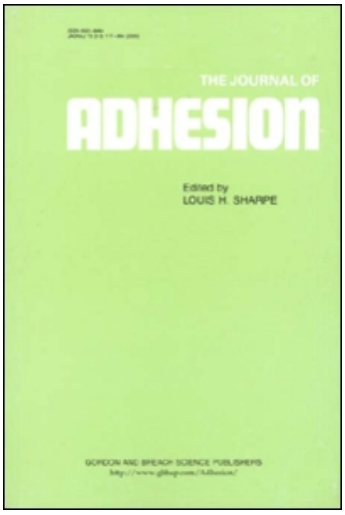

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NOTE

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INTRODUCTION

The standard FPL etch (sulfuric acid-dichromate) surface treatment of aluminum alloys for adhesive bonding has been found to suffer from bond degradation in humid atmospheres due to oxide (~200 Å thick) instability.[1] Bethune[1] reports a new preparation (phosphoric acid anodize) that reduces bond degradation by the formation of a thicker more stable hydroxide (~2000 Å). The FPL treatment involves at least five steps and the phosphoric acid treatment involves seven steps. Each step increases the cost and probability of improper preparation. In this note we will not attempt to review the vast amount of literature concerning the interaction of aluminum with water solutions but mention one of the more recent papers that is closely related to this work. Wegman *et al.*[2] found that a 30 minute tap water soak at 60°C produced strong adhesive joints that fail cohesively if the aluminum was first FPL etched. Joints made with samples that were tap water soaked after a degrease step alone were weak and failed about 85% interfacially. We have found that strong durable joints can be formed with only a degrease and tap water or carbonate soak (referred to as STAB) if these steps are properly performed. Wegman *et al.*[2] found that deionized water or deionized water plus monovalent compounds produce weak hydroxide films that cause interfacial failure. They also found that strong bonds were formed if aluminum was soaked in water solutions containing divalent ions if the aluminum had been FPL etched. Our results confirm this and show that the component in tap water responsible for the strong durable joints is the carbonate ion.

Without the carbonate ion, weak transparent hydroxide films are formed; with the carbonate ion strong, dark (light absorbing) films are formed.

This paper concerns our attempt to prepare aluminum surfaces that are equal to or better than the FPL etch or phosphoric acid anodize but with the minimum of processes steps. We have developed a two step process that appears to meet these criteria. The steps are simply: (a) proper degrease, and (b) proper tap water or carbonate soak. By proper degrease we mean complete removal of organic matter except for about a monolayer. We have found that degreasing in acetone, trichlorethylene, steam, etc. is not as good as degreasing in a solvent—"Gunk" solution. "Gunk" is a commercial trade name.[3] Our best results have been obtained by ultrasonic cleaning in a solution of one part Gunk in nine parts solvent. The only other requirements are that the tap water be near 80°C and that the water is swept past the aluminum part in a laminar flow. Laminar flow is not necessary for carbonate solutions. Contrary to other treatments, STAB leaves a uniform dark color so that improper treatment can be immediately determined by visual observation.

EXPERIMENTAL

The lap shear test was used to evaluate the static strength of bonds prepared after various pretreatments of the aluminum alloys. The wedge test was used to evaluate the bond durability. The durability test[1] involved placing the wedge joints in a humidity chamber at 120°F, 100% RH fro 24 hours. The samples were removed and split open to determine the crack growth. Two types of adhesives were used, an epoxy paste (EC–2214, 3M Co., St. Paul, Minn.) with no glass carrier and a film with glass carrier (FM73, Bloomingdale Div., American Cyanamid, Stamford, Conn.). Degreasing in acetone, trichlorethylene and one part Gunk to nine parts solvent have been used with and without ultrasonic agitation. After degreasing, the samples were placed in a Pyrex beaker of tap water that was stirred with a magnetic stirrer. The surface properties were monitored with respect to surface potential difference (SPD), photo electron emission (PEE), estimated hydroxide film thickness (from ellipsometry) and water contact angle (ϕH_2O). These instruments are described in Ref. 4.

RESULTS

Table I gives the number of samples (left column) that were used to average the surface properties. The alloy, surface treatments, average surface properties, and type of adhesive are given in Table I along with the average

joint strengths. The first set of samples (A1 2024–T3) in Table I were mated with adhesive to FPL etched samples, all of which had a water contact angle of less than 4°. The first set of six samples in Table I reveals the effect of water soak time and stirring on the surface properties. Without stirring, the hydroxide film increases about 20 Å per minute between 5 and 20 minutes. The SPD changes only slightly. Stirring the water decreases the film thickness, decreases the PEE and increases SPD and ϕH_2O. Stirring makes the film uniform over the sample if the flow is laminar. All of the six first samples in Table I were FPL etched prior to the water soak. The last two sets of samples in Table I show results of STAB for aluminum 2024–T3 and aluminum 7075–T6. The surface properties after the water soak but no prior FPL etch are essentially the same as for samples that were FPL etched prior to the soak.

