24 hr.

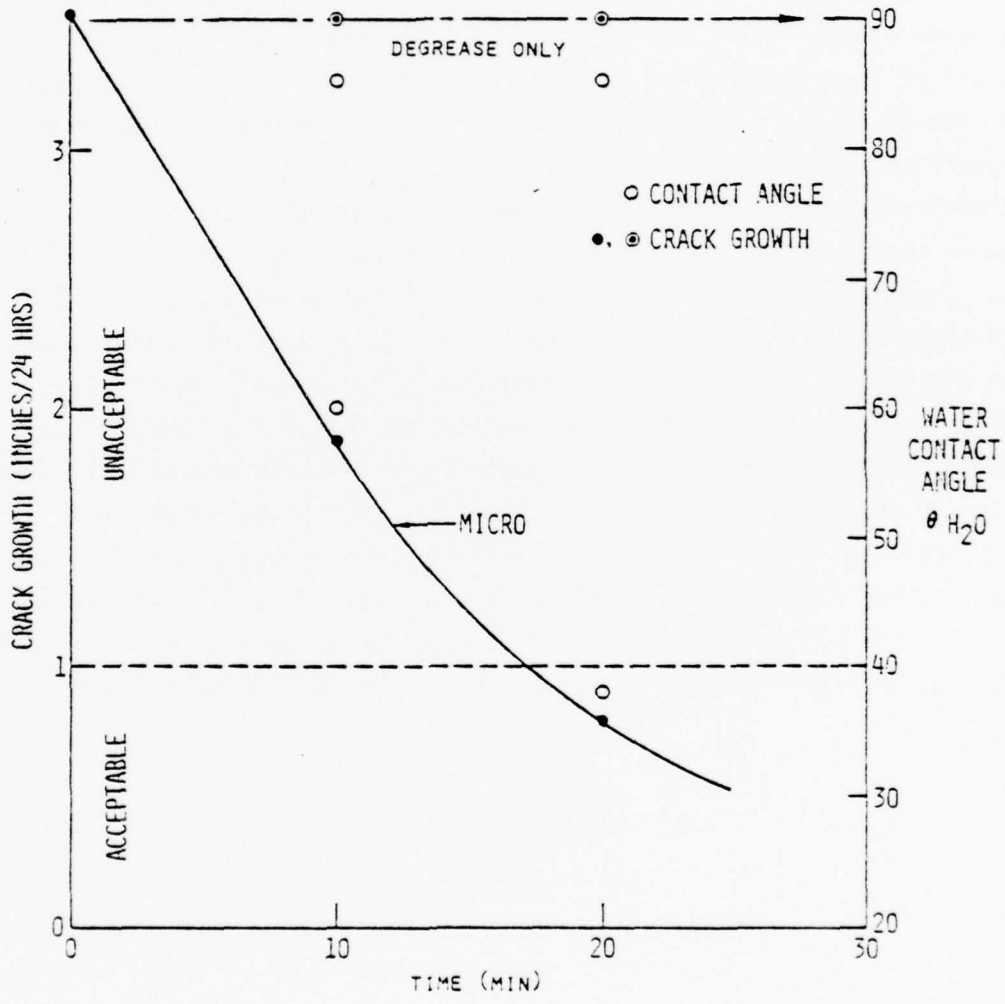



Fig. 31 Dependence of the water-drop contact angle and the growth of a crack on the length of time that an aluminum sample is exposed to a common degreasing solvent and to the micro solution.

TABLE 16

Investigator: Bivins

Alloy: 2024-T3

Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: To check STAB(2) 10 min with Hysol EA9628H adhesive.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | Clean | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-12-1H | * | 10 min | 242 | 30.7 | -.04 | 1.2 | 76 | | | 3.81 (1.5) | 1.91 (0.75) | 4.32 (1.7) |
| 12-2H | * | 10 min | 240 | 28.7 | +.03 | 1.2 | 75 | | | | | |
| 12-3 | * | 10 min | 252 | 35.3 | +.08 | 0.8 | 81 | | | 5.33 (2.1) | 0.64 (0.25) | 2.92 (1.15) |
| 12-4 | * | 10 min | 232 | 31 | +.09 | 1.0 | 71 | | | | | |
| 12-5 | * | 10 min | 230 | 33.6 | +.07 | 0.8 | 70 | | | 5.08 (2.0) | 0.76 (0.3) | 3.05 (1.2) |
| 12-6 | * | 10 min | 228 | 31 | +.07 | 1.2 | 69 | | | | | |

Remarks: *Degrease: clean surfaces with acetone and kimwipe, scrub, then into R.T. with clean soak for 10 min. with clean 60 ml into 1000 ml D.I. $H_2O$.
HPrimer EA9210-H paint samples - air dry 30 min - bake flo thru over 30 min. No.1 & 2 tabs stayed in the oven 1.2 hours.

TABLE 17

Investigator: Bivins

Alloy: 2024-T3

Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: To check 20 min STAB(2)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | MICRO | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-12-7 | Acetone & Kimwipe Rub | 20 min | 228 | 18.3 | -.3 | -.45 | 69 | 413 | | 5.33 (2.1) | 0.51 (0.2) | 1.27 (0.5) |
| 10-12-8 | " | " | 204 | 14.8 | -.3 | -.52 | 57 | 449 | | | | |
| 12-9 | " | " | 218 | 14.2 | -.31 | -.5 | 64 | 413 | | 5.46 (2.15) | 0.76 (0.3) | 2.29 (0.9) |
| 12-10 | " | " | 266 | 44.8 | -.08 | -.2 | 88 | 404 | | | | |
| 12-11 | " | " | 206 | 14.5 | -.27 | -.58 | 58 | 404 | | 5.33 (2.1) | 0.51 (0.2) | 1.78 (0.7) |
| 12-12 | " | " | 206 | 15.9 | -.25 | -.5 | 58 | 404 | | | | |

TABLE 18

Investigator: Bivins

Alloy: 2024-T3

Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: To check a 30 min STAB(2)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | MICRO | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-12-13 | Acetone & Paper wipe | 30 min clean | 220 | 22.1 | -.35 | .4 | 65 | 440 | Old 9628 | 5.33 (2.1) | 0.51 (0.2) | 1.14 (0.45) |
| 12-14 | " | " | 200 | 17 | -.35 | .6 | 55 | 476 | | | | |
| 12-15 | " | " | 228 | 21.4 | -.35 | .5 | 69 | 476 | New 9628 | 5.72 (2.25) | 0.38 (0.15) | 1.27 (0.5) |
| 12-16 | " | " | 228 | 21.4 | -.28 | .55 | 69 | 485 | | | | |
| 12-17 | " | " | 218 | 32.3 | -.3 | .3 | 64 | 426 | New 9628 | 5.84 (2.3) | 0.64 (0.25) | 1.78 (0.7) |
| 12-18 | " | " | 190 | 22.4 | -.36 | .35 | 50 | 426 | | | | |

TABLE 19

Investigator: Bivins

Alloy: 2024-T3

Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: To check 20 min STAB(2) but aging for 6 days.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Degrease | MICRO | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 10-13-7 | G + Kerosene | 20 min | | | | | 67 | | | 4.32 (1.7) | 1.02 (0.4) | 3.18 (1.25) |
| 13-8 | G + Kerosene | 20 min | | | | | 70 | | | | | |
| 13-9 | G + Kerosene | 20 min | | | | | 73 | | | 4.45 (1.75) | 1.27 (0.5) | 3.81 (1.5) |
| 13-10 | G + Kerosene | 20 min | | | | | 74 | | | | | |
| 13-11 | G + Kerosene | 20 min | | | | | 67 | | | 4.06 (1.6) | 1.02 (0.4) | 2.54 (1.0) |
| 13-12 | G + Kerosene | 20 min | | | | | 73 | | | | | |

Remarks: Degrease Gunk and kerosene u.s. 10 min, spray rinse, - clean R.T. soak 20 min using old clean solv. that had total of 50 min use.
Hysol had a bad (funny looking spot) on samples 7-9-11 about 2/3 way down sample located opposite the red covering side.
Primer - paint on - air dry 30 min - bake 150°C for 30 min - bond.

In Tables 20 and 21 the degrease step was deleted and a 10 min soak was used for the first 6 samples, a 20 min soak for the second 6 samples, 30 min for the third and 60 min for the fourth. In Table 22 the no degrease test was extended to 19 hr. Without the degrease step $\delta a$ ~5 cm (2 in)/24 hr for either the 10 or 20 min soak, with slight improvement to $\delta$ ~4.3 cm (1.7 in) for 30 and 60 min. The 19 hr soak improved the durability to 2.3 cm (0.9 in)/24 hr. In Table 21 the degrease step was included and the time of soak was 30 to 90 min. Table 21 indicates excellent durability $\delta a$ < 0.5 cm (0.2 in)/24 hr but with large initial crack length. For comparison, sample 25 was not rinsed after the MICRO soak, with resultant large increase in $\delta a$ (to 3.3 cm (1.3 in)/24 hr).

To check the effect of the rinse step between the degrease and MICRO soak, the rinse step was deleted. Table 24 indicates poor durability ($\delta a$ ~5 cm (2 in)/24 hr), but another change had been made, viz. drying with paper towels rather than blow dry with $N_2$. In Tables 25 and 27 drying was done with paper towels, with resultant $\delta a$ ~2.8 cm (1.1 in) to 4.6 cm (1.8 in)/24 hr. In Table 25, there seems to be little effect of solvent degreasing with added ultrasonic agitation and in Table 26, the 90 min soak is not quite as good as the 30 min soak. Table 27 shows that drip drying is not as good as $N_2$ blow drying ($\delta a$ ~4.8 cm (1.9 in)/24 hr).

It was noted during the photoelectron emission (PEE) measurement that the PEE current would change during UV exposure. Since most of the samples were exposed to UV in order to make this measurement, it was deemed necessary to determine if the UV exposure played a part in bond durability. The results in Table 28 indicate that the UV exposure had little, if any, effect on bond durability. As-received samples split to the end in 24 hr humidity exposure for the Wedge Test specimens. Ultrasonic degreasing in solvent does not prevent this, nor does 25 min UV exposure after 5 min degrease. Exposure to UV after 30 min MICRO gives about the same result as MICRO alone, for paper towel drying ($\delta a$ ~3.8 cm (1.5 in)/24 hr, see Tables 25 and 26).

TABLE 20

Date: 12-20-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628M
Primer: EA9210H

Purpose: Check the effect of deletion of the degrease step on STAB(2) (MICRO), 10 and 20 min soak

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(2) Time (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-20-78- | | | | | | | | | | | | |
| 1 | | 10 | 76 | 35 | 0.58 | 0.6 | 83 | | | 4.06 (1.6) | | 4.83 (1.9) |
| 2 | | 10 | 72 | 35 | 0.58 | 0.5 | 70 | | | 4.06 (1.6) | | 5.08 (2.0) |
| 3 | | 10 | 70 | 59 | 0.32 | 0.5 | 65 | | | 3.81 (1.5) | | 4.83 (1.9) |
| 4 | | 10 | 52 | 48 | 0.66 | 0.4 | 75 | | | | | |
| 5 | | 10 | 84 | 36 | 0.58 | 0.4 | 60 | | | | | |
| 6 | | 10 | 72 | 37 | 0.64 | 0.4 | 73 | | | | | |
| 7 | | 20 | 292 | 51 | 0.28 | 0.2 | 85 | | | 3.81 (1.5) | | 4.06 (1.6) |
| 8 | | 20 | 60 | 40 | 0.60 | 0.3 | 85 | | | 4.06 (1.6) | | 4.83 (1.9) |
| 9 | | 20 | 0 | 51 | 0.28 | 0.2 | 75 | | | 3.81 (1.5) | | 5.84 (2.3) |
| 10 | | 20 | 50 | 39 | 0.46 | 0.3 | 60 | | | | | |
| 11 | | 20 | 58 | 35 | 0.38 | 0.3 | 90 | | | | | |
| 12 | | 20 | 306 | 71 | 0.18 | 0.3 | 50 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Mate: 1-4, 2-5, 3-6, 7-10, 8-11, 9-12

TABLE 21

Date: 12-20-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check on effect of deletion of the degrease step on STAB(2) (MICRO), 30 and 60 min soak

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(2) (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PLL (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-20-78- | | | | | | | | | | | | |
| 13 | | 30 | 40 | 32 | 0.20 | 0.10 | 35 | | | 3.30 (1.3) | | 3.30 (1.3) |
| 14 | | 30 | 314 | 48 | 0.38 | 0.24 | 70 | | | 4.06 (1.6) | | 6.60 (2.6) |
| 15 | | 30 | 290 | 50 | 0.18 | 0.30 | 40 | | | 4.06 (1.6) | | 4.06 (1.6) |
| 16 | | 30 | 48 | 41 | 0.30 | 0.24 | 65 | | | | | |
| 17 | | 30 | 30 | 40 | 0.48 | 0.60 | 80 | | | | | |
| 18 | | 30 | 32 | 33 | 0.35 | 0.40 | 75 | | | | | |
| 19 | | 60 | 80 | 37 | 0.17 | 0.08 | 30 | | | 3.30 (1.3) | | 3.56 (1.4) |
| 20 | | 60 | 130 | 19 | 0.10 | 0.38 | 43 | | | 3.56 (1.4) | | 3.81 (1.5) |
| 21 | | 60 | 174 | 22 | 0.10 | 0.45 | 53 | | | 3.30 (1.3) | | 5.33 (2.1) |
| 22 | | 60 | 70 | 38 | 0.18 | 0.30 | 60 | | | | | |
| 23 | | 60 | 82 | 21 | 0.13 | 0.35 | 30 | | | | | |
| 24 | | 60 | 14 | 16 | 0.26 | 0.22 | 60 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Mate: 13-16, 14-17, 15-18, 19-22, 20-23, 21-24

TABLE 22

Date: 12-20-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check on effect of deletion of the degrease step on STAB(2) (MICRO), 19 hr soak

| Sample No. | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Degrease | STAB(2) (hrs) | Δ (deg) | Ψ (deg) | SPD (volts) | PEL (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-20-78- | | | | | | | | | | | | |
| 7P | | 19 | -10 | 23 | 0.76 | 0.04 | 15 | | | 5.33 (2.1) | 0.76 (0.3) | 2.28 (0.9) |
| 8P | | 19 | -26 | 17 | 0.26 | 0.07 | 12 | | | 4.57 (1.8) | 1.52 (0.6) | 2.29 (0.9) |
| 9P | | 19 | 4 | 32 | 0.71 | 0.12 | 8 | | | | | |
| 10P | | 19 | 14 | 28 | 0.52 | 0.22 | 18 | | | | | |
| 11P | | 19 | 14 | 25 | 0.76 | 0.15 | 15 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Mate: 7P-10P, 8P-11P, 9P-12P
P means roll pattern is parallel to sample axis

TABLE 23

Date: 12-30-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(2) MICRO at 30 min and 90 min

| Sample No. | Surface Treatment: Degrease Ultrasonic G (min) | Surface Treatment: STAB(2) (min) | Surface Properties: Δ (deg) | Ψ (deg) | SPD (volts) | PEL (nA) | $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-30-78- | | | | | | | | | | | | |
| 25 | 5 | 30 | 20 | 34 | 0.64 | 0.19 | 5.0 | No Rinse | | 5.08 (2.0) | | 3.30 (1.3) |
| 26 | | | 16 | 19 | 0.20 | 0.20 | 58 | | | 5.08 (2.0) | | 0.38 (0.15) |
| 27 | | | 54 | 36 | 0.23 | 0.35 | 60 | | | 5.08 (2.0) | | 0.0 |
| 28 | | | 22 | 19 | 0.18 | 0.20 | 60 | | | | | |
| 29 | | | 38 | 29 | 0.12 | 0.40 | 70 | | | | | |
| 30 | | | 184 | 3 | 0.11 | 0.50 | 70 | | | | | |
| 31 | | 90 | 56 | 33 | 0.17 | 0.20 | 38 | | | 4.83 (1.9) | | 0.51 (0.2) |
| 32 | | | 72 | 44 | 0.38 | 0.18 | 38 | | | 4.83 (1.9) | | 0.0 |
| 33 | | | 108 | 37 | 0.08 | 0.45 | 38 | | | 4.57 (1.8) | | 0.0 |
| 34 | | | 10 | 27 | 0.08 | 0.35 | 45 | | | | | |
| 35 | | | 100 | 41 | 0.20 | 0.25 | 54 | | | | | |
| 36 | | | 76 | 28 | 0.08 | 0.15 | 54 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Did not rinse sample #25
Mate: 25-28, 26-29, 27-30, 31-34, 32-35, 33-36
$N_2$ blow dry

TABLE 24

Date: 12-22-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of deletion of rinse step between degrease and STAB(2) (MICRO)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease Shell 140CC (min) | STAB(2) MICRO (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEL (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-22-78- | | | | | | | | | | | | |
| 13 | 5 | 30 | 16 | 27 | 0.17 | 0.10 | 35 | | | 3.1 (1.3) | 0.8 (0.3) | 6.1 (2.4) |
| 14 | | | 282 | 15 | 0.13 | 0.16 | 70 | | | 3.8 (1.5) | 1.3 (0.5) | 5.6 (2.2) |
| 15 | | | 24 | 22 | 0.21 | 0.22 | 45 | | | 3.5 (1.4) | 0.5 (0.2) | 4.1 (1.6) |
| 16 | | | 78 | 37 | 0.38 | 0.22 | 80 | | | | | |
| 17 | | | 70 | 17 | 0.20 | 0.26 | 68 | | | | | |
| 18 | | | 66 | 18 | 0.20 | 0.20 | 60 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. Water
Mate: 13-16, 14-17, 15-18
Dry with paper towels

TABLE 25

Date: 12-22-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check effect of deletion of ultrasonic during degrease on STAB(2) (MICRO) (7-13)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease Ultrasonic G (min) | STAB(2) MICRO (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEL (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-22-78- | | | | | | | | | | | | |
| 1 | 5 | 30 | 4 | 1 | 0.14 | 0.27 | 30 | | | 3.3 (1.3) | 0.2 (0.06) | 2.5 (1.0) |
| 2 | | | 4 | 8 | 0.18 | 0.50 | 63 | | | 3.3 (1.3) | 0.4 (0.15) | 3.3 (1.3) |
| 3 | | | 64 | 19 | 0.18 | 0.30 | 60 | | | 3.3 (1.3) | 1.5 (0.6) | 3.3 (1.3) |
| 4 | | | 240 | 31 | 0.16 | 0.75 | 80 | | | | | |
| 5 | | | 26 | 21 | 0.22 | 0.45 | 75 | | | | | |
| 6 | | | 46 | 21 | 0.24 | 0.50 | 65 | | | | | |
| 7 | No Ultrasonics | | 62 | 45 | 0.52 | 0.16 | 65 | | | 3.5 (1.4) | 0.4 (0.15) | 3.3 (1.3) |
| 8 | but solvent | | 92 | 28 | 0.14 | 0.43 | 40 | | | 3.3 (1.3) | 0.4 (0.15) | 3.5 (1.4) |
| 9 | | | 46 | 18 | 0.18 | 0.50 | 80 | | | 3.5 (1.4) | 0.5 (0.20) | 3.8 (1.5) |
| 10 | | | 56 | 30 | 0.25 | 0.50 | 78 | | | | | |
| 11 | | | 82 | 18 | 0.16 | 0.50 | 70 | | | | | |
| 12 | | | 72 | 49 | 0.32 | 0.20 | 70 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Mate: 1-4, 2-5, 3-6, 7-10, 8-11, 9-12
Dry with paper towels

TABLE 26

Date: 12-28-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628II
Primer: EA9210II

Purpose: Check STAB(2), MICRO for 30 min and 90 min with degrease

| Sample No. | Surface Treatment: Degrease (min) | Surface Treatment: STAB(2) (min) | Surface Properties: Δ (deg) | Surface Properties: ψ (deg) | Surface Properties: SPD (volts) | Surface Properties: PEL (nA) | Surface Properties: $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-30-78- | | | | | | | | | | | | |
| 1 | 10 | 30 | 274 | 20 | 0.27 | 0.7 | 50 | | | 4.32 (1.7) | | 2.79 (1.1) |
| 2 | Ultrasonic | 30 | 174 | 2 | 0.35 | 0.7 | 65 | | | 5.33 (2.1) | | 2.29 (0.9) |
| 3 | Gunk | 30 | 0 | 0 | 0.29 | 0.8 | 65 | | | 4.83 (1.9) | | 3.05 (1.2) |
| 4 | | 30 | 50 | 14 | 0.32 | 0.9 | 65 | | | | | |
| 5 | | 30 | 138 | 64 | 0.35 | 0.8 | 58 | | | | | |
| 6 | | 30 | 40 | 8 | 0.37 | 0.8 | 75 | | | | | |
| 7 | | 90 | 44 | 48 | 0.24 | 0.4 | 55 | | | 3.81 (1.5) | | 3.81 (1.5) |
| 8 | | 90 | 72 | 55 | 0.18 | 0.7 | 25 | | | 4.57 (1.8) | | 4.83 (1.9) |
| 9 | | 90 | 66 | 35 | 0.32 | 0.7 | 53 | | | 4.06 (1.6) | | 4.57 (1.8) |
| 10 | | 90 | 36 | 33 | 0.19 | 0.7 | 32 | | | | | |
| 11 | | 90 | 52 | 37 | 0.26 | 0.7 | 55 | | | | | |
| 12 | | 90 | 74 | 47 | 0.22 | 0.7 | 55 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Dried, after rinse, with paper towel blotting
Mate: 1-4, 2-5, 3-6, 7-10, 8-11, 9-12

TABLE 27

Date: 12-22-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check effect of drip dry rather than $N_2$ blow dry on STAB(2) (MICRO)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease Ultrasonic G (min) | STAB(2) (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEL (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-22-78- | | | | | | | | | | | | |
| 19 | 5 | 30 | 62 | 33 | 0.31 | 0.18 | 70 | | | | | |
| 20 | 5 | 30 | 46 | 30 | 0.18 | 0.32 | 55 | | | 3.56 (1.4) | 0.51 (0.2) | 4.57 (1.8) |
| 21 | 5 | 30 | 64 | 25 | 0.19 | 0.35 | 70 | | | 3.56 (1.4) | 1.02 (0.4) | 5.08 (2.0) |
| 23 | 5 | 30 | 68 | 27 | 0.24 | 0.45 | 70 | | | | | |
| 24 | 5 | 30 | 86 | 31 | 0.33 | 0.50 | 70 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Mate: 20-23, 21-24, 22 was not treated

TABLE 28

Date: 12-30-78 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of UV light exposure on STAB(2) (MICRO)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease Ultrasonic G (min) | STAB(2) (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 12-30-78- | | | | | | | | | | | | |
| 10 | 0 | as- received | 22 | 37 | | | | | | 6.86 (2.7) | | >7.62 (3) |
| 11 | 0 | " | 18 | 49 | | | | | | | | |
| 12 | 0 | " | 84 | 40 | | | | | | 5.08 (2.0) | | >7.62 (3) |
| 6 | 5 | MICRO 30 | 262 | 22 | | | | | | | | |
| 8 | 5 | 0 | 74 | 36 | | | | | | 4.57 (1.8) | | >7.62 (3) |
| 9 | 5 | 0 | 74 | 38 | | | | | | | | |
| 1 | 5, UV 25 | 0 | 90 | 40 | 0.67 | 0.13 | 20 | | | 5.03 (1.98) | | >7.62 (3) |
| 7 | 5, UV 25 | 0 | 74 | 37 | | 0.06 | 28 | | | | | |
| 4 | 5, UV 2 | 30 | 12 | 18 | | 0.29 | 90 | | | 3.81 (1.5) | | 3.81 (1.4) |
| 5 | 5, UV 2 | 30 | -14 | 24 | | 0.30 | 75 | | | | | |
| 2 | 5, UV 20 | 30 | 290 | 23 | 0.20 | 0.15 | | | | 3.81 (1.5) | | 3.81 (1.5) |
| 3 | 5, UV 20 | 30 | -16 | 38 | | 0.10 | 20 | | | | | |

Remarks: 90 cc MICRO/1500 cc D.I. water
Rinse flowing D.I. water, dry with paper tower

## 2.4 Post Fracture Analysis

Figure 32 is SEM pictures of the metal side of Al 2024-T3 that gave a good bond endurance wedge test (~0.5 cm (0.2 in)/2 hr) after STAB(2). A piece of adhesive has remained attached to the substrate in the debond region in Fig. 32a. Figures 32b, c and d reveal the porous nature of the Hysol EA9628 adhesive.

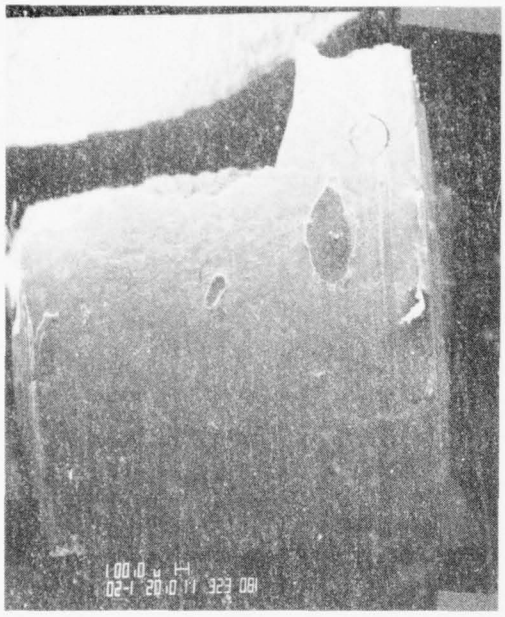
Figures 32e-h show the hydroxide layer that debonded from the adhesive during the wedge test. The stringers stretching between fractured hydroxide in Fig. 32h indicate that for a good bond, adhesive has penetrated into the hydroxide.

## 3. STAB(3)

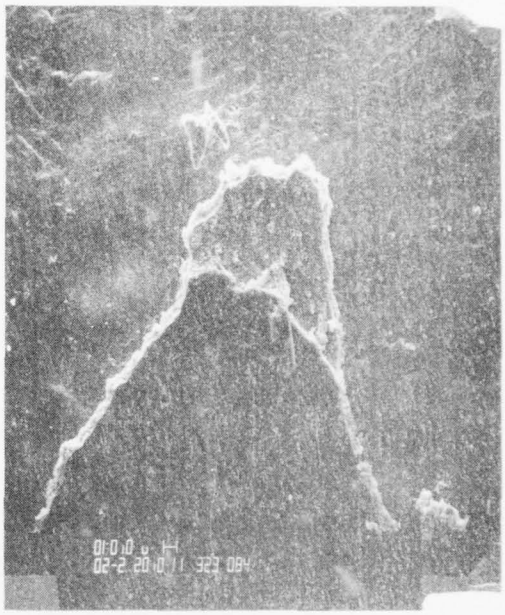
Problems in reproducibly producing good wedge test joints by STAB(1) and STAB(2) prompted an investigation of the effect of NaOH concentration on bond endurance. This led to the surface treatment referred to as STAB(3), which appears to be very successful. STAB(3) has the advantage that it is very simple and inexpensive.

## 3.1 Experimental Procedure

Al 2024-T3 is dipped in a super-concentrated solution of NaOH (568 g/l D.I. water) at room temperature for 3 minutes, rinsed in D.I. water and dried in flowing nitrogen. No degrease step is involved, at least on the as-received Al 2024-T3 used at the Science Center. The NaOH solution can be in glass or plastic but we have used stainless steel tanks without noticeable attack over a 1 yr period. A variation on STAB(3) is referred to as STAB(3) with second dip. This procedure involves a 2-10 min dip in concentrated NaOH solution, followed by a rinse, then a second much shorter dip (5-10 sec) to strip off the black hydroxide, rinse and dry.

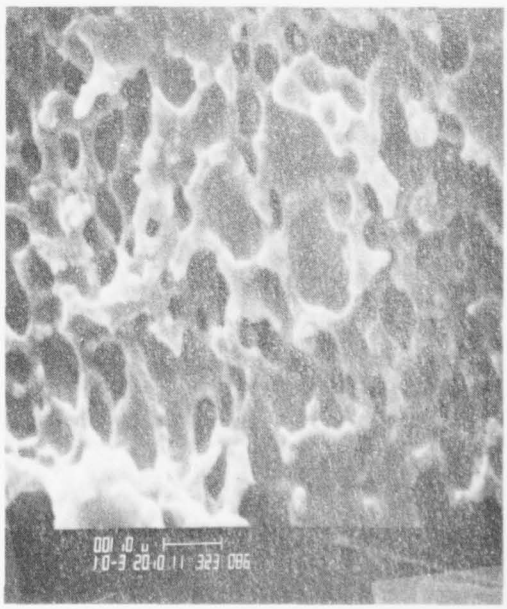


a



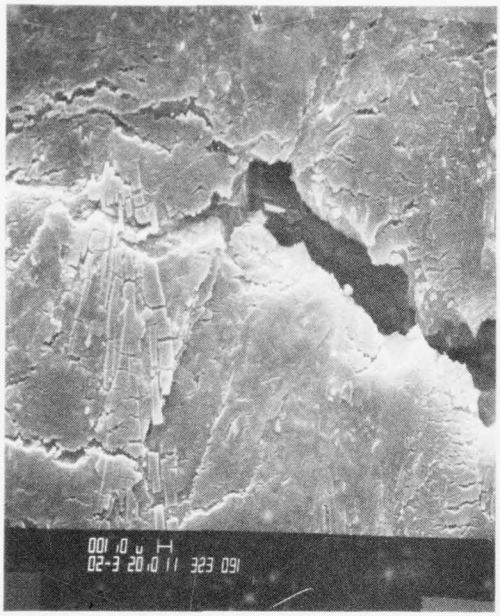
b

c

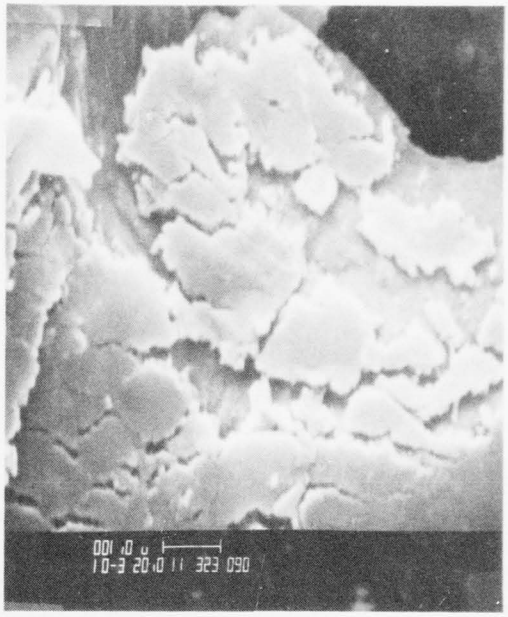


d

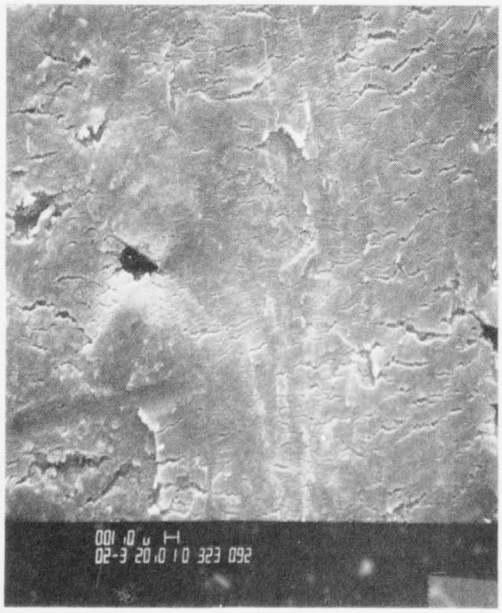
Fig. 32 SEM pictures of Al 2024-T3 after STAB(2), good bond.



