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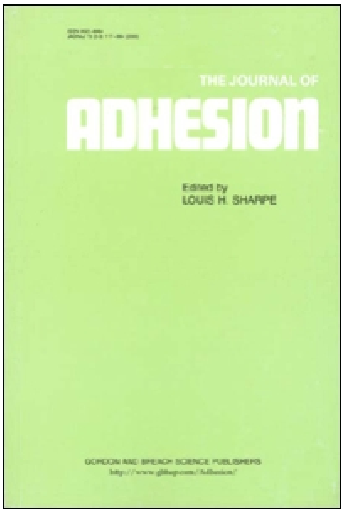

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Improved Durability of Aluminum Adhesive Bonds with Phosphonic Acid Inhibitors

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In this paper, we review our work on the use of hydration inhibitors to improve the durability of adhesively-bonded aluminum structures. Treatment of adherends given the Forest Products Laboratory (FPL) surface preparation in a solution of nitrilotris methylene phosphonic acid (NTMP) increases bond durability so that hydration of the adherend is no longer the limiting factor on crack propagation. In bonds with phosphoric-acid-anodized (PAA) adherends treated with NTMP, the transition to failure in the adhesive occurs at a shorter crack length. The initial strength of epoxy adhesive bonds is not changed by such pretreatments. Adsorption of NTMP onto FPL surfaces displaces the water initially present and forms P–O–Al bonds. Saturation coverage is approximately one monolayer. NTMP adsorbed onto PAA surfaces, which have little initial water, occupies residual active sites. Hydration of a PAA surface or an inhibited FPL surface proceeds in three steps: 1) reversible physisorption of water, 2) slow dissolution of the inhibitor-aluminum complex followed by rapid transformation of the freshly-exposed amorphous aluminum oxide to boehmite, and 3) formation of bayerite on the surface. We have identified several important criteria for inhibitors designed to improve bond durability; i.e. they should 1) displace water and occupy all active sites on the Al_2O_3 surface, 2) form strong inhibitor-surface bonds, 3) form a water-insoluble complex with aluminum, 4) be chemically compatible with the adhesive or primer, and 5) couple chemically or mechanically to the adhesive.

I INTRODUCTION

The performance of an adhesively-bonded structure is judged both by the initial strength and the long-term durability of the bond. Both of these properties depend critically on the physical and chemical interactions of the adhesive (and/or primer) with an adherend. Two mechanisms of adhesion are prominent in structural adhesive bonding: mechanically interlocking of the polymer with a microscopically-rough adherend surface and chemical bonding of the adhesive to adherend oxide.[1–3] The relative importance of the mechanisms depends greatly on the morphology and chemistry of the adherend surface and on the rheology and chemistry of the adhesive. It also depends on the environment seen by the bond and the conditions used to evaluate or define bond performance.

When an aluminum-epoxy bond is exposed to hot, humid conditions, the chemical bonds between the oxide and polymer are readily disrupted.[4] If the oxide is smooth so that bond strength is governed solely by chemical forces, the bond will fail. If the oxide is microscopically rough, such as those of commercial aerospace bonding processes,[5,6] the physically-interlocking composite interface[7–9] can maintain the initial high bond strength. In this case, a crack propagates only if the interlocking is destroyed by degradation of the oxide or if the adhesive itself fails. It has been shown that crack propagation during exposure to high humidity occurs as the aluminum oxide hydrates to the oxyhydroxide, boehmite, resulting in failure at the boehmite-metal interface.[4,10]

Oxide hydration can be slowed and, consequently, bond durability can be increased by reducing the amount of water present at the bondline[11] or by using inhibitors that act to stabilize the adherend surfaces against hydration and also to form chemical bonds with the adhesive,[8,12–19] In this paper, we concentrate on the use of one particular family of hydration inhibitors—amino phosphonates—which have proven very effective in improving bond performance. In particular, we review investigations of: 1) the surface chemistry of Forest Products Laboratory (FPL)-etched adherends and phosphoric-acid-anodized (PAA) adherends during adsorption of various hydration inhibitors, such as nitrilotris methylene phosphonic acid (NTMP); 2) the mechanism by which the treated PAA and FPL surfaces eventually hydrate; 3) the mechanism of crack propagation in a moist environment for treated and untreated FPL- and PAA-prepared structures; 4) the relative effectiveness of several related inhibitors in improving durability of FPL bonds; and 5) the effect of these inhibitors on the initial bond strength. The intent of the review is to synthesize a fuller understanding of the mechanism controlling hydration inhibition and bond durability using both published and unpublished results, mostly from our Laboratories, than is possible from the individual publications.

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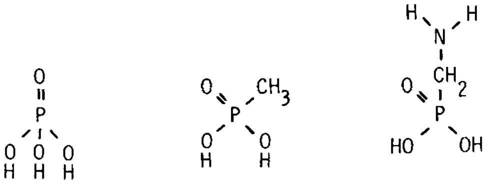
II EXPERIMENTAL

To achieve the results that we report in this review, we have used an interdisciplinary, multitechnique approach. We have used X-ray photoelectron spectroscopy (XPS), supplemented by Auger Electron Spectroscopy (AES), to examine the surface chemistry of the adherends. To analyze these data, we developed surface behavior diagrams (SBD's)[19,20] which provide a means to display graphically the XPS compositional data. They have proven invaluable in the study of these and other surface and interfacial reactions.[20] The high resolution microscopy needed to resolve the morphology of the adherend surfaces was achieved using a scanning transmission electron microscope in the scanning mode (X-SEM).[7] Charge dissipation was accomplished by sputtering a very thin coating of platinum to avoid masking the fine morphological features of the surface.

Mechanical testing was performed using T-peel specimens (ASTM D-1876) for initial strength measurements and wedge tests to determine the durability of bonded structures. The wedge test (ASTM D-3762) provides a severe test of a bonded structure by exposing the crack tip to moisture while it is under stress. To provide a stringent test for the bonded surfaces, we used a water-wicking adhesive (American Cyanamid FM-123-2) without a corrosion-inhibiting primer.

III INHIBITOR SELECTION

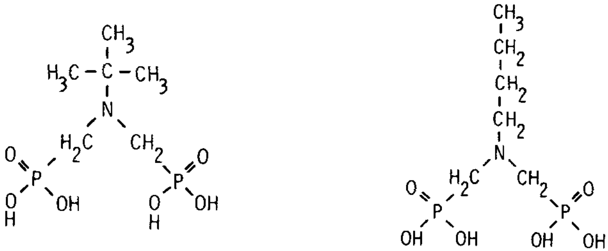
We were particularly interested in investigating the effects on bond strengths of stabilization of the oxide against moisture attack *versus* chemical coupling between the inhibitor and the adhesive. Therefore, we selected a number of compounds to produce one or the other effect[13] (Figure 1). NTMP served as a compound that both adsorbs onto the Al-oxide surface and chemically bonds to the adhesive. Adsorption of phosphoric acid (PA) onto FPL surfaces provided a



Phosphoric Acid[a] [PA]

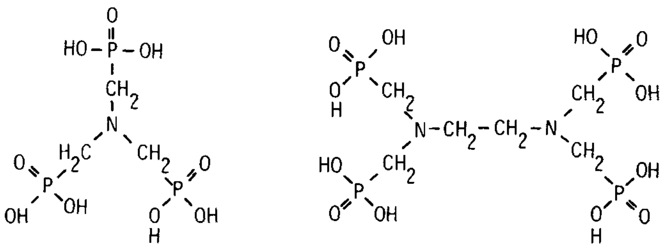
Methylene Phosphonic Acid[a] [MP]

Amino Methylene Phosphonic Acid[a] [AMP]



(t Butyl) Nitrilobis Methylene Phosphonic Acid[b] [(t Bu) NBMP]

(n Butyl) Nitrilobis Methylene Phosphonic Acid[b] [(n Bu) NBMP]



Nitrilotris Methylene Phosphonic Acid[a] [NTMP]

Ethylene Diamine Tetramethylene Phosphonic Acid[b] [EDTMP]

FIGURE 1 Inhibitors tested: a) compounds commercially available, and b) compounds synthesized (from Ref. 16).

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chemical approximation to the PAA surface without its more evolved oxide morphology.[7] Methylene phosphonic acid (MP) and amino methylene phosphonic acid (AMP) were specific portions of the NTMP molecule that represent a chemical bonding/inert pair, thus allowing us to understand better the contribution to bond durability of coupling to the adhesive. The two (butyl) nitrilobis methylene phosphonic acid isomers [(*n* Bu)NBMP and (*t* Bu)NBMP], each with two phosphonic acid groups, were selected for similar features. The first exposes an extended hydrophobic hydrocarbon chain for possible micro-mechanical interlocking with the adhesive, while the second exposes a compact hydrocarbon cluster which should be chemically and mechanically inert. Ethylene diamine tetramethylene phosphonic acid (EDTMP) provides additional phosphonic acid bonding groups (POH) to the aluminum oxide surface.

