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Environmental and adhesive durability of aluminium–polymer systems protected with organic corrosion inhibitors

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The protection of pretreated aluminium against environmental corrosion has been accomplished in varying degrees by incorporating selected organophosphonates and organosilanes on the metal surface. Ionizable phosphonates, such as nitrilo-tris methylene phosphonic acid (NTMP), adsorbed at monolayer concentrations, are effective inhibitors against hydration and are compatible with a nitrile-modified epoxy adhesive material. Aqueous 0.1 vol% solutions of selected organosilane compounds containing reactive side chains (e.g. epoxy, mercapto) exhibit protection against both hydration corrosion and the action of an aggressive species (Cl^-) and provide good adhesive bond durability with both nitrile-modified and polyamide (primer) epoxy resin systems. Wedge test results suggest that the curing process (e.g. the percentage crosslinking) of the epoxy–polyamide primer system is not affected by the addition of organosilanes, but may be affected by NTMP. The results of substrate surface characterization, adsorption behaviour of applied films, and evaluation of candidate inhibitors by chemical, mechanical, and electrochemical test methods are presented. Mechanisms to explain the observed behaviour of the phosphonate and silane systems are discussed.

1. Introduction

The aircraft industry has a vital need for compounds that protect aluminium against corrosion and are compatible with organic polymeric films used as protective coatings. Proper pretreatment of the aluminium prior to epoxy bonding remains essential for developing high bond strengths [1–8]. The incentive to eliminate environmentally undesirable materials, such as chromates, has led to the consideration of organic inhibitor compounds as anticorrosion additives.

Previous investigators have demonstrated the importance of the microscopic morphology of the oxide surface for good bondability of aluminium adherends [6–8]. The surface roughness, which controls the degree of mechanical interlocking with the overlying polymer (for thermosetting polymer systems), is regarded as an important factor in determining both initial bond strength and long-term durability of a given adherend–adhesive system.

A second critical requirement for long-term durability is the stability of the aluminium oxide in a humid environment [9–12]. The inevitable hydration of the oxide to the oxyhydroxide severely degrades the overall bond strength and polymer adhesion to the base aluminium. Certain organic aminophosphonic acids [12–14] have been shown to improve bond durability of aluminium adhesive joints by inhibiting the oxide-to-hydroxide conversion process. Although the ability of an inhibitor to chemically couple with an applied polymeric topcoat has been found to be important for improved durability [14], the effectiveness of various well-known coupling agents (e.g. organosilanes) as corrosion inhibitors for these systems has not been investigated until recently [15].

It is common practice to protect metal surfaces from environmental effects with organic polymeric coatings. These coatings, like adhesives, must be properly applied to a suitably prepared surface. Thus, a process that combines adequate substrate pretreatment with an effective organic corrosion inhibitor (that can maintain or improve the adhesion of the applied paint coating) should provide a superior protective system for the metal without the use of hazardous agents.

The results of our investigations on metal–polymer systems treated with selected inhibitors are presented in this paper. Using etched aluminium substrates, we evaluated organosilane and organophosphonate compounds with respect to their resistance to environmental degradation and overall bond durability. Many of the organosilanes contain functional groups designed to couple chemically with applied polymeric epoxy systems. Adsorption studies for the well-characterized organophosphonates are extended to consider effects of the solution pH for samples prepared by an anodization process that produces a more protective oxide surface. Mechanisms for the interaction of the ionic (ionizable) phosphonates and neutral (trialkoxy) silanes, including their respective polymerization tendencies, will be discussed.

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2. Experimental techniques

2.1. Substrate characterization

Test coupons and panels of 7075–T6 aluminium, an alloy used extensively for aircraft structures, were degreased in a commercial alkaline cleaning solution and rinsed in distilled, deionized water. The samples were then subjected to either a standard Forest Products Laboratories (FPL) treatment [1] (15 min immersion in an agitated, aqueous solution of $60\,g\,l^{-1}$ sodium dichromate dihydrate and 17 vol % sulphuric acid at 65° C, followed by rinsing in distilled, deionized water and air drying) or the sulphuric acid anodization (SAA) process (anodization in 10 wt % sulphuric acid solution at 15 V for 20 min at 25° C). Both preparations are used extensively for the adhesive bonding or corrosion protection of aircraft structural components.

Surfaces were examined in a JEOL–100CX scanning transmission electron microscope (STEM) operated in the high resolution (2 to 3 nm) SEM mode. A thin platinum layer was deposited on the specimen to suppress charging of the oxide surface.

X-ray photoelectron spectroscopy (XPS) surface analysis measurements were obtained with a Physical Electronics (Eden Prairie, Minnesota) Model 548 spectrometer consisting of a double-pass cylindrical mirror analyser with pre-retarding grids and an Mg$K\alpha$ X-ray source. The reported elemental concentrations were determined from peak height or peak area measurements, using sensitivity factors derived from standards measured by the instrument.