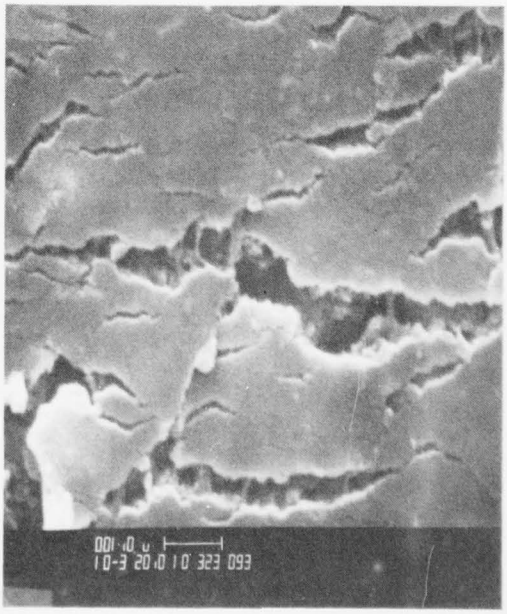

e




f




g




h

Fig. 32 continued

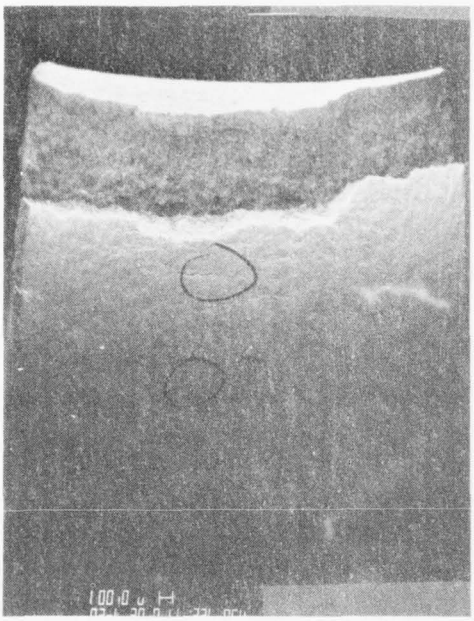
## 3.2 Surface Characterization

Figure 33 shows different magnification (a is X20, b is X200, c is X2000 and d is X10,000) SEM pictures of Al 2024-T3 after STAB(3). The hydroxide layer is quite distinct from that for STAB(1) and (2). Except for a few patches of a second layer (see Fig. 33c), STAB(3) produces a single layer of hydroxide with a very open (corn flake) structure that appears ideal for mechanical interlocking with adhesive.

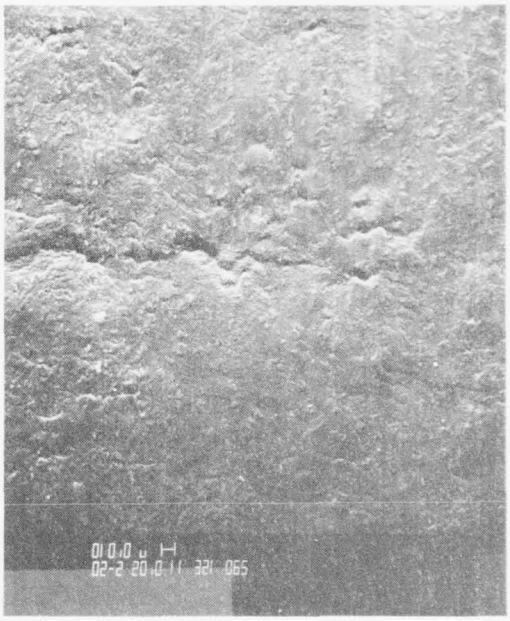
Figure 34 is an AES for Al 2024-T3 after STAB(3). The oxide contains the Mg and Cu alloy constituents, and some C and Cl surface contamination. The sputter profile (Fig. 35) shows that the film is stable to the electron beam (no 60 eV Al, no decrease in O) and has a peculiar C profile. The C remains high for 10 min and is removed sharply between 10 and 12 min. The significance of this is not understood, normal organic contamination is usually removed in 2 or 3 min or less. The carbon contamination may be a more stable compound than usual.

Figures 36a-d shows the surface property changes as the STAB(3) samples are given the thermal-humidity history of normal adhesive joint preparation. A duplicate set of samples were used to check reproducibility. The trends are reproducible and reveal definite structural changes. During the first 30 min of air exposure after STAB(3) no changes occur. Exposure to the cure oven, increase $\Delta$, PEE and $\theta_{H_2O}$. This is interpreted as a decrease in film thickness and/or density. Surprisingly, SPD does not change during the oven exposure. This, plus the small change in $\theta_{H_2O}$ may indicate, as did the C sputter profile, that the carbon contamination is peculiar and more stable for STAB(3). Exposure to the humidity chamber decreases $\Delta$ and PEE but increases $\theta_{H_2O}$ and SPD. This is interpreted as due to organic contamination but AES or ESCA results are needed to confirm this.

There is always the concern that a surface treatment does not remove enough metal to significantly thin or weaken the metal sheet. To check this for STAB(3), samples were etched for various lengths of time (0-10 min), rinsed, dried and weighed. The weight loss proved linear with time, with a

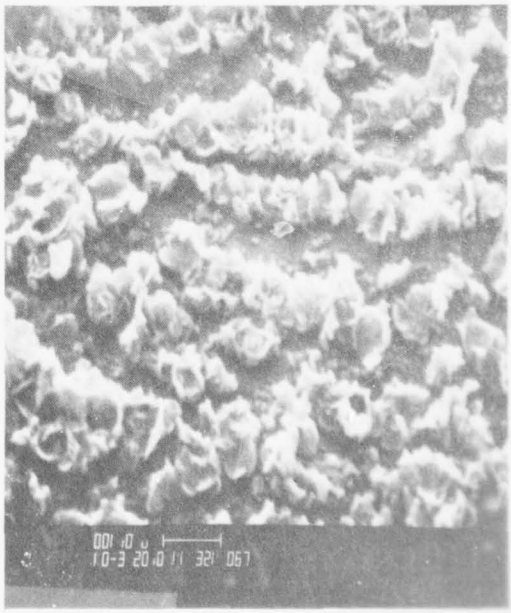


a



b

c

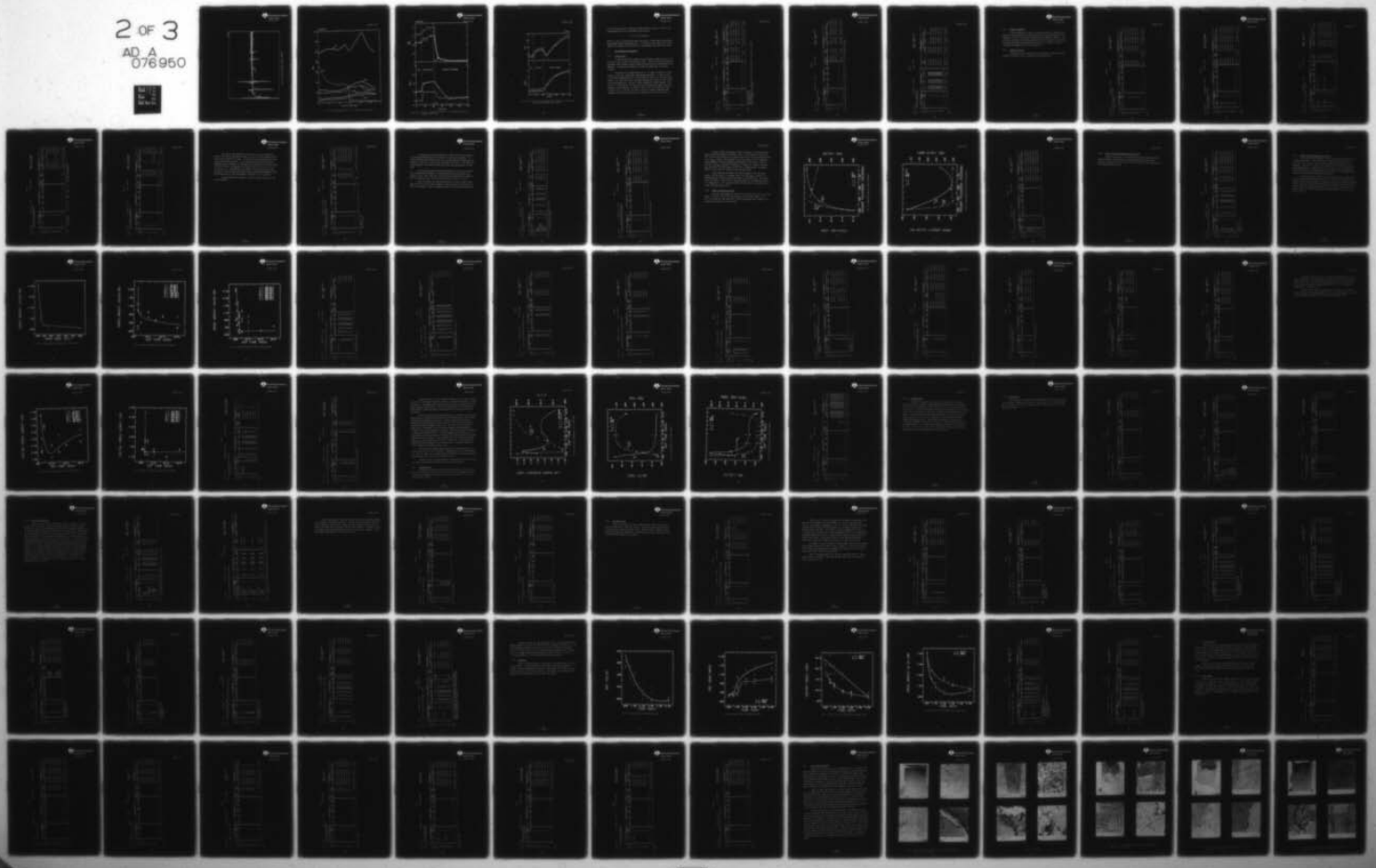


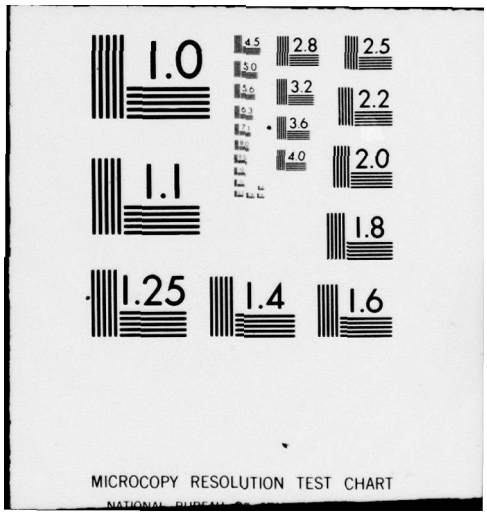
d

Fig. 33 SEM pictures of Al 2024-T3 after STAB(3).

AD-A076 950 ROCKWELL INTERNATIONAL THOUSAND OAKS CA SCIENCE CENTER F/G 11/6
SURFACE TREATMENT FOR ALUMINUM BONDING.(U)
OCT 79 T SMITH
UNCLASSIFIED SC5180.17FTR DAAK10-78-C-0274
NL

2 OF 3
AD A 076950




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART

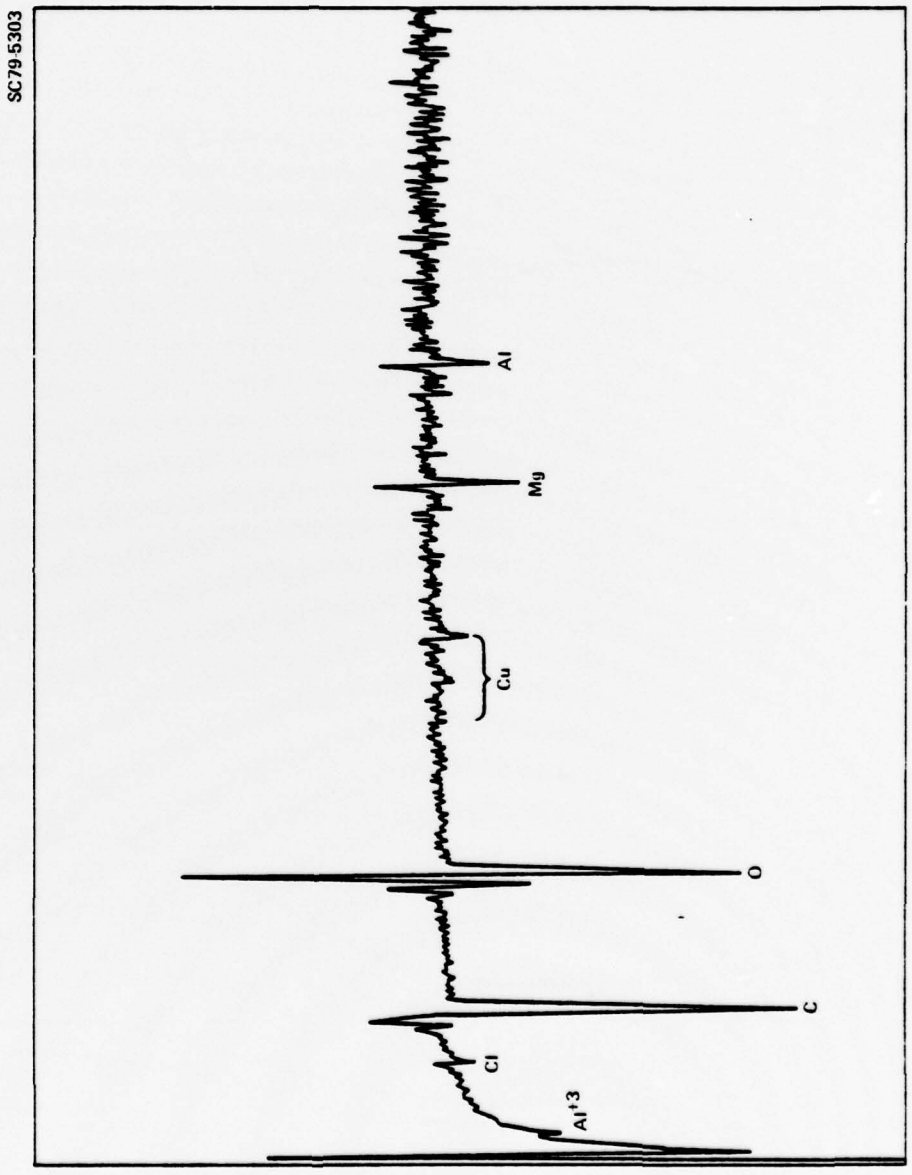



Fig. 34 AES of Al 2024-T3 after STAB(3).

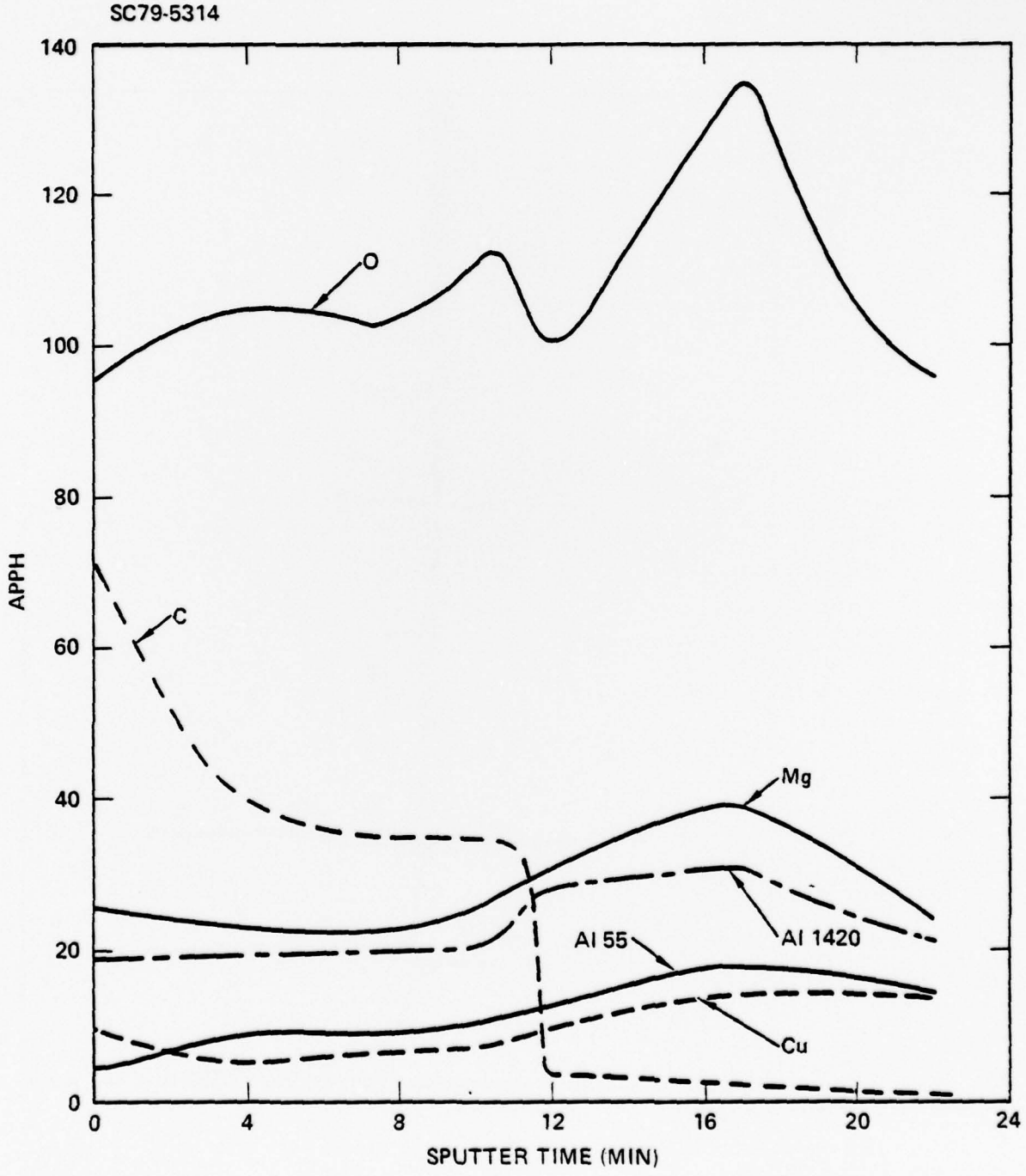



Fig. 35 AES sputter profile of Al 2024-T3 after STAB(3).

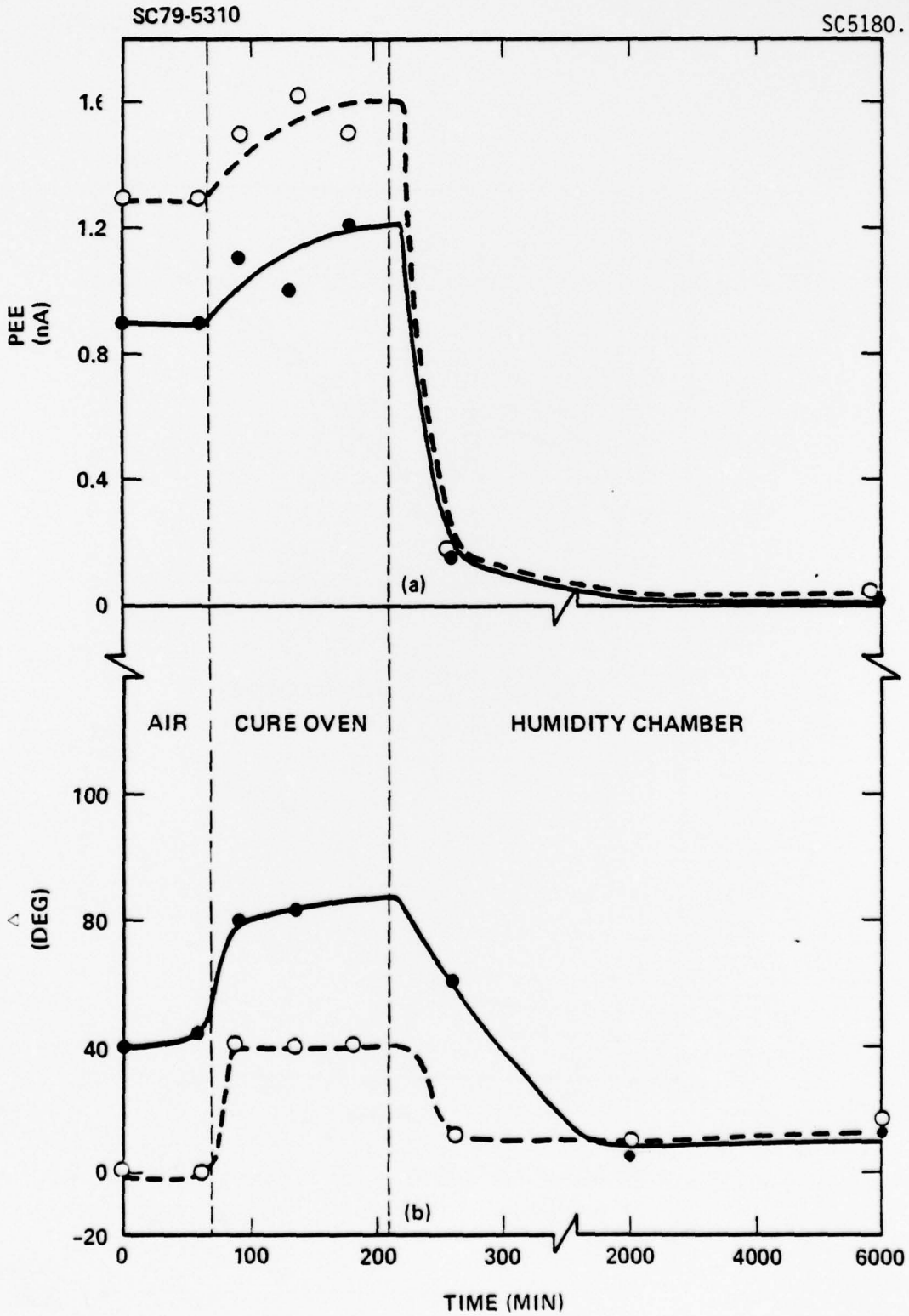



Fig. 36a,b PEE and Δ track of Al 2024-T3 in cure oven and humidity chamber after STAB(3).

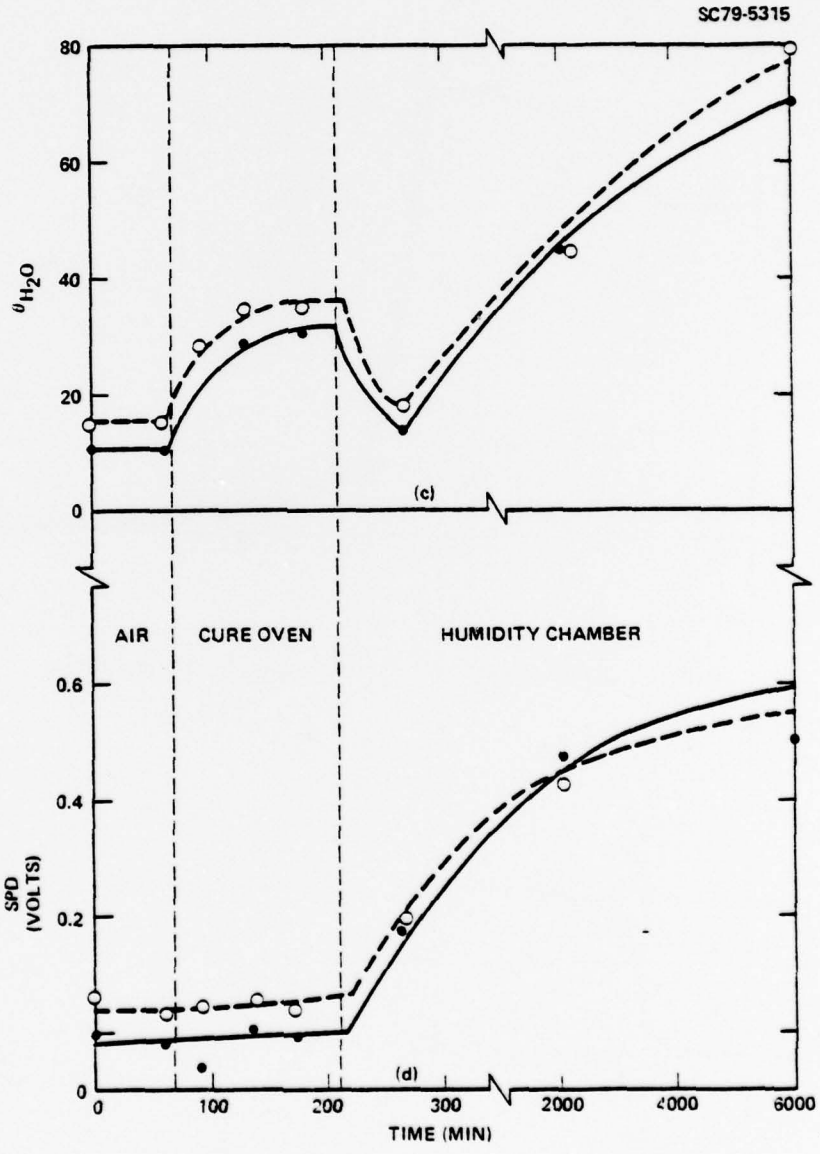



Fig. 36 c,d Track of SPD and $\theta_{H_2O}$ for Al 2024-T3 in cure oven and humidity chamber after STAB(3).

1 min initiation period. The depth of metal removal (using 2.7 g/cm$^3$ as the hydroxide density) can be expressed by the equation

$$d \simeq (5 \times 10^{-5} \text{ cm/min})t$$

where t is time in minutes after the first minute. Other samples were etched and weighed yielding the same result. It follows that the normal 3 min dip of STAB(3) only removes $10^{-4}$ cm (0.04 mil), considerably less than the FPL etch.

## 3.3 Bond Strength and Endurance

### 3.3.1 Effect of GLT

In Table 29 the crack growth was satisfactory, except for joint (7-8) which had a very low glue line thickness (GLT). There are instances when some specimens receive excess pressure, breaking the nylon scrim and extracting the adhesive. In these rare instances, lap shear and wedge tests are usually inferior.

The normal GLT averages about 4 mils. To check the effect of larger values, 5 and 10 mil shims were placed between adherends. In Table 30 the 5 mil shims produced actual GLT values between 4.1 and 4.6 mil and gave normal results, i.e. ~34.4 MPa (5 Ksi) lap shear strength and ~0.305 cm (0.12 in)/24 hrs for the wedge test. The 10 mil shims produced GLT values between 7 and 9.3 mils. The actual GLT was less than 10 mils because the copper wires were pressed into the aluminum. In Table 31 the initial crack length was large (~5.24 cm (2.11 in) for GLT of ~0.02 cm (9 mil), indicating weakened peel strength and the crack growth was low, probably due to the low value of $G_I$.

TABLE 29

Date: 01/22/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628II
Primer: EA9210II

Purpose: STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | BT (cm)(in) | Estimated GLT mm (mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-22-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | 0.64 (0.25) | 0.15 (6) | 5.08 (2.0) | 0.38 (0.15) | 0.64 (0.25) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | 0.64 (0.25) | 0.10 (4) | 4.32 (1.7) | 0.51 (0.20) | 0.76 (0.30) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | 0.64 (0.25) | 0.11 (4.5) | 4.06 (1.6) | 0.20 (0.08) | 0.91 (0.36) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | 0.64 (0.25) | -.05 (2) | 4.06 (1.6) | 0.31 (0.12) | 2.54 (1.0) |
| -8 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg. | 4.32 (1.7) | 0.36 (0.14) | 1.22 (0.48) |

Remarks: New primer, new adhesive
Rinse flowing D.I. water
Prime, oven cure
Avg. Bond Thickness (BT) = 0.1245 ± 0.0002, with primer but no adhesive. Estimated Glue Line Thickness (GLT) = BT -(0.1245 x 2) = BT -0.249

TABLE 30

Date: 01/24/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628II
Primer: EA9210H

Purpose: Effect of GLT on STAB(3)
Shim - 0.005"

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: ν (deg.) | Surface Properties: SPD (volts) | Surface Properties: PLE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Est. GLT (mm)(mil) | Bond Properties: Lap Shear MPa (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-24-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | 0.10 (4.1) | 35 (5.1) | 3.43 (1.35) | 0.08 (0.03) | 0.28 (0.11) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | 0.10 (4.6) | 35 (5.1) | 3.51 (1.38) | 0.08 (0.03) | 0.25 (0.10) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | 0.11 (4.4) | 32 (4.7) | 3.56 (1.40) | 0.13 (0.05) | 0.38 (0.15) |
| -6 | | 3 | | | | | | | | | | |
| | | | | | | | | Avg. | 34 (5.0) | 3.51 (1.38) | 0.10 (0.04) | 0.31 (0.12) |

Remarks: Measured thickness of samples to be 0.1245 ± 0.0002 as avg. at 2", 3", 4" & 5" along sample for 6 samples.

TABLE 31

Date: 01/25/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of GLT on STAB(3).
Used 10 mil copper wire shims.

| | Surface Treatment | | Sample Thickness | | | Bond Properties | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Before | After | Difference | Est. GLT mm (mil) | Wedge Crack Growth/Inches (Initial) | (1 hr) | (24 hr) |
| 1-25-79 | | | | | | | | | |
| -1 | | 3 | 0.1242 | 0.1241 | 0.0001 | 0.19 (7.0) | 6.35 (2.50) | 0.0 | 0.0 |
| -2 | | 3 | 0.1240 | 0.1239 | 0.0001 | | | | |
| -3 | | 3 | 0.1248 | 0.1247 | 0.0001 | 0.18 (7.0) | 5.54 (2.18) | 0.33 (0.13) | 0.33 (0.13) |
| -4 | | 3 | 0.1237 | 0.1235 | 0.0002 | | | | |
| -5 | | 3 | 0.1238 | 0.1237 | 0.0001 | 0.21 (8.3) | 5.49 (2.16) | 0.61 (0.24) | 0.61 (0.24) |
| -6 | | 3 | 0.1231 | 0.1230 | 0.0001 | | | | |
| -7 | | 3 | 0.1239 | 0.1239 | 0.0000 | 0.23 (9.3) | 5.23 (2.06) | 0.33 (0.13) | 0.51 (0.20) |
| -8 | | 3 | 0.1228 | 0.1228 | 0.0000 | | | | |
| -9 | | 3 | 0.1245 | 0.1242 | 0.0003 | 0.18 (7.3) | 3.58 (1.41) | 0.18 (0.07) | 0.51 (0.20) |
| -10 | | 3 | 0.1241 | 0.1240 | 0.0001 | | | | |
| -11 | | 3 | 0.1244 | 0.1241 | 0.0003 | 0.21 (8.4) | 5.97 (2.35) | 0.25 (0.10) | 0.38 (0.15) |
| -12 | | 3 | 0.1247 | 0.1245 | 0.0002 | | | | |
| | | Avg. | 0.1243 | 0.1242 | 0.0001 | 0.20 (7.9) | 5.36 (2.11) | 0.28 (0.11) | 0.38 (0.15) |

Remarks:

### 3.3.2 Effect of Degrease

A great advantage of STAB(3) is the elimination of a degrease step. However, some aluminum may be so contaminated that a degrease step will be necessary. To see if a degrease step would be detrimental to STAB(3), a set of contol specimens (Table 32) was compared with a set processed in the same way except the samples were degreased in MEK prior to STAB(3). Table 33 indicates the degrease step was not deleterious.