IV SURFACE CHEMISTRY

A. Inhibitor adsorption

1 *Surfaces produced by Forest Products Laboratory Etch* The dependence of the surface coverage and composition on solution concentration at ambient temperature is shown in the adsorption isotherm[12,14] (Figure 2) and in the Al_2O_3–NTMP–H_2O SBD (Figure 3).[15,16,20] The approximately horizontal portion of the curve above ~10 ppm corresponds to the saturation coverage P/Al ~ 0.15 (~1 molecular layer). Saturation coverage was obtained in a short immersion time on FPL

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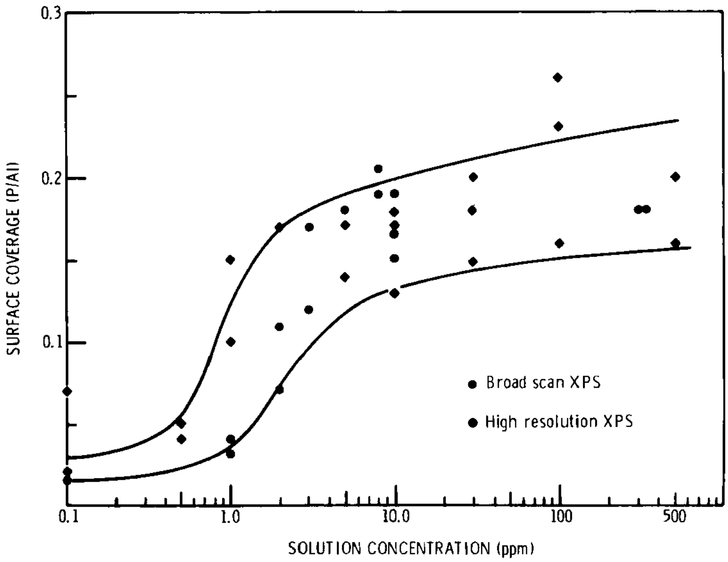

FIGURE 2 Surface coverage of NTMP-treated FPL oxide surface (P/Al) as a function of NTMP solution concentration (from Ref. 14).

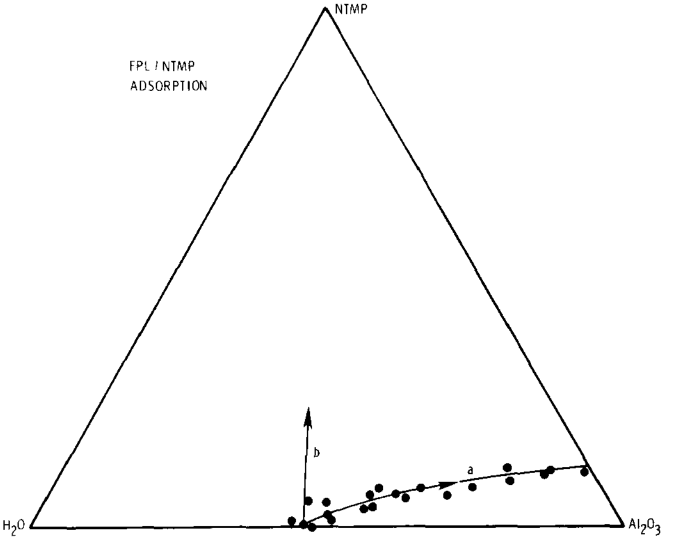

FIGURE 3 Al_2O-NTMP-H_2O SBD showing a) FPL-etched surface compositions after 30-min immersion in aqueous solutions of NTMP at concentrations ranging from 0.1 to 500 ppm (solution concentration increases from left to right); and b) the path representing no displacement of water (from Ref. 15, 16).

surfaces—no change in the coverage was seen following immersions of 5 s or greater.[16] In contrast, at 80°C, multiple inhibitor layers formed.[12]

The Al_2O_3–NTMP–H_2O SBD indicates that the adsorption process at room temperature can be described as the displacement by NTMP of water or hydroxyl groups initially bound to the aluminum oxide surface. This occurs with the formation of P–O–Al bonds, which were detected by Fourier transform infrared (FTIR) spectroscopy measurements on NTMP and an Al-NTMP complex.[16] Similar studies of phosphonic acid adsorbed on oxidized aluminum using inelastic electron tunneling spectroscopy (IETS) also showed that adsorption occurs *via* condensation and dehydration reactions.[21] Their analysis indicated a resonance between the phosphoryl and hydroxyl oxygens and the formation of ionic P–O–Al bonds to the surface.

Some differences were noted between NTMP and AMP adsorption behavior, as reflected in the evolutionary paths in the A–P–O elemental SDB (Figure 4). These will be discussed below.

2 *Phosphoric-acid-anodized surfaces* The inhibitor surface coverage on PAA oxide surfaces saturated at solution concentrations above 10 ppm (Figure 5) was much like that on FPL oxide surfaces.[17] Even though the P/Al ratio of the untreated PAA oxide was 0.1, P/Al ratios were 0.15–0.20 for both oxides following saturation treatment at room temperature. However, the adsorption path of NTMP on FPL and PAA oxides differed markedly, as illustrated by the SBD of Figure 6.[15] Because the initial PAA surface consists of the equivalent of

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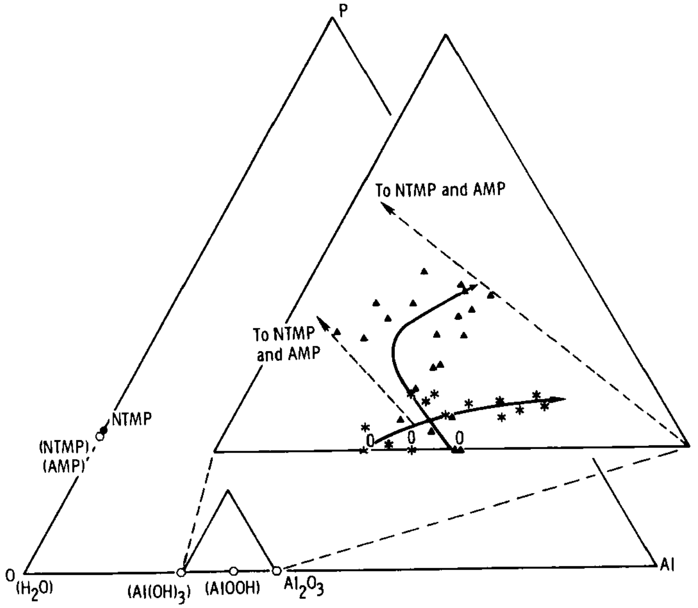

FIGURE 4 Al-P-O SBD of FPL-etched surface compositions after immersion in solutions of NTMP (triangles) or AMP (stars) at various concentrations. Open hexagons are calculated compositions. Compositions denoted by "O" represent surfaces not immersed in NTMP solutions (from Ref. 16).

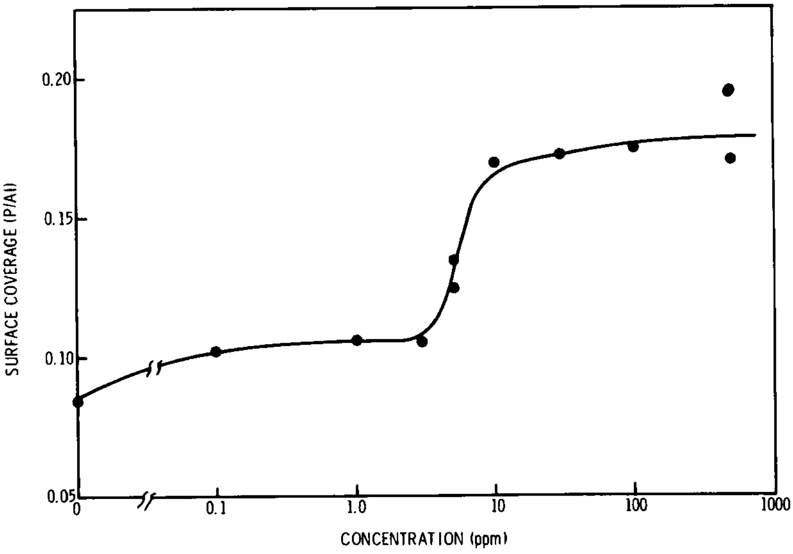

FIGURE 5 Surface coverage of NTMP-treated PAA oxide surfaces (P/Al) as a function of NTMP solution concentration (from Ref. 17).

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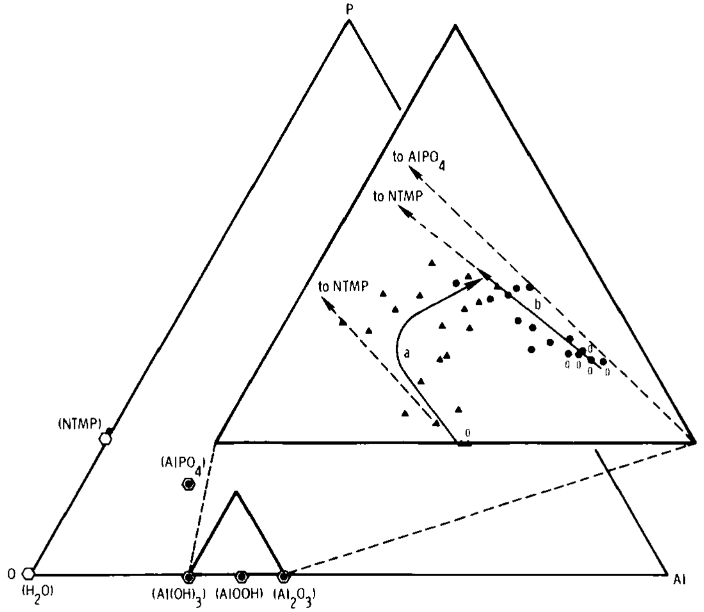

FIGURE 6 Al-P-O SBD showing the surface composition of FPL-etched surfaces (triangles) and PAA-treated surface (circles) after immersion in various concentrations of NTMP solution. Open hexagons are calculated compositions. Closed symbols are measured compositions. Compositions denoted by "O" represents surfaces not immersed in NTMP solutions (from Ref. 15).

