WL-TR-95-4060

ENVIRONMENTALLY BENIGN SOL-GEL SURFACE TREATMENT FOR ALUMINUM BONDING APPLICATIONS

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April, 1996

Final Report for Period May 1993 - March 1996

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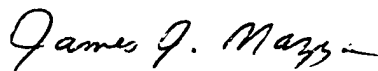AIR FORCE MATERIEL COMMAND
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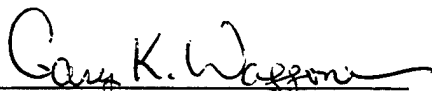
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REPORT DOCUMENTATION PAGE

Form approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*LEAVE BLANK*)	2. REPORT DATE April 22, 1996	3. REPORT TYPE AND DATES COVERED Final Report 5/93 - 3/96

4. TITLE AND SUBTITLE

Environmentally Benign Sol-Gel Surface Treatment for Aluminum Bonding Applications

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5. FUNDING NUMBERS

C: F33615-93-C-5322
PE: 62102
PR: 2418
TA: 04
WU: FN

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Boeing Defense & Space Group
P.O. Box 3999, M/S 82-32
Seattle, WA 98124-2499

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Materials & Manufacturing Directorate
Air Force Research Laboratory
Air Force Materiel Command
Wright-Patterson AFB OH 45433-7734
POC: James Mazza, AFRL/MLS, 937-255-7778

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

WL-TR-95-4060

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release: distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

A surface treatment process for aluminum using sol-gel chemistry has been developed that produces strong adhesive bonds without the rinse water requirements of traditional anodizing or etching processes. In this process, an acid catalyzed sol composed of zirconium alkoxide and a silane coupling agent in water was applied to etched or grit blasted aluminum substrates by immersion or spraying. After drying at 212°F for 1 hour, panels were primed with Cytec BR127 or XBR6757 (nonchromated, waterborne) primer and bonded in an autoclave using Hysol 9628 adhesive. The ASTM D 3762 Wedge Test was used to screen performance. The waterbased sol-gel formulation has superior performance to more traditional alcohol-based formulations used early in this program. The best formulation, using glycidoxytrimethoxysilane as the coupling agent, showed less than 0.25 inch crack extension after exposure to 140°F and 100% relative humidity for 336 hours. Failure in the crack growth region appears to be cohesive. In general, the waterborne XBR6757 showed better performance than the solvent based BR127. Further characterization of the coating is needed to understand interaction effects between adherend alloy, surface preparation, sol preparation, and application technique.

14. SUBJECT TERMS

Adhesive binder. sol-gel. aluminum. bonding. surface treatment

15. NUMBER OF PAGES
34

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE. UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

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1. Summary

Program Objective

The program objectives were to identify, develop, and evaluate a new aluminum surface treatment for adhesive bonding of Air Force components. The goal of this program was to produce a surface preparation system that minimizes rinse water use and uses environmentally benign materials. This surface treatment system must meet or exceed the performance of the phosphoric acid anodize (PAA) and Forest Products Laboratory (FPL) etch systems.

Program Approach

The approach was to use sol-gel systems to achieve a morphology similar to the etch/anodize processes to ensure an optimal mechanical linkage. Coupling agents were incorporated into the sol-gel to increase the adhesive-to-substrate bonding via chemical linkages. The PAA and FPL processes were used as benchmark controls. The first round of testing using alcohol-based sols was completed in 1994. The second round of testing used advanced aqueous sol-gel formulations and sample preparation techniques. The Appendix documents the second round testing results.

Aluminum 2024-T3 and 7075-T6 were used as the test substrates. Screening level testing was conducted using the wedge test, ASTM D 3762, with exposure at 140°F and greater than 95% relative humidity. First round test specimens were bonded using BMS 5-89 (American Cyanamid BR 127) chromated adhesive bonding primer and BMS 5-101 Type II Grade 10 (Dexter-Hysol EA 9628) 250°F cure adhesive. Second round tests used the EA 9628 adhesive with both BR 127 and the new nonchromated low VOC XBR 6757 primer.