The important result in Table I is that all water-soaked samples, with or without the FPL pretreatment, failed cohesively within the adhesive and with average bond strengths of the adhesive, i.e., $\sim$5000 psi, as are found for the standard FPL or phosphoric acid anodize processes.

Table II gives the surface properties and bond durability for various surface pretreatments as well as the two step degrease–water soak process. The crack growth for FPL etch plus an 80°C, 10 minute, stirred tap water soak is the same as for the phosphoric acid anodize, $\sim$0.12 inches/24 hours. The two step process, degrease–tap water soak, is slightly better than the FPL etch, $\sim$0.50 *vs.* 0.56 inches/24 hours, but not as good as the phosphoric acid anodize. The two step process, degrease–water soak in carbonate solution, approaches the anodize (i.e. 0.2 *vs.* 0.12 inches/24 hours). The water soak after degrease and alkaline clean yields a crack growth of $\sim$0.62 inches/24 hours. Alclad and bare aluminum 2024 with the two step process yield 0.4 ± 0.1 and 0.1 ± 0.05 inches/24 hours respectively. For comparison, the sample that was only degreased had a crack growth rate much greater than that for the others, $\sim$3 inches/24 hours. These crack growth rates can be compared with 0.1 to 0.3 inch in the first hour reported in Ref. 1 as acceptable rates. Our results are well within the 0.75 inches/hour criterion for acceptable preparations suggested in Ref. 1.

The principal mineral ingredient in our tap water is $CaCO_3$. We therefore added carbonates and bicarbonates to deionized water to see if carbonate caused dark films. Since carbonate produced dark films whereas chlorides and sulfates did not, it was concluded that the ingredient in tap water necessary for forming stable strong films is carbonate ion. Table III gives the dark film properties and bond crack growth. Adding K_2CO_3 to deionized water increased the pH to 9.8 and caused rapid reaction with aluminum at 80°C. Adding $NaHCO_3$ to deionized water to give a pH of 8.3 produced dark films with different properties, but cleavage of the wedge joints was cohesive in either case and the crack growth well within the 0.75 inches per

TABLE I

Surface properties and bond strengths for the two step degrease–water soak process

Number of samples	alloy	Treatment: Degrease	FPL	Water-soak Time min.	Water-soak Temp. °C	Properties: SPD (volts)	PEE amps × 10^{11}	Hydroxide film thickness Å	ϕH_2O deg.	Adhesive	Joint strength σ psi
1	2024–T3	Ultra	yes	5	90	0.2	48	580	5	3M–2214	4640
1		Sonic	yes	10	90	0.2	87	690	3	3M–2214	5380
1		Acetone	yes	15	90	0.2	65	750	3	3M–2214	5100
1			yes	20	90	0.3	76	850	4	3M–2214	4760
1	Stir last 10 minutes		yes	25	90	0.4	19	800	29	3M–2214	4800
1	Stir		yes	10	90	0.5	18	660	13	3M–2214	5400
6	2024–T3	Gunk 5 minutes	no	10	85	0.3±0.1	25±10	700±150	10±5	3M–2214	5000±500
6	7075–T6 Ultrasonic	Gunk 10 minutes	no	10	85	0.4±0.1	80±20	700±150	15±5	3M–2214	5000±500

TABLE II

Surface properties and bond durability for the two step degrease–tap water soak process

Number of samples	Alloy	Treatment				Properties				Adhesive	Crack growth inches/24 hr
		Degrease	FPL	Tap water soak Time	Temp.	SPD (volts)	PEE amps $\times 10^{11}$	Hydroxide film thickness Å	ϕH_2O deg.		
6	7075–T6	Phosphoric acid anodize				0.16±0.04	5±1	3500±300	0	FM73	0.12
1	7075–T6	Ultrasonic Gunk 10 minutes	yes	10	80	0.4	48	600	2	FM73	0.12
	7075–T6	Ultrasonic Gunk 10 minutes	no	10	80	0.2	240	700	8	FM73	0.50
1	7075–T6	Ultrasonic Gunk 10 minutes	yes	no		1.1	450	300	1	FM73	0.56
1	7075–T6	Ultrasonic Gunk 10 minutes	Alk clean	10	80	0.1	380	800	2	FM73	0.62
1	7075–T6	Ultrasonic Gunk 10 minutes	no	no		1.3	26	500	50	FM73	3.0
6	Al ClAD 2024–0	Ultrasonic Gunk 10 minutes	no	10	80	0.70±0.1	130±10	340±20	10±4	FM73	0.4±0.1
6	Al 2024–T3	Ultrasonic Gunk 10 minutes	no	10	77	0.22±0.02	6±2	900±50	30±10	3M–2214	0.10±0.05

first hour criterion. The ellipsometric results indicated a large absorption index as expected from the dark color but we have been unable to estimate a film thickness as yet.