2.2. Epoxy coatings

Two conventional epoxy coatings were used for these studies: a nitrile-modified epoxy structural adhesive (American Cyanamid FM 123–2) and an unpigmented epoxy–polyamide primer topcoat system. The epoxy primer formulation consisted of two components, Shell Epon 1001–T75 epoxy resin and Versamid 115 amidopolyamine, mixed 1 : 1 by volume, which were qualitatively characterized using a Nicolet (Madison, Wisconsin) 7199 Fourier transform infrared (FTIR) spectrometer in the absorbance mode.

2.3. Inhibitor coverage

The FPL- or SAA-prepared coupons and panels were immersed for 30 min in an aqueous (or aqueous–alcoholic) inhibitor solution at room temperature, followed by rinsing in distilled, deionized water and forced air drying. Coverage levels of phosphonate and silane inhibitors were determined from the surface concentration ratios of their characteristic elements, P/Al or Si/Al, respectively.

2.4. Corrosion testing

The aluminium surfaces were hydrated by immersing freshly treated coupons in distilled, deionized water held at 80° C. Samples were removed at specified time intervals, air-dried and stored in a dessicator prior to analysis.

The adhesive bond durabilities of the inhibitor-treated 7075–T6 surfaces were evaluated by wedge tests (ASTM D–3762) on bonded specimens. Panels (15 cm × 15 cm) were joined with the FM 123–2 to simulate the epoxy primer and cured at 121° C under 0.276 MPa for 1 h. The panels were then cut into 2.5 cm × 15 cm strips and a wedge (2.5 cm × 2.5 cm × 0.318 cm) was driven into one end to provide a constant crack-opening displacement. The specimens were placed in a humidity chamber at 65° C and 95% relative humidity and removed at specified time intervals to record the crack-tip locations; after each examination, they were returned to the humidity chamber.

Primed, inhibitor-pretreated specimens were evaluated environmentally in a Singleton (Cleveland, Ohio) Opti-Mist Test Cabinet, which was maintained at an atmosphere of 5% NaCl, pH 6.5 to 7.2 and 35° C, according to ASTM B–117. The specimens were supported on grooved wooden racks and removed only for brief periodic examinations during the test.

The electrochemical behaviour of the 7076–T6 alloy was analysed by anodically polarizing specimens with a PAR (Princeton, New Jersey) Model 273 potentiostat/galvanostat to assess the ability of the inhibitors to promote passivation in chloride-containing electrolytes. The aluminium surfaces were polished to a 4000-grit finish with SiC paper, degreased with a solvent, and washed in an alkaline detergent solution. Each sample to be polarized was then placed for 30 min in degassed electrolytic solutions containing chloride (0.002 N KCl) as the aggressive ion species and 0.1 N Na_2SO_4 to minimize the impedance of the electrolyte. Inhibitors were added to the solution in concentrations known to provide the optimum surface coverage [16]. Each sample was scanned anodically at a rate of $0.5\,mV\,sec^{-1}$.

3. Results

3.1. Aluminium oxide morphology

The morphology of the FPL oxide surface was characterized in previous studies at these laboratories [7] using the STEM in the SEM mode. The isometric drawing shown in Fig. 1 was derived from that work. The FPL oxide is characterized by a cell structure and a high concentration of 5 nm thick, 40 nm high oxide whiskers, which protrude from the surface.

In contrast to the FPL-prepared surface, the SAA process produces a much thicker oxide layer which exhibits a "cracked mud" morphology at low SEM magnifications and a dense porous network at high resolution. A structural representation, shown in Fig. 2, illustrates the network of closely packed pore cells (20 to 60 nm in diameter with 10 to 30 nm pores) oriented in long columnar bundles and separated by

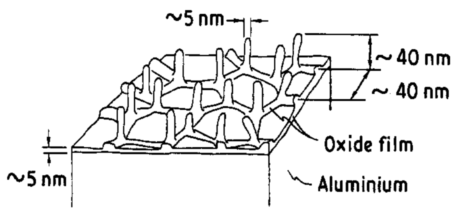

Figure 1 Structure of a Forest products Laboratories (FPL)-prepared aluminium surface [7].