Results and Conclusions

- **Sol-gel systems have initial crack performance equivalent to PAA**

  Significant progress has been made to meeting the goals of this program, that is, to develop a sol-gel process that has the same adherence characteristics as the phosphoric acid anodize or Forest Products Laboratory etch processes. Both the first round sol-gels (alcohol-based mixture of zirconium isopropoxide and glycidoxytrimethoxysilane (GTMS) with acetic acid catalyst) and the second round sol-gels (water-based formulation of the same components) produced wedge crack specimens which did not extend under laboratory ambient conditions.

- **Environmental durability is equal to control samples**

    Wedge crack specimens produced using the water-based sol had environmental durability equal to or better than control samples using PAA through 336 hours of humidity exposure. Crack extensions of less than 0.15 inch are typical. The failure is cohesive in the adhesive layer. Specimens prepared using the alcohol-based sols failed adhesively (crack extension greater than 0.5 inch) in less than 24 hours exposure to a hot humid environment.

- **Processing parameters defined**

    Important parameters are identified for a producible system. These include surface cleaning and activation of the substrate aluminum as well as sol characteristics such as type of catalyst (acid), coupling agent (GTMS), and curing process (flash dry then 200-300°F bake).

- **Surface preparation is critical to producing good bonding**

    Absorbent cleaning techniques, such as wheat starch blasting of the aluminum surface, were efficient at removing most soils from the aluminum surface with minimal etching. However, this method left a residue on the surface and failed to produce a surface that was clean enough or active enough for direct application of the sol-gel coating. A clean and chemically active uniform surface was obtained using a nonchromated etching deoxidizer (Boeclene). Grit blasting with aluminum oxide is also an effective surface preparation method when used with the water-based sols.

- **Bond primer may not be required for good bonding performance**

    Crack extension results were found to be similar with or without the use of the bond primer in some alcohol-based sol-gel systems. Eliminating the primer would result in considerable cost and time savings as well as elimination of a chromated material containing a high level of volatile organic compound (VOC).

2. Introduction

This report describes the results of screening level research to develop an environmentally friendly prebond surface preparation process for aluminum alloys commonly used in USAF aircraft. The goal is to use only non-toxic materials, to generate minimal waste streams, and to eliminate the need for large amounts of rinse water. A process based on sol-gel chemistry is reported here. First round tests using an alcohol-based sol are discussed in the main body of this report. The results of a second round of tests using a water-based sol are reported in the Appendix.

3. Background

Conventional processes to treat aluminum surfaces for bonding applications include anodizing (most often using phosphoric acid, PAA) or chromic acid-sulfuric acid etching (the Forest Products Laboratory process, FPL). Both of these systems produce a microrough surface into which an adhesive primer, a very thin adhesive solution, can penetrate. Adherence results from mechanical interlocking between the porous aluminum oxide layer and the adhesive primer. These systems have been extensively studied and an excellent review has been published.[i]

The desired failure mode of conventional bond systems is cohesive in the organic adhesive layer. In a hot humid environment, failure can also occur cohesively in the aluminum oxide binder layer. The failure results from hydration processes that cause breakdown of the stable aluminum oxide. Hydration of aluminum oxide is inhibited by a variety of anions, with phosphate having the greatest effect.[ii] Adhesive bonding using PAA as the adhesive binder produces the most durable bonding system currently used for aluminum.