### 3.3.3 Effect of Primer

Tables 34, 35 and 36 indicate that the lengths of time the primers had been in use had little if any effect on bond durability.

TABLE 32

Date: 02/05/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of degrease step on STAB(3)
No degrease (Control)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT mm (mil) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-05-79 | | | | | | | | | | | | |
| -13 | | 3 | | | | | | 0.11 (4.5) | | 3.56 (1.4) | 0.20 (0.08) | 0.20 (0.08) |
| -14 | | 3 | | | | | | | | | | |
| -15 | | 3 | | | | | | 0.10 (4) | | 3.81 (1.5) | 0.23 (0.09) | 0.58 (0.23) |
| -16 | | 3 | | | | | | | | | | |
| -17 | | 3 | | | | | | 0.10 (4) | | 3.30 (1.3) | 0.25 (0.10) | 0.64 (0.25) |
| -18 | | 3 | | | | | | | | | | |
| -19 | | 3 | | | | | | 0.07 (3) | | 3.56 (1.4) | 0.13 (0.05) | 0.25 (0.10) |
| -20 | | 3 | | | | | | | | | | |
| -21 | | 3 | | | | | | 0.10 (4) | | 3.56 (1.4) | 0.15 (0.06) | 0.43 (0.17) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | 0.10 (4) | | 3.81 (1.5) | 0.23 (0.09) | 0.53 (0.21) |
| -24 | | 3 | | | | | | | | | | |
| | | | | | | | | Avg. | | 3.56 (1.4) | 0.20 (0.08) | 0.38 (0.15) |

Remarks:

TABLE 33

Date: 02/05/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628II
Primer: Hysol EA9210I

Purpose: Effect of degrease step on STAB(3)
MEK degrease 10 min.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease MEK | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT (mm)(mil) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-05-79 | | | | | | | | | | | | |
| -1 | 10 min. | 3 | | | | | | 0.11 (4.5) | | 4.12 (1.62) | 0.31 (0.12) | 0.43 (0.17) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | 0.09 (3.5) | | 3.51 (1.38) | 0.10 (0.04) | 0.33 (0.13) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | 0.09 (3.5) | | 3.71 (1.46) | 0.15 (0.06) | 0.51 (0.20) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | 0.10 (4.0) | | 3.94 (1.55) | 0.20 (0.08) | 0.48 (0.19) |
| -8 | | 3 | | | | | | | | | | |
| -9 | | 3 | | | | | | 0.07 (3.0) | | 3.66 (1.44) | 0.31 (0.12) | 1.02 (0.40) |
| -10 | | 3 | | | | | | | | | | |
| -11 | | 3 | | | | | | 0.10 (4.0) | | 3.66 (1.44) | 0.31 (0.12) | 1.02 (0.40) |
| -12 | | 3 | | | | | | | | | | |
| | | | | | | | | Avg. | 3.89 (1.53) | | 0.20 (0.08) | 0.53 (0.21) |

Remarks:

TABLE 34

Date: 01/29/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of old or new primer on STAB(3)

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: ∀ (deg.) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Est GLT mm (mil) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-05-79 | | | | | | | | | | | |
| -13 | Old Primer | 3 | from stock | 1/18/79 | | | | | | | |
| -14 | ↓ | 3 | | | | | | 0.08 (3) | 4.65 (1.83) | 0.31 (0.12) | 1.30 (0.51) |
| -15 | | 3 | | | | | | | | | |
| -16 | | 3 | | | | | | 0.08 (3) | 5.54 (2.18) | 0.48 (0.19) | 0.74 (0.29) |
| -17 | | 3 | | | | | | | | | |
| -18 | | 3 | | | | | | 0.08 (3) | 4.60 (1.81) | 0.33 (0.13) | 0.43 (0.17) |
| -19 | New Primer | 3 | from stock | 1/29/79 | | | | | | | |
| -20 | | 3 | | | | | | 0.10 (4) | 3.81 (1.50) | 0.43 (0.17) | 0.43 (0.17) |
| -21 | | 3 | | | | | | | | | |
| -22 | | 3 | | | | | | 0.10 (4) | 3.87 (1.52) | 0.20 (0.08) | 0.41 (0.16) |
| -23 | | 3 | | | | | | | | | |
| -24 | ↓ | 3 | | | | | | 0.10 (4) | 3.58 (1.41) | 0.23 (0.09) | 0.38 (0.15) |
| | | | | | | | | Avg | 4.32 (1.70) | 0.33 (0.13) | 0.61 (0.24) |

Remarks:

TABLE 35

Date: 02/05/79 Investigator: R. Haak Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of primer age and use, STAB(3)
Primer taken from stock 02/05/79

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-05-79 | | | | | | | | | | | | |
| -13 | | 3 | | | | | | | | 3.51 (1.38) | 0.13 (0.05) | 0.56 (0.22) |
| -14 | | 3 | | | | | | | | | | |
| -15 | | 3 | | | | | | | | 3.51 (1.38) | ~0 | 0.38 (0.15) |
| -16 | | 3 | | | | | | | | | | |
| -17 | | 3 | | | | | | | | 3.51 (1.38) | ~0 | 0.81 (0.32) |
| -18 | | 3 | | | | | | | | | | |
| -19 | | 3 | | | | | | | | 3.61 (1.42) | ~0 | 0.64 (0.25) |
| -20 | | 3 | | | | | | | | | | |
| -21 | | 3 | | | | | | | | 3.51 (1.38) | 0.51 (0.02) | 0.41 (0.16) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | | | 4.04 (1.59) | ~0 | 0.25 (0.10) |
| -24 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg. | 3.61 (1.42) | ~0.03 (0.01) | 0.51 (0.20) |

Remarks:
After fracture 70, 218 47 0.18 0.12 --- #18 Interfacial Failure Region
After fracture 12 23 -0.15 0.08 15 #17 Mate to Failure Region

TABLE 36

Date: 02/05/79 Investigator: R. Haak Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of primer age and use STAB(3)
Primer taken from stock 1/18/79

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No | No Degrease | STAB(3) Time (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Est. GLT (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-05-79 | | | | | | | | | | | | |
| -1 | 3 | | | | | | | | 3.51 (1.38) | | ~0 | 1.52 (0.6) |
| -2 | 3 | | | | | | | | | | | |
| -3 | 3 | | | | | | | | 3.51 (1.38) | | ~0 | 0.38 (0.15) |
| -4 | 3 | | | | | | | | | | | |
| -5 | 3 | | | | | | | | 3.76 (1.48) | | ~0 | 0.25 (0.10) |
| -6 | 3 | | | | | | | | | | | |
| -7 | 3 | | | | | | | | 4.32 (1.70) | | ~0 | 0.71 (0.28) |
| -8 | 3 | | | | | | | | | | | |
| -9 | 3 | | | | | | | | 3.63 (1.43) | | 0.13 (0.05) | 0.46 (0.18) |
| -10 | 3 | | | | | | | | | | | |
| -11 | 3 | | | | | | | | 3.81 (1.63) | | ~0 | 0.56 (0.22) |
| -12 | 3 | | | | | | | | | | | |
| | | | | | | | | Avg | 3.81 (1.50) | | ~0 | 0.64 (0.25) |

Remarks:

The usual primer treatment involves warm up to room temperature, shake to mix solids, dip sample, leave in air for 1/2 hour followed by oven cure at 121°C (250°F) for 1 hour. In Table 37 the primed samples were left over night without oven cure. In this experiment not curing the primer weakened the peel strength, as indicated by the average initial crack length of 4.83 cm (1.9 in) as compared to a normal value of ~3.56 cm (1.4 in) to 3.81 cm (1.5 in). Although the crack growth in 24 hours was good, other experiments indicate that leaving the primer uncured causes degradation with failure occurring at the primer-adhesive interface or in the primer.

The bond endurance and mode of failure is rather sensitive to the primer thickness.

TABLE 37

Date: 01/18/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: STAB(3), to check air overnight dry or oven dry
Overnight dry primer, old primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) time (min) | $\Delta$ (deg.) | $\Psi$ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est. GLT mm (mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-18-79 | | | | | | | | | | | | |
| -13 | | 3 | | | | | | | 0.10 (4) | 1.75 | 0.38 (0.15) | 0.38 (0.15) |
| -14 | | 3 | | | | | | | | | | |
| -15 | | 3 | | | | | | | 0.12 (5) | 1.75 | 0.33 (0.13) | 0.76 (0.30) |
| -16 | | 3 | | | | | | | | | | |
| -17 | | 3 | | | | | | | 0.10 (4) | 2.0 | 0.51 (0.20) | 0.51 (0.20) |
| -18 | | 3 | | | | | | | | | | |
| -19 | | 3 | | | | | | | 0.10 (4) | 2.2 | 0.41 (0.16) | 0.64 (0.25) |
| -20 | | 3 | | | | | | | | | | |
| -21 | | 3 | | | | | | | 0.10 (4) | 2.0 | 0.25 (0.10) | 0.38 (0.15) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | | 0.10 (4) | 1.85 | 0.25 (0.10) | 0.43 (0.17) |
| -24 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg. | 4.88 (1.92) | 0.36 (0.14) | 0.51 (0.20) |

Remarks: Rinse flowing D.I. water
$N_2$ blow dry
Prime, dry overnight

To estimate the primer thickness, as-received primer was brushed on to carefully weighed pieces of aluminum foil, cured, and reweighed. The primer thickness was estimated to be 1.5 μ by the weighing technique as compared to 5 μ (0.2 mil) with calipers for normal application. The reason for the discrepancy is not known, unless the solids cause the calipers to read high.

Table 38 shows surface property and wedge test results for samples with varying primer thickness. The as-received primer was brushed onto samples 7 and 8, this primer was diluted by 50% by adding MEK for samples 5 and 6, diluted again for 3 and 4, and no primer was used for 1 and 2.

Table 39 reveals that dipping the sample into (well mixed) primer, then allowing it to drip drain produces a layer too thin at the top and too thick at the bottom. This is evidenced further in the scale up study later.

TABLE 38

Date: 01/23/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of primer thickness on STAB(3)
New primer

| Sample No. | Surface Treatment: No Degrease Primer | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: Ψ (deg.) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Peel Force (g/cm) | Bond Properties: Est. GLT mm (mil) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-23-79 | | | | | | | | | | | | |
| -1 | None | 3 | 2 | 25 | -0.03 | 1.4 | 14 | | 0.08 (3.0) | 3.56 (1.4) | 0.25 (0.1) | 1.17 (0.46) |
| -2 | None | 3 | 26 | 29 | -0.01 | 1.2 | 28 | | | | | |
| -3 | Dilute 1/4 | 3 | 0 | 18 | 0.65 | 0.2 | 102 | | 0.09 (3.5) | 3.56 (1.4) | 0.46 (0.08) | 0.66 (0.26) |
| -4 | Dilute 1/4 | 3 | 18 | 30 | 0.60 | 0.2 | 100 | | | | | |
| -5 | Dilute 1/2 | 3 | 18 | 21 | 0.75 | 0.2 | 94 | | 0.08 (3.0) | 3.81 (1.5) | 0.13 (0.05) | 0.25 (0.10) |
| -6 | Dilute 1/2 | 3 | 14 | 18 | 0.80 | 0.3 | 95 | | | | | |
| -7 | Normal | 3 | 2 | 19 | 0.80 | 0.2 | 86 | | 0.09 (2.5) | 3.81 (1.5) | 0.20 (0.80) | 0.56 (0.18) |
| -8 | Normal | 3 | 0 | 20 | 0.90 | 0.2 | 84 | | | | | |

Remarks: Primer applied on horizontal samples with brush.
Surface properties after priming

TABLE 39

Date: 01/23/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of primer application (dip and drain)
Overnight air dry after oven cure, new primer

| | Surface Treatment | | Surface Properties | | | | | | Bond Properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est. GLT mm (mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-23-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | 0.14 (5.5) | 3.81 (1.5) | 0.28 (0.11) | 1.40 (0.55) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | | 0.11 (4.5) | 3.71 (1.46) | 0.20 (0.08) | 2.03 (0.80) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | | 0.07 (3.0) | 3.80 (1.5) | 0.20 (0.08) | 1.27 (0.52) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | | 0.05 (2.0) | 3.56 (1.4) | 0.15 (0.06) | 0.66 (0.26) |
| -8 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg | 3.81 (1.5) | 0.20 (0.08) | 1.32 (0.53) |

Remarks: Prime, oven cure, left over night before bonding.

Figure 37 shows the effect of primer thickness on the water contact angle and surface potential difference (SPD). The increase and leveling of SPD is normal for the addition of organic material to a clean aluminum surface as for $\theta_{H_2O}$. However, the decrease in $\theta_{H_2O}$ for thicker film is unexpected, unless chromates are being exposed at the surface of the primer. The fact that SPD and $\theta_{H_2O}$ continue to increase up to about 0.6 μ (6000A) indicates that the primer is either porous or the film is discontinuous. The porous nature of the primer is indicated in SEM pictures later.

Figure 38 shows the effect of primer thickness on PEE and crack growth. The PEE drops to a constant value (~0.2 μA) about a factor of 10 above background, indicating that the primer is photo emitting. The optimum primer thickness is about 0.8μ for bond endurance in a stressed-humid condition (wedge test). It is evident from Fig. 37 and 38 that a good monitor for primer thickness might be SPD.

### 3.3.4 Effect of Primer Cure Time

Table 40 gives wedge test results for a primer cure of 10 min. vs the normal 1 hr. cure. The 10 min cure produces initial cracks about 1.3 cm (0.5 in) longer than the normal cure, indicating reduced peel strength. The average crack growth is about the same.

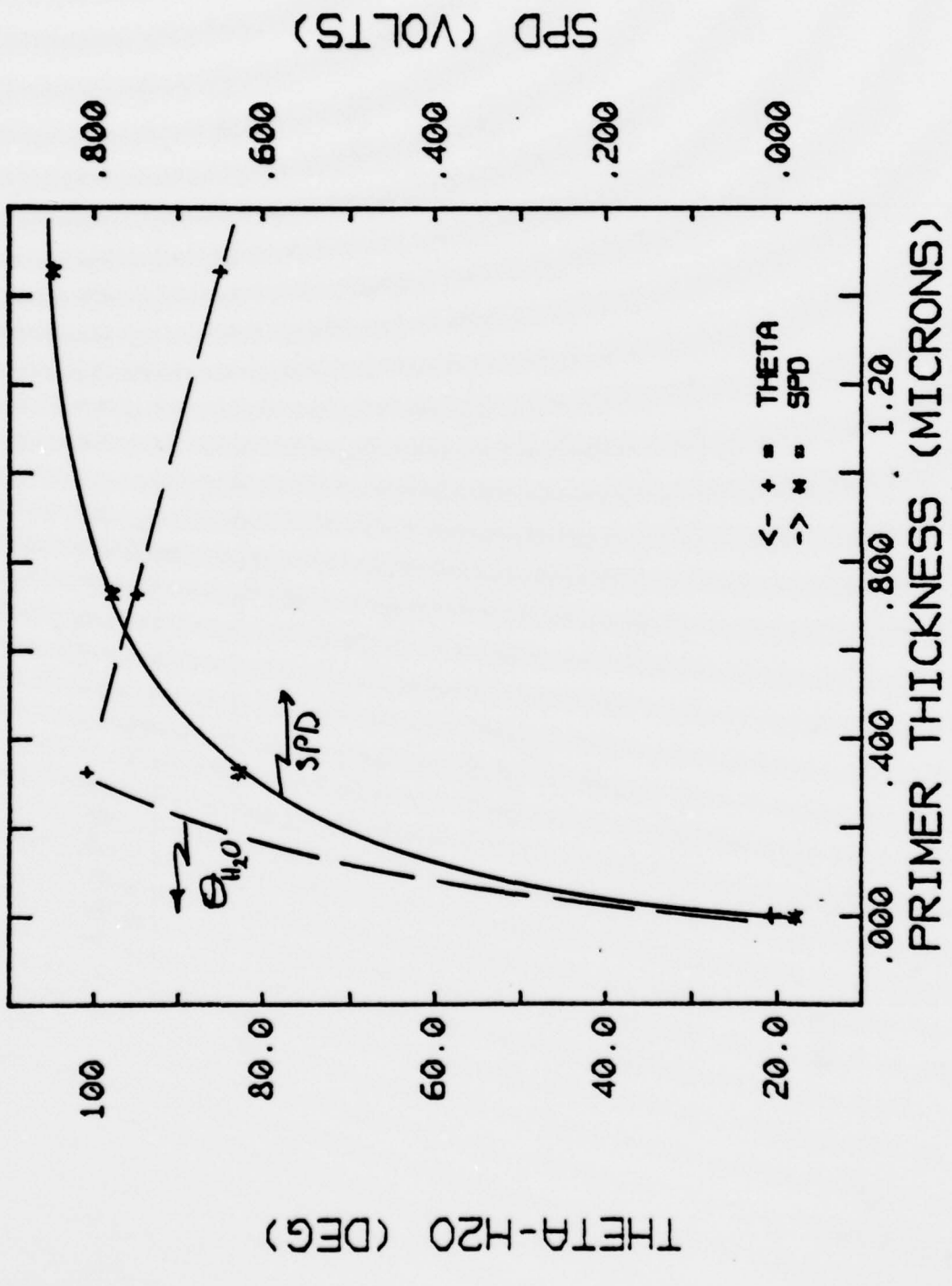



Fig. 37 Theta-$H_2O$ & SPD vs primer thickness.

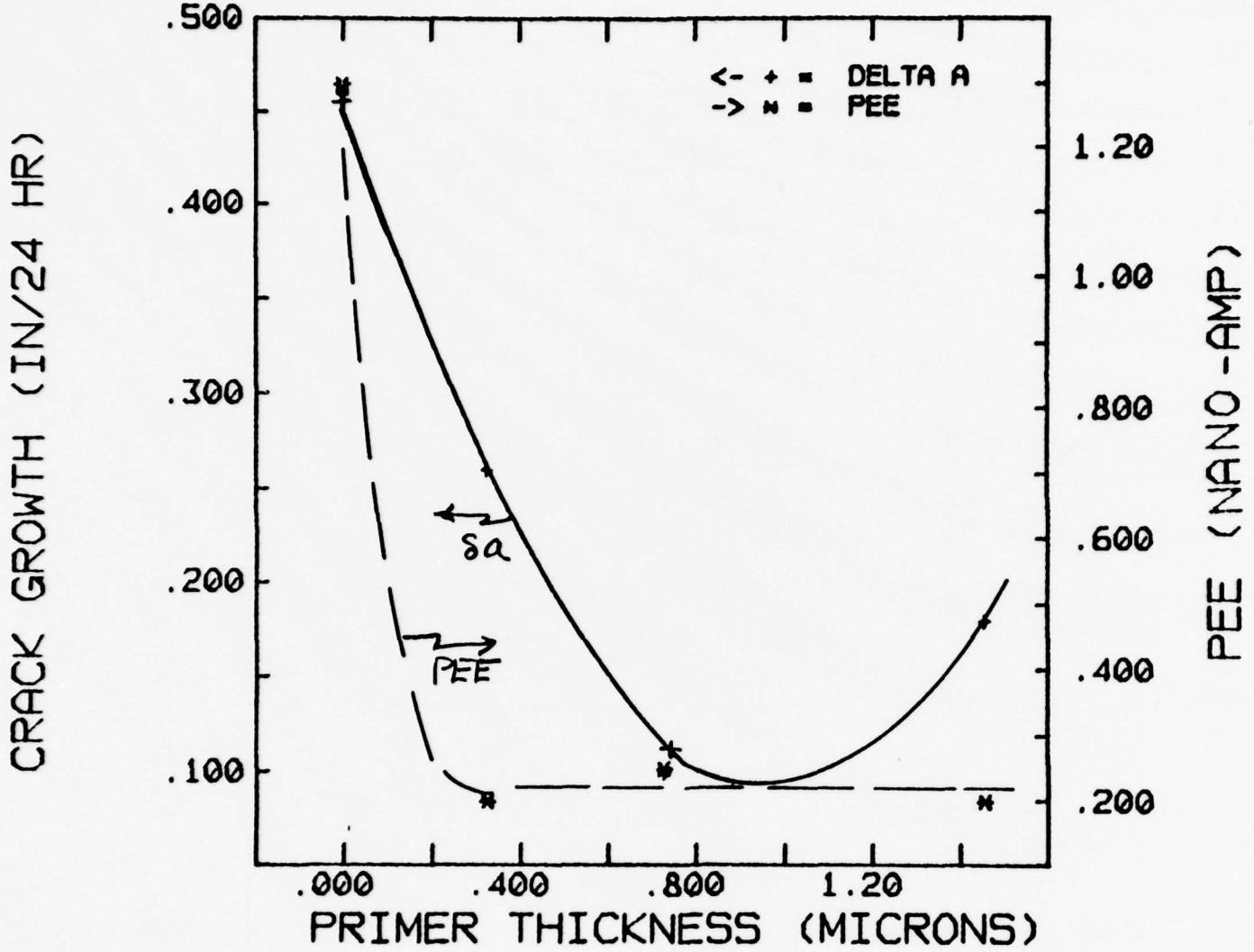



Fig. 38 Crack growth & PEE vs primer thickness.

TABLE 40

Date: 01/22/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of oven cure time for STAB(3)

| Sample No. | Surface Treatment: No Degrease Oven Cure 120°C | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: ψ (deg.) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Peel Force (g/cm) | Bond Properties: Est. GLT mm (mil) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-05-79 | | | | | | | | | | | | |
| -1 | 10 min | 3 | | | | | | | 0.08 (3) | 5.33 (2.1) | 0.51 (0.20) | 0.41 (0.16) |
| -2 | 10 min | 3 | | | | | | | | | | |
| -3 | 10 min | 3 | | | | | | | 0.05 (2) | 5.84 (2.3) | 0.31 (0.12) | 0.38 (0.15) |
| -4 | 10 min | 3 | | | | | | | | | | |
| -5 | 10 min | 3 | | | | | | | 0.06 (2.5) | 5.08 (2.0) | 0.56 (0.22) | 0.56 (0.22) |
| -6 | 10 min | 3 | | | | | | | | | | |
| -7 | 1 hr | 3 | | | | | | | 0.05 (2) | 4.32 (1.7) | 0.38 (0.15) | 0.38 (0.15) |
| -8 | 1 hr | 3 | | | | | | | | | | |
| -9 | 1 hr | 3 | | | | | | | 0.06 (2.5) | 4.06 (1.6) | 0.52 (0.06) | 0.38 (0.15) |
| -10 | 1 hr | 3 | | | | | | | | | | |
| -11 | 1 hr | 3 | | | | | | | 0.10 (4) | 4.06 (1.6) | 0.25 (0.10) | 0.41 (0.16) |
| -12 | 1 hr | 3 | | | | | | | | | | |

Remarks: New primer, new adhesive

### 3.3.5 Effect Of Delay Between STAB(3) and Prime

Table 41 shows there is little effect of delay between the STAB(3) surface treatment and the prime, on surface properties or wedge tests. Excellent crack growth results (~0.37 cm (0.18 in)/24 hrs) are obtained ater 24 hrs delay before priming.

TABLE 41

Date: 01/29/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of delay time between STAB(3) and prime

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Delay Time | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PLL (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est. GLT mm (mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-29-79 | | | | | | | | | | | | |
| -1 | 5 min | 3 | 30 | 24 | -0.04 | 0.9 | 10 | | 0.09 (3.5) | 3.94 (1.55) | 0.08 (0.03) | 0.25 (0.10) |
| -2 | 5 min | 3 | 0 | 33 | 0.10 | 1.3 | 15 | | | | | |
| -3 | 1 hr | 3 | 40 | 25 | -0.04 | 0.9 | 10 | | 0.08 (3.0) | 4.37 (1.72) | 0.23 (0.09) | 0.38 (0.15) |
| -4 | 1 hr | 3 | -6 | 32 | 0.05 | 1.3 | 15 | | | | | |
| -5 | 4 hr | 3 | -50 | 16 | 0.00 | 0.09 | 9 | | 0.08 (3.0) | 4.04 (1.59) | 0.23 (0.09) | 0.25 (0.15) |
| -6 | 4 hr | 3 | 14 | 9 | -0.01 | 0.09 | 8 | | | | | |
| -7 | 8 hr | 3 | 56 | 28 | 0.17 | 1.0 | 13 | | 0.10 (4.0) | 3.85 (1.54) | 0.28 (0.11) | 0.38 (0.20) |
| -8 | 8 hr | 3 | 60 | 22 | -0.06 | 1.0 | 23 | | | | | |
| -9 | 16 hr | 3 | 66 | 16 | -0.02 | 0.8 | 11 | | 0.08 (3.0) | 4.42 (1.74) | 0.13 (0.05) | 0.51 (0.15) |
| -10 | 16 hr | 3 | 72 | 12 | -0.07 | 0.7 | 10 | | | | | |
| -11 | 24 hr | 3 | 66 | 43 | -0.18 | 0.7 | 11 | | 0.08 (3.0) | 4.42 (1.38) | 0.13 (0.05) | 0.46 (0.18) |
| -12 | 24 hr | 3 | 66 | 40 | -0.20 | 0.6 | 11 | | | | | |

Remarks: 500 g NaOH/ℓ Soln.
3 min dip
Flowing D.I. water rinse
$N_2$ blow dry

3.3.6 Effect of NaOH Concentration and Time

Tables 42-51 show the effect of time in various NaOH concentrations on wedge crack growth. The large numbers of samples yielding ≤ 0.51 cm (0.2 in)/24 hrs at 580 g/ℓ and 3 min dip indicate these parameters to be adequate. Figure 39 is a plot of crack growth for a 3 min dip, at various NaOH concentrations. Concentrations as low as 100 g/ℓ may be adequate but below 100 g/ℓ the crack growth dramatically increases. More experiments are needed for concentrations between 100 and 600 g/ℓ.

Figure 40 shows the effect of time in NaOH solution on crack growth rate for concentration between 15 and 124 g/ℓ. The first few minutes of dip greatly reduces the crack growth but (except for 125 g/ℓ) at these low concentrations, even 30 minutes does not reduce crack growth below 0.63 cm (0.25 )/ 24 hrs. Figure 41 shows that above 125 g/ℓ, dip times of ≥3 min will give good results. All told 41 joints gave crack extensions of <0.2"/24 hr at 3 min dip, 568 g/ℓ.

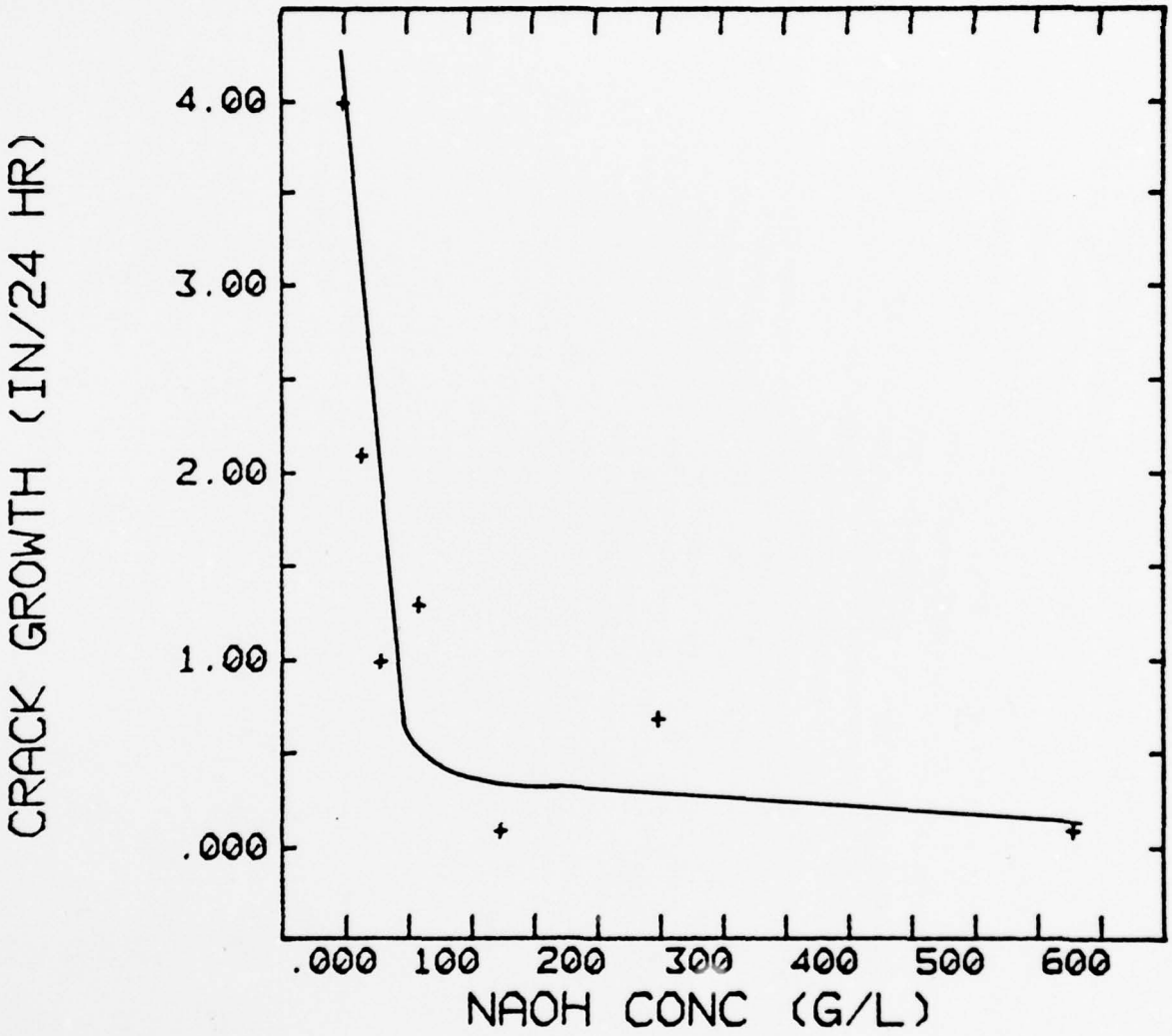



Fig. 39 Crack growth vs NaOH conc for 3 minute dip.