TABLE III

Surface properties and bond durability for degrease $-CO_3^{=}$ in DI water soak

Number of samples	Alloy	Treatment: Degrease	FPL	Tap water soak: time	Tap water soak: temp.	Properties: SPD (volts)	Properties: PEE amps $\times 10^{11}$	Properties: ϕH_2O deg.	Adhesive	Crack growth inches/24 hr
						K_2CO_3 pH = 9.8				
6	7075-T6	Ultrasonic Gunk 10 minutes	no	10	80	0.94	2.5	10	FM73	0.2
						$Na\ HCO_3$ pH = 8.3				
4	7075-T6	Ultrasonic Gunk 10 minutes	no	10	80	0.55	5	10	FM73	0.4

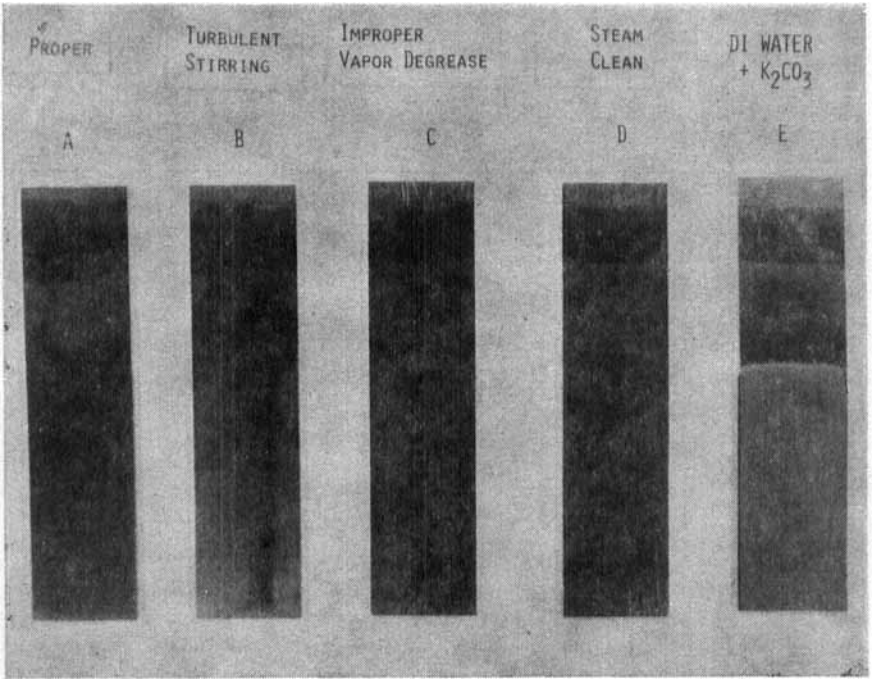

FIGURE 1 Photographs of proper A and improper B, C and D samples, STAB Process, DI Water + K_2CO_3 Sample E.

Figure 1 compares a properly prepared sample A by STAB with improperly prepared samples, B, C and D. Each sample was water soaked (bottom) in stirred tap water at 80°C for 10 minutes after the degrease treatment. Sample B shows the nonuniform film that results from turbulent stirring. Sample C shows fingerprints and patchy film that result from improper vapor degrease in trichlorethylene and sample D shows patchy film that results from steam cleaning prior to the water soak. Sample E was soaked in deionized water with K_2CO_3.

CONCLUSIONS

Although the results reported here are very limited, they indicate that a simple two step surface treatment process may be adequate for preparation of aluminum alloys for adhesive bonding. Comparison of the number of steps with other processes in Table IV indicates that STAB should be considerably less expensive and because of simplicity, more reliable than the

TABLE IV

Comparison of STAB process steps with the standard FPL and phosphoric acid anodize

FPL	Phosphoric Acid Anodize	STAB
VAPOR DEGREASE	DEGREASE	DEGREASE
↓	↓	↓
ALKALINE CLEAN	ALKALINE CLEAN	WATER SOAK
↓	↓	
RINSE	RINSE	
↓	↓	
FPL ETCH	DEOXIDIZE	
↓	↓	
RINSE	RINSE	
	↓	
	ANODIZE	
	↓	
	RINSE	

other processes. It has the advantage that the color allows an immediate visual check on the process. Nonuniform, streaky or patchy colored surfaces are not satisfactory. Fingerprints and improperly degreased areas are easily detected as seen in Figure 1. It is yet to be seen if scale up to factory facilities will introduce complexity not encountered in the small laboratory equipment.

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