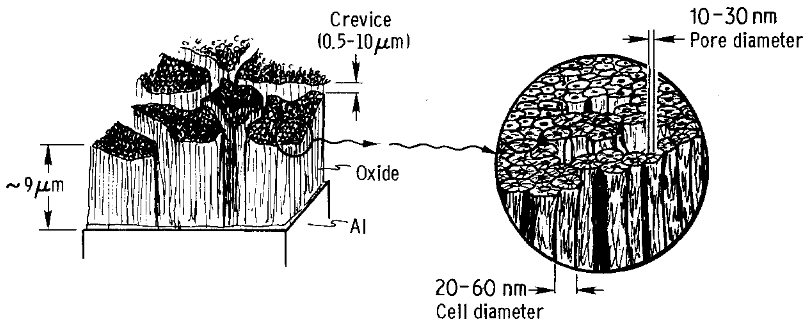

Figure 2 Structure of sulphuric acid-anodized (SAA) aluminium surface.

wide crevices. The oxide thickness, obtained from cross-sectional SEM examination, is > 9000 nm after the 20 min SAA process. After 5 min of anodization, the chemical composition (in at %) of the anodized 7075–T6 surface remained essentially homogeneous at approximately 30% Al, 60% O and 3.5% S, with 6.4% C due to adventitious hydrocarbon contamination. These values correspond to essentially one monolayer of $Al_2(SO_4)_3$ on top of the Al_2O_3 matrix.

3.2. Inhibitor surface coverage

The adsorption behaviour of phosphonate compounds, including those shown in Fig. 3, on FPL-prepared aluminium surfaces has been reported [11, 12, 14]. The respective concentrations of phosphorus or silicon and aluminium were measured by XPS. Fig. 4 shows the correlation of phosphorus coverage on SAA surfaces following treatment in nitrilo-tris methylene phosphonic acid (NTMP) solution, ranging in concentration from 10 to 10^5 p.p.m. An immersion time of 30 min was used to ensure constant saturation coverage. The adsorption maximum observed was attributed to a multilayer build-up of the inhibitor compound in the pH 2 to 4 region [16].

The relationship between the level of NTMP coverage and the solution pH has been reported previously [16]. Essentially, if the NTMP solution concentration is maintained at 100 p.p.m., an adsorption maximum is observed between pH 2 and 4.

The surface coverages for three silanes using different solution adsorption conditions, including type of solvent system, solution pH, and total immersion time, are shown in Table I. The results indicate that adsorption for these materials depends primarily upon the aqueous composition and pH of the inhibitor solution.

3.3. Hydration studies

Visual examination of a series of inhibitor-treated FPL-prepared 7075–T6 aluminium coupons exposed to high humidity conditions for specified time intervals indicated good short-term hydration resistance for several phosphonate and silane compounds (no visible discoloration). The most effective silane compound tested contained the mercapto (–SH) functional group.

3.4. Stability of aluminium–polymer systems

3.4.1. Wedge test results

The corrosion resistance and adhesive coupling capability of the inhibitors were evaluated by the wedge test. Results obtained on SAA-prepared surfaces (Fig. 5) indicated that two inhibitor treatments (100 p.p.m. NTMP and 5000 p.p.m. epoxysilane) outperformed

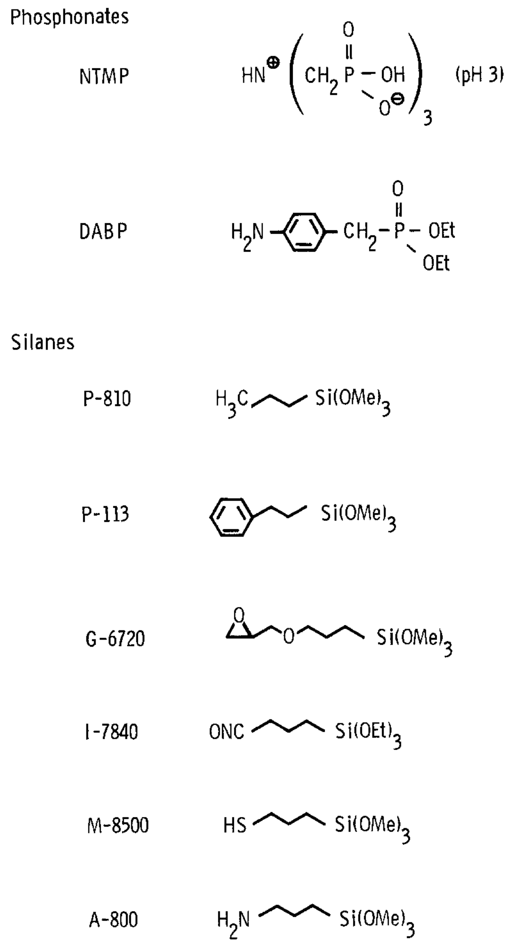

Figure 3 Structures of corrosion inhibitor compounds.

