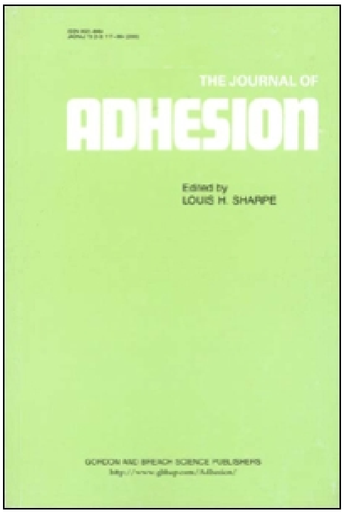

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Inorganic Adhesive Primers: Effect of Metal Surface Treatments

R. A. Pike[a]; F. P. Lamm[a]
[a] United Technologies Research Center, East Hartford, CT, U.S.A.

To cite this Article Pike, R. A. and Lamm, F. P.(1988) 'Inorganic Adhesive Primers: Effect of Metal Surface Treatments', The Journal of Adhesion, 26: 2, 171 — 179
To link to this Article: DOI: 10.1080/00218468808071284
URL: http://dx.doi.org/10.1080/00218468808071284

J. Adhesion, 1988, Vol. 26, pp. 171–179
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Inorganic Adhesive Primers: Effect of Metal Surface Treatments†

R. A. PIKE and F. P. LAMM

United Technologies Research Center, East Hartford, CT 06108, U.S.A.

(Received November 11, 1987; in final form April 18, 1988)

Wedge crack test results of adhesively bonded, inorganic primed, short time, room-temperature acid-treated aluminum surfaces have demonstrated the feasibility of this approach in field repair of bonded structures. The required thickness of inorganic primer has been shown to be directly related to the metal adherend oxide structure. Satisfactory long term inorganic primer storage stability has been demonstrated.

KEY WORDS Aluminum; metal surface treatments; inorganic primer; primer thickness; primer stability; oxide structure.

INTRODUCTION

The use of inorganic primers in adhesively bonded joints offers an alternate approach to standard resin-based primers or coupling agents for improving the environmental resistance of bonded structures. The inorganic primers investigated to data, formed by hydrolysis of metal alkoxides on acid-etched (FPL) or anodized (PAA) aluminum adherends, are equally effective after room or elevated temperature conversion to the hydrated oxide form.[1] Surface analysis suggests that the resulting primer is a stable form of an amorphous Boehmite $[Al(O)OH]_x$ which can form on exposure of the alkoxide to limited amounts of moisture.[2,3]

† Presented at the International Conference "Adhesion '87" of the Plastics and Rubber Institute held at York University, England, September 7–9, 1987.

The effect of inorganic primer with PAA- and FPL-treated aluminum bonded with 121°C and 177°C curing adhesives was previously found to produce improved crack resistance compared with organic primed controls.[1,4] Unexpectedly, it was discovered that with the inorganic primer generated from the aluminum alkoxide the crack propagation resistance of both FPL-treated and PAA surfaces was essentially the same with both types of adhesives; the difference normally associated with the two surface treatments using organic primers was negated by application of the amorphous alumina primer.

In order to ascertain the potential application of the inorganic primer concept for use in field repair applications the effectiveness of an inorganic primer on aluminum surfaces treated with room temperature acid systems has now been determined. In addition, results of bonded joint tests using aged inorganic primed adherends and the effect of primer thickness as it relates to oxide thickness produced by different surface treatments are presented.

EXPERIMENTAL PROCEDURE

The 2024-T3 aluminum alloy was phosphoric acid anodized (PAA) at room temperature using 12% aqueous phosphoric acid at either 8 v for 25 min. or 10 v for 20 min., or treated by FPL acid etch at room temperature using the standard sodium dichromate-sulfuric acid formulation. Pasa Jel 101 acid etch from Smetco Corp. was applied to the aluminum adherends for 5 min. at room temperature. Chromic acid anodization (CAA) was carried out using standard procedures per MIL-A-8625. The inorganic primer was formed by applying a one percent toluene solution of sec-butyl aluminum alkoxide from Stauffer Chemical Co. (E-8385) to the treated surfaces. The alkoxide was converted to oxide primer by solvent evaporation at room temperature followed by heating at 75°C in air. American Cyanamid BR-127 epoxy primer was used for control samples.