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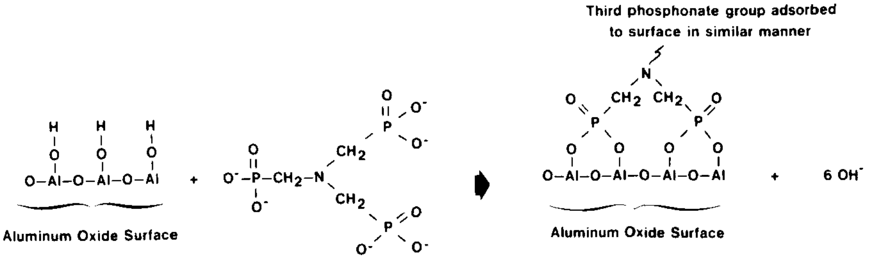
a monolayer of phosphate on top of Al_2O_3, with very little adsorbed water (assuming an electron attenuation length of ~16 Å),[22] adsorption is a simple addition reaction, with the PAA surface composition evolving along a line drawn to the NTMP composition point.

At 80°C, multilayer surface coverages were observed similar to the FPL case. For example, at a solution concentration of 300 ppm, the P/Al ratio for both FPL and PAA oxides ranged from 0.4–0.5.

3 *Discussion* The adsorption of each amino phosphonate inhibitor onto FPL surfaces proceeds by the displacement of adsorbed water on the surface. For NTMP, this reaction continues at room temperature until most, if not all, of the water is replaced by approximately one monolayer of chemisorbed inhibitor. However, AMP displaces water less efficiently, so that some water remains even at the highest AMP coverages achieved at room temperature.[16] The presence of residual water is reflected in the lower phosphorus content on the surface at saturation. The adsorption model (Figure 7) suggests that one phosphorus atom is added for every two water molecules removed from the surface (assuming that all the inhibitor's POH groups bond to the Al_2O_3). Since the AMP-treated surface has a significantly lower P/Al ratio, less water would be displaced from the surface. Recent results of Zanzucchi and Thomas[23] using NTMP as corrosion



MODEL FOR ADSORPTION OF NTMP ON Al_2O_3

FIGURE 7 Schematic model for the adsorption of NTMP onto an Al_2O_3 surface. Possible resonances between the POH and P=O bonds are not shown.

inhibitors for thin Al films are consistent with this model. Using infrared spectroscopy and XPS they found, for NTMP-treated surfaces, a surface aluminum-phosphonate formed by chemical bonding between Al and the phosphorus-oxygen functional group, as we have previously suggested (Figure 7).

The data for NTMP on FPL oxides (Figure 3) show the adsorption isotherm to be concave downward, which is indicative of a two-step adsorption process.[16] This is more clearly illustrated in Figure 4, where the isotherm proceeds first in the direction of NTMP, and then away from the H_2O vertex. These results suggest that at very low solution concentrations, only one of NTMP's $PO_3^=$ moieties bonds to the surface. Consequently, the inhibitor coverage, as determined by the amount of P on the surface, increases faster than the water concentration on the surface decreases. At higher concentrations, the NTMP competes more successfully with water for adsorption sites, and the other $PO_3^=$ moieties of the molecule bond to the surface, displacing additional water without increasing the inhibitor coverage.

In contrast, a single-step process is expected for AMP, since it has only one phosphonic acid group per molecule. The SBD shown in Figure 4 supports this hypothesis; it clearly shows only a slight curvature in the surface composition evolutionary path for AMP on FPL, as opposed to the concave isotherm characteristic of NTMP adsorption.

The adsorption of NTMP on PAA surfaces (Figure 6) is quite different because little initial water is present.[15] The resulting evolution of the surface composition suggests a simpler direct adsorption process. Nonetheless, the saturation coverage by phosphorus-containing groups is very similar to that of NTMP on FPL. Although these data alone do not allow us to differentiate between NTMP adsorption on unoccupied active sites only and the NTMP displacement of the phosphate incorporated onto the surface during anodization, we can make such a determination by comparing the ratio of typical N concentrations on the NTMP/PAA and the NTMP/FPL surfaces (~1.5% and ~2.5–3.0%, respectively) to the corresponding ratio of additional P(~1:2, Figure 5). This analysis

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shows that the two ratios are equal, thus eliminating the possibility of a significant displacement of the original phosphate, i.e., NTMP adsorbs only on unoccupied active sites. Regardless of the details of the adsorption process, however, NTMP stabilizes the Al_2O_3 surface against hydration.

B Surface hydration

1 *PAA and FPL surfaces* The change in the surface composition of PAA adherends as a function of time at 80°C and 95–100% RH is shown in the $AlPO_4$–Al_2O_3–H_2O SBD of Figure 8.[19] Auger sputter-depth profiles of samples before and after hydration are shown in Figure 9. An upper limit of 20% of the phosphorus originally present in the oxide was detected after hydration.

The SBD shows hydration to be a three-step process (Figure 8).[19] The first step (line I) is the adsorption of water and can occur prior to exposure to high humidity and temperature. This adsorption involves no change in the oxide mophology and is reversible, as evidenced by points *b* and *b'*, which correspond to the same sample before and after exposure to a dehydrating ultrahigh-vacuum environment for several days. More extensive hydration occurs once the sample is placed in the humidity chamber (line II). At this point, the surface morphology transforms from a porous oxide with protruding whiskers to a "cornflake" structure, and the surface evolves from a phosphate-covered oxide (with some adsorbed water) to the oxyhydroxide boehmite (AlOOH). At longer exposure

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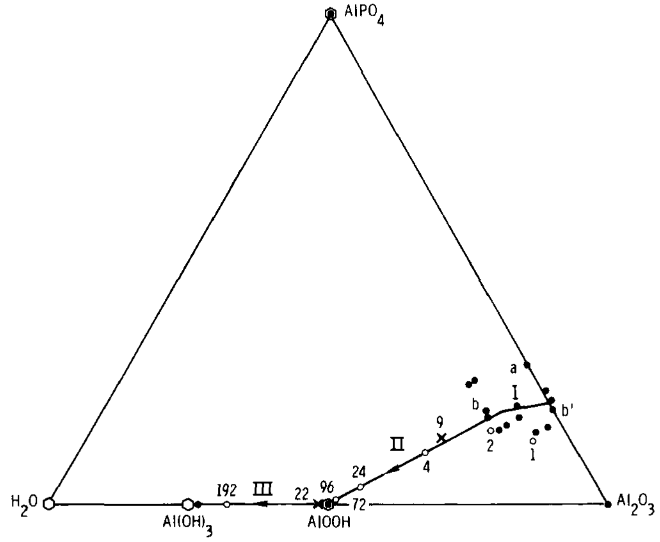

FIGURE 8 Al_2O_3–$AlPO_4$–H_2O SBD showing the three steps of hydration of PAA oxides in 100% relative humidity at 50°C (circles) and at 60°C (crosses). Hexagons represent calculated compositions; solid circles represent compositions of standards and of PAA samples prior to hydration; open circles and crosses represent compositions of samples at various stages of hydration. The numbers beside the points correspond to the exposure time in hours to the humid environment (adapted from Ref. 19).

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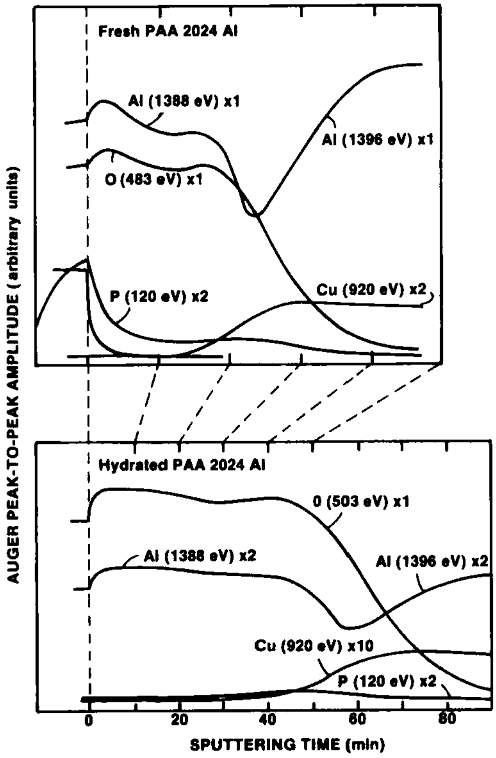

FIGURE 9 Auger sputter-depth profiles of a) unhydrated and b) hydrated PAA oxides. The numbers in parentheses are the kinetic energies of the Auger transitions used (from Ref. 19).

times, further hydration ensues with the formation of bayerite [$(Al(OH)_3$] crystallites on the surface (line III).

An investigation of the hydration of NTMP-treated FPL surfaces (Figure 10) shows a similar three-step process: physisorption of water (movement of the surface composition from line b to line a), hydration of the oxide to boehmite (movement along line a), and further hydration to bayerite. As with the PAA samples, the initial adsorption of water is reversible. Sputter-depth profiles of several hydrated samples revealed no subsurface concentration of phosphorous in coupons without surface phosphorous.