TABLE I Silane adsorption to FPL 7075–T6 surfaces

Silane	Concentration (p.p.m.)	Solvent system*	pH	Immersion time (min)	Si/Al
P–810	1000	W	4	40	0.04
		W	7	40	0.07
		M/W	4	40	0.076
		W	4	240	0.10
G–6720	1000	W	4	40	0.148
		W	7	40	0.083
		M/W	4	40	0.127
		W	4	240	0.158
A–800	1000	W	4	40	0.364
		W	7	40	0.460
		M/W	4	40	0.330

*W = water, M/W = methanol–water, 1 : 1.

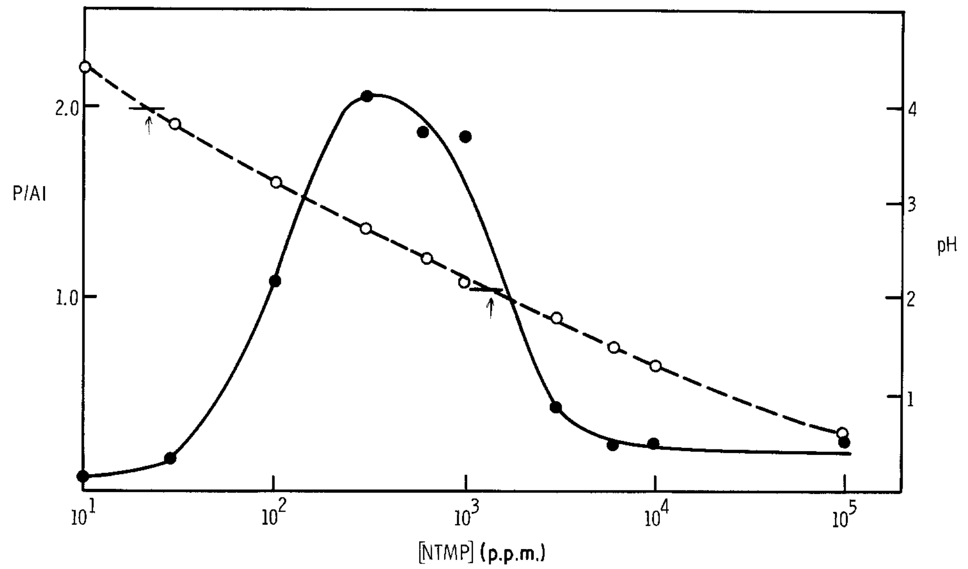

Figure 4 NTMP coverage as a function of concentration on SAA-prepared 7075–T6 aluminium surface. (○) pH, (●) P/Al ratio.

those treated with higher concentrations of NTMP and by FPL alone, but were apparently no more effective than the SAA control with respect to overall adhesive bond durability. However, XPS analysis (Fig. 6), in conjunction with SEM examination of the failed debonded sides, identified the true modes of failure. The SAA control (hydrated oxide on both sides under SEM; high aluminium and oxygen levels on both sides) failed within the oxide. Examination of the specimen treated with multilayer-forming 5000 p.p.m. NTMP solution (distinct "metal" and "adhesive" sides under SEM; high aluminium and oxygen, low carbon levels on "metal"side; high carbon, low aluminium and oxygen levels on "adhesive" side) indicated that the failure occurred between the metal and the adhesive (known as *adhesive failure*). Although distinct "metal" and "adhesive" sides were apparent upon visual examination of the debonded surfaces treated with 100 p.p.m. NTMP, SEM analysis indicated the presence of an adhesive layer on the "metal" side. XPS analysis showed low aluminium and oxygen and identical high carbon levels on both debonded sides, confirming a failure within the adhesive layer (*cohesive failure*), i.e. the best possible performance in a given adherend–adhesive system. This result is similar to that obtained using a 2024 aluminium alloy prepared by the phosphoric acid anodization (PAA) process [17], and indicates the importance of monolayer NTMP coverage for good bond durability (Fig. 4). SEM and XPS analyses indicated that the epoxysilane system failed by a "mixed mode" process).

A second wedge test was performed to evaluate six silanes and NTMP on the thinner, more sensitive FPL oxide (Fig. 7). The results indicated that four silanes performed better than the FPL control but not as well as NTMP; one silane (an aminopropyl derivative) performed very poorly with respect to the control; and one silane (M–8500, mercaptopropyl derivative) outperformed all the other inhibitor systems, including NTMP and organosilanes containing methyl, phenyl, isocyanate, and epoxide side chains. Subsequent XPS analysis of the adsorbed mercaptosilane inhibitor showed high concentrations of silicon and sulphur near the surface, with correspondingly low aluminium,