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. Reliabond 398 epoxy adhesive was used by Northrup Corporation. Wedge crack tests were carried out according to ASTM D-3762 at 71°C/95% relative humidity. Exposure times ranged up to 250 hrs. Crack lengths were measured under 20X magnification in millimeters. Tensile lap shear specimens prepared by Northrup Corp. were 1.27 cm overlap, 12.7 cm long, 2.54 cm wide and 0.635 cm in thickness.

RESULTS

Room Temperature Adherend Surface Treatments

Wedge crack tests on 2024 aluminum using an acid etch system, SmutGo, which reportedly leaves a very smooth oxide layer on the surface have been carried out by workers at Martin–Marietta.[5] These workers found that there was a substantial improvement in the crack resistance of FM-300 bonded specimens using the inorganic alumina primer compared to BR-127 organic primer as shown in Figure 1. For example, the organic-primed specimens completely failed in 2 hours compared to the inorganic primer which showed a crack growth of 2.7 cm in 200 hours. In addition, the initial crack length produced by wedge insertion was 2.2 cm less for the inorganic primed test group, indicating that the aluminum surface was not completely wetted by organic primer. A marked improvement in reproducibility of crack propagation in the bonded joint also resulted with the use of the inorganic primer.

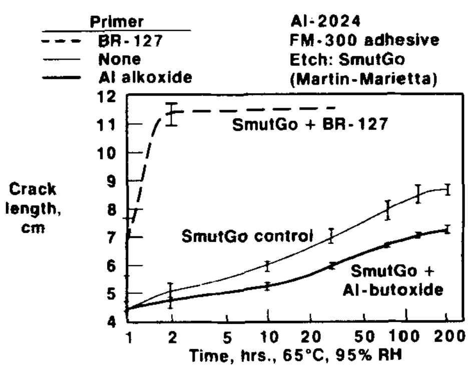

FIGURE 1 Effect of RT acid etch on crack growth.

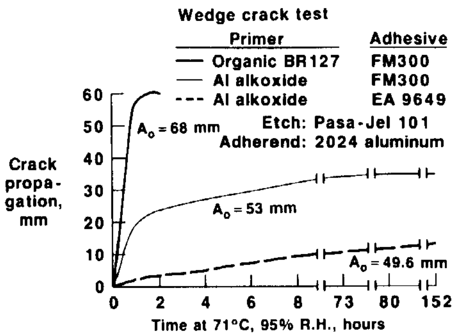

FIGURE 2 Effect of non-chromate etch on crack growth.

Similar results on 2024 aluminum have been obtained in our laboratories (UTRC) using the Pasa Jel 101 acid etch system which contains no chromic acid. The inorganic primer showed marked improvement over BR-127 primed control specimens, particularly with EA-9649 adhesive, as illustrated in Figure 2. The difference in the response of EA-9649 and FM-300 on inorganic primed PAA and standard FPL treated 2024 aluminum has been previously noted.[6]

FM-300 is the only adhesive tested to date using the treatment which gave larger crack growth for the inorganic primed surfaces compared to organic primed systems. With FPL treated 2024 aluminum, UTRC results showed the inorganic primer to be better than organic primed, in contrast to Martin–Marietta tests which showed that organic-primed 2024 was superior.[5]

Preliminary investigation indicates that the difference in adhesive composition, particularly the rubber content and filler type, may be responsible for the inferior performance of the FM-300 on inorganic primed surfaces. Visual inspection of the fractured joints showed that the EA-9649 failed 95 percent cohesively while the FM-300 exhibited only 25 percent cohesive failure.

It was also demonstrated that a five-minute application of FPL etch at RT was an effective surface treatment when combined with the inorganic primer as illustrated in Figure 3. Normally, FPL etching is carried out at 70°C for 10–15 minutes.[7] Thus, short-time, room-temperature acid etching, essential for field repair situations,

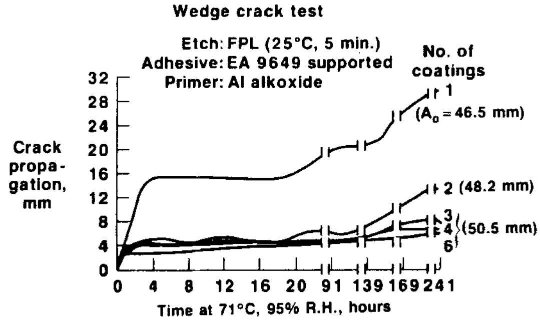

FIGURE 3 Effect of primer thickness and RT FPL etch on crack growth.

can be used to obtain a high level of environmental resistance in bonded joints when combined with the inorganic primer.

