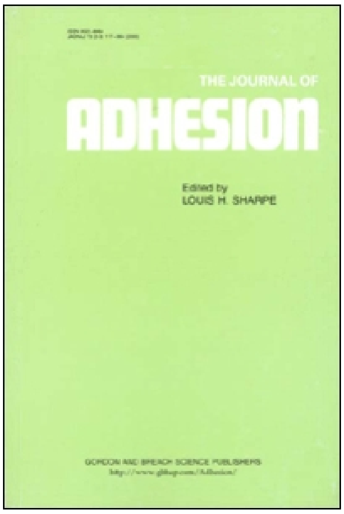

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NOTE

A Water Soluble Hydrated Metal Oxide Primer for Adhesively Bonded Joints†

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KEY WORDS Aluminum; titanium; inorganic primer; water solubility.

INTRODUCTION

Weight saving and manufacturing cost benefits have led to the increase in use of adhesively-bonded structures in the automotive, aerospace and marine industries. In order to be a viable alternative to, for example, metal fasteners, these adhesive bonds should maintain the strength typical of conventional fastener systems. In many applications, the bonds are put under a variety of environmental and mechanical stresses. For example, frequently these bonds are exposed over long periods of time to wet environments which can result in a loss of bond strength. The loss of strength can result from the extension of cracks and other deformations that occur in the adhesive or metal oxide which are accelerated by the moist environment. As a result of this deficiency, extensive research and development efforts have been undertaken to define methods and identify materials which improve bonded joint performance in humid conditions. For example, it is known that surface preparation is important in the bonding of aluminum and titanium, and cleanliness in the bonding of ceramic articles. Thus, it is essential that, before bonding, the adherend is cleaned and chemically pretreated to produce a surface which in combination with the adhesive develops the bond strengths which meet application requirements. The normal procedure after surface treatment is to apply a corrosion-inhibiting primer by a spray technique for surface protection prior to bonding and to insure resin penetration into the oxide structure which provides improved environmental resistance. A major drawback of spray application is the large volume of organic solvent

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(normally MEK) emitted to the atmosphere. A successful alternative is the recently-developed electrodeposited primer by Northrup Corp., which consists of water solubilized primer particles which migrate in an electric field to a conductive work piece where they are deposited in a dense, continuous coating.[1] The primer was developed for use with 121°C (250°F) curing epoxy adhesives. An Air Force sponsored contract is currently under way, the objective of which is to develop an electrodeposited water-based primer for use with 177°C (350°F) curing epoxy systems.[2] A water-based epoxy primer system for application using the more conventional spray techniques has also been described.[3]

An alternate approach to the use of standard resin-based organic primers is the inorganic primers generated from metal alkoxide.[4] Investigation has shown that an inorganic hydrated metal oxide primer provides an effective method for elimination of toxic, chromium-containing organic primers in adhesive bond preparation. Such inorganic primers are generated by application of an organic solution of a metal alkoxide to the surface treated metal adherends. Solvents such as toluene, tetrahydrofuran or butyl alcohol have been employed. Because of increased environmental considerations the thrust of current adhesive technology is to eliminate organic solvents by replacement with aqueous solutions or dispersions of organic adhesives and primers. This paper describes the effectiveness of a water-based inorganic primer system for the adhesive bonding of both aluminum and titanium adherends.

EXPERIMENTAL PROCEDURE

The 2024-T3 aluminum alloy was phosphoric acid anodized (PAA) at room temperature using 12% aqueous phosphoric acid at 10 v for 20 min. Methylethylketone cleaned titanium 6Al-4V alloy was grit blasted then treated with Pasa Jel 107 acid etch, from Smetco Corp, for 20 min. at room temperature. The inorganic primer was applied as a three percent by weight colloidal solution in water. The water was allowed to evaporate at room temperature after each coat followed by oven drying at 180°C with or without applied vacuum for 30 min.