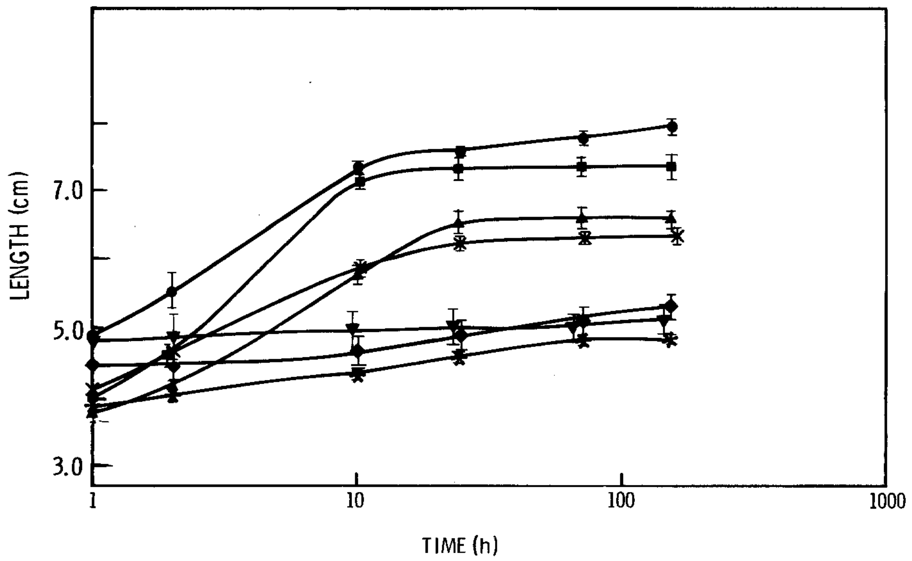

Figure 5 Wedge test results for inhibitor-treated SAA 7075–T6 aluminium specimens. (●) NTMP (500 p.p.m.), (■) NTMP (1500 p.p.m.), (▲) FPL, (×) NTMP (5000 p.p.m.), (♦) Z-6040 (5000 p.p.m.), (▼) NTMP (100 p.p.m.), (∗) SAA.

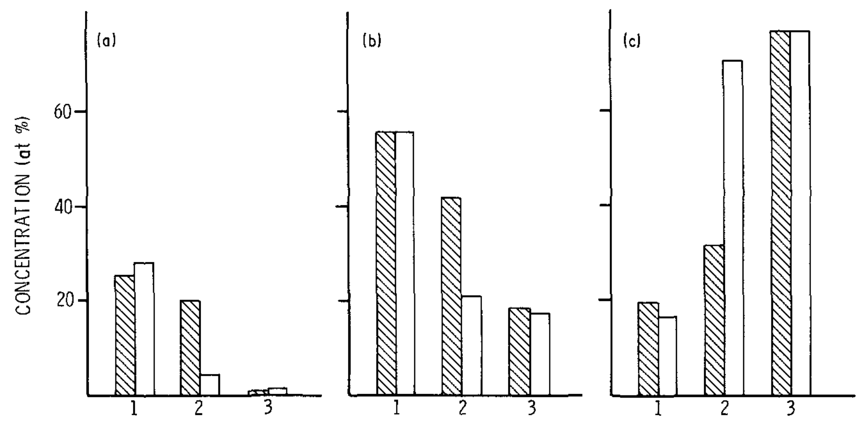

Figure 6 XPS surface analysis results for debonded SAA 7075–T6 aluminium specimens. (a) Aluminium, (b) oxygen, (c) carbon; (1) SAA, (2) SAA + NTMP (500 p.p.m.), (3) SAA + NTMP (100 p.p.m.); metal side shaded, adhesive side unshaded.

the sulphur being primarily in the reduced "inhibitor" (i.e., R–SH) form relative to sulphate $(–SO_4)^{2-}$, resulting from the FPL pretreatment.

The compatibility of the epoxy–polyamide primer with the nitrile-modified epoxy adhesive facsimile and the aluminium oxide surface was also evaluated by the wedge test, since earlier tests using the primer as the adhesive had failed immediately. As shown in Fig. 8, the addition of the primer improved the overall durability of the aluminium–adhesive system. The application of the mercaptopropyl silane derivative by pre-adsorption onto the substrate surface effectively maintained or slightly enhanced the bond strength between the primer and the FPL oxide. In contrast, adsorbed NTMP, which preserves the integrity of the (nitrile-modified) adhesive–metal bond, failed to prevent rapid deterioration of the polyamide primer–metal bond.

XPS analysis of the debonded specimens provided evidence to explain these results. Using atomic concentrations for the respective metal/adhesive debonded sides, the unprimed (30.0/28.6% Al, 58.2/61% O) and primed (24.6/26.4% Al, 59.4/57.3% O) FPL control and mercaptosilane-treated (27.1/25.0% Al, 54.1/51.3% O) specimens were found to have failed primarily within the oxide, which represented the weakest layer in the system. The higher levels of carbon on the adhesive side (24.7%) of the NTMP-treated oxide specimens compared to the metal (9.2%) indicated an adhesive failure (i.e. between the oxide and the polyamide primer).