2 *Discussion* It is important to understand the mechanisms occurring during the hydration process if we are to improve bond durability. A study of different possible mechanisms[19] shows that only one process is compatible with the evolution of surface composition directly to that of boehmite and with the absence of phosphorus in or below the hydration product—a slow dissolution of the inhibitor followed by the rapid hydration of the freshly-exposed amorphous aluminum oxide. That is, hydration occurs only as the inhibitor-Al complex

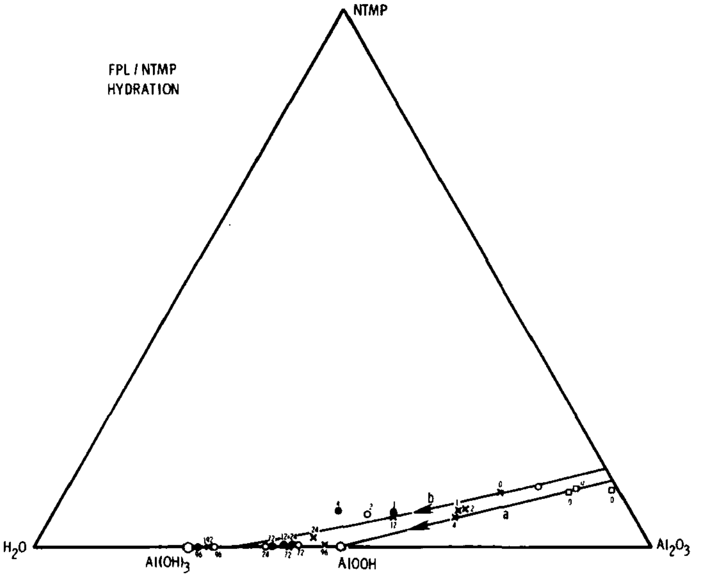

FIGURE 10 Al_2O_3–NTMP–H_2O SBD showing the evolution of FPL-etched surfaces treated with saturation coverages of NTMP, as a function of exposure time in 100% relative humidity at 50°C. The different symbols represent different experimental runs; the numbers are the exposure time in hours. Line "a" represents the hydration path with no physisorbed water, line "b" represents the hydration path with a monolayer of physisorbed water (from Ref. 16).

slowly dissolves from the surface into the condensed water vapor. This complex apparently forms an ultra-thin protective coating by adsorbing onto active sites and, as it is removed, the amorphous oxide becomes subject to hydration. This sequence of events is consistent with recent results of Zanzucchi and Thomas[23] for thin Al films. In their work they found that phosphonates and silanes are effective inhibitors for corrosion protection by extending the lifetime of the film in water. Superior performance was exhibited by the phosphonate compounds, particularly NTMP.

V MECHANICAL TESTING

A Initial bond strength

The initial strength of bonds formed with treated FPL adherends was compared with that of control adherends for several adhesives. The T-peel strength values given in Table I indicate that for each of the epoxy adhesives, the treated bonds, including those with multilayer inhibitor coverage, exhibited the same strengths as the control bonds using untreated FPL adherends, i.e., there was no degradation of dry interfacial strength. In fact, each specimen failed cohesively in adhesive, as indicated by visual examination and the high C and low O

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TABLE I
T-peel strengths for FPL-etched adherends

	Adhesives			
Treatment	FM-123-5 Nitrile epoxy	FM 238/BR238[a] Nitrile phenolic	FM 1000 Polyamide epoxy	FM 53 Epoxy
Control	172 ± 26 kPa	259 ± 21 kPa	554 ± 13 kPa	351 ± 52 kPa
MP 300 ppm	152 ± 16	201 ± 18	—	
NTMP				
10 ppm, RT	225 ± 23	195 ± 11	576 ± 11	350 ± 54
100 ppm, RT	164 ± 6	164 ± 6	550 ± 6	353 ± 36
100 ppm, 80°C	156 ± 10	204 ± 21	576 ± 0	—
(*n*-Bu)NBMP				
10 ppm, RT	161 ± 6	241 ± 11	569 ± 8	—
100 ppm, RT	165 ± 12	185 ± 18	569 ± 8	—
100 ppm, 80°C	159 ± 14	169 ± 7.6	576 ± 0	—
Locus of failure				
Visual	Cohesive	Adhesive[b]	Cohesive/adhesive	Cohesive
XPS	Cohesive	Cohesive	—	—

[a] Primed with BR 238.
[b] Between primer and adhesive.

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concentrations seen with XPS on each side of the failed bond. Such a failure mode indicates that the weakest link of the system is the strength of the polymer. For structures consisting of adherends primed and bonded with a nitrile phenolic adhesive, those made with inhibitor-treated adherends showed a slight degradation of strength. The cause of this effect is not known; however, since failure occurred within the polymeric material, close to the adherend/adhesive interface, the inhibitor may have caused a weaker interphase region of the adhesive, perhaps by interfering with the adhesive cure.

B Bond durability in moist environments

1 *Surfaces produced by Forest Products Laboratory Etch* Typical wedge-test data for FPL adherends showed that NTMP significantly improved bond durability (Figure 11).[12] Indeed, bond performance approached that of untreated PAA adherends. Wedge tests on adherends treated with NTMP at 80°C and room temperature (Figure 12) showed nearly the same results even though NTMP coverage at the high temperature was 2–3 times greater.

Fracture energy, G, obtained using the crack-length data generated by the wedge tests, was plotted against crack velocity, v (Figure 13).[14] From these plots, we determined the value of G at which crack velocity was below the level of experimental detectability, G_I (Table II). Data are also included for the PAA adherends sprayed with a corrosion-inhibiting primer and bonded with the adhesive FM 123–2. Because the crack was completely cohesive through the center of the adhesive layer in this last case, the wedge test provides information on the fracture behavior of the adhesive without any influence from interfacial effects.

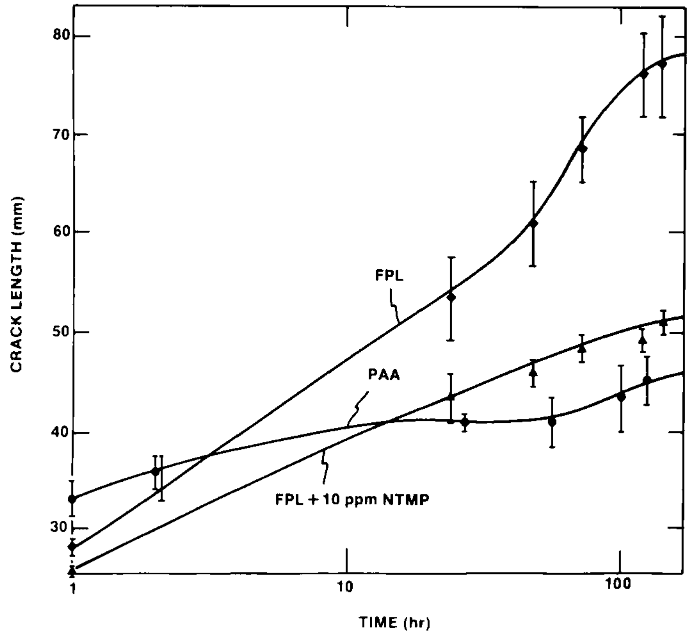

FIGURE 11 Wedge-test results (crack length as a function of time) for FPL, NTMP-treated FPL, and PAA adherends treated at room temperature (from Ref. 12).

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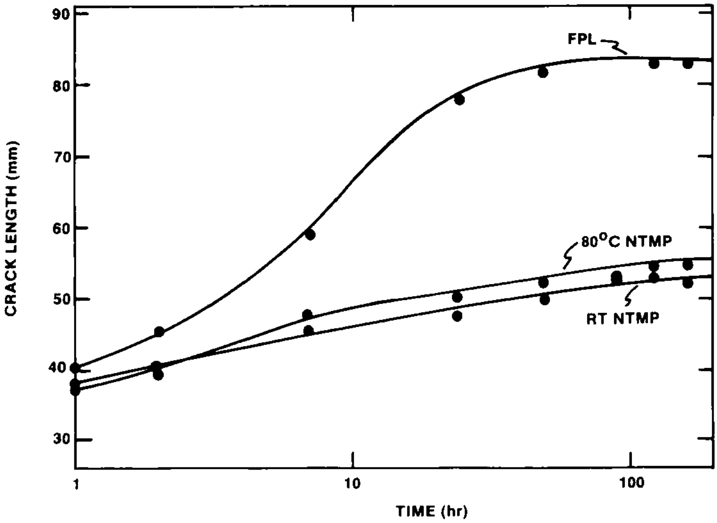

FIGURE 12 Wedge-test (crack length as a function of time) for FPL- and NTMP-treated FPL adherends treated at room temperature and at 80°C. NTMP solution concentration was 10 ppm (from Ref. 12).

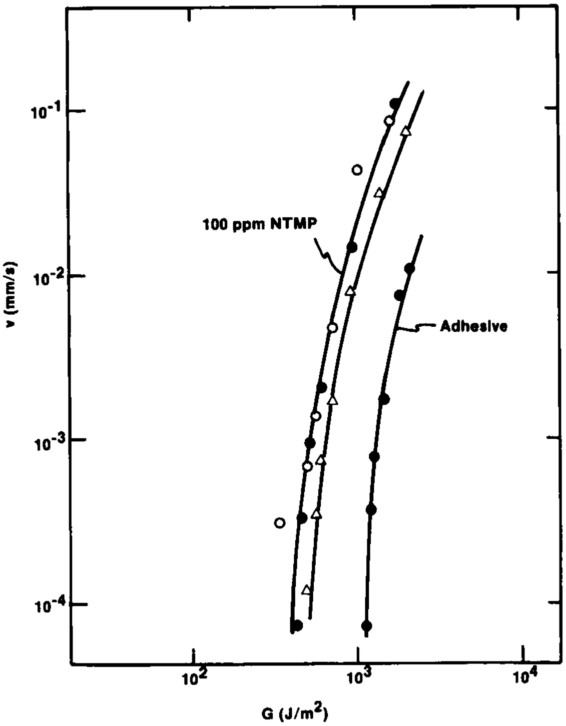

FIGURE 13 Wedge-test results (crack velocity as a function of fracture energy) for FPL adherends treated in 100-ppm NTMP solutions. Also shown are results from a PAA-prepared sample with a corrosion inhibiting primer that forced cohesive failure. The different symbols correspond to different experimental runs; the two lines define the band of values (from Ref. 14).