Adhesive-bonded joints were prepared using commercial samples of scrim-supported Hysol EA-9649 and American Cyanamid FM-300, both 177°C curing epoxy adhesives. Wedge crack tests were carried out according to ASTM D-3672 at 71°C/95% relative humidity. Exposure times ranged up to 150 hrs. Crack lengths were measured under 20 × magnification in millimeters. Fluorescence examination of failed fracture surfaces was carried out using an Instrument Technology Inc. light source, model 125120. The water-based inorganic primer was synthesized in water using a modification of a previously reported method to produce a colloidal solution of approximately 9.5 weight percent of a hydrated polymeric aluminum oxide.[5] The composition of the primer has been designated as $Al_2(OH)_{6-y}X_y$ for identification purposes. X can be a number of different anions and y is a small number. Anions were chosen which, after primer application, could be eliminated by volatilization.

RESULTS

Aluminum adherends

Initial wedge crack tests were carried out on PAA-treated 2024-T3 aluminum adherends by water evaporation of one to three coats of the water-soluble hydrated aluminum oxide, followed by heat treatment at 180°C for 30 min. in an air circulating oven. The adherends were bonded with Hysol EA-9649 according to the manufacturer's instructions and tested. The crack propagation results are shown graphically in Figure 1. The initial crack length due to wedge insertion was nearly the same for the three coating thicknesses. One coat was estimated to be approximately 200 nm thick based on prior studies with metal alkoxides. With the elevated temperature drying of the inorganic primer there was a difference in performance, with the thicker primer providing crack resistance values nearly identical to those previously obtained with the organic-solvent-applied aluminum sec-butyl alkoxide. A comparison of the two systems is given in Table I.

To determine if the level of hydration of the primer had an effect on the performance of the bonded joint a second set of adherends was similarly treated and after primer application heated at 180°C under vacuum. The results of the wedge test, illustrated in Figure 2, showed that there was essentially no difference in performance between a 2 to 4 primer coating thickness with all specimens producing an average crack growth of 5–9 mm in the 148-hour exposure time period. These results indicated that there may be a hydration effect on primer performance and that use of vacuum drying probably removed the excess water which would be detrimental to formation of a strong bond. It was found that heating a neat sample of primer to 180–200°C under vacuum resulted in formation of a water-insoluble oxide. The optimum level of hydration and structure of the heat-treated primer has not been determined.

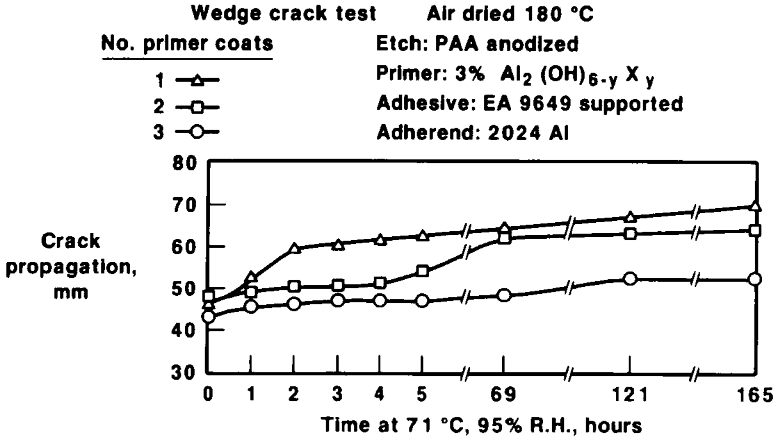

FIGURE 1 Effect of primer thickness and heat treatment on crack growth.

TABLE I
Comparison of water soluble and metal alkoxide inorganic primers on PAA aluminum

	Crack growth, mm	
Exposure time, hours[a]	Water soluble primer, 3 coats[b]	Metal alkoxide primer, 4 coats[b]
A_0 (wedge insertion)[c]	49.5	48.0
1	1.8	1.4
4	2.2	2.1
20	3.3	3.3
100	7.0	3.5
150	7.8	3.6
Total crack length:	57.3	51.6

[a] Wedge crack tests carried out at 71°C/95% RH.

[b] Adhesive—EA-9649; metal alkoxide applied from organic solution.

[c] A_0 = initial crack length.