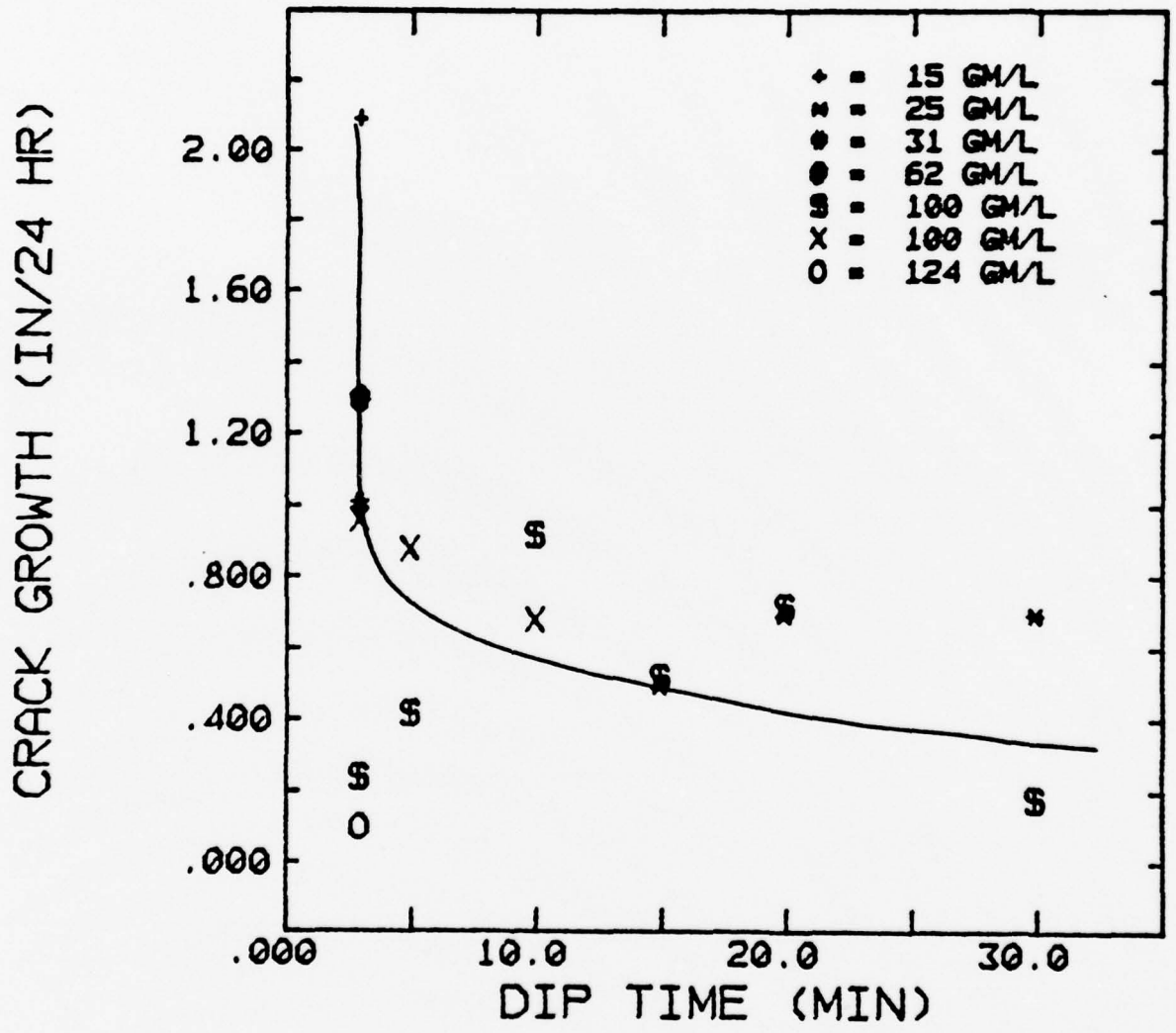



Fig. 40 Effect of NaOH conc & dip time on stab(3).

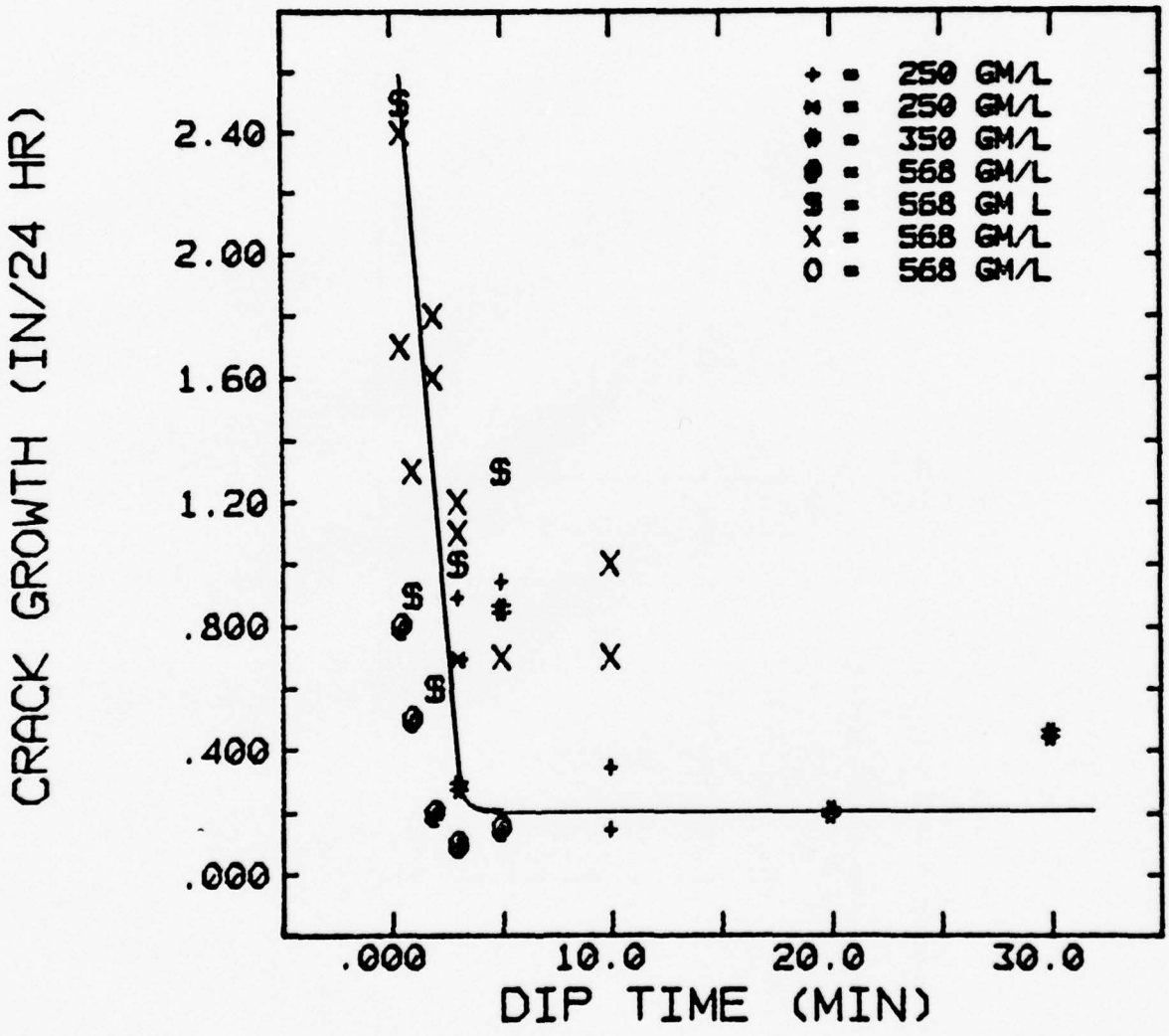



Fig. 41 Effect of NaOH conc & dip time on stab(3)

TABLE 42

Date: 1-6-79 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of time in NaOH solution, STAB(3), no degrease

| Sample No. | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Degrease | STAB(3) Time (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEE (mA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-6-79- | | | | | | | | | | | | |
| 1 | as-received | 0 | 68 | 41 | 0.53 | 0.22 | 50 | | | | | >10.16 (4) |
| 2 | " | 0 | 74 | 46 | 0.71 | 0.28 | 66 | | | | | |
| 3 | | 0.5 | 44 | 30 | 0.35 | 0.26 | 66 | | | | | 2.03 (0.8) |
| 4 | | 0.5 | 48 | 24 | 0.30 | 0.20 | 66 | | | | | |
| 5 | | 1.0 | 82 | 26 | 0.04 | 1.00 | 23 | | | | | 1.27 (0.5) |
| 6 | | 1.0 | 70 | 8 | 0.23 | 0.24 | 30 | | | | | |
| 7 | | 2.0 | 96 | 28 | 0.00 | 1.24 | 18 | | | | | 0.51 (0.2) |
| 8 | | 2.0 | 8 | 29 | 0.07 | 0.08 | 40 | | | | | |
| 9 | | 3.0 | 26 | 19 | -0.02 | 1.20 | 8 | | | | | 0.25 (0.1) |
| 10 | | 3.0 | 38 | 28 | -0.03 | 1.20 | 9 | | | | | |
| 11 | | 5.0 | 16 | 37 | -0.03 | 1.40 | 5 | | | | | 0.38 (0.15) |
| 12 | | 5.0 | 16 | 38 | -0.05 | 1.40 | 8 | | | | | |

Remarks: 360 g NaOH/600 cc D.I. water
Mate: 1-2, 3-4, 5-6, 7-8, 9-10, 11-12

TABLE 43

Date: 1-6-79 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of time in NaOH solution, STAB(3)

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg) | Surface Properties: Ψ (deg) | Surface Properties: SPD (volts) | Surface Properties: PLE (nA) | Surface Properties: $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-6-79- | | | | | | | | | | | | |
| 13 | as-received | 0 | -12 | 48 | 0.55 | 0.30 | 70 | 175 | | | | >10.16 (4) |
| 14 | " | 0 | 62 | 44 | 0.62 | 0.26 | 54 | 219 | | | | |
| 15 | | 0.5 | 264 | 15 | 0.30 | 0.65 | 33 | 263 | | | | 6.35 (2.5) |
| 16 | | 0.5 | 74 | 38 | 0.54 | 0.38 | 85 | 263 | | | | |
| 17 | | 1.0 | 54 | 40 | 0.44 | 0.34 | 65 | 350 | | | | 2.89 (0.9) |
| 18 | | 1.0 | 40 | 27 | 0.40 | 0.32 | 52 | 306 | | | | |
| 19 | | 2.0 | 24 | 29 | 0.28 | 0.80 | 52 | 350 | | | | 1.52 (0.6) |
| 20 | | 2.0 | 56 | 48 | 0.14 | 1.40 | 18 | 263 | | | | |
| 21 | | 3.0 | 4 | 26 | 0.22 | 1.60 | 11 | 482 | | | | 2.54 (1.0) |
| 22 | | 3.0 | 24 | 33 | 0.13 | 1.60 | 11 | 350 | | | | |
| 23 | | 5.0 | 0 | 37 | 0.01 | 2.00 | 8 | 438 | | | | 3.30 (1.3) |
| 24 | | 5.0 | -4 | 32 | 0.03 | 1.50 | 11 | 87 | | | | |

Remarks: 360 g NaOH/600 cc D.I. water
Mate: 13-14, 15-16, 17-18, 19-20, 21-11, 23-24

TABLE 44

Date: 1-5-79 Investigator: R. Haak Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: LA9210H

Purpose: Effect of time in NaOH solution, STAB(3) (0.5-2 min)

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg) | Surface Properties: ψ (deg) | Surface Properties: SPD (volts) | Surface Properties: PLE (nA) | Surface Properties: $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | Bond Properties: Wedge Crack Growth/cm(in) (1 hr) | Bond Properties: Wedge Crack Growth/cm(in) (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-5-79- | | | | | | | | | | | | |
| 1 | | 0.5 | | | | 0.3 | 50 | | | 3.81 (1.5) | | 4.32 (1.7) |
| 2 | | 0.5 | | | | 0.4 | 35 | | | | | |
| 3 | | 0.5 | | | | 0.3 | 40 | | | 3.81 (1.5) | | 4.10 (2.4) |
| 4 | | 0.5 | | | | 0.3 | 34 | | | | | |
| 5 | | 1.0 | | | | 1.1 | 27 | | | 3.81 (1.5) | | 3.30 (1.3) |
| 6 | | 1.0 | | | | 0.7 | 30 | | | | | |
| 7 | | 1.0 | | | | 0.6 | 33 | | | 3.81 (1.5) | | 3.30 (1.3) |
| 8 | | 1.0 | | | | 0.6 | 28 | | | | | |
| 9 | | 2.0 | | | | 1.0 | 20 | | | 3.81 (1.5) | | 4.57 (1.8) |
| 10 | | 2.0 | | | | 0.8 | 18 | | | | | |
| 11 | | 2.0 | | | | 0.8 | 18 | | | 3.81 (1.5) | | 4.06 (1.6) |
| 12 | | 2.0 | | | | 1.0 | 15 | | | | | |

Remarks:

TABLE 45

Date: 1-5-79 Investigator: R. Haak Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of time in NaOH solution, STAB(3) (3-10 min)

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg) | Surface Properties: Ψ (deg) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-5-79- | | | | | | | | | | | | |
| 13 | | 3 | | | | 1.0 | 18 | | | 3.81 (1.3) | | 4.32 (1.2) |
| 14 | | 3 | | | | 0.9 | 16 | | | | | |
| 15 | | 3 | | | | 1.0 | 15 | | | 3.81 (1.4) | | 6.10 (1.1) |
| 16 | | 3 | | | | 0.8 | 15 | | | | | |
| 17 | | 5 | | | | 1.1 | 15 | | | 3.81 (1.3) | | 3.30 (0.7) |
| 18 | | 5 | | | | 1.0 | 15 | | | | | |
| 19 | | 5 | | | | 1.0 | 15 | | | 3.81 (1.7) | | 3.30 (0.7) |
| 20 | | 5 | | | | 0.9 | 15 | | | | | |
| 21 | | 10 | | | | 0.9 | 9 | | | 3.81 (1.4) | | 4.57 (0.7) |
| 22 | | 10 | | | | 1.0 | 9 | | | | | |
| 23 | | 10 | | | | 1.0 | 9 | | | 3.81 (1.5) | | 4.57 (1.0) |
| 24 | | 10 | | | | 0.9 | 6 | | | | | |

Remarks:

TABLE 46

Date: 1-15-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of NaOH concentration, STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease NaOH (Conc) | STAB(3) $H_2O$ (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-15-79- | | | | | | | | | | | | |
| 1 | 360 g 600 cc | 3 | | | | | | | | 3.30 (1.9) | | 3.05 (0.1) |
| 2 | 360 600 | 3 | | | | | | | | | | |
| 3 | 180 600 | 3 | | | | | | | | 3.56 (1.8) | | 2.79 (0.7) |
| 4 | 180 600 | 3 | | | | | | | | | | |
| 5 | 90 600 | 3 | | | | | | | | 3.30 (2.3) | | 1.79 (0.1) |
| 6 | 90 600 | 3 | | | | | | | | | | |
| 7 | 45 600 | 3 | | | | | | | | 4.32 (2.0) | | 1.78 (1.3) |
| 8 | 45 600 | 3 | | | | | | | | | | |
| 9 | 23 600 | 3 | | | | | | | | 3.56 (2.1) | | 1.78 (1.0) |
| 10 | 23 600 | 3 | | | | | | | | | | |
| 11 | 12 600 | 3 | | | | | | | | 3.81 (2.4) | | 2.54 (2.1) |
| 12 | 12 600 | 3 | | | | | | | | | | |

Remarks:

TABLE 47

Date: 01/18/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of time and concentration on STAB(3)
Concentration = 25 g NaOH/ℓ solution (i.e. 25 g NaOH + 889cc D.I. water)
Old primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est. GLT (mm)(mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-18-79 | | | | | | | | | | | | |
| -25 | | 3 | | | | | | | 0.09 (3) | 5.33 (2.1) | 0.76 (0.3) | 3.30 (1.3) |
| -26 | | 3 | | | | | | | | | | |
| -27 | | 5 | | | | | | | 0.06 (2.5) | 8.64 (3.4) | >10.16 (4) | >10.16 (4) |
| -28 | | 5 | | | | | | | | | | |
| -29 | | 10 | | | | | | | - | >10.16 (4) | >10.16 (4) | >10.16 (4) |
| -30 | | 10 | | | | | | | | | | |
| -31 | | 15 | | | | | | | 0.09 (3.0) | 7.62 (3) | 0.76 (0.3) | 1.27 (0.5) |
| -32 | | 15 | | | | | | | | | | |
| -33 | | 20 | | | | | | | 0.06 (2.5) | 6.10 (2.4) | 0.50 (0.2) | 1.79 (0.7) |
| -34 | | 20 | | | | | | | | | | |
| -35 | | 30 | | | | | | | 0.06 (2.5) | 8.38 (3.3) | 0.25 (0.1) | 1.79 (0.7) |
| -36 | | 30 | | | | | | | | | | |

Remarks: Rinse flowing D.I. water
$N_2$ blow dry
Prime, dry 0.5 hr, oven 123°C 1 hr.

TABLE 48

Date: 01/24/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of NaOH concentration and time on STAB(3)
Concentration - 100 g NaOH/ℓ solution

| Sample No. | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Degrease | STAB(3) Time (min) | δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT (mm)(mil) | Lap Shear (MPa)(Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-24-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | 0.11 (4.3) | - | 10.57 (4.16) | 0.41 (0.16) | 0.61 (0.24) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 5 | | | | | | 0.08 (3.0) | - | 9.61 (3.57) | 0.56 (0.22) | 1.07 (0.42) |
| -4 | | 5 | | | | | | | | | | |
| -5 | | 10 | | | | | | 0.08 (3.0) | 7.5 (1.09) | 6.24 (2.45) | 1.79 (0.70) | 2.34 (0.92) |
| -6 | | 10 | | | | | | | | | | |
| -7 | | 15 | | | | | | 0.06 (3.0) | 11.3 (1.64) | 5.08 (2.00) | 1.27 (0.50) | 1.32 (0.52) |
| -8 | | 15 | | | | | | | | | | |
| -9 | | 20 | | | | | | 0.05 (2.0) | 17.4 (2.52) | 6.10 (2.40) | 1.68 (0.66) | 1.83 (0.72) |
| -10 | | 20 | | | | | | | | | | |
| -11 | | 30 | | | | | | 0.05 (2.0) | 19.5 (2.87) | 6.60 (2.60) | 0.30 (0.12) | 0.46 (0.18) |
| -12 | | 30 | | | | | | | | | | |

Remarks:

TABLE 49

Date: 01/19/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of time and concentration on STAB(3)
Concentration = 100g NaOH/ solution

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | (deg.) | (deg.) | SPD (volts) | PEE (nA) | $H_2O$ (deg.) | Peel Force (g/cm) | Est. GLT (mm)(mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-19-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | 0.08 (3.0) | 7.12 (2.8) | 1.02 (0.4) | 2.4 (0.96) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 5 | | | | | | | 0.09 (3.5) | 8.90 (3.5) | 0.69 (0.27) | 2.2 (0.88) |
| -4 | | 5 | | | | | | | | | | |
| -5 | | 10 | | | | | | | 0.08 (3.0) | 4.32 (1.7) | 0.38 (0.15) | 1.7 (0.68) |
| -6 | | 10 | | | | | | | | | | |

Remarks: Primer applied, left over weekend then oven cured.

TABLE 50

Date: 01/26/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628II
Primer: EA9210II

Purpose: Effect of concentration and time on STAB(3)
Concentration = 250g NaOH/ℓ solution

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: Ψ (deg.) | Surface Properties: SPD (volts) | Surface Properties: PLE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Peel Force (g.cm) | Bond Properties: Est. GLT (mm)(mil) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-26-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | 0.08 (3) | 7.62 (3.0) | 0.51 (0.2) | 2.29 (0.90) |
| -2 | | 3 | | | | | | | 0.06 (2.5) | | | |
| -3 | | 5 | | | | | | | | 4.83 (1.9) | 0.76 (0.3) | 2.41 (0.95) |
| -4 | | 5 | | | | | | | | | | |
| -5 | | 10 | | | | | | | | 3.30 (1.3) | 0.25 (0.1) | 0.89 (0.35) |
| -6 | | 10 | | | | | | | | | | |
| -7 | | 10 | | | | | | | | 3.30 (1.3) | 0.25 (0.1) | 0.38 (0.15) |
| -8 | | 10 | | | | | | | | | | |

Remarks:

TABLE 51

Date: 01/29/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of NaOH concentration and time on STAB(3).
Concentration = 350g NaOH/ℓ solution

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLL (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est GLT (mm)(mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-29-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | 0.08 (3.0) | 3.68 (1.45) | 0.76 (0.03) | 7.11 (0.28) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 5 | | | | | | | 0.10 (4.0) | 4.65 (1.83) | 0.38 (0.15) | 2.16 (0.85) |
| -4 | | 5 | | | | | | | | | | |
| -9 | | 20 | | | | | | | 0.08 (3.0) | 2.92 (1.15) | 0.76 (0.03) | 1.14 (0.20) |
| -10 | | 20 | | | | | | | | | | |
| -11 | | 30 | | | | | | | 0.08 (3.0) | 3.86 (1.52) | 0.20 (0.08) | 1.14 (0.45) |
| -12 | | 30 | | | | | | | | | | |

Remarks:

Figure 42 and 43 are plots of initial cracks length on dip time in NaOH. Below 100g/ℓ (Fig. 42) there is a minimum in initial crack length at about a 10 min dip. At the higher NaOH concentration (Fig. 43) the initial crack length is sensitive to concentration for a 3 min dip, but becomes insensitive to time above 3 min.

Table 52 and 53 show the effect of time in 580g/ℓ NaOH on the lap shear strength. As-received samples give high lap shear values (~4.8 Ksi) but high %IF (percent interfacial failure) and terrible wedge tests.

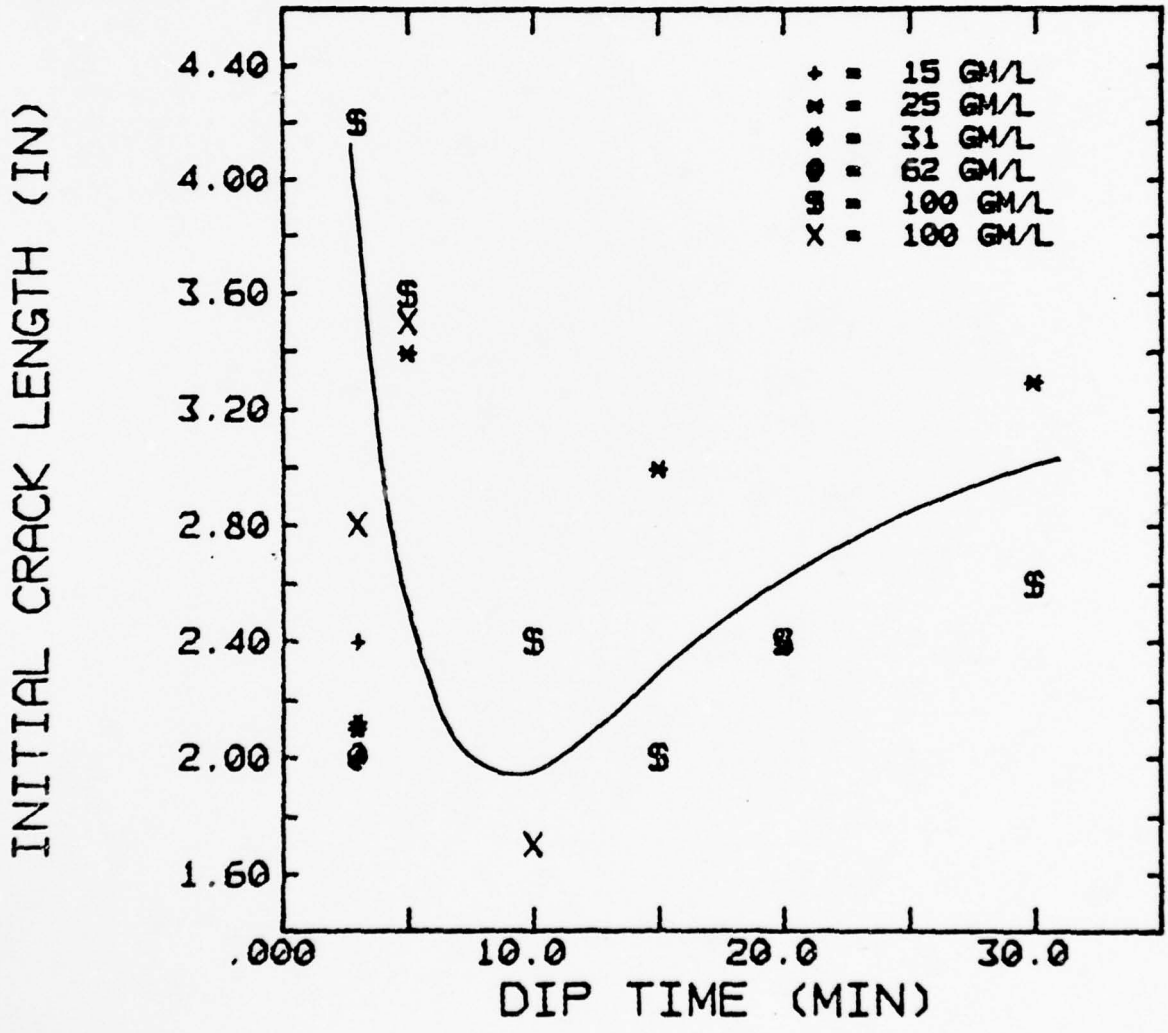



Fig. 42 Effect of NaOH conc & dip time on stab(3).

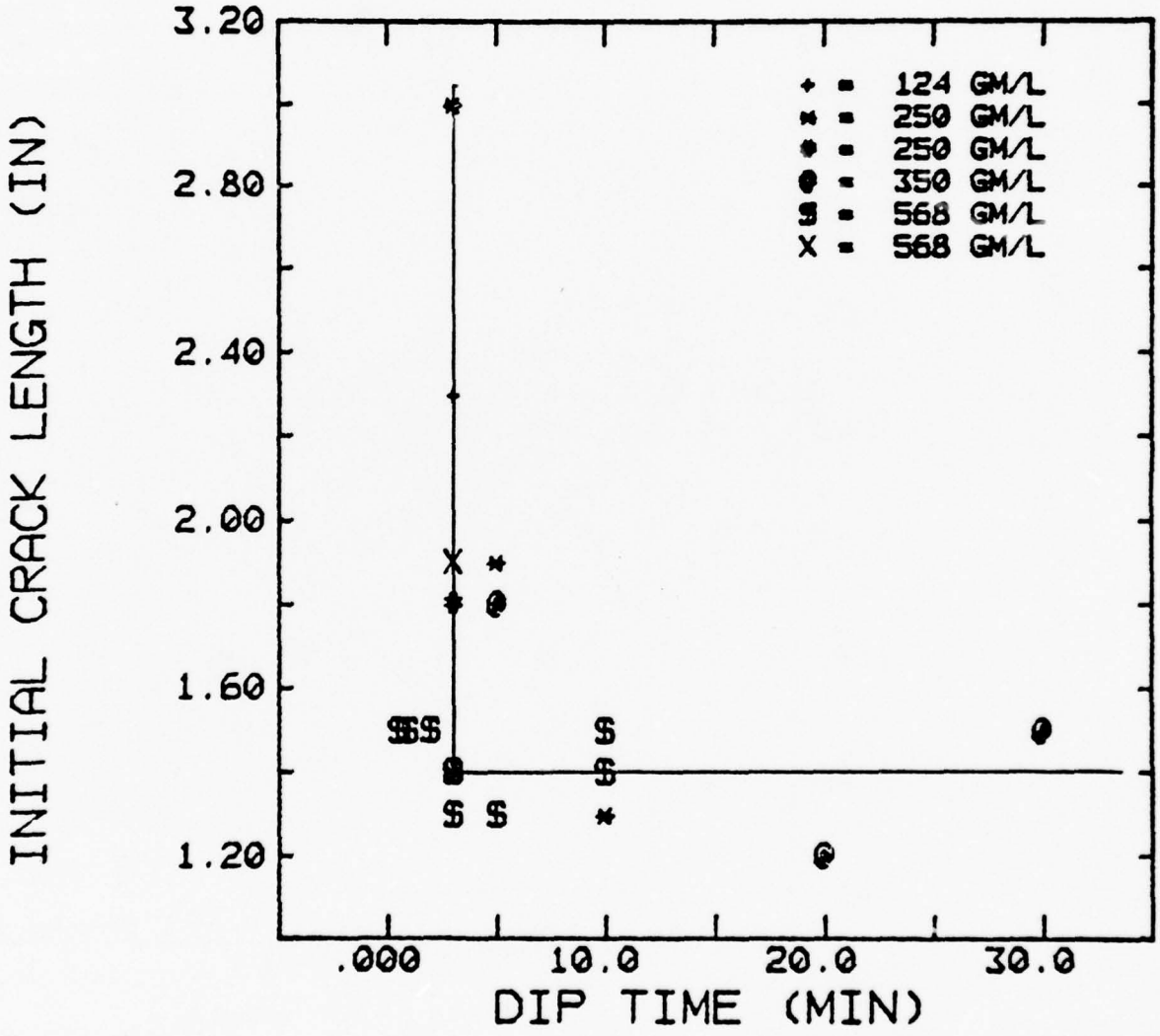



Fig. 43 Effect of NaOH conc & dip time on stab(3).

TABLE 52

Date: 02/12/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of time in NaOH on STAB(3)
Lap shear tests

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (MPa) (Ksi) | %IF |
| 2-12-79 | | | | | | | | | | |
| -1 | As Received | 0 | 93 | 37 | 0.46 | 0.08 | 30 | | 33.1 (4.81) | 80 |
| -2 | As Received | 0 | 97 | 35 | 0.38 | 0.11 | 38 | | | |
| -3 | | 0.5 | 76 | 33 | 0.10 | 0.14 | 48 | | 36.2 (5.26) | 5 |
| -4 | | 0.5 | 62 | 27 | 0.18 | 0.10 | 60 | | | |
| -5 | | 1.0 | 34 | 28 | 0.80 | 0.42 | 35 | | 33.8 (4.90) | 5 |
| -6 | | 1.0 | 18 | 28 | 0.40 | 0.56 | 35 | | | |
| -7 | | 3.0 | 10 | 25 | 0.00 | 0.95 | 18 | | 31.1 (4.51) | 30 |
| -8 | | 3.0 | 10 | 25 | -0.02 | 0.95 | 14 | | | |
| -9 | | 5.0 | 10 | 28 | -0.02 | 1.05 | 13 | | 32.2 (4.68) | 65 |
| -10 | | 5.0 | 20 | 31 | 0.00 | 0.98 | 18 | | | |
| -11 | | 10.0 | 10 | 33 | 0.26 | 0.78 | 6 | | 29.6 (4.31) | 85 |
| -12 | | 10.0 | 10 | 28 | 0.01 | 0.80 | 8 | | | |

Remarks:

TABLE 53

Date: 02/14/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of time in NaOH on lap shear strength, STAB(3).