At the conclusion of the humidity exposure, the wedge-test assemblies were separated. The original crack through the adhesive had not continued to propagate after exposure to humidity. Instead, a new crack had initiated at the oxide/adhesive interface and had continued at this location until crack arrest.

2 *Phosphoric-acid-anodized surfaces* The wedge-test performance of PAA adherends was similar to that for NTMP-treated FPL adherends (Figure 14).[17]

TABLE II
G_I obtained from wedge tests of FPL-etched adherends

Sample description[a]	G_I (J/m^2)
Control	35–175
2 ppm NTMP	105–440
10 ppm NTMP	
100 ppm NTMP	350–525

[a] All NTMP treatments were at room temperature.

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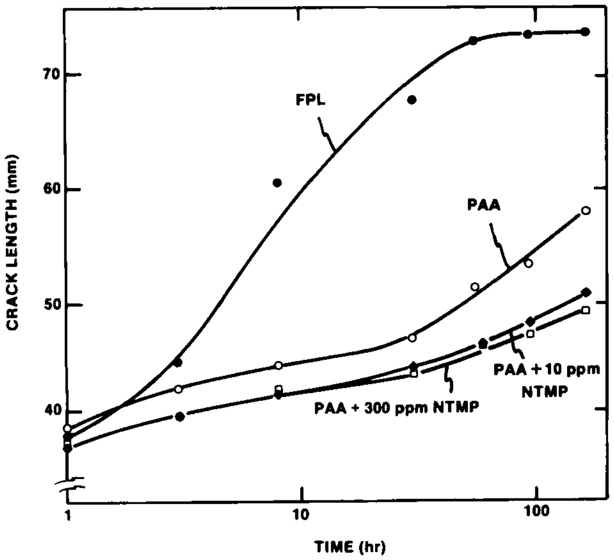

FIGURE 14 Wedge-test results (crack length as a function of time) for untreated FPL and PAA adherends and PAA adherends treated with 10-ppm and 300-ppm NTMP solutions (from Ref. 17).

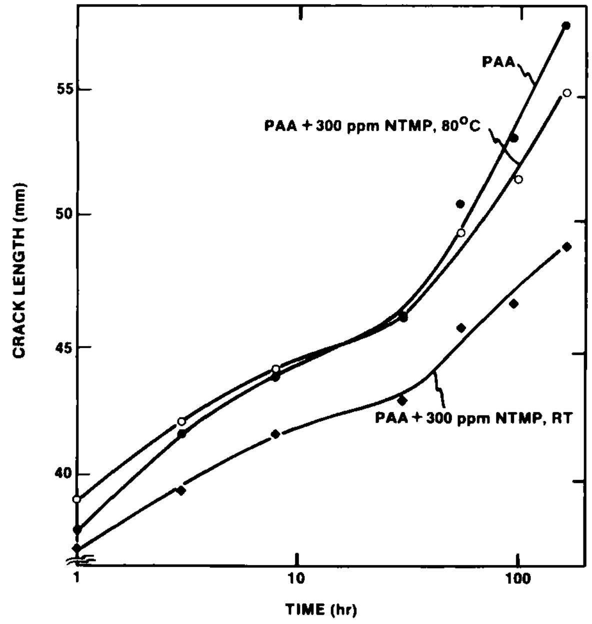

FIGURE 15 Wedge-test results (crack length as a function of time) for untreated PAA adherends and PAA adherends treated in 300-ppm NTMP solutions at either room temperature of 80°C (from Ref. 17).

Treatment in NTMP solutions led to an improved performance that was independent of treatment solution concentration, provided room-temperature saturation coverage was obtained. At higher coverages, bond durability was reduced relative to that provided by room-temperature treatment (Figure 15), but never fell below that of untreated PAA surfaces.

Crack extension forces and resultant crack velocities derived from the wedge-test results are plotted in Figure 16.[17] A two-step crack propagation process is clearly seen as discussed below. As with FPL adherends, X-SEM examination confirmed that a warm, humid environment at the crack tip always initiated a new crack at the oxide/adhesive interface, even on inhibitor-treated PAA adherends. The re-initiation and initial propagation of the crack were associated with conversion of the original oxide to boehmite.

Visual examination of both treated and untreated adherends indicate that the failure surface on the aluminum side was dull or stained where the initial crack propagated, but was shiny and had a slight purple sheen near the final crack tip.[17] For the adherends treated both in concentrated (200–500 ppm) NTMP solutions and at 80°C, the final increment of crack extension often led to crack propagation wholly within the adhesive layer. X-SEM and XPS examination of the Al side of the fracture surface revealed that the dull regions corresponded to a hydrated surface, and the shiny regions corresponded to an oxide surface coated with a thin adhesive layer (Figure 18); the transition from dull to shiny corresponded to the horizontal portion of the crack length *vs* time curves of Figure 14 and to the

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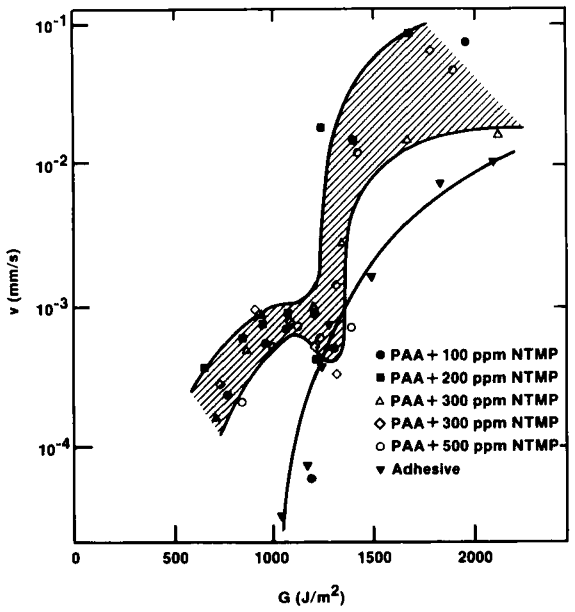

FIGURE 16 Wedge-test results (crack velocity as a function of fracture energy) for NTMP-treated PAA adherends and FM 123–2 adhesive, determined from the same cohesive failure described in Fig. 13. (from Ref. 17).

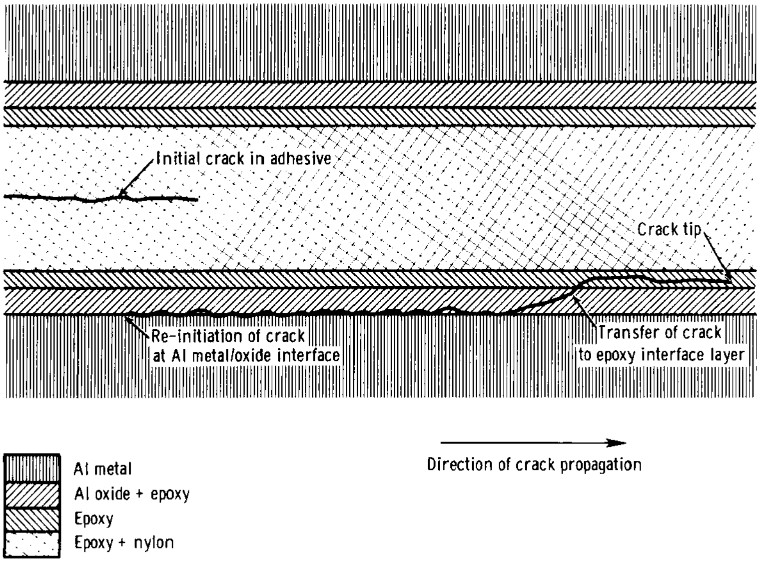

FIGURE 17 Schematic of crack path in wedge-test samples (from Ref. 17).

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discontinuity of the crack velocity *vs* fracture energy curves of Figure 16. Since the shiny region on the failure surfaces showed no evidence of the Dacron mat, the crack evidently progressed in the epoxy resin between the oxide surface and the Dacron scrim.

Conversion of oxide to hydroxide at the transition apparently occurs so slowly that it is no longer a precursor to crack propagation, and propagation through the adhesive becomes a more favorable mechanism of crack growth. Thus, the crack moves progressively away from the interface region until it is wholly within the layer (Figure 17). When adhesive deformation due to passage of the crack front exceeds a certain limit, the adhesive recoils. On PAA-treated adherends treated with NTMP, the crack path moves away from the oxide/adhesive interface at a shorter crack length, but at approximately the same exposure time.

3 *Inhibitor evaluation* The wedge test was also used to evaluate the effectiveness of the various inhibitors shown in Figure 1 in improving bond durability. Based on the results shown in Figures 19–21, we classified the inhibitors into three groups:[16] (I) MP and PA, which provide either worse performance or no improvement over the untreated FPL specimens; (II) AMP and (*t* Bu)NBMP, which provide some improvement over the control; and (III) NTMP, (*n* Bu) NBMP, and EDTMP, which provide the best performances.