The failure mode of the wedge crack specimens was examined using a microscope analysis. Visual examination initially indicated a mixture of adhesive and cohesive failure. However, further analysis of what appeared to be adhesive failure on the metal failure side, showed that a thin layer of adhesive remained on the surface of the primed adherend. The crack propagated from surface to surface leaving portions of adhesive on both adherends. The surface photographs shown in Figure 3 illustrate the character of the failed surfaces. Thus, the main fracture path occurred in the adhesive in what could be identified as an interphase region between the primer surface and the support scrim. The presence of the thin layer of adhesive was verified by exposure of the surface to ultra violet light. The adhesive was found to fluoresce under the lamp while the bare aluminum surface

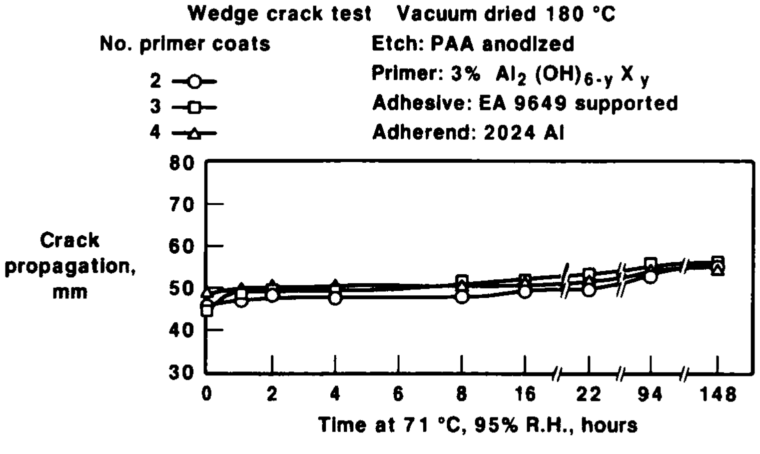

FIGURE 2 Effect of primer thickness and vacuum heat treatment on crack growth.

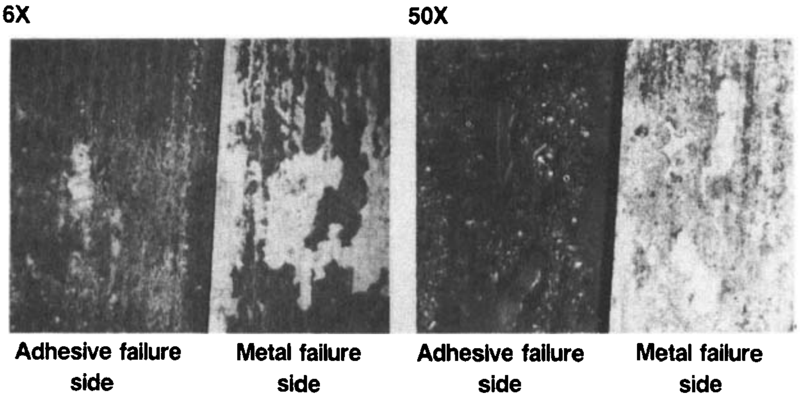

FIGURE 3 Fracture surfaces of EA-9649 bonded aluminum wedge crack specimens.

did not. Exposure of PAA, FPL and Pasa Jel treated metal adherends and inorganic primed surfaces did not result in a fluorescent response. With these types of adhesive systems this test appears to be a simple, inexpensive method of detecting the presence of resin on the metal surface.

Similar wedge crack tests were performed using PAA-treated aluminum 2024 bonded with FM-300 adhesive. As had been found using the aluminum alkoxide based inorganic primer, FM-300 gave a longer crack propagation than the Hysol EA-9649 adhesive. As previously reported under the same test conditions, metal alkoxide primed adherends gave a total crack growth of 64 mm and BR-127 organic primed adherends a growth of 74 mm.[4] The results with the water-soluble primer are tabulated in Table II.

There was minimum effect on crack growth due to primer thickness. The fracture surfaces of both the adhesive and metal failure side are shown in Figure 4. As found with the Hysol adhesive, a thin uniform layer of resin coated the metal failure side which indicated that the failure was cohesive and occurred in a

TABLE II
Crack growth of FM-300 bonded aluminum adherends[a]

		Crack growth, mm		
Exposure time, hours[b]	No. of primer coats:	2	3	4
A_0, (wedge insertion)[c]		47.7	45.8	47.3
1		7.0	6.6	6.3
20		20.4	18.5	17.3
100		21.0	20.8	18.6
150		22.0	21.0	18.7
Total crack length:		69.7	66.8	66.0

[a] PAA treated 2024 aluminum, water soluble primer.
[b] Wedge crack tests carried out at 71°C/95% RH.
[c] A_0 = initial crack length.