3.4.2. Salt fog results

To evaluate the effectiveness of inhibitor-treated specimens exposed to an environmentally corrosive (Cl^--containing) atmosphere, a series of salt fog tests was conducted on primed specimens. The SAA-prepared surfaces proved too resistant for evaluation in a reasonable (< 1200 h) time-frame. Standard and accelerated salt fog tests on FPL-prepared specimens indicated that at least two silanes (mercaptopropyl and epoxy derivatives) generally maintained or enhanced protection in the scribed and unscribed areas of the primed panels, whereas NTMP actually increased the degree of deterioration (pitting/blistering) in the corresponding regions.

3.5. Electrochemical test results

Potentiodynamic polarization measurements provided a more sensitive means of evaluating the inhibitors, with respect to environmental (Cl^-) corrosion protection, than the salt fog tests. The results obtained from

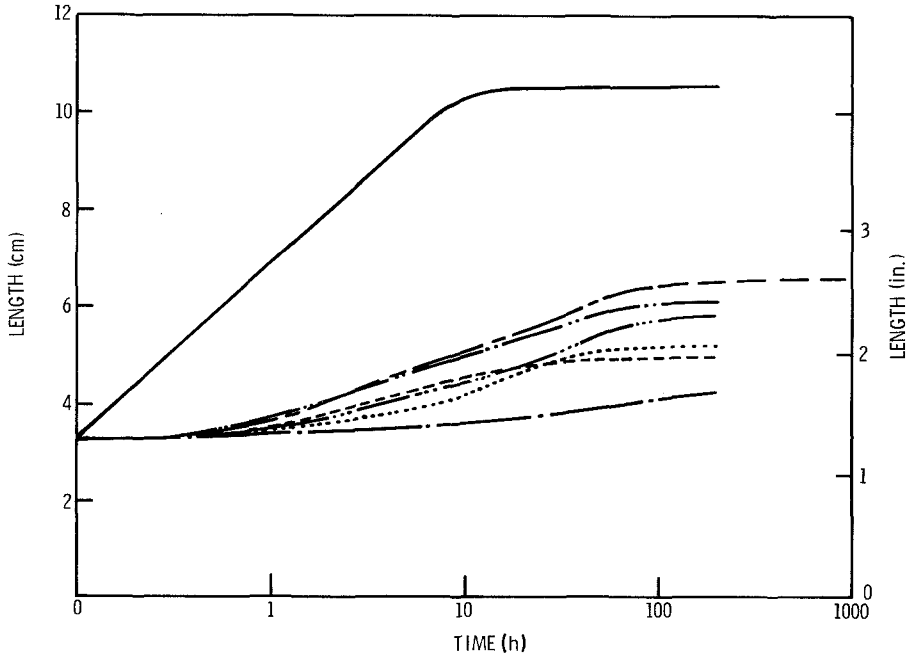

Figure 7 Wedge test results for inhibitor-treated FPL–7075–T6 aluminium specimens. (—) A-0800, (——) FPL, (-···-) P-810, (-····-) P-113/I-7840, (···) G-6720, (– – –) NTMP, (–·–) M-8500.

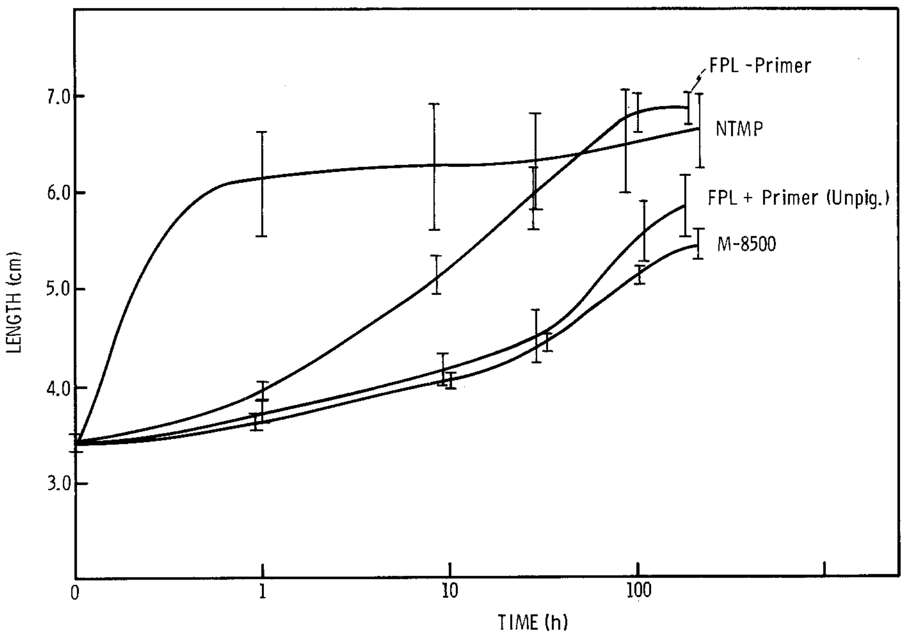

Figure 8 Wedge test results for primed FPL 7075–T6 specimens.