Effect of Primer Thickness

It is well known that organic primers are used at a preferred thickness, generally on the order of 0.2–0.4 mil ($\sim 5 - 10 + 10^3$ nm). To determine if there was a thickness effect with the inorganic primer, related to crack propagation, a series of three wedge crack tests were run with PAA-, FPL- and CAA-treated 2024 aluminum bonded with Hysol EA-9649 adhesive. A summary of the surface characteristics resulting from each surface treatment is listed in Table I.

It had been established that at the one percent concentration used, one coat of the aluminum alkoxide resulted in approximately 150 nm of primer thickness.[4] The results for the first two surface

TABLE I
Aluminum surface treatments: effect on oxide structure[a]

	FPL	PAA	CAA
Oxide height, nm	~5	~300	~1500
Cell width, nm	~40	~40	~40
Protrusion height, nm	~40	~100	has profile of
Protrusion width, nm	~5	~10	metal surface

[a] Data taken from J. D. Venables *et al.*[8]

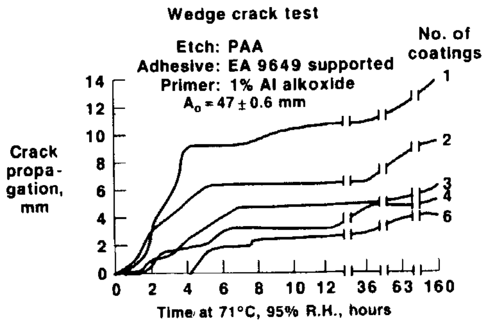

FIGURE 4 Effect of primer thickness on crack growth of PAA treated aluminum.

treatments are shown in Figures 3 and 4 for specimens exposed to temperature and humidity for over 160 hours. With the PAA-treated surface bonded with EA-9649, it was apparent that coatings made with a thickness greater than 450 nm (3 coats) were superior to thinner coatings and that after 6–7 hours exposure, very little additional cracking occurred; failure was cohesive within the bondline. With three to six coats of the primer an induction period of 2–4 hours occurred before the crack propagated. The one- and two-coat primed specimens exhibited some degree of adhesive failure. The FPL-treated surface bonded with the same adhesive indicated that two coats of the inorganic primer, ~300 nm, was sufficient to produce a low level of crack propagation with all cohesive failure. The CAA-surface treated aluminum was found to exhibit no substantial difference between the organic primed surface and one coating of the inorganic primer. Up to four coats gave the same low 3–4 mm crack extension in 172 hours, as illustrated by the data in Table II. The organic-primed specimen and one with no primer produced joints which had essentially the same crack resistance as the inorganic coated adherends.

Thus, it appears that the effectiveness of the inorganic primer is directly related to the degree of oxide porosity and the depth of the porous oxide layer resulting from each of the three surface treatments. As has been reported[7] these factors decrease in terms of surface treatment PAA > FPL > CAA. The latter treatment produces a thick, dense oxide (low porosity) having no oxide protrusions.

TABLE II
Effect of primer thickness on crack growth

Etch: CAA	Adhesive: EA-9649 supported					
Primer:	1% Al alkoxide				BR-127	None
No. of coats	1	2	3	4	—	—
A_0, mm[a]	47.5	49.0	51.0	48.0	50.2	52.0
Crack growth[b] after 172 hours, mm	3.2	3.7	3.9	4.1	5.0	4.3

[a] A_0 = initial crack length of wedge insertion.
[b] Test at 71°C, 95% R.H.