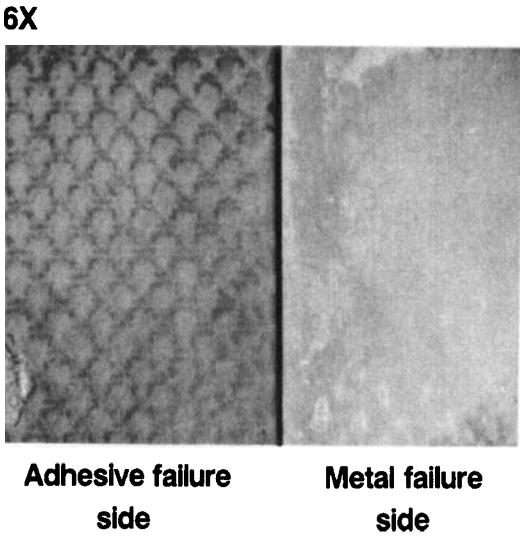

FIGURE 4 Fracture surfaces of FM-300 bonded aluminum wedge crack specimens.

thin layer adjacent to the primed surface. The crack, however, propagated only near one adherend in contrast to the Hysol EA-9649 fracture. The presence of the resin was verified using the fluorescence test as described above. Preliminary mechanical surface measurements estimated the thin layer was approximately 59 micrometers in depth. These results showed that good adhesion of resin to water soluble inorganic primed aluminum was obtained with both adhesives and the failure path in each case appeared to be governed by the characteristics of the interphase associated with the adhesive composition.

A schematic representation of the fracture mode difference between the two adhesives is shown in Figure 5. The results imply that FM-300 is a more brittle epoxy adhesive than EA-9649. The latter has aluminum powder filler and is rubber modified. FM-300 has no aluminum, a minimum amount of titanium

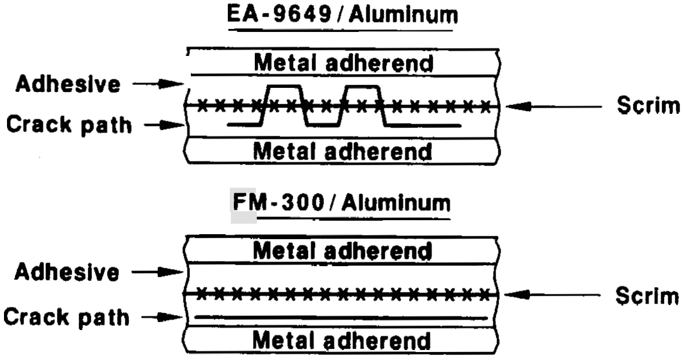

FIGURE 5 Failure mode of wedge test specimens.

oxide, and contains a brominated epoxy component and a rubber modifier. The effect of these compositional differences on the fracture mode remains unclear. Fracture toughness tests (G_{Ic}) on the two adhesives using the unsupported films must be carried out to verify the above hypothesis.

Titanium adherends

Wedge crack tests were carried out on Pasa Jel 107 etched titanium 6-4 adherends primed with two to four coats of water soluble inorganic primer. The primer was air dried at 180°C, 30 min. prior to bonding with Hysol EA-9649. The crack propagation results are shown graphically in Figure 6. The results indicated that the specimens with 3 or 4 coats of primer performed slightly better than the specimen which had 2 coats of primer. These results are similar to those previously obtained using sec-butyl aluminum alkoxide or tetrabutyl titanate as a primer for titanium.[6] A comparison of wedge crack test results of the bonded specimens using the organic solvent applied and water soluble primers is listed in Table III.

Even though acceptable crack growth rates were obtained it was found that the primary failure mode was 85% adhesive with the fracture path propagating through the inorganic primer or between the primer and metal oxide. Only small islands of adhesive were detected on the metal failure side by the fluorescence test. Surface analysis based on XPS must be carried out to identify the exact crack route.

The results using FM-300 adhesive were similar to those with EA-9649 with 98 percent adhesive failure on one adherend. Fluorescence analysis showed only minor traces of adhesive present on the metal failure side. The wedge crack test results are listed in Table IV.