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | %IF | Lap Shear (MPa) (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-14-79 | | | | | | | | | | | | |
| -1 | | 0 | | | | | | P | 18 (4.1) | | | |
| -2 | | 0 | | | | | | | | | | |
| -3 | | 0.5 | | | | | | P | 31 (4.5) | | | |
| -4 | | 0.5 | | | | | | | | | | |
| -5 | | 1.0 | | | | | | P | 34 (4.9) | | | |
| -6 | | 1.0 | | | | | | | | | | |
| -7 | | 3.0 | | | | | | P | 31 (4.5) | | | |
| -8 | | 3.0 | | | | | | | | | | |
| -9 | | 5.0 | | | | | | 70 | 27 (3.9) | | | |
| -10 | | 5.0 | | | | | | | | | | |
| -11 | | 10.0 | | | | | | 90 | 27 (3.9) | | | |
| -12 | | 10.0 | | | | | | | | | | |

Remarks: P means failure at primer - adhesive interface.

Figure 44 shows a plot of lap shear strength and %IF vs time in NaOH solution. As indicated in Table 54, there is a problem with respect to primer application. The samples were dipped in primer and drip drained with the lap shear bond area at the bottom. Too thick primer layers give failure at the metal-primer or adhesive-primer interface and thus do not test the surface preparation.

Figure 45 and 46 show surface properties as a function of dip time in NaOH solution. The results are consistent with the wedge tests that indicate good durability between 3 and 10 min. Figure 45 shows that the surface properties change dramatically during the first 2 or 3 min but then remain essentially constant between 3 and 10 min. The drop in the ellipsometric phase shift $\Delta$ corresponds to film thickening, whereas the corresponding increase in PEE might be thought to indicate film thinning since the hydroxide is not emitting and the metal is. Both measurements are consistent if it is assumed that a thick porous layer is formed with decreasing barrier-electron-attenuating-layer thickness. Figure 46 shows that the SPD and water contact angle, $\theta_{H_2O}$, also decrease and level off at about 3 min. The as-received samples are rather hydrophilic, as indicated by the low contact angles, but first increase then decrease with dip time.

The fact that all measurements remain fairly constant beyond 3 min indicate that the film that is formed is independent of the dip time beyond 3 min. That is, after 3 min in NaOH solution the surface is about the same and forms the same type of film upon rinsing and drying.

Figures 45 and 46 indicate that all of the surface tools can be used for quality assurance that STAB(3) has been properly performed.

### 3.3.7 Process Errors

A number of process errors have been defined thus far, such as too short a time in NaOH, too thick or too thin primer, time allowed for uncured primer before bonding etc. However, the primary process error to avoid is improper rinse and dry.

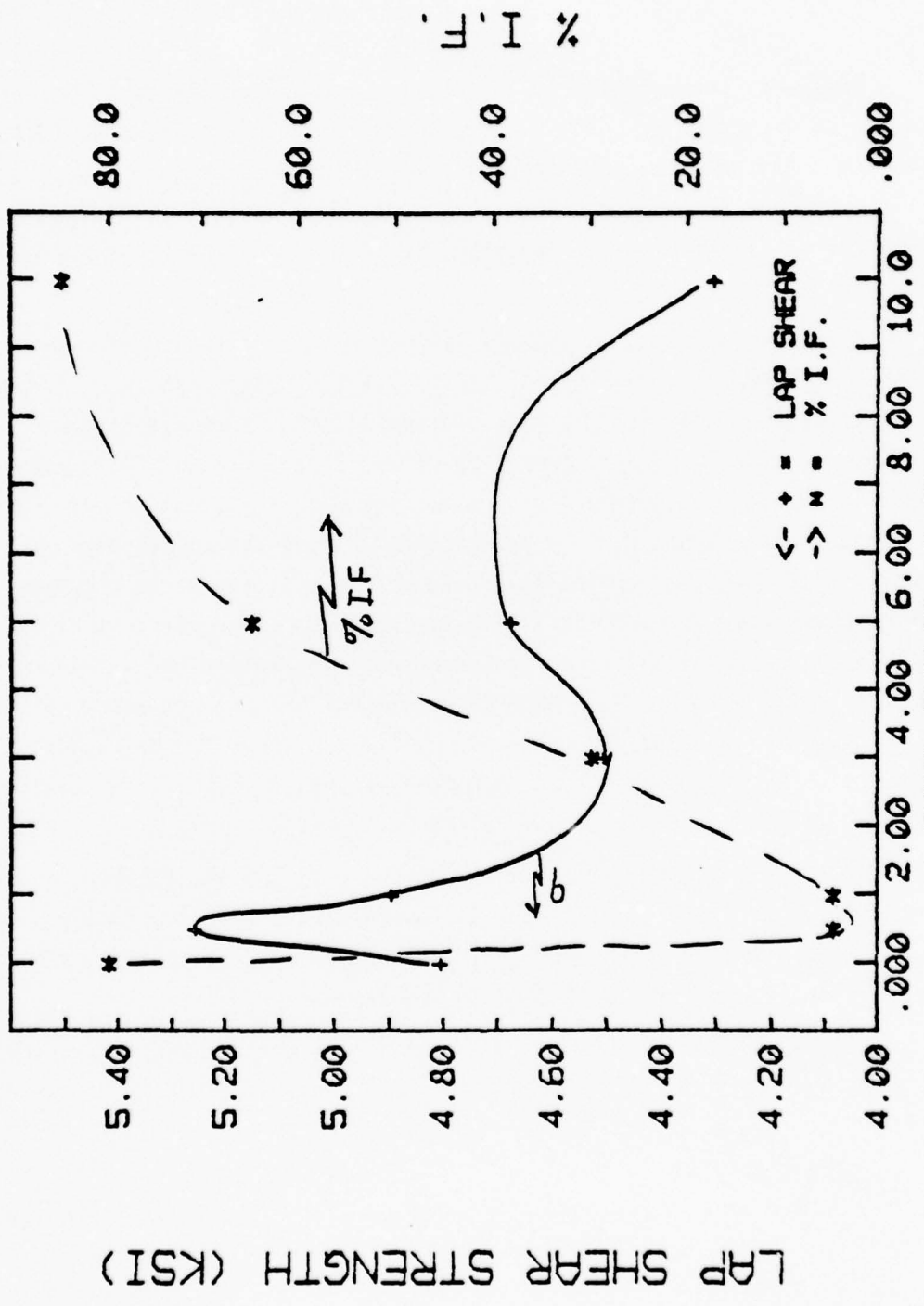



Fig. 44 Lap shear strength & % I.F. vs dip time.

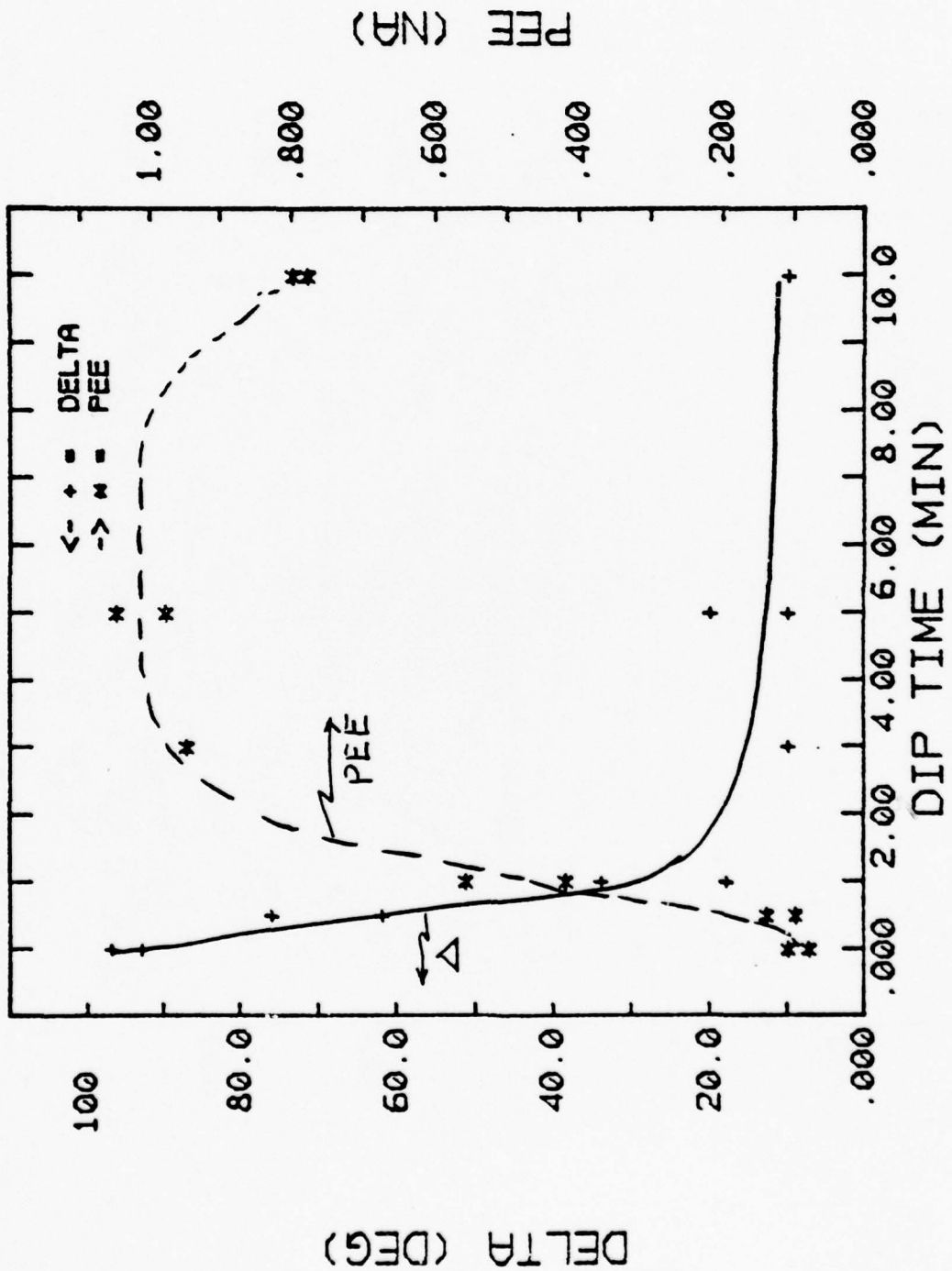



Fig. 45 Delta & PEE vs dip time in NaOH.

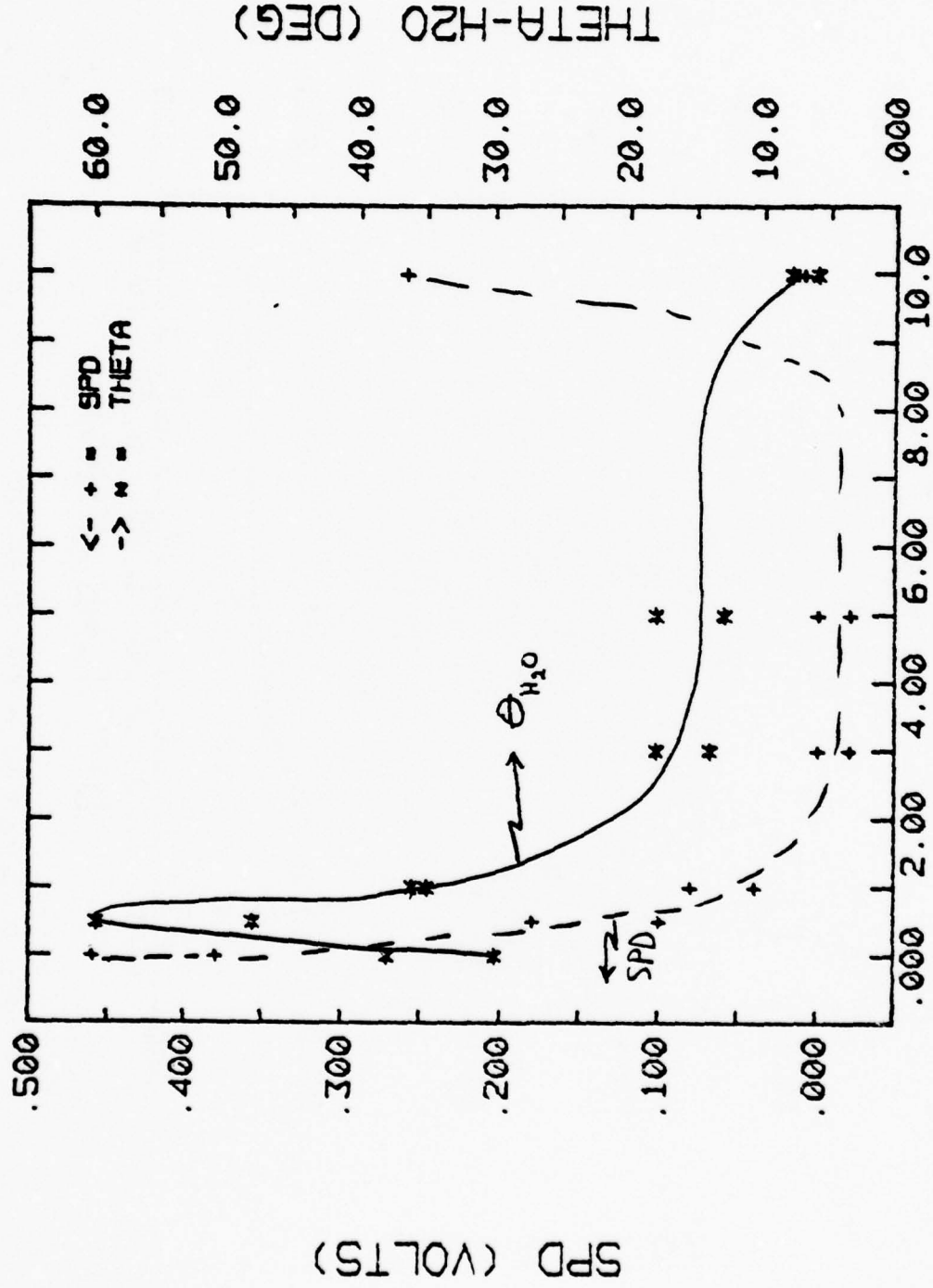



Fig. 46 SPD & theta-$H_2O$ vs dip time in NaOH.

TABLE 54

Date: 03/30/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Br 127

Purpose: STAB(3), 0.5 min spray rinse, 1 min $N_2$ dry.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PLE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | pH | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 3-30-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | | 3.51 (1.38) | 0.20 (0.08) | 0.33 (0.13) |
| -2 | | 3 | | | | | | | | 3.51 (1.38) | 0.10 (0.04) | 0.25 (0.10) |
| -3 | | 3 | | | | | | | | 3.63 (1.45) | 0.10 (0.04) | 0.48 (0.09) |
| -4 | | 3 | | | | | | | | 3.43 (1.35) | 0.51 (0.02) | 0.41 (0.06) |
| -5 | | 3 | | | | | | | | 3.38 (1.33) | 0.10 (0.04) | 0.33 (0.13) |
| -6 | | 3 | | | | | | | | 3.51 (1.38) | 0.10 (0.04) | 0.25 (0.10) |
| -7 | | 3 | | | | | | | 6 | 3.53 (1.39) | 0.51 (0.02) | 0.41 (0.06) |
| -8 | | 3 | | | | | | | 6 | 3.79 (1.49) | 0.03 (0.01) | 0.51 (0.02) |
| -9 | | 3 | | | | | | | >8 | 3.79 (1.49) | 0.41 (0.16) | 3.18 (1.25) |
| -10 | | 3 | | | | | | | >7 | 3.86 (1.52) | 0.08 (0.03) | 1.58 (0.62) |
| -11 | | 3 | | | | | | | >8 | 3.68 (1.45) | 0.25 (0.10) | 6.10 (2.40) |
| | | | | | | | | | Avg | 3.61 (1.42) | 0.08 (0.03) | 2.29 (0.09) |

3.3.7.1 Improper Rinse

An example of samples that were properly and improperly rinsed is given in Table 54. Samples 1-8 were properly rinsed yielding an average of 0.08 (0.03 in)/1 hr and 0.23 (0.09 in)/24 hr with an initial crack length of 3.56 (1.4 in). A small drop of water was placed on the region of crack growth after splitting the joints. The pH of the water drop was checked with litmus paper. It was consistently found that for regions of failure at the metal interface (as for .... 9, 10, 11, Table 54) a direct correlation exists between crack growth and pH. Crack growth increases with increasing pH, indicating inadequate rinsing prior to priming. Checking the pH of samples that were dipped in D.I. water without agitation revealed the surface pH to be 11 for a 15 sec dip, 9 for 1 min dip and about 7 for spray rinsed sample. These results point up the necessity of a spray rinse.

3.3.7.2 Improper Dry

The experiments in Tables 55-57 were performed to test $N_2$ blow drying vs drip drying. However, the results in Tables 55-57 are too large, probably due to a process error such as improper primer thickness or cure rather than the drying process.

TABLE 55

Date: 02/02/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of dry process on STAB(3).
$N_2$ blow dry.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-02-79 | | | | | | | | | | | | |
| 13 | | 3 | | | | | | | | 3.73 (1.47) | | 2.03 (0.8) |
| 14 | | 3 | | | | | | | | | | |
| 15 | | 3 | | | | | | | | 3.30 (1.30) | | 6.60 (2.6) |
| 16 | | 3 | | | | | | | | | | |
| 17 | | 3 | | | | | | | | 3.30 (1.30) | | 7.37 (2.9) |
| 18 | | 3 | | | | | | | | | | |
| 19 | | 3 | | | | | | | | 4.83 (1.90) | | 3.56 (1.4) |
| 20 | | 3 | | | | | | | | | | |
| 21 | | 3 | | | | | | | | 5.08 (2.00) | | 4.83 (1.9) |
| 22 | | 3 | | | | | | | | | | |
| 23 | | 3 | | | | | | | | 4.19 (1.65) | | 4.06 (1.6) |
| 24 | | | | | | | | | | | | |

TABLE 56

Date: 02/01/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of dry process on STAB(3).
Drip dry #1-6, $N_2$ blow dry #7-12.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-01-79 | | | | | | | | | | | | |
| -1 | Drip dry | 3 | | | | | | | | 6.35 (2.5) | | 1.78 (0.7) |
| -2 | 0.5 hr | 3 | | | | | | | | | | |
| -3 | 0.5 hr | 3 | | | | | | | | 4.83 (1.9) | | 1.78 (0.7) |
| -4 | 0.5 hr | 3 | | | | | | | | | | |
| -5 | 0.5 hr | 3 | | | | | | | | 4.06 (1.6) | | 1.78 (0.7) |
| -6 | 0.5 hr | 3 | | | | | | | | | | |
| -7 | $N_2$ blow dry | 3 | | | | | | | | 5.33 (2.1) | | 3.30 (1.3) |
| -8 | $N_2$ blow dry | 3 | | | | | | | | | | |
| -9 | $N_2$ blow dry | 3 | | | | | | | | 3.55 (1.4) | | 3.81 (1.5) |
| -10 | $N_2$ blow dry | 3 | | | | | | | | | | |
| -11 | $N_2$ blow dry | 3 | | | | | | | | 4.06 (1.6) | | 3.81 (1.5) |
| -12 | $N_2$ blow dry | 3 | | | | | | | | | | |

TABLE 57

Date: 02/02/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of dry process on STAB(3).
Drip dry 0.5 hr before prime.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-02-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | | 3.89 (1.53) | | 4.57 (1.8) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | | | 3.38 (1.33) | | 3.05 (1.2) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | | | 3.81 (1.50) | | 4.32 (1.7) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | | | 3.81 (1.50) | | 3.81 (1.5) |
| -8 | | 3 | | | | | | | | | | |
| -9 | | 3 | | | | | | | | 4.72 (1.86) | | 5.33 (2.1) |
| -10 | | 3 | | | | | | | | | | |
| -11 | | 3 | | | | | | | | 3.43 (1.35) | | 5.08 (2.0) |
| -12 | | 3 | | | | | | | | | | |

3.3.7.3 Organic Contamination

Tables 58 and 59 are for experiments to check the effect of organic contamination on lap shear strength of samples that had STAB(3) treatment. The surface properties were measured before and after deliberate contamination with hexane, decane, tetradecane, paraffin oil and stearic acid. Unfortunately, the primer was too thick in some cases and caused failure at the primer-adhesive interface. The contamination procedure was to dip the sample into the pure compound and allow it to drain from the sample. It is not surprising that hexane and decane had little effect on surface properties and the joint strengths were high, as these organics should immediately evaporate from the surface. It is indeed surprising that the thick layers left by tetradecane, paraffin oil and stearic acid had such a small effect on lap shear strength. The ability of the STAB(3) surface to accommodate organic contamination not absorbed by the adhesive is similar to that found for the phosphoric acid anodize treatment of aluminum. FPL etch treatment is very sensitive to organic contamination decreasing lap shear strength by 300 psi for a single monolayer of Myristic acid.[3]

TABLE 58

Date: 02/16/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of organic contamination after STAB(3).

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Contamination | STAB(3) Time (min) | Δ (deg.) | Ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | %IF | Lap Shear MPa (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-16-79 | | | | | | | | | | | | |
| -1 | None | 3 | 10 | 26 | -0.06 | 0.82 | 28 | P | 25 (3.60) | | | |
| -2 | None | 3 | 20 | 24 | -0.09 | 0.88 | 20 | | | | | |
| -1 | None | 3 | 11 | 24 | -0.10 | 1.00 | 15 | P | 27 (3.91) | | | |
| -2 | None | 3 | 20 | 26 | -0.12 | 1.10 | 13 | | | | | |
| -5 | Hexane/before | 3 | 10 | 26 | -0.05 | 0.70 | 25 | P | 27 (3.86) | | | |
| -6 | Hexane/before | 3 | 20 | 29 | -0.09 | 0.86 | 21 | | | | | |
| -5 | after | 3 | 10 | 26 | -0.08 | 0.09 | 15 | 50 | 36 (5.29) | | | |
| -6 | after | 3 | 16 | 33 | -0.12 | 1.00 | 16 | | | | | |
| -9 | Decane/before | 3 | 16 | 25 | -0.08 | 0.86 | 16 | 10 | 37 (5.39) | | | |
| -10 | before | 3 | 10 | 22 | -0.09 | 0.94 | 23 | | | | | |
| -9 | after | 3 | 36 | 32 | -0.06 | 0.90 | 21 | 5 | 37 (5.34) | | | |
| -10 | after | 3 | 10 | 24 | -0.07 | 1.00 | 21 | | | | | |

Remarks: P means failure at primer-adhesive interface
Samples 3 and 4 treated as 1 and 2, 7 and 8 as 5 and 6, 11 and 12 as 9 and 10.

TABLE 59

Date: 02/16/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of organic contamination after STAB(3).

| Sample No. | Surface Treatment: No Degrease Contamination | STAB(3) Time (min) | Surface Properties: Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Bond Properties: %IF | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tetradecane | | | | | | | | | | | |
| 13 | before | 3 | 14 | 24 | -0.08 | 0.9 | 21 | 0 | 30 (4.34) | | | |
| 14 | before | 3 | 15 | 31 | -0.08 | 0.9 | 14 | | | | | |
| 13 | after | 3 | 46 | 31 | -0.22 | 0.3 | 40 | 30 | 32 (4.60) | | | |
| 14 | after | 3 | 46 | 29 | -0.21 | 0.6 | 34 | | | | | |
| | Paraffin Oil | | | | | | | | | | | |
| 17 | before | 3 | 14 | 27 | -0.08 | 0.9 | 20 | - | - | | | |
| 18 | before | 3 | 14 | 27 | -0.08 | 0.9 | 18 | | | | | |
| 17 | after | 3 | 0 | 22 | -0.09 | 0.02 | 38 | P | 27 (4.02) | | | |
| 18 | after | 3 | 0 | 22 | -0.14 | 0.02 | 44 | | | | | |
| | Stearic Acid | | | | | | | | | | | |
| 21 | before | 3 | 14 | 26 | -0.04 | 0.8 | 18 | P | 27 (3.86) | | | |
| 22 | before | 3 | 14 | 30 | -0.10 | 0.9 | 28 | | | | | |
| 21 | after | 3 | 14 | 22 | 0.05 | 0.1 | 110 | P | 24 (3.56) | | | |
| 22 | after | 3 | 0 | 23 | 0.03 | 0.3 | 140 | | | | | |

Remarks: P means failure at primer-adhesive interface samples 15 and 16 treated as 13 and 14, 19 and 20 as 17 and 18, 23 and 24 as 21 and 22.

Some aluminum panels were obtained with teflon film adhesively bonded to the surface for handling protection. Removal of the teflon left patches of contact cement on the aluminum. Tables 60 and 61 show the effect of time in NaOH on the wedge tests for panels that had teflon removed. The general trend is to weaken the peel strength causing long initial cracks. However, a 3 min dip reduced crack growth to ~0.76 (0.3 in)/24 hr.

TABLE 60

Date: 02/09/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of time in NaOH on STAB(3).

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm( in) (Initial) | (6 hr) | (24 hr) |
| 2-9-79 | | | | | | | | | | | | |
| -1 | | 0 | | | | | | | | 6.73 (2.65) | 10.16 (74) | >10.16 (4) |
| -2 | | 0 | | | | | | | | | | |
| -3 | | 0 | | | | | | | | 6.10 (2.40) | 3.05 (1.2) | 3.81 (1.5) |
| -4 | | 0 | | | | | | | | | | |
| -5 | | 1 sec | | | | | | | | 7.49 (2.95) | 1.78 (0.7) | 2.79 (1.1) |
| -6 | | 1 sec | | | | | | | | | | |
| -7 | | 1 sec | | | | | | | | 8.64 (3.40) | 2.29 (0.9) | 4.06 (1.6) |
| -8 | | 1 sec | | | | | | | | | | |
| -9 | | 30 sec | | | | | | | | 5.59 (2.20) | 2.29 (0.9) | 3.05 (1.2) |
| -10 | | 30 sec | | | | | | | | | | |
| -11 | | 30 sec | | | | | | | | 5.46 (2.15) | 3.81 (1.5) | 4.06 (1.6) |
| -12 | | 30 sec | | | | | | | | | | |

Remarks: Teflon covering removed.

TABLE 61

Date: 02/09/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of time in NaOH on STAB(3)
Wedge tests

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | %IF | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (6 hr) | (24 hr) |
| 2-9-79 | | | | | | | | | | | | |
| -13 | | 1 | | | | | | | | 4.57 (1.8) | 1.52 (0.6) | 2.03 (0.8) |
| -14 | | 1 | | | | | | | | | | |
| -15 | | 1 | | | | | | | | 4.83 (1.9) | 1.27 (0.5) | 2.03 (0.8) |
| -16 | | 1 | | | | | | | | | | |
| -17 | | 2 | | | | | | | | 6.35 (2.5) | 1.02 (0.4) | 1.27 (0.5) |
| -18 | | 2 | | | | | | | | | | |
| -19 | | 2 | | | | | | | | 4.57 (1.8) | 0.51 (0.2) | 1.27 (0.5) |
| -20 | | 2 | | | | | | | | | | |
| -21 | | 3 | | | | | | | | 4.82 (1.9) | 0.51 (0.2) | 0.76 (0.3) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | | | 4.82 (1.9) | 0.25 (0.1) | 0.51 (0.2) |
| -24 | | 3 | | | | | | | | | | |

Remarks: Teflon covering removed.

### 3.3.8 Tap Water Rinse

Table 62 indicates that local (Thousand Oaks, California) tap water may be as good as D.I. water for rinsing. The two bad wedge specimens (no's 15-16 and 23-24) may have resulted from an improper rinse. However, further testing with tap water showed that severe pitting resulted. The effect of the pitting on bond endurance is not known.

TABLE 62

Date: 01/26/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of using tap water rather than D.I. water for STAB(3).

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Est. GLT mm (mil) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-26-79 | | | | | | | | | | | | |
| -13 | | 3 | | | | | | | 0.09 (3.7) | 5.33 (2.1) | 0.13 (0.05) | 0.38 (0.15) |
| -14 | | 3 | | | | | | | | | | |
| -15 | | 3 | | | | | | | 0.13 (5.2) | 5.59 (2.2) | 0.15 (0.60) | 2.54 (1.0) |
| -16 | | 3 | | | | | | | | | | |
| -17 | | 3 | | | | | | | 0.12 (4.7) | 4.06 (1.6) | 0.0 | 0.08 (0.03) |
| -18 | | 3 | | | | | | | | | | |
| -19 | | 3 | | | | | | | 0.11 (4.4) | 3.81 (1.5) | 0.0 | 0.13 (0.05) |
| -20 | | 3 | | | | | | | | | | |
| -21 | | 3 | | | | | | | 0.06 (2.4) | 3.56 (1.4) | - | 0.89 (0.35) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | | 0.09 (3.4) | 3.81 (1.5) | - | 2.79 (1.1) |
| -24 | | | | | | | | | | | | |

Tables 63, 64, 65 and 66 indicate that the delay time between drying and priming the samples, has little effect, up to 1 hr, consistent with Table 41, which shows no degradation in 24 hr. Table 67 and other experiments indicated that leaving the primer uncured prior to bonding degraded the humidity-stress endurance. The effect of solution temperature, in Table 68, is inconclusive, but the result at room temperature (26°C) is much better than the higher temperature results. Tables 69 and 70 show improved results with shorter rinse times. In the case of Table 70, the samples were dipped in rinse water rather than flushed with flowing D.I. water from the hose.

An attempt to test the effect of delay between removal of the samples from the NaOH solution and rinse is given in Table 71. A delay of 15 sec has little effect, and longer than this degrades the durability, but the test is inconclusive due to excessive crack growth.

Table 72 compares results for used and fresh NaOH solution. There seems to be no distinction. Note that the poor bond (11-12) was treated for 10 min rather than 3 min.