Effect of Inorganic Primer Aging

The ability of any primer system to be protective and usable over an extended time period after application is one of the primary reasons for using a primer, since it acts as a protective coating for the activated metal oxide surface. In actual practice it is not unusual for treated and primed metal surfaces to be placed in storage for up to two years prior to bonding. To determine the effect of aging on inorganic-primed, PAA-treated 2024 aluminum, wedge crack tests were performed over a period of a year after initial primer application. The specimens were bonded initially and after 5-month and one-year exposure to atmospheric conditions, using EA-9649 adhesive. In each instance, the same low level (~5 mm) of crack extension in 178 hours at 71°C/95% RH was obtained with failure within the adhesive bondline. Thus, the inorganic primer demonstrated adequate stability under laboratory atmosphere exposure. The test data are listed in Table III.

Samples of PAA-treated 2024 aluminum specimens primed with the inorganic primer were also shipped from UTRC to Northrup Corp. for bonding and testing.[9] Northrup compared the UTRC inorganic-primed specimens with Northrup-primed BR-127 organic primer using Reliabond 398 film adhesive. The tensile lap shear test results are listed in Table IV.

As shown, the inorganic primer provided improved room temperature strength retention after a 50-hour soak at 177°C. In contrast, the organic-primed samples lost all strength after the heat treatments.

TABLE III
Effect of inorganic primer aging on crack propagation

	Initial crack length, mm[a]	Increase in crack length, mm	Test time, hours[b]
As fabricated	47	5.4	122
Five months aging[c]	44	4.8	172
Twelve months aging[c]	46	5.1	176

[a] Crack length A_0 resulting from wedge insertion.
[b] At 71°C/95% RH, 2024 aluminum adherends, PAA treated, EA9649 adhesive.
[c] At RT-uncovered.

These results reflect not only the room temperature stability of the inorganic-primed surfaces but indicate the level of thermal stability which can be achieved with inorganic-primed bonded structures relative to the organic primers.

TABLE IV
Aluminum lap shear strengths of inorganic and BR-127 primers with Reliabond 398 adhesive[a]

Primer	Lap Shear Strength MPa(psi) RT[d]	177°C[d]
As-Fabricated		
Inorganic[b]	33.9 (4920 ± 275)	17.9 (2600 ± 50)
BR-127[c]	23.4 (3400 ± 240)	primer failure
After 50 hours aging at 177°C:		
Inorganic	26.6 (3860 ± 250)	19.7 (2860 ± 150)
BR-127	Too weak to test	

[a] 2024-T3, PAA anodized 20 min. at 10V (UTRC).
[b] Aluminum alkoxide applied from 1% toluene solution heated at 85°C for 20 minutes.
[c] BR-127 primer spray applied (0.2 mils) at Northrup and cured at 121°C for 30 minutes.
[d] Each test an average of 4–8 specimens.

CONCLUSIONS

Based on previous results and the work reported herein, the following factors appear to influence the performance of inorganic primers:

- inorganic primer effectiveness is independent of conversion temperature
- Required thickness of inorganic primer is controlled by oxide surface structure
- Adhesive composition affects inorganic primer-adhesive interaction
- RT aging of primer coating does not affect performance

Acknowledgements

The technical assistance of R. W. Girouard and J. P. Pinto and the willingness of H. Clearfield of Martin Marietta and G. Beckwith of Northrup Corp. to share their results pertaining to testing of the inorganic primer concept and the supply of metal alkoxides by Mr. Kelly Triplett of Stauffer Chemical Co. is gratefully acknowledged.

References

1. R. A. Pike, *Int J. of Adhesion and Adhesives* **6,** 21 (1986).
2. B. E. Yoldas, *J. Am. Ceramic Soc.* **65,** 387 (1982).
3. D. G. Altenpohl, *Corrosion* **18,** 143 (1962).
4. R. A. Pike, *Int. J. Adhesion and Adhesives* **5,** 3 (1985).
5. H. Clearfield, *Martin Marietta,* private communication: J. S. Ahearn and G. D. Davis, *Plastic and Rubber Inst., Proc. of 3rd International Conf. "Adhesion* '87", York Univ., (Sept. 1987), p. 29.
6. R. A. Pike, *Proc. of 5th Ann. Program Review/Workshop,* Virginia Tech. Center for Adhesion Science (May 1987), p. 75.
7. A. V. Pocius, in *Adhesion Aspects of Polymeric Coatings,* K. L. Mittal, Ed. (Plenum Press, NY, 1983), p. 173.
8. J. D. Venables, *et al. Appl. Surface Sci.* **3,** 88 (1979).
9. G. T. Beckwith, *Northrup Corporation,* private communication.