These results again illustrate the effect that adhesive composition can have on the performance as well as the mode of failure on a bonded joint.

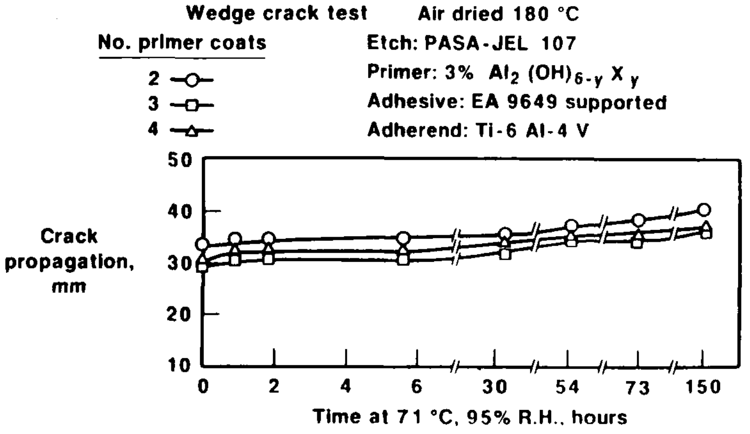

FIGURE 6 Effect of primer thickness on crack growth.

TABLE III
Comparison of water soluble and organic solvent applied metal alkoxide inorganic primers on Pasa Jel treated titanium

	Crack growth, mm.			
Exposure time, hours[a]	Water soluble primer[b]	Aluminum alkoxide[b]	Titanium alkoxide[b]	Hysol EA-9205[c]
A_0 (wedge insertion)[d]	30.0	31.0	32.0	57.0
4	1.7	2.3	1.7	57.0
20	2.8	2.7	2.2	57.0
100	5.0	4.9	3.8	57.0
160	7.0	6.7	4.9	57.0
Total crack length:	37.0	37.7	36.9	Stopped test

[a] Wedge crack tests carried out at 71°C/95% RH.
[b] Adhesive—Hysol EA-9649.
[c] Hysol EA-9205 primer.
[d] A_0 = initial crack length.

TABLE IV
Crack growth of FM-300 bonded titanium adherends[a]

		Crack Growth, mm.			
Exposure time, hours[b]	No. of primer coats:	0	2	3	4
A_0 (wedge insertion)[c]		51.0	28.3	28.1	29.1
1		—	1.6	2.6	2.2
6		3.7	5.9	4.2	4.2
30		5.2	12.0	9.4	9.1
75		—	12.8	12.0	13.2
150		7.1	12.8	12.6	14.1
Total Crack Length:		58.1	41.1	40.7	43.2

[a] Pasa Jel etched adherends; water soluble primer.
[b] Wedge crack tests carried out at 71°C/95% RH.
[c] A_0 = initial crack length.

CONCLUSIONS

It has been demonstrated that water based inorganic primer compositions present a viable approach to the elimination of both environmentally undesirable chromium normally present in organic primers and organic solvent from the adhesive bonding process. The scope and optimized processing parameters remain to be defined. The fracture path (failure mode) of an adhesive joint will be influenced to some extent by adhesive composition.

Acknowledgements

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References

1. G. T. Beckwith, and T. Pollard, Proc. 17th Nat. SAMPE Tech. Conf., Oct. 1985, p. 400.
2. R. H. Greer, Rohr Ind., WPAFB Contract F33615-86-R-5009, P. Tydings, Program Officer.
3. A. V. Pocius and T. H. Wilson, Jr., Proc. 19th SAMPE Internat. Tech. Conf., Oct. 1987, p.
4. R. A. Pike and F. P. Lamm, *Preprints, Am. Chem. Soc. Div. of Polymeric Materials,* Sci. & Engg. **56,** 299 (1987); R. A. Pike, F. P. Lamm, *Polymer Sci. and Technology* **37,** L. H. Lee, Ed. (Plenum Press, NY, 1988), p. 141.
5. A. W. Thomas and A. P. Tai, *J. Am. Chem. Soc.* **54,** 841 (1932).
6. R. A. Pike, F. P. Lamm, and J. P. Pinto, Proc. 5th Int. Joint Military/Government–Industry Sym. Picatinny Arsenal, Nov. 1987, p. 177.