TABLE 63

Date: 8-6-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of delay in air between $N_2$ blow dry and prime (STAB(3))

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Delay to Prime (min) | STAB(3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-8-79- | | | | | | | | | | | | |
| 13 | 1 | 3 | | | | | | | | 5.08 (2.0) | 0.25 (0.1) | 1.78 (0.7) |
| 14 | 1 | 3 | | | | | | | | | | |
| 15 | 5 | 3 | | | | | | | | 4.83 (1.9) | 0.25 (0.1) | 1.27 (0.5) |
| 16 | 5 | 3 | | | | | | | | | | |
| 17 | 10 | 3 | | | | | | | | 5.33 (2.1) | 0.13 (0.05) | 1.52 (0.6) |
| 18 | 10 | 3 | | | | | | | | | | |
| 19 | 20 | 3 | | | | | | | | 5.33 (2.1) | 0.38 (0.15) | 4.57 (1.8) |
| 20 | 20 | 3 | | | | | | | | | | |
| 21 | 30 | 3 | | | | | | | | 5.08 (2.0) | 0.25 (0.1) | 2.03 (0.8) |
| 22 | 30 | 3 | | | | | | | | | | |
| 23 | 60 | 3 | | | | | | | | 4.82 (1.9) | 0.36 (0.14) | 1.27 (0.5) |
| 24 | 60 | 3 | | | | | | | | | | |

Remarks:

TABLE 64

Date: 1-15-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(3), prime within 5 min after dry.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) (min) | Δ (deg) | Ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-15-79- | | | | | | | | | | | | |
| 13 | | 3 | | | | | | | | 4.83 (1.9) | | 0.76 (0.3) |
| 14 | | 3 | | | | | | | | | | |
| 15 | | 3 | | | | | | | | 4.83 (1.9) | | 0.25 (0.1) |
| 16 | | 3 | | | | | | | | | | |
| 17 | | 3 | | | | | | | | 5.59 (2.2) | | 0.0 |
| 18 | | 3 | | | | | | | | | | |
| 19 | | 3 | | | | | | | | 5.84 (2.3) | | 0.25 (0.1) |
| 20 | | 3 | | | | | | | | | | |
| 21 | | 3 | | | | | | | | 4.83 (1.9) | | 0.25 (0.1) |
| 22 | | 3 | | | | | | | | | | |
| 23 | | 3 | | | | | | | | 6.10 (2.4) | | 0.0 |
| 24 | | 3 | | | | | | | | | | |

REMARKS: 568 g NaOH/l D.I. water
Rinse flowing D.I. water
Dry blowing $N_2$
Prime within 5 min

TABLE 65

Date: 1-8-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of delay in air between $N_2$ blow dry and prime STAB(3)

| Sample No. | Surface Treatment: No Degrease Delay to Prime (min) | Surface Treatment: STAB(3) (min) | Surface Properties: Δ (deg) | Surface Properties: ψ (deg) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-8-79- | | | | | | | | | | | | |
| 1 | 1 | 3 | | | | | | | | 4.83 (1.9) | 0.15 (0.06) | 0.76 (0.3) |
| 2 | 1 | 3 | | | | | | | | | | |
| 3 | 5 | 3 | | | | | | | | 5.08 (2.0) | 0.13 (0.5) | 2.54 (1.0) |
| 4 | 5 | 3 | | | | | | | | | | |
| 5 | 10 | 3 | | | | | | | | 4.83 (1.9) | 0.25 (0.10) | 0.76 (0.3) |
| 6 | 10 | 3 | | | | | | | | | | |
| 7 | 20 | 3 | | | | | | | | 4.83 (1.9) | 0.20 (0.08) | 1.52 (0.6) |
| 8 | 20 | 3 | | | | | | | | | | |
| 9 | 30 | 3 | | | | | | | | 4.57 (1.8) | 0.38 (0.15) | 1.27 (0.4) |
| 10 | 30 | 3 | | | | | | | | | | |
| 11 | 60 | 3 | | | | | | | | 4.57 (1.8) | 0.15 | 1.27 (0.5) |
| 12 | 60 | 3 | | | | | | | | | | |

Remarks:

TABLE 66

Date: 1-12-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: To have a different investigator check delay time in air between dry and prime, STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Degrease | STAB(3) | | | | | | Peel | Lap | | | |
| Sample No. | Time Before Prime (min) | (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Force (g/cm) | Shear (Ksi) | (Initial) | Wedge Crack Growth/cm(in) (1 hr) | (24 Hr) |
| 1-12-79- | | | | | | | | | | | | |
| 13 | 96 | 3 | 22 | 38 | -0.03 | 2.0 | 10 | | | 4.32 (1.7) | | 0.05 (0.02) |
| 14 | 96 | 3 | 44 | 22 | 0.00 | 2.0 | 10 | | | | | |
| 15 | 90 | 3 | 24 | 38 | -0.04 | 2.2 | 9 | | | 4.32 (1.7) | | 0.05 (0.02) |
| 16 | 90 | 3 | 20 | 35 | 0.00 | 2.1 | 10 | | | | | |
| 17 | 84 | 3 | 10 | 37 | 0.02 | 2.0 | 10 | | | 4.57 (1.8) | | 0.05 (0.02) |
| 18 | 84 | 3 | 14 | 34 | -0.03 | 2.2 | 11 | | | | | |
| 19 | 79 | 3 | 14 | 33 | 0.00 | 2.2 | 11 | | | 3.81 (1.5) | | 0.08 (0.30) |
| 20 | 79 | 3 | 20 | 36 | 0.00 | 2.1 | 11 | | | | | |
| 21 | 72 | 3 | 18 | 30 | -0.07 | 1.6 | 11 | | | 4.32 (1.7) | | 0.38 (0.15) |
| 22 | 72 | 3 | 24 | 25 | -0.05 | 1.0 | 12 | | | | | |
| 23 | 68 | 3 | 22 | 30 | -0.06 | 1.2 | 9 | | | 4.32 (1.7) | | 0.13 (0.05) |
| 24 | 68 | 3 | 24 | 28 | -0.05 | 1.1 | 11 | | | | | |

Remarks: 3 min in NaOH solution (568 g/l)
Rinse in flowing D.I. water ~10 sec
Dry with blowing $N_2$
Prime as indicated, left overnight before bonding

TABLE 67

Date: 1-16-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(3), prime within 30 min after dry but did not cure primer.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No. Degrease | STAB (3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm (in) (Initial) | (1 hr) | (24 Hr) |
| 1-16-79- | | | | | | | | | | | | |
| 1 | | 3 | 32 | 28 | 0.04 | 1.1 | 20 | | | 5.08 (2.0) | 0.0 | 0.25 (0.1) |
| 2 | | 3 | 56 | 22 | 0.05 | 1.0 | 17 | | | | | |
| 3 | | 3 | 38 | 22 | 0.10 | 1.0 | 15 | | | 5.08 (2.0) | 0.51 (0.2) | 0.76 (0.3) |
| 4 | | 3 | 20 | 21 | 0.00 | 0.9 | 30 | | | | | |
| 5 | | 3 | 10 | 36 | -0.04 | 0.9 | 11 | | | 4.32 (1.7) | 0.51 (0.2) | 3.30 (1.3) |
| 6 | | 3 | 32 | 29 | 0.00 | 1.1 | 14 | | | | | |
| 7 | | 3 | 20 | 29 | -0.05 | 1.0 | 29 | | | 4.83 (1.9) | 0.25 (0.1) | 0.51 (0.2) |
| 8 | | 3 | 32 | 38 | 0.00 | 1.1 | 29 | | | | | |
| 9 | | 3 | 20 | 29 | 0.09 | 0.8 | 12 | | | 4.57 (1.8) | 0.25 (0.1) | 1.02 (0.4) |
| 10 | | 3 | 32 | 34 | -0.06 | 1.1 | 10 | | | | | |
| 11 | | 3 | 2 | 24 | -0.05 | 0.9 | 13 | | | 3.81 (1.5) | 1.52 (0.6) | 3.81 (1.5) |
| 12 | | 3 | 10 | 29 | -0.02 | 0.8 | 11 | | | | | |

REMARKS: 568 g NaOH/l D.I. water
Rinse flowing D.I. water
Dry blowing $N_2$
Prime within 0.5 hr
Leave overnight, no oven bake of primer

TABLE 68

Date: 1-11-79 Investigator: L. Bivins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of NaOH solution temperature on STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease (Temp °C) | STAB(3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Color | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-11-79- | | | | | | | | | | | | |
| 1 | 35 | 3 | | | | | | Dark Brown | | 5.08 (2.0) | 0.41 (0.16) | 2.03 (0.8) |
| 2 | 35 | 3 | | | | | | Dark Brown | | | | |
| 3 | 50 | 3 | | | | | | Black | | 6.60 (2.6) | 0.08 (0.3) | 1.27 (0.5) |
| 4 | 50 | 3 | | | | | | Black | | | | |
| 5 | 40 | 3 | | | | | | | | 5.33 (2.1) | 1.27 (0.5) | 3.56 (1.4) |
| 6 | 40 | 3 | | | | | | | | | | |
| 7 | 26 | 3 | | | | | | Gold | | 5.08 (2.0) | 0.38 (0.15) | 0.25 (0.1) |
| 8 | 26 | 3 | | | | | | Gold | | | | |
| 9 | 30 | 3 | | | | | | Dark Grey | | 4.83 (1.9) | 1.02 (0.4) | 4.32 (1.7) |
| 10 | 30 | 3 | | | | | | Dark Grey | | | | |
| 11 | 45 | 3 | | | | | | Soot Black | | 5.33 (2.1) | 2.03 (0.8) | 2.79 (1.1) |

Remarks: 360 g NaOH/600 ml D.I. water
Rinse in flowing D.I. water
Dry in blowing $N_2$

TABLE 69

Date: 1-9-79 Investigator: L. Bivins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of rinse time for STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Rinse Time (sec) | STAB(3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-9-79- | | | | | | | | | | | | |
| 1 | 1 | 3 | | | | | | | | 3.30 (1.3) | | 3.81 (1.5) |
| 2 | 1 | 3 | | | | | | | | 3.81 (1.5) | | 4.06 (1.6) |
| 3 | 5 | 3 | | | | | | | | 4.06 (1.6) | | 5.08 (2.0) |
| 4 | 5 | 3 | | | | | | | | 3.56 (1.4) | | 4.83 (1.9) |
| 5 | 30 | 3 | | | | | | | | 4.06 (1.6) | | 4.83 (1.9) |
| 6 | 30 | 3 | | | | | | | | | | |
| 7 | 120 | 3 | | | | | | | | | | |
| 8 | 120 | 3 | | | | | | | | | | |
| 9 | 300 | 3 | | | | | | | | | | |
| 10 | 300 | 3 | | | | | | | | | | |

Remarks: 360 g NaOH/600 ml D.I. water
Rinse in flowing D.I. water
Dry in blowing $N_2$
Prime within 5 min

TABLE 70

Date: 1-9-79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of rinse time on STAB(3)
This rinse was not flowing. The samples were dipped in rinse water

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Rinse Time (sec) | STAB(3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-9-79- | | | | | | | | | | | | |
| 11 | 1 | 3 | | | | | | | | 4.32 (1.7) | | 3.81 (1.5) |
| 12 | 1 | 3 | | | | | | | | | | |
| 13 | 5 | 3 | | | | | | | | 4.57 (1.8) | | 3.81 (1.5) |
| 14 | 5 | 3 | | | | | | | | | | |
| 15 | 30 | 3 | | | | | | | | 4.57 (1.8) | | 3.05 (1.2) |
| 16 | 30 | 3 | | | | | | | | | | |
| 17 | 120 | 3 | | | | | | | | 3.56 (1.4) | | 4.57 (1.8) |
| 18 | 120 | 3 | | | | | | | | | | |
| 19 | 300 | 3 | | | | | | | | 3.56 (1.4) | | 4.32 (1.7) |
| 20 | 300 | 3 | | | | | | | | | | |
| 21 | 600 | 3 | | | | | | | | 3.56 (1.4) | | 5.84 (2.3) |
| 22 | 600 | 3 | | | | | | | | | | |

Remarks: 360 g NaOH/600 ml D.I. water
Rinse in beaker of D.I. water
Dry in blowing $N_2$

TABLE 71

Date: 1-12-79 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Effect of delay time in air between the NaOH dip and rinse STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease Delay in Air (sec) | STAB(3) (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-12-79- | | | | | | | | | | | | |
| 1 | 1 | 3 | 16 | 20 | -0.02 | 1.9 | 6 | | | 3.56 (1.4) | 1.02 (0.4) | 3.05 (1.2) |
| 2 | 1 | 3 | 60 | 31 | +0.04 | 1.6 | 10 | | | | | |
| 3 | 5 | 3 | 10 | 23 | 0.02 | 1.4 | 5 | | | 3.81 (1.5) | 0.76 (0.3) | 3.81 (1.5) |
| 4 | 5 | 3 | 8 | 30 | -0.04 | 2.0 | 5 | | | | | |
| 5 | 10 | 3 | 26 | 26 | 0.03 | 1.6 | 11 | | | 3.56 (1.4) | 1.52 (0.6) | 3.56 (1.4) |
| 6 | 10 | 3 | 78 | 46 | 0.00 | 1.5 | 10 | | | | | |
| 7 | 15 | 3 | 28 | 26 | -0.02 | 2.0 | 6 | | | 3.81 (1.5) | 1.52 (0.6) | 3.56 (1.4) |
| 8 | 15 | 3 | 22 | 30 | 0.00 | 1.4 | 2 | | | | | |
| 9 | 20 | 3 | 6 | 29 | 0.00 | 1.2 | 10 | | | 4.06 (1.6) | 1.02 (0.4) | 3.05 (2.2) |
| 10 | 20 | 3 | 12 | 36 | -0.04 | 2.0 | 3 | | | | | |
| 11 | 30 | 3 | 18 | 32 | 0.00 | 1.5 | 5 | | | 4.06 (1.6) | 1.52 (0.6) | 7.12 (2.8) |
| 12 | 30 | 3 | 16 | 35 | -0.02 | 1.5 | 5 | | | | | |

Remarks:

TABLE 72

Date: 1-13-79 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check the effect of used vs new NaOH solution. STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB (3) Time (min) | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Color | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-13-79- | | | | | | | | | | | | |
| 1 | Used Solution | 3 | 28 | 25 | 0.13 | 1.5 | 10 | Greenish-Grey | | 3.30 (1.3) | 0.25 (0.1) | 3.56 (1.4) |
| 2 | " | 3 | 26 | 26 | 0.06 | 1.8 | | " | | | | |
| 3 | " | 3 | 26 | 28 | 0.11 | 1.7 | 11 | " | | 2.54 (1.0) | 0.0 | 0.76 (0.3) |
| 4 | " | 3 | 12 | 25 | 0.20 | 1.5 | | " | | | | |
| 5 | " | 3 | 28 | 32 | 0.11 | 1.7 | | " | | 3.05 (1.2) | 0.51 (0.2) | 2.79 (1.1) |
| 6 | " | 3 | 16 | 32 | 0.04 | 1.8 | | " | | | | |
| 7 | New Solution | 3 | 26 | 23 | 0.28 | 1.0 | 20 | " | | 2.79 (1.1) | 0.51 (0.2) | 2.79 (1.1) |
| 8 | " | 3 | 16 | 27 | 0.17 | 1.7 | 10 | " | | | | |
| 9 | " | 3 | 30 | 24 | 0.17 | 1.7 | 10 | " | | 2.79 (1.1) | 0.25 (0.1) | 1.78 (0.7) |
| 10 | " | 3 | 30 | 28 | 0.12 | 1.7 | 5 | " | | | | |
| 11 | " | 10 | 26 | 33 | 0.04 | 1.3 | 5 | Black | | 5.33 (2.1) | 2.54 (1.0) | 6.35 (2.5) |
| 12 | " | 10 | 18 | 33 | -0.02 | 1.5 | | " | | | | |

REMARKS: Samples 1-6: used solution, 3 min dip, flowing D.I. water rinse, blow $N_2$ dry
Samples 7-10: new solution, 3 min dip, flowing D.I. water rinse, blow $N_2$ dry
Samples 11, 12: new solution, 10 min dip, flowing D.I. water rinse, blow $N_2$ dry
Solutions were 568 g NaOH in 1 l D.I. water

Figures 47, 48 and 49 show the effect of time in concentrated NaOH on surface properties and Fig. 50 shows the effect on Wedge Test durability. The SPD decreases from about 0.6 to 0 in 5 min. The PEE increases from about $0.25 \times 11^{-9}$ amps to about $1.5 \times 10^{-9}$ amps and $\theta_{H_2O}$ decreases to 10° in about 5 min. The Wedge Test crack growth decreases from >4"/24 hr to ~1"/24 hr in 1 min NaOH exposure, if the rinse and dry steps are optimized.

### 3.3.10 Second Dip

Table 73 compares results of the second dip treatment with the single dip treatment. It would appear that the simpler single dip treatment is better. Table 74 compares the effect of various times for the first dip, new vs. old solution, for the two dip process. The results are inconsistent and generally less durable than for the single step process.

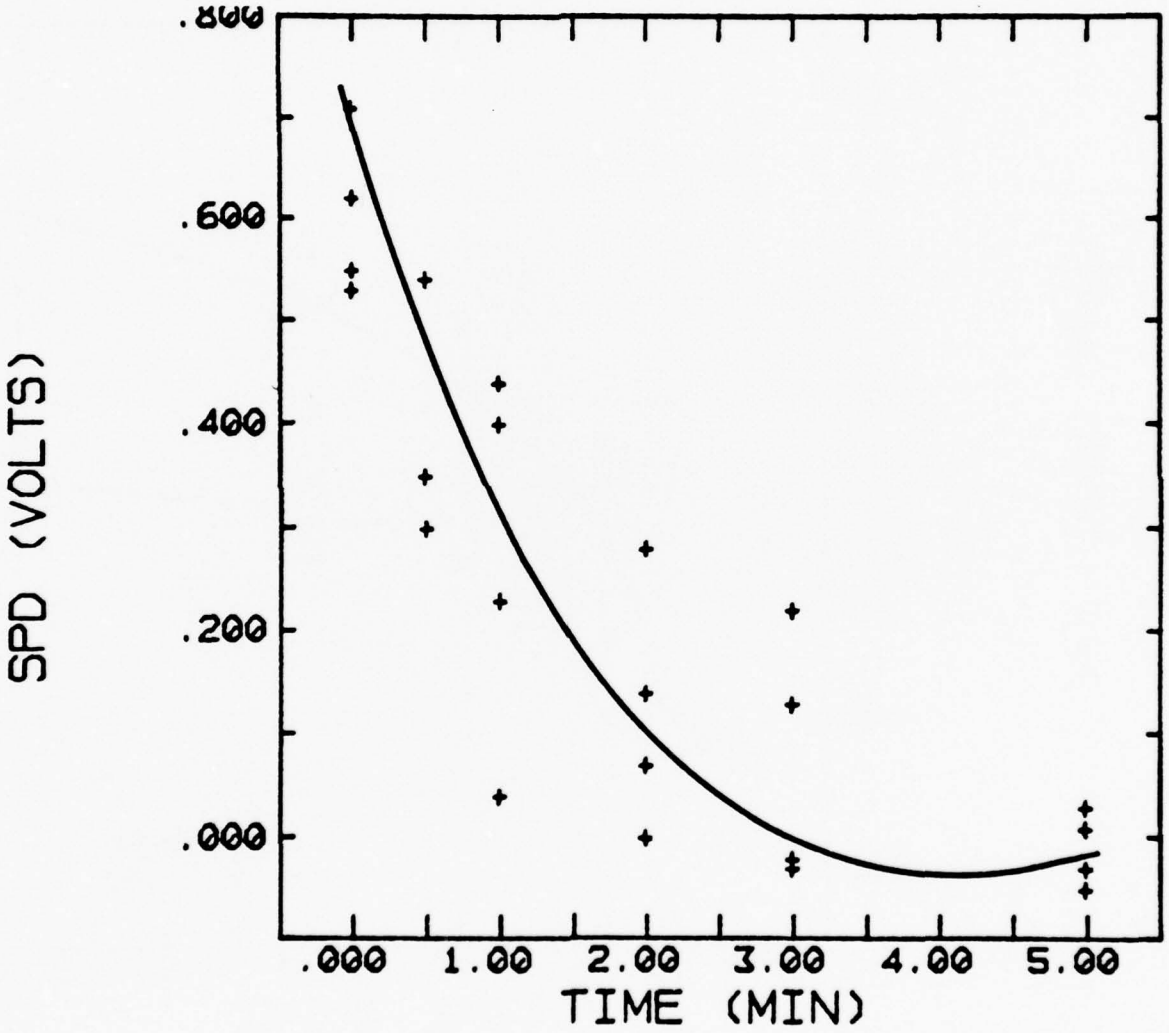



Fig. 47 Effect of time in NaOH soln on SPD.

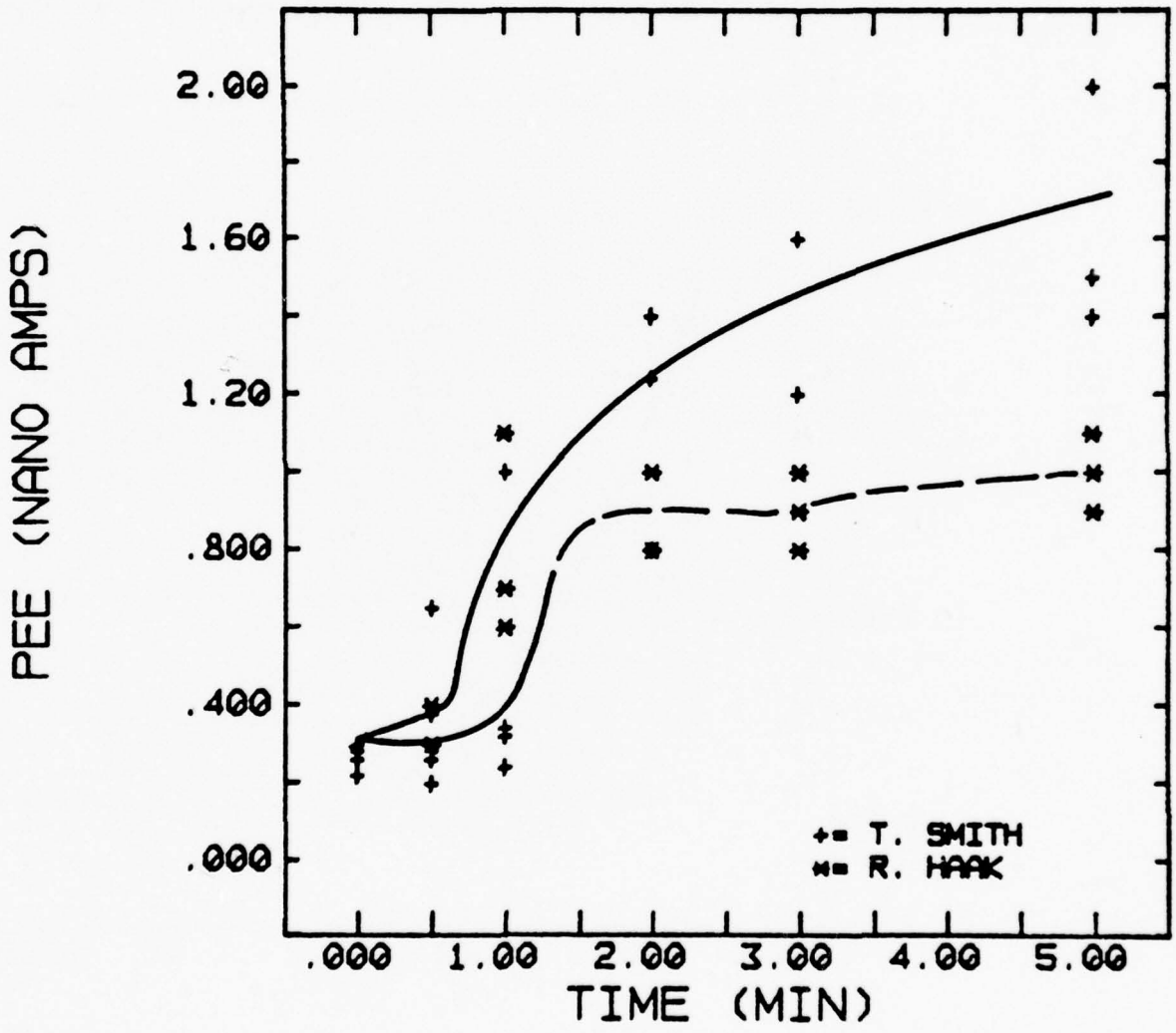



Fig. 48 Effect of time in NaOH soln on PEE.

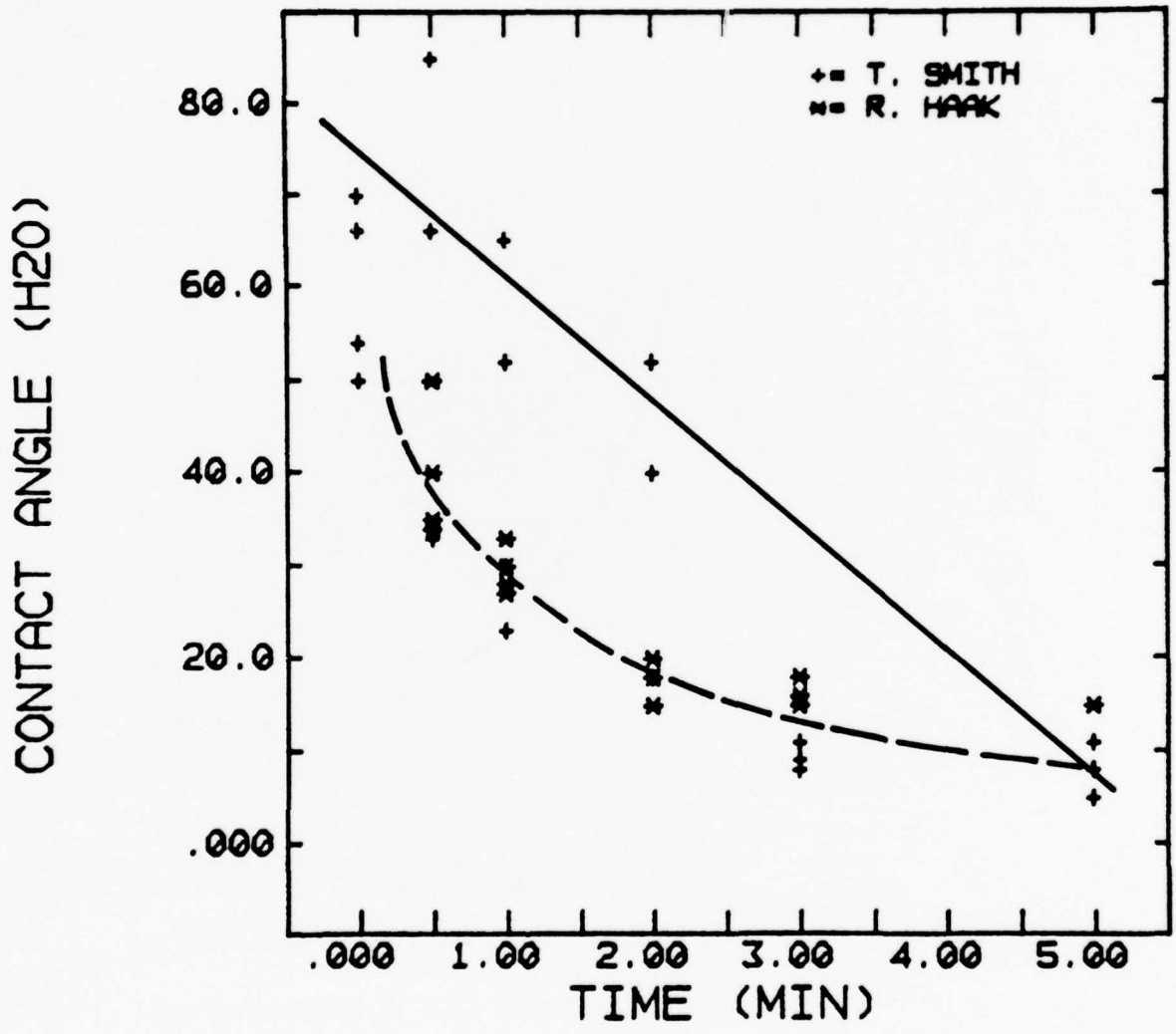



Fig. 49 Effect of time in NaOH soln on contact angle.

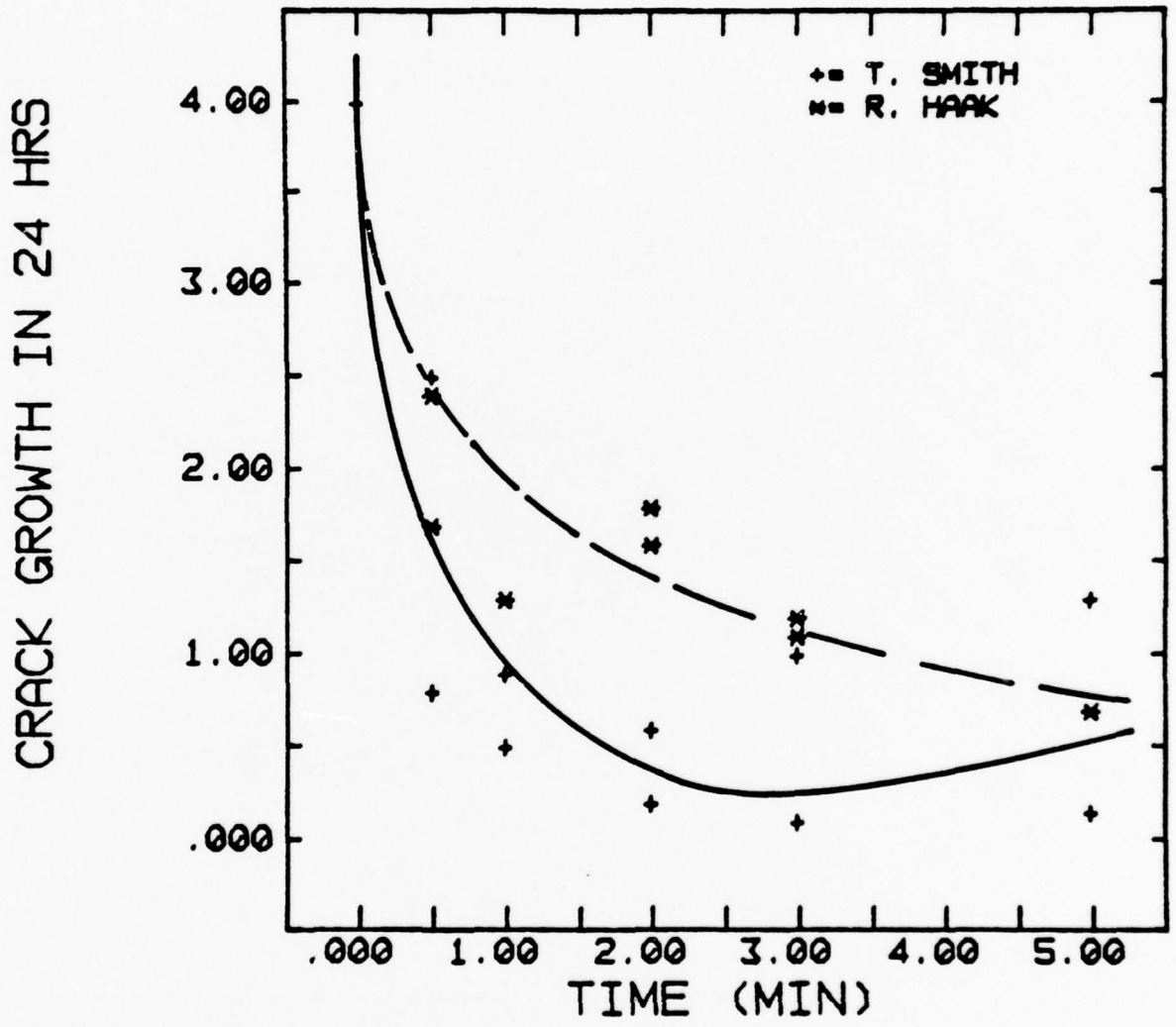



Fig. 50 Effect of time in NaOH soln on crack growth.