As before, we used X-SEM and XPS to determine the microscopic locus of failure of selected wedge-test specimens.[16] The XPS results are summarized in Table III. The failures of specimens treated with MP, PA (66 ppm), NTMP (100 ppm at room temperature, 10 ppm at 80°C), and EDTMP occurred near or at the adhesive-adherend interface, as indicated by the substantial differences

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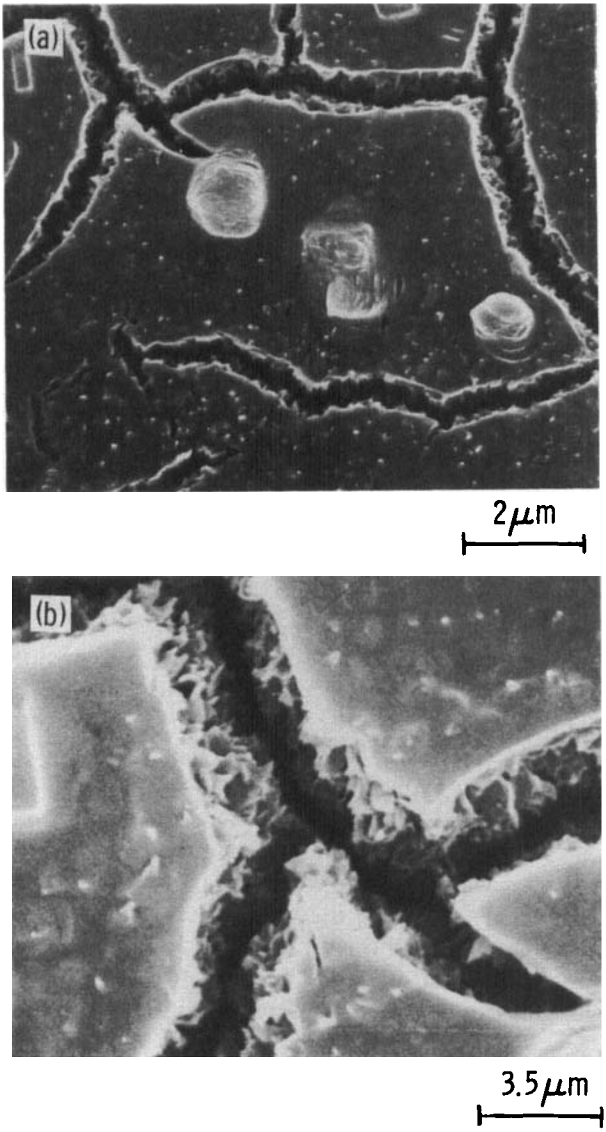

FIGURE 18 SEM micrographs of Al side of failure surface on PAA adherend treated in 200-ppm NTMP solution showing hydroxide formation after crack propagation through the adhesive layer; (b) is a higher magnification of (a) (from Ref. 17).

seen between the metal and adhesive sides of the failure. In contrast, the two surfaces of the FPL control and specimens treated with (*t* Bu)NBMP and (*n* Bu)NBMP exhibited high Al and O and low C, indicating that the locus of failure was in the oxide/hydroxide or at the interface between the oxide/hydroxide and the metal, resulting in hydration or corrosion of the metal surface.

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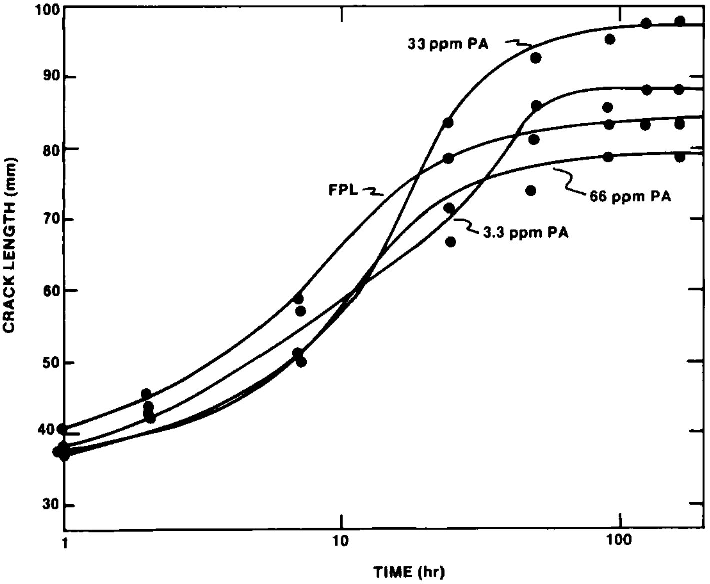

FIGURE 19 Wedge-test results (crack length as a function of time) for FPL adherends treated in solutions of PA and for untreated FPL adherends (from Ref. 14).

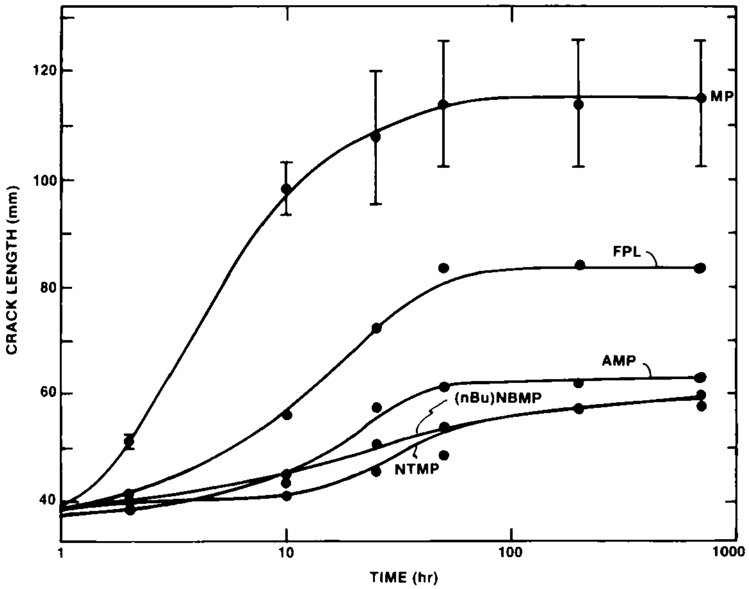

FIGURE 20 Wedge-test results (crack length as a function of time) for untreated FPL adherends and for FPL adherends treated in MP, AMP, (*n*-Bu)NBMP, and NTMP solutions (from Ref. 16).

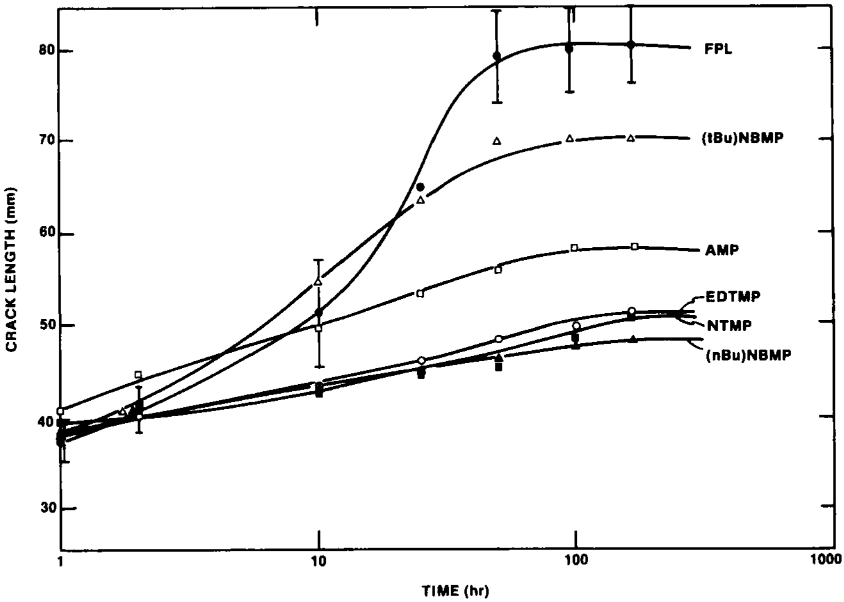

FIGURE 21 Wedge-test results (crack length as a function of time) for untreated FPL adherends and for FPL adherends treated in AMP, (*t*-Bu)NBMP, (*n*-Bu)NBMP, NTMP, and EDTMP solutions (from Ref. 16).

In most specimens that exhibited better performance than the control, bond failure was due to hydration of the adherend surface. For example, panels treated with AMP (and *n* Bu)NBMP exhibited the cornflake morphology of boehmite up to the crack-tip (Figure 22). More extensive hydration was also seen in some areas.

In contrast, visual observations of the near-crack-tip region of NTMP-treated

TABLE III
XPS surface composition of wedge-tested FPL adherends pretreated with various inhibitors

	Composition (at. %)†							
	Al		O		C		P	
Group sample description	M	A	M	A	M	A	M	A
Adhesive	—	0	—	8	—	92	—	—
Control	22	24	44	47	34	30	—	—
I MP, 300 ppm	20	0	50	21	29	78	—	—
I PA, 3.3 ppm	18	15	46	43	36	42	—	—
I PA, 33 ppm	17	17	52	42	21	41	—	—
I PA, 66 ppm	25	2	49	25	25	73	0.6	—
II (*t*-Bu)NBMP, 300 ppm	30	29	59	58	10	12	—	—
III NTMP, 100 ppm, RT	30	14	56	38	13	47	—	—
III NTMP, 10 ppm, 80°C	14	2.5	40	25	45	72	1	0.5
III EDTMP, 300 ppm	29	19	59	45	12	36	—	—
III (*n*-Bu)NBMP, 300 ppm	31	30	56	58	13	11	—	—

† M = metal side of failure, A = adhesive side of failure.