anodically polarizing polished 7075–T6 aluminium samples are presented in Fig. 9. For the control electrolyte (0.1 N Na_2SO_4, 0.002 N KCl, no inhibitor), pitting was observed almost immediately on the surface, and the aluminium showed no evidence of passivation. The addition of NTMP to the solution did not appear to protect the metal surface, when compared to the solutions containing no inhibitors. In contrast, the sample polarized in the electrolyte solution containing 1000 p.p.m. mercaptopropyl silane (M–8500) did passivate up to −200 mV (saturated calomel electrode) and had a distinct pitting potential well above (more noble than) the potential where pitting initiates in NTMP-containing electrolytes. The alloy surface remained free from pits up to −200 mV, above which small pits began to form.

4. Discussion

The corrosion resistance and polymer-bonding compatibility of the ionizable (acidic) organophosphonates and the neutral organosilanes are directly related to their inherent chemical properties. Specifically, NTMP inhibits the hydration of Al_2O_3 and maintains or improves bond durability with a nitrile-modified epoxy adhesive (depending on the surface treatment). The mercaptopropyl silane, in addition to having these properties, is compatible with an epoxy–polyamide primer and resistant to localized environmental corrosion. These results are discussed in conjunction with the nature of the adsorbed films and the metal substrate surfaces.

The initial integrity of an adhesively bonded system depends on the surface oxide porosity and microscopic roughness features resulting from the etching or anodization pretreatments [18]. The thin FPL oxide [7] provides a suitable substrate surface for evaluating some of the candidate inhibitors. The SAA surface characterized in this study consists of a thick (9 μm), porous, columnar layer that provides excellent corrosion resistance in both humid and

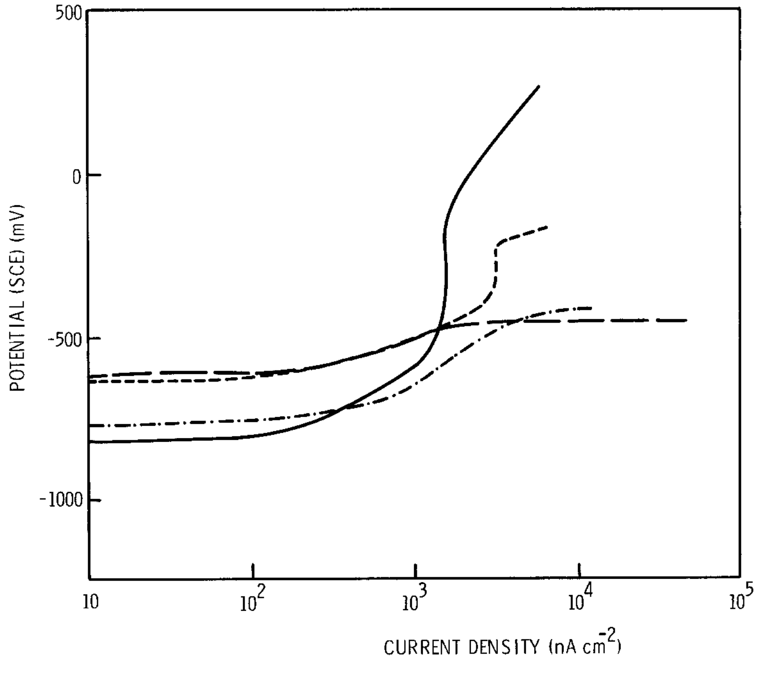

Figure 9 Electrochemical test results for two different inhibitors in 0.1 N Na_2SO_4 electrolyte with added KCl and inhibitors. The working electrode is polished 7075–T6 aluminium. (—) 0.1 N Na_2SO_4; (–––) 100 p.p.m. M–8500, 0.1 N Na_2SO_4, 0.002 N KCl; (–·–) 0.1 N Na_2SO_4, 0.002 N KCl; (——) 100 p.p.m. NTMP, 0.002 N KCl, 0.1 N Na_2SO_4.

aggressive (i.e. Cl^-) media due, in large part, to its thickness.