TABLE 73

Date: 1-2-79 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(3) with and without 2nd NaOH dip

| Sample No. | Surface Treatment: No Degrease | STAB(3) (min) 1st | STAB(3) (sec) 2nd | Surface Properties: Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Bond Properties: Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-2-79- | | | | | | | | | | | | | |
| 1 | With 2nd dip | 2 | 10 | 266 | 34 | 0.20 | 0.20 | 0 | | | 3.56 (1.4) | | 1.78 (0.7) |
| 2 | " | 2 | 10 | 248 | 35 | 0.16 | 0.50 | 5 | | | | | |
| 3 | " | 2 | 10 | 206 | 8 | 0.10 | 0.85 | 5 | | | 3.30 (1.3) | | 2.29 (0.9) |
| 4 | " | 2 | 10 | 130 | 53 | 0.14 | 0.70 | 5 | | | | | |
| 5 | " | 2 | 10 | 160 | 59 | 0.15 | 0.85 | 12 | | | 3.81 (1.5) | | 2.29 (0.9) |
| 6 | " | 2 | 10 | 28 | 36 | 0.11 | 1.40 | 19 | | | | | |
| 7 | Without 2nd dip | 2 | 0 | 120 | 25 | 0.21 | 2.2 | 10 | | | 3.30 (1.3) | | 0.76 (0.3) |
| 8 | " | 2 | 0 | 0 | 36 | 0.23 | 1.1 | 4 | | | | | |
| 9 | " | 2 | 0 | 66 | 31 | 0.20 | 1.6 | 2 | | | 3.56 (1.4) | | 0.76 (0.3) |
| 10 | " | 2 | 0 | -1.6 | 35 | 0.20 | 1.1 | 2 | | | | | |
| 11 | " | 2 | 0 | 20 | 5 | 0.20 | 1.3 | 8 | | | 3.81 (1.5) | | 1.02 (0.4) |
| 12 | " | 2 | 0 | 72 | 13 | 0.21 | 0.5 | 5 | | | | | |

Remarks: 360 g NaOH/600 ml D.I. water
Rinse flowing D.I. water (~10 sec)
Dry in blowing $N_2$
2nd dip 10 sec in NaOH solution, added steps for 1-6
Rinse flowing D.I. water
Dry in blowing $N_2$

TABLE 74

Date: 1-139 Investigator: T. Smith Alloy: Al 2024-T3 Adhesive: Hysol EA9628H
Primer: EA9210H

Purpose: Check STAB(3) with 2nd dip in NaOH solution

| | Surface Treatment | | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) (min) 1st | (sec) 2nd | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 Hr) |
| 1-13-79- | | | | | | | | | | | | | |
| 13 | New Solution | 10 | 5 | 104 | 38 | 0.20 | 1.7 | 8 | | | 3.04 (1.2) | 0.51 (0.2) | 3.81 (1.5) |
| 14 | " | 10 | 5 | 100 | 39 | 0.15 | 1.2 | 8 | | | | | |
| 15 | " | 5 | 5 | 102 | 39 | 0.16 | 1.2 | 7 | | | 3.30 (1.3) | 2.29 (0.9) | 5.08 (2.0) |
| 16 | " | 5 | 5 | 104 | 38 | 0.16 | 1.2 | 7 | | | | | |
| 17 | " | 10 | 5 | 102 | 39 | 0.14 | 1.3 | 13 | | | 3.04 (1.2) | 0.25 (0.1) | 1.02 (0.4) |
| 18 | " | 10 | 5 | 110 | 42 | 0.11 | 3.0 | 8 | | | | | |
| 19 | " | 10 | 5 | 106 | 39 | 0.13 | 1.6 | 10 | | | 3.04 (1.2) | 0.51 (0.2) | 1.78 (0.7) |
| 20 | " | 10 | 5 | 102 | 40 | 0.14 | 1.5 | 8 | | | | | |
| 21 | Used Solution | 5 | 5 | 102 | 41 | 0.12 | 2.5 | 8 | | | 2.54 (1.0) | 1.78 (0.7) | 2.03 (1.8) |
| 22 | " | 5 | 5 | 100 | 39 | 0.12 | 1.7 | 8 | | | | | |
| 23 | " | 10 | 5 | 96 | 40 | 0.07 | 3.2 | 3 | | | 3.30 (1.3) | 1.02 (0.4) | 4.83 (1.9) |
| 24 | " | 10 | 5 | 98 | 39 | 0.12 | 2.0 | 8 | | | | | |

Remarks: Samples 13-16 drip dried (no $N_2$ blowing)
Samples 17-24 $N_2$ blow dried
568 g NaOH/l D.I. water

### 3.3.11 Other Adhesives

Tables 75-78 are for experiments with STAB(3) but using FM73 adhesive without primer. For 48 wedge test joints the initial crack lengths average 0.94 cm (1.55 in), the crack growths in 1 hr average 0.58 cm (0.23 in) and crack growths in 24 hr average 1.80 cm (0.71 in). By using BR 127 primer with FM 73, (Table 79) the crack growth decreased to 0.24 cm (0.1 in)/1 hr and 0.38 cm (0.15 in)/24 hr and failure was cohesive, which is as good as the PAA or FPL treatment.

Table 80 gives results for another adhesive (AF 163 with XB 3944 primer). Again the crack growth was reduced to 0.38 cm (0.15 in)/24 hrs. This was not affected by primer cure: air dry for 2 hr vs. oven cure for 1 hr.

### 3.3.12 Other alloys

Table 81 gives results for STAB(3) with Al 7075-T6. The crack growth of 4.06 cm (1.6 in)/24 hrs is poor. The durability is much improved by adding a degrease step (Table 82) i.e. 2.29 cm (0.9 in)/24 hrs, but is still good with respect to result for Al2024-T3. Table 83 gives results for STAB(3) with Al 6061-T6. The average crack growth is 2.29 cm (0.9 in)/24 hr, which is poor compared to Al2024-T3. Considerable work is needed to optimizing STAB(3) for other alloys.

TABLE 75

Date: 01/31/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: FM 73
No Primer

Purpose: STAB(3) with FM 73, no primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-31-79 | | | | | | | | | | | | |
| -1 | | | | | | | | | | 3.56 (1.4) | 1.78 (0.7) | 3.30 (1.3) |
| -2 | | | | | | | | | | | | |
| -3 | | | | | | | | | | 3.94 (1.55) | 0.25 (0.1) | 1.35 (0.53) |
| -4 | | | | | | | | | | | | |
| -5 | | | | | | | | | | 3.81 (1.50) | 0.25 (0.1) | 1.58 (0.62) |
| -6 | | | | | | | | | | | | |
| -7 | | | | | | | | | | 3.18 (1.25) | 0.76 (0.3) | 1.73 (0.68) |
| -8 | | | | | | | | | | | | |
| -9 | | | | | | | | | | 4.45 (1.75) | 0.25 (0.1) | 2.41 (0.95) |
| -10 | | | | | | | | | | | | |
| -11 | | | | | | | | | | 4.06 (1.6) | 0.25 (0.1) | 9.14 (0.36) |
| -12 | | | | | | | | | | | | |
| | | | | | | | | | Avg | 3.81 (1.5) | 0.51 (0.2( | 1.80 (0.74) |

Remarks:

TABLE 76

Date: 01/31/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: FM 73

Purpose: STAB(3) with FM 73, no primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT (mil) | Lap Shear MPa (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-31-79 | | | | | | | | | | | | |
| -13 | | | | | | | | | 27 (4) | 4.27 (1.68) | 0.31 (0.12) | 1.17 (0.46) |
| -14 | | | | | | | | | | | | |
| -15 | | | | | | | | | 27 (4) | 3.94 (1.55) | 0.51 (0.20) | 1.32 (0.52) |
| -16 | | | | | | | | | | | | |
| -17 | | | | | | | | | 34 (5) | 4.17 (1.64) | 0.66 (0.26) | 1.90 (0.75) |
| -18 | | | | | | | | | | | | |
| -19 | | | | | | | | | 27 (4) | 4.01 (1.58) | 1.75 (0.18) | 2.08 (0.82) |
| -20 | | | | | | | | | | | | |
| -21 | | | | | | | | | 24 (3.5) | 4.01 (1.58) | 1.75 (0.69) | 2.44 (0.96) |
| -22 | | | | | | | | | | | | |
| -23 | | | | | | | | | 27 (4) | 3.86 (1.52) | 3.56 (0.14) | 2.08 (0.82) |
| -24 | | | | | | | | | | | | |
| | | | | | | | | | Avg. | 4.04 (1.59) | 0.56 (0.22) | 1.83 (0.72) |

Remarks:

TABLE 77

Date: 01/31/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: FM 73
No Primer

Purpose: STAB(3) with FM 73, no primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-31-79 | | | | | | | | | | | | |
| -1 | | | | | | | | | | 3.56 (1.4) | 1.78 (0.7) | 3.30 (1.3) |
| -2 | | | | | | | | | | | | |
| -3 | | | | | | | | | | 3.81 (1.5) | 0.25 (0.1) | 1.27 (0.5) |
| -4 | | | | | | | | | | | | |
| -5 | | | | | | | | | | 3.81 (1.5) | 0.25 (0.1) | 1.52 (0.6) |
| -6 | | | | | | | | | | | | |
| -7 | | | | | | | | | | 3.30 (1.3) | 0.76 (0.3) | 1.78 (0.7) |
| -8 | | | | | | | | | | | | |
| -9 | | | | | | | | | | 4.32 (1.7) | 0.25 (0.1) | 2.28 (0.9) |
| -10 | | | | | | | | | | | | |
| -11 | | | | | | | | | | 4.06 (1.6) | 0.25 (0.1) | 1.02 (0.4) |
| -12 | | | | | | | | | | | | |
| | | | | | | | | | Avg. | 3.81 (1.5) | 0.51 (0.2) | 1.78 (0.7) |

Remarks:

TABLE 78

Date: 01/31/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: FM 73
No Primer

Purpose: STAB(3) with FM 73, no primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT (mil) | Lap Shear Mpa(ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-31-79 | | | | | | | | | | | | |
| -13 | | | | | | | | | 21 (3) | 4.32 (1.7) | 0.25 (0.1) | 0.5 |
| -14 | | | | | | | | | | | | |
| -15 | | | | | | | | | 21 (3) | 4.06 (1.6) | 0.51 (0.2) | 0.5 |
| -16 | | | | | | | | | | | | |
| -17 | | | | | | | | | 27 (4) | 4.06 (1.6) | 0.76 (0.3) | 0.7 |
| -18 | | | | | | | | | | | | |
| -19 | | | | | | | | | 21 (3) | 4.06 (1.6) | 0.51 (0.2) | 0.8 |
| -20 | | | | | | | | | | | | |
| -21 | | | | | | | | | 21 (3) | 4.06 (1.6) | 1.78 (0.7) | 1.0 |
| -22 | | | | | | | | | | | | |
| -23 | | | | | | | | | 21 (3) | 3.81 (1.5) | 0.25 (0.1) | 0.8 |
| -24 | | | | | | | | | | | | |
| | | | | | | | | | Avg | 4.06 (1.6) | 0.76 (0.3) | 1.78 (0.7) |

Remarks:

TABLE 79

Date: 01/30/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: FM 73
Primer: BR 127

Purpose: Effect of adhesive on STAB(3)
Adhesive FM 73, Primer BR 127

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Est. GLT (mil) | Lap Shear MPa (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1-30-79 | | | | | | | | | | | | |
| -1 | | 3 | | | | | | | 14 (2) | 4.09 (1.61) | 0.20 (0.08) | 0.38 (0.15) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | | 27 (4) | 4.06 (1.60) | 0.20 (0.08) | 0.38 (0.15) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | | 24 (3.5) | 4.04 (1.59) | 0.28 (0.11) | 0.38 (0.15) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | | 14 (2) | 4.19 (1.65) | 0.23 (0.09) | 0.33 (0.13) |
| -8 | | 3 | | | | | | | | | | |
| -9 | | 3 | | | | | | | 21 (3) | 3.81 (1.50) | 0.20 (0.08) | 0.31 (0.12) |
| -10 | | 3 | | | | | | | | | | |
| -11 | | 3 | | | | | | | 21 (3) | 4.29 (1.69) | 0.33 (0.13) | 0.53 (0.21) |
| -12 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg. | 4.06 (1.6) | 0.25 (0.10) | 0.38 (0.15) |

Remarks: Cohesive failure

TABLE 80

Date: 02/1/79 Investigator: D. Collins Alloy: Al 2024-T3 Adhesive: AF 163
Primer: XB 3944

Purpose: Effect of adhesive on STAB(3)
AF 163 with XB 3944 primer

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-1-79 | | | | | | | | | | | | |
| -25 | Primer air dry | 3 | | | | | | | | 3.81 (1.50) | 0.56 (0.18) | 0.46 (0.18) |
| -26 | 2 hr | 3 | | | | | | | | | | |
| -27 | | 3 | | | | | | | | 3.43 (1.35) | 0.38 (0.15) | 0.38 (0.15) |
| -28 | | 3 | | | | | | | | | | |
| -29 | | 3 | | | | | | | | 3.43 (1.35) | 0.25 (0.10) | 0.38 (0.15) |
| -30 | | 5 | | | | | | | | | | |
| -31 | Oven cure | 5 | | | | | | | | 4.57 (1.80) | 0.25 (0.10) | 0.25 (0.10) |
| -32 | 1 hr | 5 | | | | | | | | | | |
| -33 | | 3 | | | | | | | | 3.56 (1.4) | 0.25 (0.10) | 0.41 (0.16) |
| -34 | | 3 | | | | | | | | | | |
| -35 | | 3 | | | | | | | | 3.81 (1.5) | 0.33 (0.13) | 0.51 (0.20) |
| -36 | | | | | | | | | | | | |
| | | | | | | | | | Avg. | 3.81 (1.5) | 0.33 (0.13) | 0.38 (0.15) |

Remarks: Brush on primer

TABLE 81

Date: 02/5/79 Investigator: D. Collins Alloy: Al 7075-T6 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of alloy on STAB(3)
Al 7075-T6, no degrease step.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-5-79 | | | | | | | | | | | | |
| -13 | | 3 | | | | | | | | 3.43 (1.35) | 1.07 (0.42) | 3.30 (1.3) |
| -14 | | 3 | | | | | | | | | | |
| -15 | | 3 | | | | | | | | 3.56 (1.40) | 0.20 (0.08) | 2.79 (1.1) |
| -16 | | 3 | | | | | | | | | | |
| -17 | | 3 | | | | | | | | 4.32 (1.70) | 0.51 (0.20) | 3.56 (1.4) |
| -18 | | 3 | | | | | | | | | | |
| -19 | | 3 | | | | | | | | 3.30 (1.30) | 5.94 (2.34) | 6.60 (2.6) |
| -20 | | 3 | | | | | | | | | | |
| -21 | | 3 | | | | | | | | 3.30 (1.30) | 4.57 (1.80) | 5.33 (2.1) |
| -22 | | 3 | | | | | | | | | | |
| -23 | | 3 | | | | | | | | 4.06 (1.60) | 0.51 (0.20) | 2.54 (1.0) |
| -24 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg. | 3.66 (1.44) | 1.27 (0.5) | 4.06 (1.6) |

Remarks:

TABLE 82

Date: 02/5/79 Investigator: D. Collins Alloy: Al 7075-T6 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Effect of alloy on STAB(3)
Al 7075-T6 with degrease step.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-5-79 | | | | | | | | | | | | |
| -1 | 10 min in MEK | 3 | | | | | | | | 3.56 (1.4) | 0.24 | 3.81 (1.5) |
| -2 | | 3 | | | | | | | | | | |
| -3 | | 3 | | | | | | | | 3.81 (1.5) | 0.25 | 2.29 (0.9) |
| -4 | | 3 | | | | | | | | | | |
| -5 | | 3 | | | | | | | | 3.81 (1.5) | 0.07 | 1.52 (0.6) |
| -6 | | 3 | | | | | | | | | | |
| -7 | | 3 | | | | | | | | 3.81 (1.5) | 0.31 | 1.52 (0.6) |
| -8 | | 3 | | | | | | | | | | |
| -9 | | 3 | | | | | | | | 4.06 (1.6) | 0.31 | 1.52 (0.6) |
| -10 | | 3 | | | | | | | | | | |
| -11 | | 3 | | | | | | | | 3.56 (1.4) | 0.30 | 2.79 (1.1) |
| -12 | | 3 | | | | | | | | | | |
| | | | | | | | | | Avg | 3.81 (1.5) | 0.64 (0.25) | 2.89 (0.9) |

Remarks:

TABLE 83

Date: 03/23/79 Investigator: D. Collins Alloy: Al 6061-T6 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Different alloy - STAB(3) - 3 min in NaOH, DI rinse, $N_2$ dry

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Lap Shear (ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 1 | | 3 | | | | | | | 3.96 (1.56) | 0.25 (0.1) | 2.34 (0.92) |
| 2 | | 3 | | | | | | | | | |
| 3 | | 3 | | | | | | | 3.43 (1.35) | 0.19 (0.08) | 2.24 (0.88) |
| 4 | | 3 | | | | | | | | | |
| 5 | | 3 | | | | | | | 4.06 (1.6) | 1.14 (0.45) | 2.54 (1.00) |
| 6 | | 3 | | | | | | | | | |
| 7 | | 3 | | | | | | | 3.45 (1.36) | 0.13 (0.05) | 2.44 (0.96) |
| 8 | | 3 | | | | | | | | | |
| 9 | | 3 | | | | | | | 4.78 (1.88) | 0.44 (0.175) | 1.27 (0.50) |
| 10 | | 3 | | | | | | | | | |
| 11 | | 3 | | | | | | | 4.29 (1.69) | 1.40 (0.55) | 2.67 (1.05) |
| 12 | | 3 | | | | | | | | | |
| | | | | | | | | Avg | 3.99 (1.57) | 0.58 (0.23) | 2.29 (0.9) |

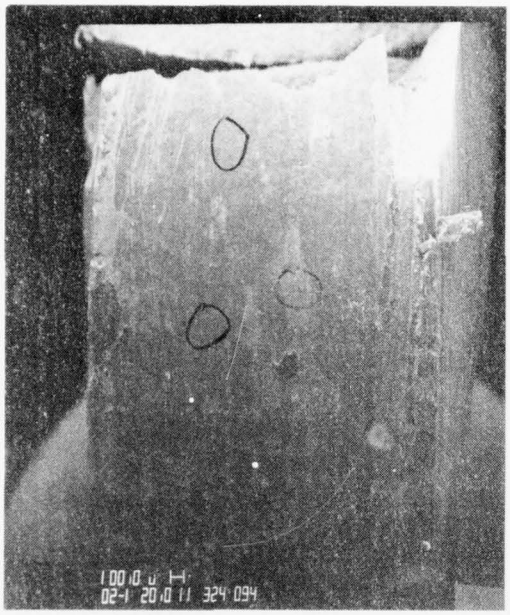
Remarks:

## 3.4 Post Fracture Analysis

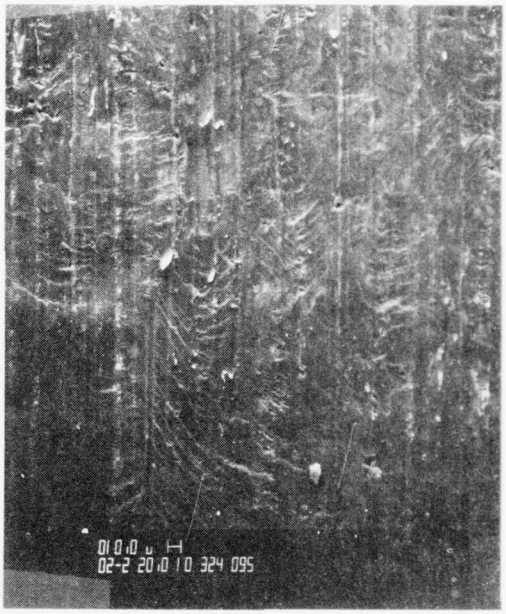
Figure 51 shows SEM pictures of the debond region of a STAB(3) joint after the wedge test. Figure 51d reveals that failure is near the hydroxide-primer interface but cohesive in the primer. Figures 51e-h shows larger magnifications of region 99 in Fig. 51a. In this region, occasional failure in the hydroxide can be noted. In Fig. 52 considerable cohesive failure in the adhesive is observed. Figure 52c magnifies the region 24 in Fig. 52b, where cohesive failure was near the metal interface. Figure 52d shows the porous structure of the cohesively failed adhesive (area 28, Fig. 52b).

Figure 53 shows SEM pictures of Al 2024-T3 after STAB(3) with second dip, and wedge test. Figure 53 is for the mating adherend that failed after bending the metal and shows failure to be in the primer at the hydroxide interface (i.e., the hydroxide is filled with primer). Figure 54 is SEM pictures for Al 2024-T3 after STAB(3) with 2nd dip and wedge test, but at the metal side (i.e, the interface that failed during the wedge test). In this case there has been much less penetration of the hydroxide by the primer and failure appears to be right at the hydroxide-primer interface.

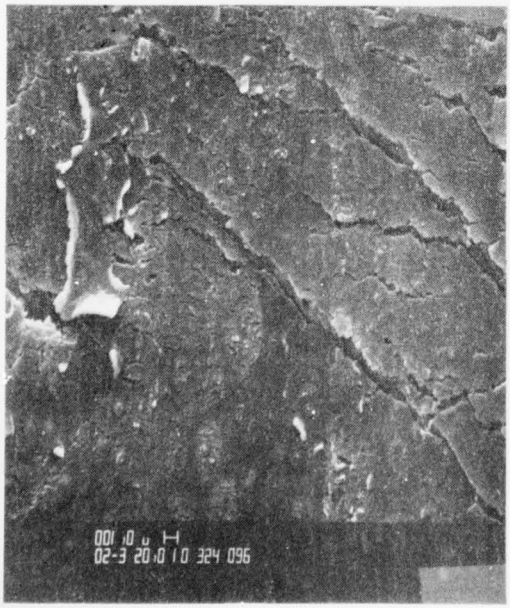
It was supposed that if failure occurred in the hydroxide film for poor bond endurance that hydroxide would be on both mating surfaces, and thus the surface properties of the mating surfaces would be approximately the same especially for $\theta_{H_2O}$ that is sensitive to the outer atomic layers. Table 84 reports surface properties of mating (metal vs. adhesive) sides of joints that had poor wedge test results (~2.03 cm-5.08 cm (0.8-2 in)/24 hr). The surface properties are very similar and the water contact angle (~36°) closer to that for hydroxide (~10°) than adhesive (~90°). Except for $\theta_{H_2O}$ the properties of primed, unbonded Al 2024-T3 surface are surprisingly similar to that of the fractured joint which would indicate failure in the primer. The results indicate mixed failure in the hydroxide and primer for the medium to poor bonds.



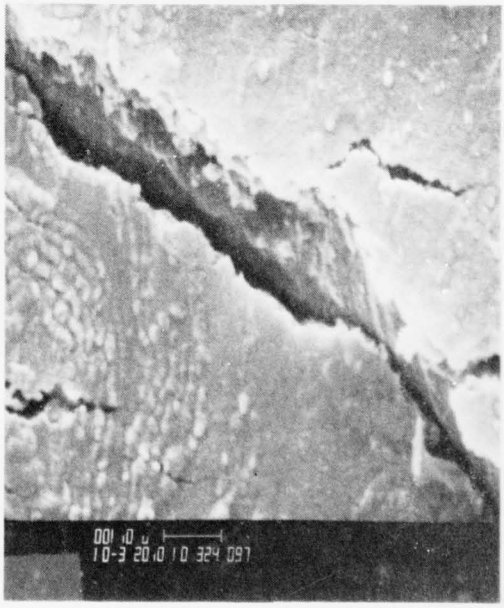

a




b




c

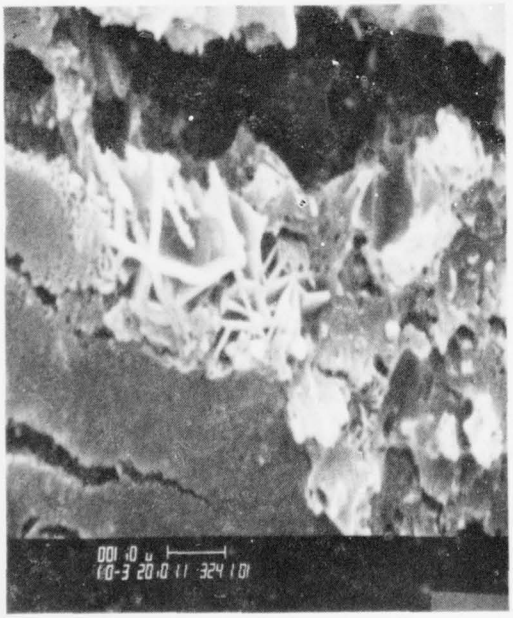



d

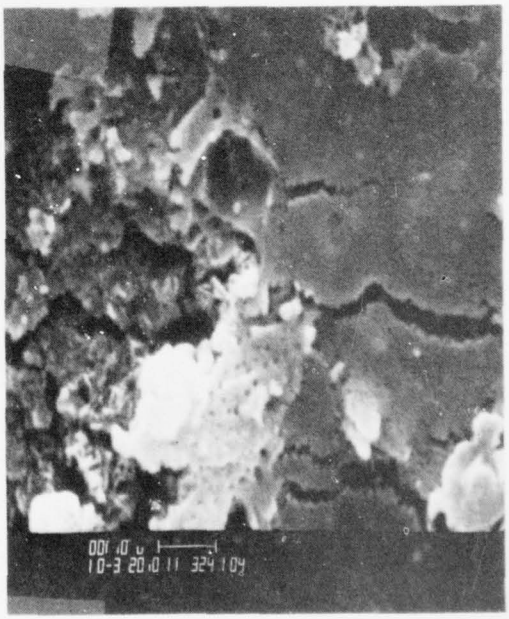
Fig. 51 SEM pictures of Al 2024-T3 after STAB(3) and wedge test. Good bond (~0.3"/24 hr).

e

f



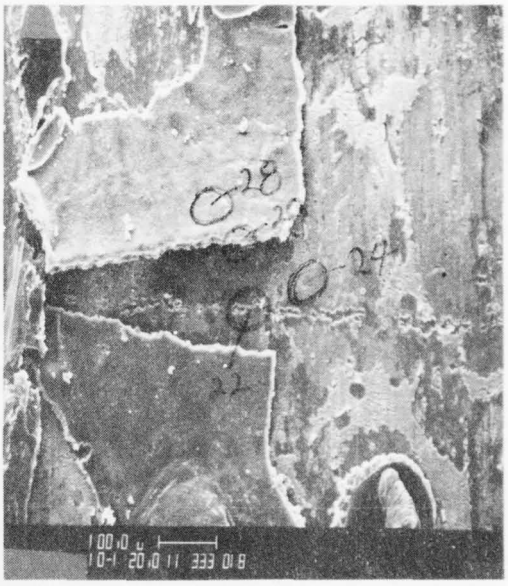
g



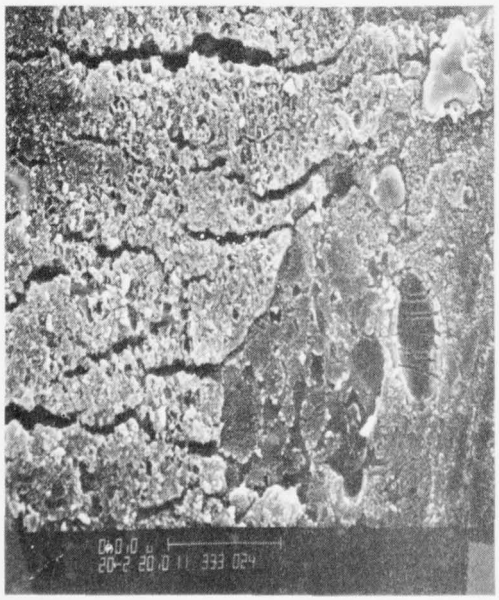
h

Fig. 51 continued

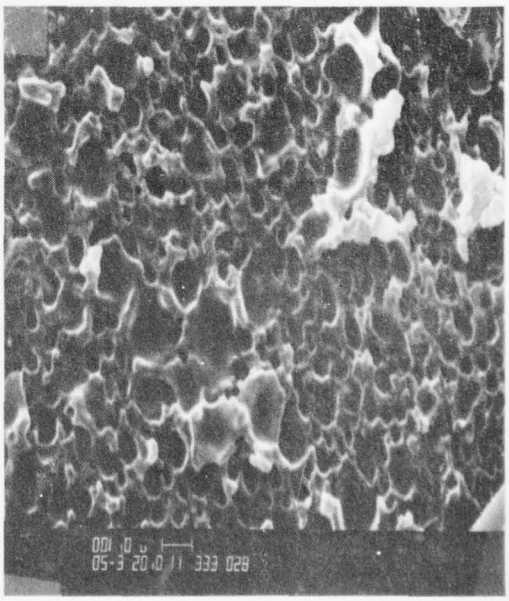
a



b

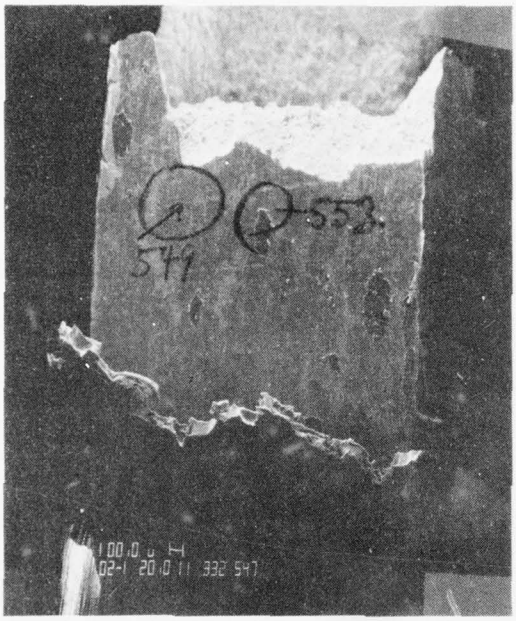


c

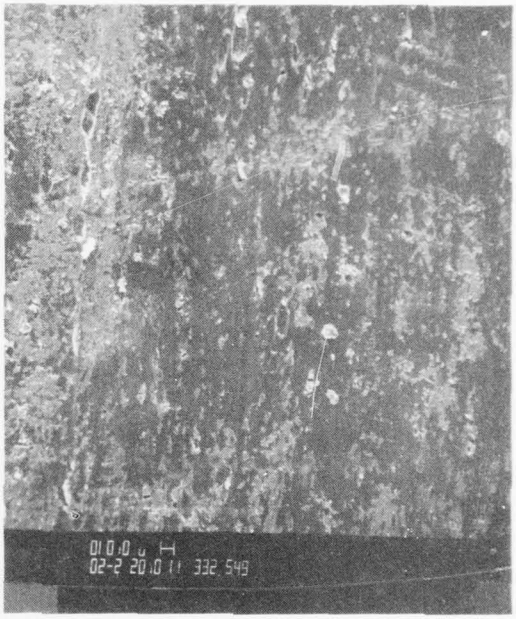


d

Fig. 52 SEM pictures of Al 2024-T3 after STAB(3) and wedge test. Good bond (~0.3"/24 hr).