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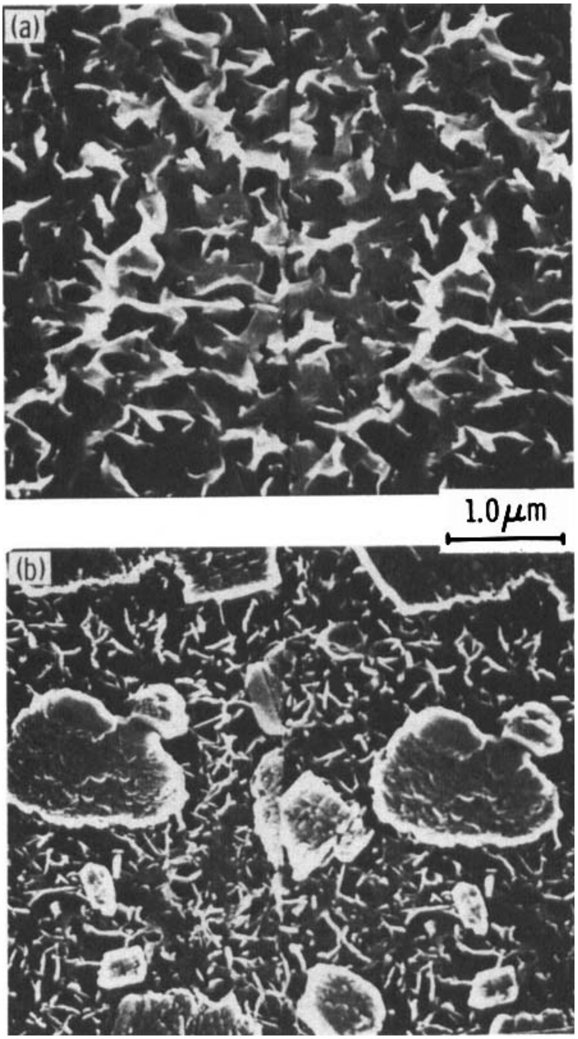

FIGURE 22 Scanning electron mcirographs of the near-crack-tip region of the aluminum side of two inhibitor-treated FPL-etched wedge-test specimens: a) AMP-treated surface exhibiting cornflake (boehmite) morphology and b) (*n*-Bu)NBMP-treated surfaces exhibiting bayerite crystallites on top of boehmite (from Ref. 16).

panels revealed a "shiny" aluminum area right at the crack tip and a "dull" region further along the crack (Figure 23). Upon closer examination, the shiny area was seen to exhibit an FPL morphology, whereas the dull area exhibited the cornflake morphology.[16] In this case, the crack apparently propagated in advance of the hydration of the aluminum oxide and hydration occurred only after additional exposure to the moist environment.

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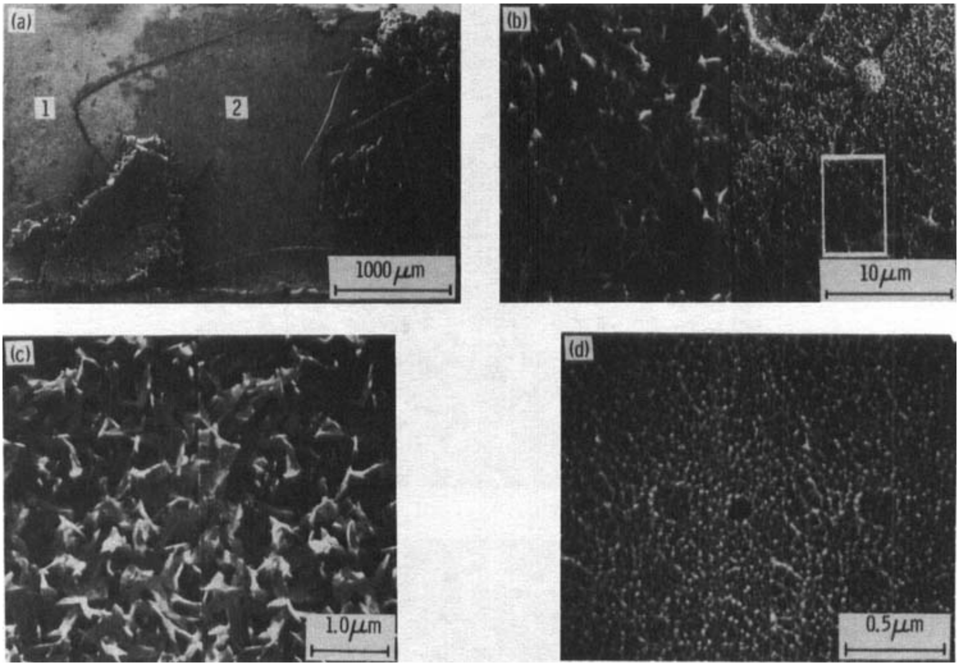

FIGURE 23 Scanning electron micrographs of the near-crack-tip region of the aluminum side of an NTMP-treated FPL-etched wedge test specimen: a) low magnification view showing 1) the dull aluminum area and 2) the shiny aluminum area, and the cohesive failure in the adhesive after the wedge test was completed (at right); b) the beginning of hydration in the boundary region between dull and shiny areas, (enlargement of the blocked-in area is at left); c) higher magnification stereo view of the dull area showing the cornflake boehmite structure; and d) higher magnification stereo view of the shiny area showing the original FPL morphology (from Ref. 16).

C Discussion

1 *Initial strength* Based on T-peel tests of treated and untreated structures bonded with epoxy adhesives, the control specimens exhibited optimum initial strength, i.e., failure was cohesive in the adhesive (Table I). Consequently, no improvement was expected or observed for inhibitor-treated adherends. Since the dry performance of the control and treated specimens was equal, it appears that the interfacial strength between the oxide and adhesive for the treated adherends was also stronger than the cohesive strength of the adhesive.

The small degradation of T-peel strengths for primed, treated structures bonded with the nitrile phenolic adhesive (FM 238) suggests that the inhibitors used here may not be compatible with all types of adhesives. In these cases, failure occurred with the polymer system, possibly at the primer-adhesive interface. The inhibitors did not weaken the primer-aluminum oxide interface below the cohesive strength of the polymer system, but did apparently reduce the cohesive strength itself, possibly by inhibiting the cure of the polymer.

2 *Bond durability* The wedge test results for FPL adherends treated in NTMP solutions at room temperature indicate marked improvements in environmental durability, as measured by the final crack length after exposure to a humid environment. The observation of similar Al concentrations on both sides of the failure surface (Table III) of the FPL adherends indicates that the locus of failure was through a hydrated oxide layer. When the original Al oxide is converted to Al hydroxide the resulting boehmite occupies a larger volume and exhibits a less dense cornflake morphology compared to the original amorphous oxide. This oxide-to-hydroxide conversion disrupts the mechanical interlocking between the oxide and the adhesive and creates stresses that promote crack propagation along the weak hydroxide-metal interface.[16]

Maximum improvements in bond durability were associated with room-temperature saturation surface converage (approximately one monolayer). Higher coverage, such as that produced by NTMP treatment at 80°C, did not further improve the bond durability[12] and XPS results suggest that crack propagation occurred at least partially through the NTMP multilayer at the oxide-adhesive interface.

The improvements in bond durability that accompany NTMP surface pretreatments result from stabilization of the surface against hydration. In some cases, the hydration rate of NTMP-treated specimens was slowed sufficiently so that it was no longer the limiting factor in bond durability. Instead, at least at the latter stages of crack growth, failure occurred along the inhibitor-adhesive interface and only after subsequent exposure did the oxide surface hydrate (Figure 23).[16]

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Failure in these cases (and in the experiment involving NTMP treatment at elevated temperatures) may be caused by slow, moisture-induced changes in the adhesive (similar to those seen by Albrecht and Mecklenburg[24]) which allow the adhesive to relax and withdraw from the pores of the FPL oxide. Such a phenomenon would be seen only with configurations such as those used in wedge tests, where water is in contact with the adhesive at the crack tip for extended periods of time.[16] In addition, this relaxation of the adhesive would be observed only in conjunction with a very stable oxide.

In all cases, insertion of the wedge-test assemblies into the warm, humid environment resulted in the initiation of a crack at or near the oxide/adhesive interface. This crack initiation has also been observed by other investigators[25] and is apparently due to hydration of the oxide and the associated breakdown of interface integrity. If moisture is excluded from the interface, interfacial failure does not occur.

The bond durability of PAA-treated adherends was also increased by treatment in NTMP solutions at room temperature.[17] Again, additional adsorbed NTMP (from high-temperature solutions) did not further increase wedge-test performance; in fact, performance of the panels with higher NTMP coverage was inferior to that of panels treated at room temperatures. Crack propagation at the latter stages was not hydration controlled even in the untreated specimens, but might have been influenced by inhibitor-induced coupling of the oxide to the adhesive (coupling will be discussed in more detail in the comparison of different inhibitors). An NTMP multilayer would be limited by weak intermolecular bonding although chemical coupling to the adhesive is probably maintained.

It is clear the adherend behavior is strongly dependent on surface treatment prior to bonding. The failure mode of PAA adherends changed from cohesive to adhesive as did that for FPL adherends upon exposure to the humid environment. This transition was less abrupt for the PAA adherends and, on PAA treated with saturation surface coverages of NTMP, there was effectively an "incubation period" before interfacial failure was observed. Once interfacial cracking began on FPL adherends, the initial crack velocity was maintained to very low G values, indicating that the mechanism of crack growth was independent of the stress (Figure 13).[14] Indeed, the conversion of oxide to hydroxide is such a stress-independent mechanism. The behavior of PAA adherends was quite different.[17] At relatively high G levels, the crack velocity fell two orders of magnitude below its initial value. Examination of these fracture surfaces by X-SEM revealed that the locus of failure was initially through the oxide but, in the latter stages, went through the adhesive near the oxide-adhesive interface. The discontinuity in the behavior of these adherends, evident in Figure 16, is probably a reflection of this change in the locus of failure. The behavior at the higher G levels is evidence of failure of the bond through oxide hydration whereas, at the lower G levels, it is characteristic of adhesive failure near the interface. The v-G curve for the inhibited PAA adherends approaches that for the adhesive. The crack velocity does not follow the adhesive curve because the locus of failure is in the near-interface region where the adhesive may have different properties.