There are some interesting differences between the adsorption of ionizable (aminophosphate) and neutral (organosilane) compounds on to FPL- and SAA-prepared aluminium surfaces. The acidic NTMP species, consisting of a quaternary $\equiv N^+$ and unprotonated $-O^-$ groups in solution [19], exhibits a pH-dependent multilayer adsorption maximum in an aqueous solution. At low solution concentrations (< 100 p.p.m.), the coverage is essentially monolayer, corresponding to a P/Al ratio of 0.15 [12]. Wedge test results confirmed that this monolayer of NTMP leads to better long-term bond durability than multilayer films, which probably are formed by weak intermolecular hydrogen bonding and fail by a mixed-mode process.

On the other hand, alkoxysilane coupling agents produce structures which probably consist of a fused network of polymeric six-membered Si–O rings [20]. Although multiple layers of adsorbed silane (siloxane) films can be obtained, only the first few layers are bound to the metal by Si–O–Al bonds, through the silanol (hydroxyl) groups, and cannot be removed by aqueous rinsing [21]. The remaining film is available for general corrosion protection and possible coupling to the adhesive primer.

The corrosion behaviour of inhibitor-treated aluminium oxide systems provides clues to the mechanism of action for the phosphonates and silanes. In a purely hydrating environment, the hydrophilic NTMP provides short-term protection relative to untreated controls, probably by displacing H_2O in the oxide and forming a more stable complex [14, 22]. Used on SAA surfaces with the nitrile-modified epoxy adhesive, NTMP leads to a bond that fails only within the adhesive, i.e. cohesive failure. The FM 123–2 adhesive contains the curing agent dicyanodiamide, which does not release low-molecular weight amines until temperatures are above 90° C [23]. The curing sequence and/or kinetics of this adhesive system may be important factors with respect to its compatibility with adsorbed NTMP. On the other hand, the epoxy–polyamide primer contains free amino groups at room temperature and may be inhibited by the electrophilic NTMP species prior to curing. Another example of curing inhibition in an acidic medium was observed when moderate amounts of salicylic acid were added to an epoxy–amine matrix system [24]. Such behaviour could be responsible for the weak bond strengths observed for the NTMP-containing oxide–primer specimens. In environments containing an aggressive species (e.g. Cl^-), the anion may interact with and become incorporated into the NTMP–oxide matrix, whereby it can attack the metal surface.

Silanes applied to an aluminium substrate can protect the surface from hydration [15]. This hydration resistance was reflected by the wedge test performances of our silane-treated systems. Furthermore, electrochemical and salt fog results indicated that the oligomeric film maintained the resistance in environments containing aggressive species and oxidizing conditions. In contrast to NTMP, however, certain silanes are compatible and reactive with the epoxy polyamide primer as well as with the nitrile-modified adhesive which, in most cases, strengthens the oxide–epoxy bond. This result is presumably due to a chemical coupling of functional epoxide or mercapto side chains on the organosilane with the epoxy coatings during the curing process, and indicates the true bifunctional nature of such inhibitors. The poor performance of the aminosilane compound (expected to strengthen the metal–adhesive bond) is not completely understood at this time. Using similar concentrations, Walker [25] has shown that some silanes are effective adhesion promoters for urethane and epoxy paints on aluminium and mild steel surfaces and significantly improve the initial, wet, and recovered bond strengths.

5. Conclusions

Ionic phosphonates, e.g. NTMP, are effective hydration inhibitors because they can form an insoluble complex with the oxide surface. They are useful as epoxy adhesive couplers in cases where the adhesive is compatible with the adsorbed phosphonate molecule [14]. The wedge test results indicate that in both epoxy–aluminium systems studied, certain organosilanes tend to both increase the epoxy–metal bond durability and maintain hydration resistance. The results of the salt fog and anodic polarization experiments further suggest that these silane films are effective against localized pitting. Such systems could have application beyond the aircraft industry, i.e. these durability improvements are also generally relevant to the field of corrosion and corrosion prevention.

The addition of certain organophosphonate and organosilane compounds to polymeric epoxy–metal systems used in adhesively bonded aluminium leads to improved overall durability. With respect to adsorption conditions, NTMP exhibits a pH-dependent surface coverage, which includes a region characterized by a multilayer of hydrogen-bonded phosphonate molecules. These thick layers are weak and fail to provide good bond durability in a humid environment. However, NTMP monolayers are protective against hydration and are compatible with a nitrile-modified epoxy adhesive, although not with an epoxy–polyamide primer topcoat.

In contrast to NTMP, hydrolysed silane compounds are adsorbed as oligomeric films, and confer corrosion resistance in both hydrating and aggressive ion, e.g. Cl^-, environments. These inhibitors can also couple with applied epoxy primer or adhesive formulations to further protect the metal against corrosion. The organosilanes do not appear to affect the curing process, e.g. the percentage crosslinking, of the polymeric epoxy systems.

Such multifunctional compounds may represent new, environmentally desirable alternatives for corrosion protection.

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