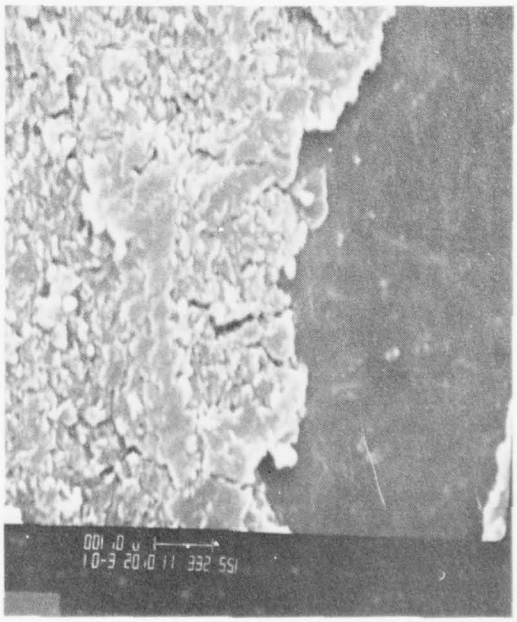



a



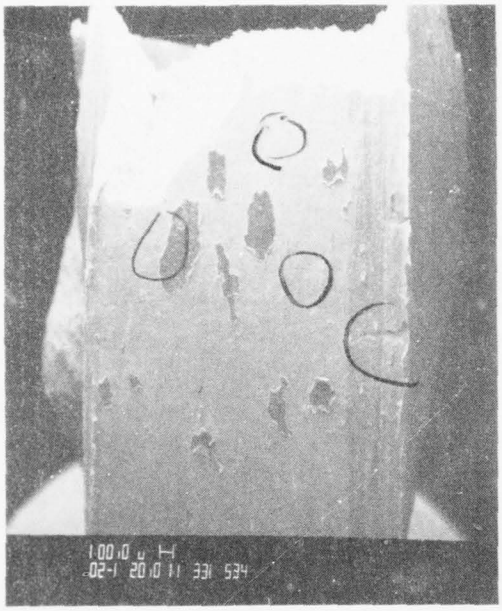
b

c

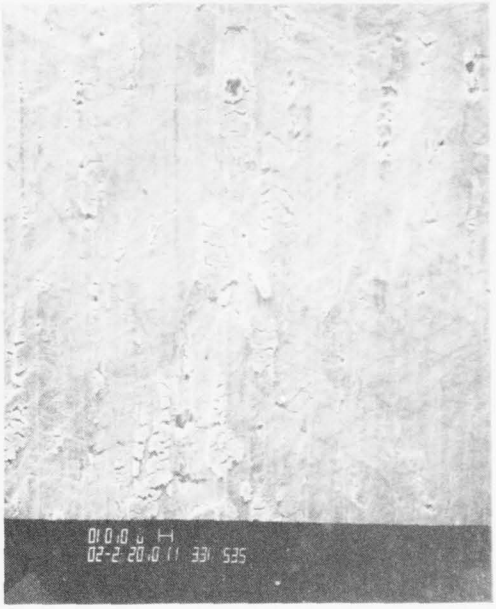


d

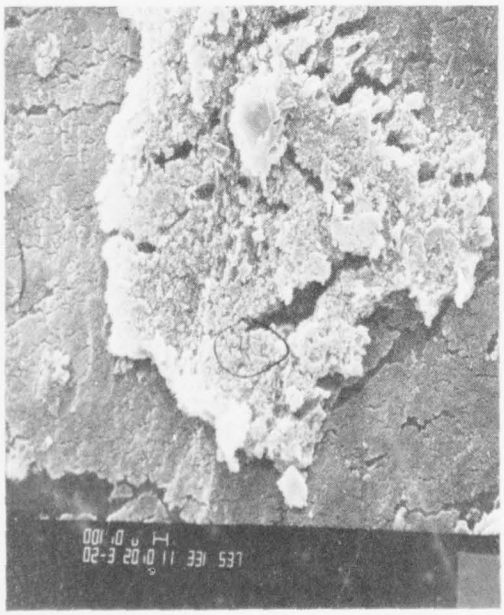
Fig. 53 SEM pictures of Al 2024-T3 after STAB(3) with 2nd dip and wedge test. Medium bond (~0.7"/24 hr).



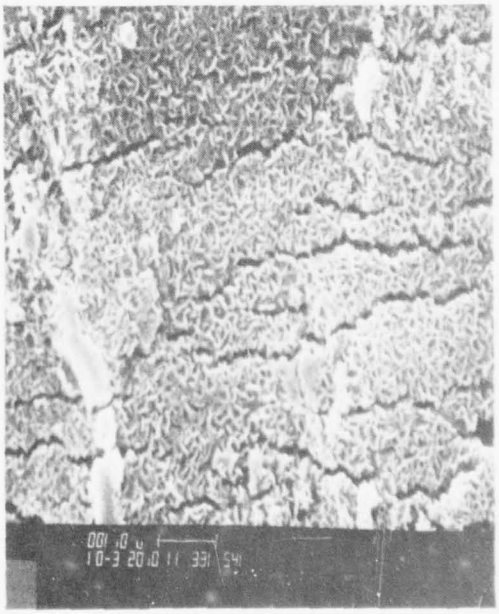
a



b



c



d

Fig. 54 SEM pictures of Al 2024-T3 after STAB(3) with 2nd dip and wedge test. Medium bond (~0.7"/24 hr), metal ride.

AD-A076 950 ROCKWELL INTERNATIONAL THOUSAND OAKS CA SCIENCE CENTER F/G 11/6
SURFACE TREATMENT FOR ALUMINUM BONDING.(U)
OCT 79 T SMITH DAAK10-78-C-0274
UNCLASSIFIED SC5180.17FTR NL

3 OF 3
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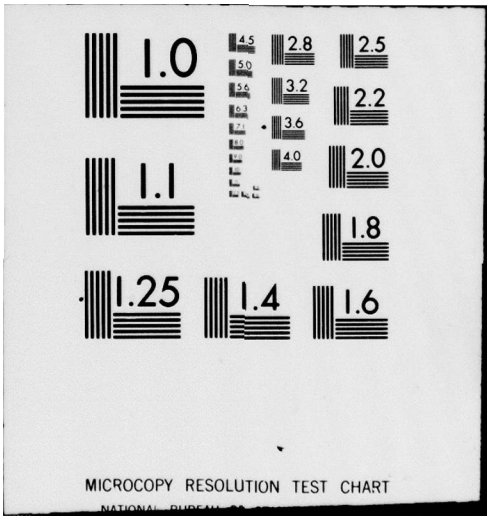
1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART

TABLE 84

Comparison of Surface Properties of
Mating Surfaces After Wedge Tests

| Sample No. | Condition | Surface Properties Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Crack Growth cm (in)/24 hr |
|---|---|---|---|---|---|---|---|
| 2-1-79-2 | Primed Unbonded side | 2 | 20 | 0.38 | 0.18 | 63 | |
| 9 | " | 0 | 19 | | 0.08 | 62 | |
| 10 | " | 4 | 24 | | 0.22 | 60 | |
| | Avg. | 2 | 21 | 0.38 | 0.16 | 62 | |
| 2-2-79-14 | Interfacial Failure, Metal | 8 | 26 | 0.19 | 0.08 | 43 | 2.03 (0.8) |
| 2-1-79-2 | " | 4 | 20 | - | 0.10 | 45 | 2.03 (0.8) |
| 2-1-79-9 | " | 10 | 20 | - | 0.06 | 45 | 3.81 (1.5) |
| 2-1-79-10 | " | (74) | (43) | - | 0.12 | 32(80) | 3.81 (1.5) |
| 2-2-79-11 | " | 12 | 22 | 0.46 | 0.22 | 32 | 5.08 (2.0) |
| | Avg. | 8 | 22 | 0.37 | 0.10 | 33 | 3.30 (1.3) |
| 2-2-79-13 | Interfacial Failure, Adhesive | 16 | 24 | 0.30 | 0.05 | 23 | 2.03 (0.8) |
| 2-1-79-11 | " | 8 | 21 | 0.22 | 0.10 | 38 | 5.08 (2.0) |
| 2-1-79-12 | " | 14 | 23 | 0.40 | 0.10 | 47 | 4.06 (2.0) |
| | Avg. | 13 | 23 | 0.30 | 0.08 | 36 | 4.06 (1.6) |

## III. SCALE UP

For laboratory scale up, 1' × 1' panels were processed in stainless steel containers that contained 13 liters of solution. The panels were dipped in the NaOH tank then hung from hooks on a frame that was automatically cycled up and down at controlled speed. Limit switches reversed the motor when the panel reached the upper and lower desired position in the rinse and dry tank. The panels were lowered into the rinse tank before the spray water was turned on. Both sides were sprayed simultaneously. The panel was then lowered before turning on the $N_2$ drying tube. This tube has a line of holes to allow forced gas to impinge uniformly across the panel. The panel was slowly raised, drying from top to bottom to avoid water dripping over the dried region.

The panels were then primed and cut into two pieces 30.48 cm × 15.24 cm (1 ft × 0.5 ft) that were bonded together and then cut into 2.54 cm × 15.24 cm (1 in × 6 in) wedge specimens. The wedge specimens were labeled A-K with A for the sample that was at the top of the panel during STAB(3) treatment and K at the bottom.

Tables 85 and 86 show results for STAB(3) scale up to 2.54 cm × 2.54 cm (1 ft × 1 ft) panels. The average initial crack length is 1.36", the average crack growth is 0.23 cm (0.09 in)/1 hr, 0.28 (0.11 in)/24 hr (Table 85) and 0.10 cm (0.04 in)/1 hr, and 0.51 cm (0.20 in)/24 hr (Table 86). Samples E and F in Table 86 gave high crack growth values. The pH of the surface proved to be about 8 in each case, indicating insufficient rinse in this area.

TABLE 85

Date: 01/28/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: BR 127

Purpose: Scale Up: Panel #1, rinse 1 min, $N_2$ dry 1 min.

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 2-28-79 | | | | | | | | | | | | |
| -A | | 3 | | | | | | | | 3.56 (1.40) | 0.18 (0.07) | 0.38 (0.15) |
| -B | | 3 | | | | | | | | 3.61 (1.42) | 0.25 (0.10) | 0.37 (0.14) |
| -C | | 3 | | | | | | | | 3.36 (1.32) | 0.25 (0.10) | 0.38 (0.15) |
| -D | | 3 | | | | | | | | 3.40 (1.34) | 0.25 (0.10) | 0.25 (0.10) |
| -E | | 3 | | | | | | | | 3.45 (1.36) | 0.25 (0.10) | 0.25 (0.10) |
| -F | | 3 | | | | | | | | 3.63 (1.43) | 0.15 (0.06) | 0.18 (0.07) |
| -G | | 3 | | | | | | | | 3.50 (1.38) | 0.13 (0.05) | 0.25 (0.10) |
| -H | | 3 | | | | | | | | 3.43 (1.35) | 0.25 (0.10) | 0.28 (0.11) |
| -I | | 3 | | | | | | | | 3.43 (1.35) | 0.18 (0.07) | 0.15 (0.06) |
| -J | | 3 | | | | | | | | 3.30 (1.30) | 0.25 (0.10) | 0.25 (0.10) |
| -K | | 3 | | | | | | | | 3.38 (1.33) | 0.25 (0.10) | 0.25 (0.10) |
| | | | | | | | | | Ave | 3.45 (1.36) | 0.23 (0.09) | 0.28 (0.11) |

TABLE 86

Date: 03/28/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: BR 127

Purpose: Scale up: Panel #2, rinse 0.5 min, $N_2$ dry 0.5 min

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Wedge Crack Growth/cm( in) (Initial) | (1 hr) | (24 hr) |
| 3-28-79 | | | | | | | | | | | |
| -A | | 3 | | | | | | | 3.30 (1.3) | 0.13 (0.05) | 0.33 (0.13) |
| -B | | 3 | | | | | | | 3.45 (1.36) | 0.03 (0.01) | 0.48 (0.09) |
| -C | | 3 | | | | | | | 3.30 (1.32) | 0.08 (0.03) | 0.33 (0.14) |
| -D | | 3 | | | | | | | 3.18 (1.25) | 0.10 (0.04) | 0.13 (0.05) |
| -E | | 3 | | | | | | pH 8 | 3.56 (1.4) | 0.10 (0.04) | 1.90 (0.75) |
| -F | | 3 | | | | | | pH 8 | 3.30 (1.3) | 0.18 (0.07) | 1.32 (0.52) |
| -G | | 3 | | | | | | | 3.56 (1.4) | 0.10 (0.04) | 0.25 (0.10) |
| -H | | 3 | | | | | | | 3.50 (1.38) | 0.08 (0.03) | 0.43 (0.07) |
| -I | | 3 | | | | | | | 4.32 (1.7) | 0.10 (0.04) | 0.36 (0.14) |
| -J | | 3 | | | | | | | 3.43 (1.35) | 0.08 (0.03) | 0.38 (0.15) |
| -K | | 3 | | | | | | | 3.43 (1.35) | 0.13 (0.05) | 0.38 (0.15) |
| | | | | | | | | Ave | 3.48 (1.37) | 0.10 (0.04) | 0.51 (0.20) |

Table 87 shows successful STAB(3) for a 30.48 × 30.48 × 0.16 cm (1 fт × 1 ft × 1/16 in) panel, used for lap shear testing. Except for the bottom two samples K and L, the average lap shear strength is 5.5 ksi, normal for primarily cohesive failure. The bottom two samples received too much pressure in the press, which broke the scrim and allowed the adhesive to escape, leaving a thin GLT.

Table 88 gives successful scale up STAB(3) results for Al 2024-T3, Hysol EA9628H and BR 127 primer. A different investigator made the test and used a drip dry rather than $N_2$ blow dry. The average initial crack length was 3.32 cm (1.35 in), the crack growth was 0.13 cm (0.05 in)/1 hr and 0.51 cm (0.2 in)/24 hr. This is encouraging for the simpler drip dry process.

In Table 89 the standard STAB(3) process was used but the sides of the aluminum panels with the painted marking letters were bonded. In those areas of no paint the average crack values were 3.56 cm (1.4 in), 0.23 cm (0.09 in)/1 hr and 0.36 cm (0.14 in)/24 hr. In the areas with painted letters the crack growth was much larger indicating that the process does not remove the paint in 3 min.

TABLE 87

Date: 03/14/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: Hysol EA9210H

Purpose: Scale up, STAB(3), lap shear tests
3 min in NaOH, 30 sec DI water rinse, 30 sec $N_2$ dry
Primer sprayed on

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear MPa Ksi | Wedge Crack Growth/cm-in. (Initial) | (1 hr) | (24 hr) |
| 3-14-79 | | | | | | | | | | | | |
| -A | Panel 1 | 3 | | | | | | | - | | | |
| -B | | 3 | | | | | | | 37 (5.4) | | | |
| -C | | 3 | | | | | | | 37 (5.3) | | | |
| -D | | 3 | | | | | | | 37 (5.5) | | | |
| -E | | 3 | | | | | | | 35 (5.1) | | | |
| -F | | 3 | | | | | | | 38 (5.6) | | | |
| -G | | 3 | | | | | | | 37 (5.4) | | | |
| -H | | 3 | | | | | | | 39 (5.7) | | | |
| -I | | 3 | | | | | | | 40 (5.8) | | | |
| -J | | 3 | | | | | | | 38 (5.6) | | | |
| -K | | 3 | Broken scrim indicates too much pressure | | | | | | 29 (4.2) | | | |
| -L | | 3 | Broken scrim indicates too much pressure | | | | | | 29 (4.3) | | | |
| | | | | | | | | Avg | (5.5) | | | |

TABLE 88

Date: 04/04/79 Investigator: D. Collins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer BR 127

Purpose: Scale up. Check drip dry STAB(3)

| | Surface Treatment | | Surface Properties | | | | | Bond Properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | No Degrease | STAB(3) Time (min) | Δ (deg.) | ψ (deg.) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg.) | Peel Force (g/cm) | Lap Shear (Ksi) | Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
| 4-04-79 | | | | | | | | | | | | |
| -A | | 3 | | | | | | | | 3.45 (1.36) | 0.10 (0.04) | 0.15 (0.06) |
| -B | | 3 | | | | | | | | 3.43 (1.35) | 0.13 (0.05) | 0.20 (0.08) |
| -C | | 3 | | | | | | | | 3.51 (1.38) | 0.76 (0.03) | 0.51 (0.20) |
| -D | | 3 | | | | | | | | 3.48 (1.37) | 0.18 (0.07) | 0.84 (0.33) |
| -E | | 3 | | | | | | | | 3.48 (1.37) | 0.18 (0.07) | 0.89 (0.35) |
| -F | | 3 | | | | | | | | 3.45 (1.36) | 0.08 (0.03) | 0.33 (0.12) |
| -G | | 3 | | | | | | | | 3.40 (1.34) | 0.06 (0.02) | 2.29 (0.90) |
| -H | | 3 | | | | | | | | 3.35 (1.32) | 0.10 (0.04) | 0.76 (0.30) |
| -I | | 3 | | | | | | | | 3.35 (1.32) | 0.18 (0.07) | 0.66 (0.26) |
| -J | | 3 | | | | | | | | 3.50 (1.38) | 0.15 (0.06) | 0.48 (0.19) |
| -K | | 3 | | | | | | | | 3.45 (1.36) | 0.18 (0.07) | 0.56 (0.22) |
| | | | | | | | | | Avg | 3.43 (1.35) | 0.13 (0.05) | 0.51 (0.20) |

TABLE 89

Date: 02/06/79 Investigator: L. Bivins Alloy: 2024-T3 Adhesive: Hysol EA9628H
Primer: BR 127

Purpose: Scale up: STAB(3), bond painted side.

| Sample No. | Surface Treatment: No Degrease | Surface Treatment: STAB(3) Time (min) | Surface Properties: Δ (deg.) | Surface Properties: ψ (deg.) | Surface Properties: SPD (volts) | Surface Properties: PEE (nA) | Surface Properties: $\theta_{H_2O}$ (deg.) | Bond Properties: Peel Force (g/cm) | Bond Properties: Lap Shear (Ksi) | Bond Properties: Wedge Crack Growth/cm(in) (Initial) | (1 hr) | (24 hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4-06-79 | | | | | | | | | | | | |
| -A | | 3 | | | | | | | | 3.45 (1.36) | 0.18 (0.07) | 0.38 (0.15) |
| -B | | 3 | | | | | | | | 3.58 (1.41) | 0.20 (0.08) | 0.28 (0.11) |
| -C | | 3 | | | | | | | | 3.30 (1.30) | 0.25 (0.10) | 0.28 (0.11) |
| -D | | 3 | Letter paint marks | | | | | | | 3.68 (1.45) | 0.31 (0.12) | 0.76 (0.30) |
| -E | | 3 | | | | | | | | 3.56 (1.40) | 0.18 (0.07) | 0.20 (0.08) |
| -F | | 3 | | | | | | | | 3.68 (1.45) | 0.23 (0.09) | 0.23 (0.15) |
| -G | | 3 | | | | | | | | 3.56 (1.40) | 0.25 (0.10) | 0.31 (0.12) |
| -H | | 3 | | | | | | | | 3.45 (1.36) | 0.20 (0.08) | 0.28 (0.11) |
| -I | | 3 | | | | | | | | 3.68 (1.45) | 0.20 (0.08) | (0.36 (0.14) |
| -J | | 3 | Letter paint marks | | | | | | | 3.51 (1.38) | (1.16)(0.89) | (4.27)(1.68) |
| -K | | 3 | | | | | | | | 3.61 (1.42) | 0.25 (0.10) | 0.36 (0.14) |
| | | | | | | | | | Avg. | 3.56 (1.40) | 0.23 (0.09) | 0.36 (0.14) |

# IV. ECONOMICS

The economics of any particular surface treatment must be judged on the basis of needed bond strength and endurance, initial or additional capital investments, recurring cost of maintenance and materials and any additional costs of meeting OSHA requirements to meet health and safety regulations.

Table 90 compares STAB surface treatments with the industry standard (i.e., FPL etch) and the more recent Boeing phosphoric acid anodize used in the Air Force PABST program. The Boeing PAA treatment (BAC 5555) adds two steps to the standard Forest Product Laboratories (FPL) treatment, i.e., the anodize and an additional rinse. The Boeing treatment entails 8 steps as compared to 6 for FPL, 5 for Rockwell STAB(1) and (2) and 3 for Rockwell STAB(3).

A first approximation as to relative capital investment was estimated by giving the value of one unit for each step, adding a unit to each step that needed heating and one unit for the electrical equipment needed for anodizing. In addition to relative capital investment, relative bond endurance, and hazard are listed in Table 90. It is seen that on the basis of lab scale up studies, STAB(3) with only 3 steps yields as durable joints as PAA or FPL and should be less expensive as to capital investment and maintenance. The cost of materials is listed in Table 91 and it is seen that when the cost of energy to heat the various solutions is considered, STAB(3) should be least expensive, especially if caustic soda can be used. This has yet to be demonstrated, since in this study pure NaOH flakes were used.

Of particular importance, is the low hazard of STAB(3) as compared to FPL etch or PAA, since one of the main purposes of this research was to eliminate the use of carcinogenic chromates for factory use.

TABLE 90

Comparison of Surface Treatments With Respect to Process Steps, Bond Endurance, Relative Capital Investment and Hazard

| Surface Treatment \ Step | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Bond Endurance Crack Growth (cm(in)/hr) | Relative Capital Investment | Relative Hazard |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Boeing | Vapor Degrease | Alkaline Clean | Rinse | Sulfuric Acid Dichromate Etch | Rinse | PAA | Rinse | Dry | | | |
| BAC 5555 Phosphoric Acid Anodize PAA | Tri-chloro-ethylene | TURCO 4215 31 g/ℓ 66°C | D.I. water | $Na_2Cr_2O_7$ 28.5 g $H_2SO_4$ 285 g D.I. water to 1 ℓ 66°C | D.I. water | $H_3PO_4$ 10 w/o 10 volts 20-25 min | D.I. water | Forced Air | 0.10 (0.04) | 11 | TCE (Moderate toxic) Chromates (Carcinogens) $H_2SO_4$ (toxic) |
| Forest Prod. Lab | " | " | " | " | " | Dry | | | | | |
| Sulfuric Acid Dichromate Etch FPL | " | " | " | " | " | Forced Air | | | 0.30 (0.12) | 8 | " |
| Rockwell International | Ultra-sonic solvent | Rinse | Hot Water Soak | Rinse | Dry | | | | | | Solvent (Moderate toxic] |
| STAB(1) | 9 Parts Solvent 1 part "Gunk" | D.I. water | Tap or D.I. + $K_2CO_3$ to pH 9.8 80°C, 10 min | D.I. water | $N_2$ or Air | | | | 0.76 (0.3) | 5 | Solvent (Moderate toxic) |
| STAB(2) | " | " | Room Temp Soak MICRO 60 ml/ℓ water | " | " | | | | 0.76 (0.3) | 5 | Solvent |
| STAB(3) | NaOH NaOH 36 w/o Room Temp | Rinse D.I. water | Dry $N_2$ or Air | | | | | | <0.13 (0.05) | 3 | No fumes |
| Degrease | Solvent | | | | | | | | >5.0 (2.0) | 1 | Solvent (Moderate toxic) |
| None | | | | | | | | | >0.76 (3.0) | | |

TABLE 91

Relative Cost of Materials for Surface Treatment Processes

| Material | Form | $/lb |
|---|---|---|
| Solvent (TCE) | 55 gal drums | 1.00 |
| Sulfuric Acid | 750 lb drums | 0.06 |
| Phosphoric Acid (80%) | " | 0.34 |
| Sodium Dichromate | 100 lb bags<br>1 ton lot | 0.55 |
| Sodium Hydroxide<br>(Caustic soda 50% liq) | 400 lb drum | 0.10 |
| Sodium Hydroxide | 100 lb bag<br>1 ton lot | 2.00 |

## V. SUMMARY OF RESULTS AND CONCLUSIONS

The object of this program was to find a nonacid surface treatment (no carcinogenic chromates) for Al 2024-T3 that was inexpensive but would produce strong, durable adhesive joints with Hysol EA9628H adhesive and Hysol EA9210H or BR 127 primer.

Initial studies[1] indicated that a simple degrease and hot water soak (STAB(1)) would produce strong durable joints. Further investigation revealed great difficulty in reproducing this result although occasional good results could be obtained. Investigation of surface properties revealed that as-received Al 2024-T3 has a surface layer of metal that differs from the bulk. This layer is entirely removed in the standard FPL etch, but is only partially reacted during STAB(1). If the Al 2024-T3 is FPL etched then given STAB(1) good bond endurance with wedge test results. It is concluded that in some instances STAB(1) reacts with the entire outer layer of metal yielding hydroxide that is stable to moisture (hydrothermal stress). In other instances this layer is only partially reacted, leaving an unstable layer that can corrode under hydrothermal stress. Also, SEM studies reveal the STAB(1) hydroxide to be layered, allowing fracture between the layers.

In the course of studying STAB(1), a simple degrease and water soak (room temperature) in a water solution containing a commercial cleaning agent (MICRO) gave good bond endurance results. This was labeled STAB(2). Further investigation revealed this treatment to suffer from the same reproducibility problems as STAB(1).

In the process of studying STAB(1) and (2) the effect of sodium hydroxide concentration was investigated. It was found that a 36 w/o solution of NaOH in D.I. water (STAB(3)) gave excellent bond endurance by the wedge test. Of 61 wedge test specimens, the average crack growth in the first hour was ~0.10 cm (0.04 in) and after the first 24 hr, ~0.51 cm (0.2 in). Failure during the wedge test was primarily cohesive in adhesive or primer. The results for STAB(3) are comparable with the Boeing PAA, and the standard FPL

etch treatments. The lap shear strength averages above 5.5 Ksi, with cohesive failure, and is also comparable with the PAA or FPL results.

Investigation of the surface properties of STAB(3) revealed that the outer unstable layer of metal is removed in 3 min (i.e., ~1 μ removal). After rinsing and drying a very porous hydroxide single layer is formed. These properties are similar to that for PAA in that primer becomes embedded within the hydroxide layer and the hydroxide and underlying metal is stable to corrosion under hydrothermal stress.

Auger electron spectroscopy with $Ar^+$ sputter etching reveals the chemical constitution of the outer atomic layers for films after the various treatments (see Table 92). As-received and degreased-only Al 2024-T3 have aluminum oxide layers rich in Mg whereas FPL etched and PAA do not. It has been hypothesized that the Mg-rich oxide layer causes corrosion instability of the layer and thus the layer must be removed for improved hydrothermal stress durability. However, STAB(3) leaves films with a high concentration of Mg but also gives good durability. The as-received and degreased-only Al 2024-T3 does have less stable oxide, as revealed by the effect of the electron beam. The electron beam reduces $Al^{+3}$ and desorbs oxygen whereas this does not occur for the surface treated alloy. STAB(3) forms a film with a much more stable carbon compound than normal organic contamination. The other surface properties (ellipsometric parameters, $\Delta$, $\psi$, SPD, PEE and $\theta_{H_2O}$) are fairly reproducible for FPL, PAA and STAB(3) and can be used for quality assurance. These properties are very unreproducible for STAB(1) and (2), consistent with the irreproducible bond properties.

A number of process variables were investigated to delineate the range for good bonds and the boundaries beyond which poor bonds result. Table 91 lists the parameters, range and remarks.

Although STAB(3) has been optimized for Al 2024-T3 and Hysol EA9628H adhesive and primer, it has been found to be as good for other 121°C (250°F) curing adhesives, e.g., FM 73/BR 127, AF 163/XB 3944. However, the STAB(3) parameters that give good results for Al 2024-T3 have not been found optimum for other alloys such as Al 7075-T6 or Al 6061-T6.

STAB(3) produces a pleasing gold color. This plus surface properties measured by ellipsometry, SPD, PEE and $\theta_{H_2O}$ can be used for quality assurance that the treatment has been properly performed and is the basis for non-destructive inspection techniques.

TABLE 92

Comparison of Surface Properties For The
Various Surface Treatment of Al 2024-T3

| Treatment | Δ (deg) | ψ (deg) | SPD (volts) | PEE (nA) | $\theta_{H_2O}$ (deg) | APPH Al 50 eV | APPH Al 1400 eV | APPH O 510 eV | APPH Mg 1200 eV | APPH Cu 170 eV | APPH C 270 eV |
|---|---|---|---|---|---|---|---|---|---|---|---|
| As-received | 0.6 | 52.9 | 0.45 | 0.01 | 70 | 2 | 22 | 102 | 42 | 0 | 42 |
| Degrease | 90.0 | 34.2 | 0.56 | 0.00 | 60 | 2 | 14 | 104 | 31 | 0 | 52 |
| FPL | 14 | 37 | 0.65 | 0.18 | 10 | 30 | 10 | 75 | 0 | 3 | 4 |
| PAA | 173 | 40 | 0.20 | 0.04 | 10 | 15 | 20 | 80 | 0 | 0 | 4 |
| STAB(1) | 158 | 40 | 0.16 | 0.3 | 15 | 7 | 44 | 116 | 4 | 0 | 30 |
| STAB(2) | 63 | 30 | 0.0 | 0.6 | 30 | 5 | 20 | 62 | 17 | 10 | 82 |
| STAB(3) | 20 | 27 | 0.0 | 1.3 | 10 | 4 | 19 | 96 | 25 | 9 | 73 |

TABLE 93

Process Parameter Boundaries for STAB(3)

| Parameter | Range for Good Bonds | Remarks |
|---|---|---|
| Glue line thickness | 3-7 mil | Normal ~4 mil |
| Primer thickness | 0.4-1.4 μ (wt chg.)<br>0.06-0.2 mil (calipers) | |
| Primer cure | 1 hr normal | 10 min gave poor peel strength |
| | 121°C (250°F) | Left overnight before cure gave bad bonds |
| Degrease | not needed | but does not degrade STAB(3) |
| NaOH conc. | >100 g/ℓ | Best results ~600 g/ℓ |
| Time of NaOH dip | >3 min | Best results ~3-5 min |
| Delay between NaOH dip and rinse | 1 min ok | Need more data for longer periods |
| Rinse | Spray rinse with D.I. water | Insufficient rinse leaves surface alkaline giving poor durability |
| Dry | $N_2$ blow, air blow | Drip drying may be satisfactory |
| | Drip dry? | Need more data |
| Contamination | Like PAA, very tolerant | But need more data |
| Delay before Primer | >24 hrs ok | |
| Delay between Primer and cure | 1/2 hr ok, 24 hrs bad | |

Care must be taken to insure adequate spray rinsing. Inspection for inadequate rinsing can be made with a micro pH meter or with litmus paper. The pH should be near 7 by placing wet litmus on the surface. Values of pH >8 indicates inadequate removal of NaOH and will result in poor hydrothermal durability.

Scale up studies of panels 30.48 cm × 30.38 cm (1 ft × 1 ft) processed in 13 liters of NaOH solution, bonded then cut up for wedge and lap shear tests, indicate even better results are obtained than for small coupons.

# VI. RECOMMENDATIONS

It is recommended that:

1. further research be completed as to the range of process parameters, such as, delay time between NaOH dip and rinse, time of rinse, types of drying (forced $N_2$ vs. air, drip dry etc.),
2. the trade off between NaOH concentrations, time of dip and temperature,
3. optimization with respect to other alloys,
4. optimization with respect to high temperature adhesives (polyimides),
5. scale up and optimization to factory facilities.

## VII. REFERENCES

1. T. Smith, J. Adhesion 9, 313 (1977).
2. T. Smith, Surface Science, 55, 601 (1976).
3. T. Smith, AFML-TR-74-73, Part II, Oct. 1975, p. 104.