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We speculate that the transition between crack propagation in the oxide and in the adhesive may involve the slow, moisture-induced relaxation of the adhesive. Unlike the situation with FPL adherends, the adhesive is not able to disengage from the extensive pore structure provided by the PAA oxide. However, the interlocking can be weakened, thereby allowing the crack to move upward in the oxide to the near-interfacial adhesive. Regardless of the mechanism by which the crack transfers from the oxide to the adhesive, the near interfacial adhesive is not as durable as the bulk or central region of adhesive. The failure of the crack to transfer to the near-interfacial region in tests leading to cohesive failure (primed PAA specimens and samples not exposed to high humidity) suggests that an activation energy is necessary for crack transfer or crack re-initiation.

3 *Inhibitor evaluation* Several different inhibitors beside NTMP were also investigated, but less extensively.[16] The first of these, PA, is of interest because a PA-treated FPL surface is analogous to a PAA surface in that both exhibit similar surface chemistry and hydration resistance. However, their wedge-test performances were markedly different: treatment in PA solutions provided no improvement in bond durability over that of the FPL control. Results of XPS failure analysis of a specimen treated with 66-ppm PA and, to a lesser extent, one treated with a 33-ppm PA (Table III) indicated failure along the oxide-adhesive interface, probably prior to hydration since P was detected on the metal side of

the 66-ppm samples. Apparently PA weakens this interface, relative to NTMP treatment, either by forming inhibitor-adhesive bonds that are not resistant to attack by moisture or by passivating the adherend surface and forming no chemical bonds with the adhesive. In either case, the interface provides an easy path for crack propagation, possibly following moisture-induced relaxation of the adhesive. We will return to the idea of chemical bonding between the adhesive and the inhibitor in the discussion of other inhibitors.

Given that PA-treated FPL samples provide poor bond durability despite a surface chemistry similar to PAA samples, what accounts for the superior performance of PAA specimens during wedge test? We attribute[16] this to the significantly thicker porous oxide formed by the PAA process,[6] which produces more extensive and efficient physical interlocking and bond performance that is less dependent on chemical coupling of the oxide and the adhesive. An absence of chemical bonding between the PAA surface and the adhesive should have less effect on the bond durability of PAA adherends because the substantial interlocking of oxide and adhesive retards crack propagation (provided stability of the oxide is maintained).

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Despite good initial bond strengths (Table I), bond durability of MP-treated adherends was below that of the untreated FPL control specimens.[16] Crack propagation occurred interfacially between the oxide and the adhesive. The reason for this behavior may be related to interference of MP with the adhesive cure process, or passivation of the surface, as was previously discussed for PA-treated FPL samples. The results for AMP showed that the addition of the amino group to MP made a marked difference in the performance of the respective bonds. The amino group is capable of chemically bonding with the epoxy adhesive, thus stregthening the inhibitor-adhesive interface. At the same time, AMP increases the hydration resistance of the oxide. However, water remaining on the surface following saturation coverage of AMP (Figure 4) can act as initiation sites for hydration, thus preventing the hydration resistance from reaching that of NTMP-treated oxides. Consequently, bond durability of AMP-treated adherends is not as good as that of NTMP-treated adherends.

The next set of inhibitors, the two (Bu)NBMP compounds, each provided improved durability, but (*n* Bu)NBMP treatment gave a wedge-test performance comparable with that of NTMP.[16] Failure occurred as the oxide hydrated, leading to crack propagation within the hydroxide or along the weak hydroxide-metal interface with subsequent hydration of the exposed metal surface. We attribute the improved performance of (*n* Bu)NBMP over (*t* Bu)NBMP to mechanical interlocking on a molecular scale, where the *n*-butyl tail is dispersed in the polymeric adhesive; the inert, compact *t*-butyl cluster does not provide such interlocking. The mechanical coupling or interpenetrating network makes the interface less vulnerable to aqueous attack and improves bond durability. Each (Bu)NBMP compound contains two phosphonic acid groups, but only the (*n* Bu)NBMP compound produces the same bond durability as NTMP, which contains three phosphonic acid groups. We conclude therefore, that (*n*Bu)NBMP bonding to the adhesive is equivalent as far as durability is concerned to NTMP bonding. Moreover, the XPS results of failed surfaces indicate that the locus of failure is in the oxide or at the metal/oxide interface in the (Bu)NBMP case but at the inhibitor/adhesive interface in the NTMP case. This indicates that three phosphonic acid groups per molecule are necessary to stabilize the oxide and force the failure to the inhibitor/adhesive interface. This result is also a strong indication that the weak link in the *most* durable bonds is the inhibitor-adhesive interface and not the Al-oxide-inhibitor interface.

Performance with EDTMP, with four methylene phosphonic acid groups, was similar to that for NTMP and (*n* Bu)NBMP, despite the extra bonding phosphonic acid group on EDTMP, with failure occurring at least partially at the interface. These results again suggest that a higher inhibitor-oxide bond strength compared to that with NTMP does not lead to improved bond durability.

4 *Inhibitor properties for improving bond durability* Based on the surface chemistry and mechanical test results, we identified five properties of inhibitors that are necessary to improve bond durability of aluminum structures, i.e., they must 1) occupy all chemically active sites on the Al_2O_3 surface, 2) form strong inhibitor-aluminum oxide bonds, 3) form a water-insoluble complex with aluminum, 4) be compatible with the adhesive/primer, and 5) chemically or physically couple to the adhesive/primer.[16]

The first three were derived from the models of adsorption and hydration. Strong interactions between the inhibitor and the adherend surface are needed so that a dilute solution of inhibitor can successfully compete with water for adsorption sites and effectively passive all the surface sites where hydration might initiate. Furthermore, once the aluminum-inhibitor complex is formed, it must remain on the surface to protect the underlying oxide and not go into solution.

The fourth criterion—compatibility—was suggested by T-peel experiments in which inhibited specimens exhibited lower initial strength when bonded with a nitrile phenolic adhesive than did similar control specimens. The poor durability of the MP-treated wedge test panels is also an example, we believe, of poor compatibility under moist conditions.

Finally, the importance of coupling between the inhibitor and adhesive was noted in the discussion on wedge-test data. The coupling can be chemical, as illustrated by the NTMP, AMP, and MP results, or mechanical on a molecular scale as demonstrated by the results with the two (Bu)NBMP compounds. In the NTMP case, the lone pair of electrons on the nitrogen atom apparently react with the polymeric adhesive to provide superior bond durability for the treated adherends. This reaction is not possible for PA-treated adherends; thus bond performance is not improved for FPL adherends even though PA is effective in inhibiting hydration. PA incorporated in the surface is effective in improving durability of PAA adherends because the oxide provides strong mechanical interlocking with the polymer and the PA molecule stabilizes the oxide against moisture attack. NTMP-treated PAA adherends exhibit better performance than untreated adherends presumably because the NTMP molecule provides chemical bonding across the inhibitor-polymer interface, something the PA molecule does not do.

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The criteria for inhibitor selection are clearly not independent. For example, an inhibitor that occupies all active sites on the surface will undoubtedly be strongly bonded to the surface. Similarly, an inhibitor that couples to an adhesive will also be compatible with it and will form a complex less likely to be attacked by water. When the oxide surface is stabilized with respect to hydration, coupling to the adhesive becomes important in preventing degradation of the adhesive-inhibitor interface. This is especially important for the FPL oxide but is also a factor for the PAA oxides. For the NTMP/FPL case, hydration was slowed sufficiently to transfer the locus of failure to the adhesive-inhibitor interface and to cause the failure mode to depend primarily on withdrawal of the adhesive from the oxide.

VI SUMMARY

Hydration inhibitors, such as nitrilotris methylene phosphonic acid, improve the durability of adhesively-bonded aluminum structures placed in a moist environment. Our work has shown: 1) pretreatment of FPL adherends in an inhibitor solution increases bond durability to the extent that hydration of the adherend is no longer the limiting step in crack propagation; 2) pretreatment of PAA adherends improves bond durability and focuses the failure into the adhesive at shorter crack lengths (larger stress intensity); 3) inhibitor pretreatments do not lower the initial bond strength when used with epoxy adhesives; 4) adsorption of NTMP onto an FPL surface involves the displacement of water and the formation of P–O–Al bonds, with a saturation coverage of approximately one monolayer; 5) adsorption of NTMP onto a PAA surface, which has little adsorbed water, results in occupation of residual active sites; 6) hydration of a PAA or an inhibited FPL surface proceeds in three steps: i.e., i) reversible physisorption of water, ii) slow dissolution of the inhibitor(phosphate)-aluminum complex followed by rapid hydration of the freshly-exposed amorphous aluminum oxide to boehmite, and iii) a further hydration of the boehmite to bayerite; and finally, 7) inhibitors designed to improve bond durability should i) displace water and occupy all active sites on the Al_2O_3 surface, ii) form strong inhibitor surface bonds, iii) form a water-insoluble complex with aluminum, iv) be compatible with the adhesive or primer, and v) couple to the adhesive.

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