From an environmental viewpoint, both PAA and FPL processes have the disadvantage of using strong acids and toxic materials. Both also require significant amounts of water to rinse excess process solution from parts. This rinse water must be treated prior to discharge or reuse, generating secondary hazardous waste materials. The goal of the research reported here is to develop a process that will produce adhesive bonds with equivalent strength and environmental stability to the PAA and FPL processes currently used. The new process must not require rinsing and/or use environmentally undesirable materials.
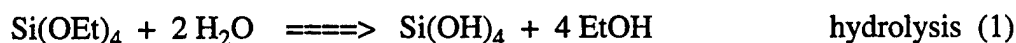
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4. Technical Approach

The program approach is to use sol-gel chemistry to develop adhesive binder coatings that mimic the microstructure of the anodize and etch processes. The surface microstructure provides a mechanical interlock between the bond primer and the metal substrate. Bond strength and durability may be increased by including hybrid inorganic-organic sol-gel precursors that modify the sol-gel metal oxide surface to allow covalent bonding between the adhesive and the inorganic adhesive binder. The strength of the system results from both mechanical and chemical interactions at the metal/sol-gel and sol-gel/primer interfaces.

Durability of the binder layer in humid conditions is a function of the susceptibility of the metal oxide layer to hydrate. Sol-gel systems based on silicon, zirconium, or other metals do not hydrate readily. They should be much more hydrolytically stable than adhesive binders based on aluminum oxide.

4.1 Sol-Gel Chemistry

The term "sol-gel," a contraction of "solution-gelation," refers to a series of reactions where a soluble metal species (typically a metal alkoxide or metal salt) hydrolyzes to form a metal hydroxide. The metal hydroxides then condense to form an inorganic polymer. Depending on reaction conditions, the polymers may condense to colloidal particles or may grow to form a network gel. Many metals are known to undergo sol-gel reactions. Silicon and aluminum sol-gel systems have been studied extensively.[iii] The sol-gel hydrolysis and condensation reactions, using silicon as an example, are shown in equations (1) and (2).

$$Si(OEt)_4 + 2\,H_2O \implies Si(OH)_4 + 4\,EtOH \qquad \text{hydrolysis (1)}$$

$$Si(OH)_4 \implies SiO_4 + 2\,H_2O \qquad \text{condensation (2)}$$

Our model of the formation of a sol-gel film on aluminum involves condensation of the sol metal hydroxide with hydroxyl groups on the aluminum substrate surface. The aluminum hydroxyl groups result from the hydrolysis of the native aluminum oxide surface film. The reactions are shown schematically in Figure 1.
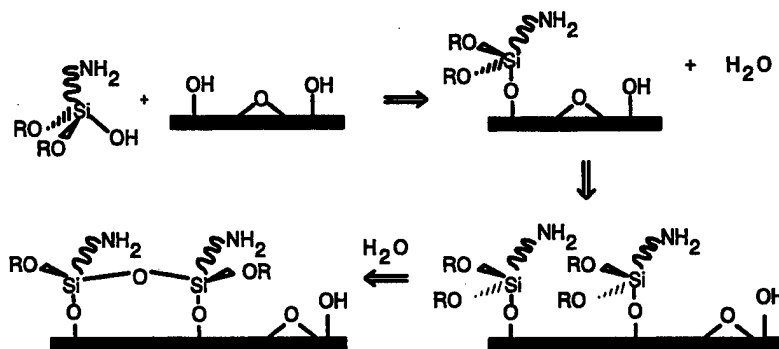
Figure 1 -- Sol-Gel Chemistry on a Hydrated Surface.

Sol-gel chemistry is quite versatile. Reaction conditions (for example concentration of reagents and catalyst type) control the relative rates of the hydrolysis and condensation reactions. Sol-gel solutions can be prepared which readily form thin films or which condense to fine colloidal particles. Starting materials and reaction conditions can produce films with morphology similar to the anodize and etch processes.[iii]

Sol-gel chemistry is also the basis for "coupling agents," i.e., a metal alkoxide sol-gel precursor where one alkoxide group is replace by a functionalized alkyl group such as the aminopropyl moiety shown in Figure 1. Unlike the metal-oxygen bonds, the metal-carbon bond is quite stable and does not hydrolyze. Coupling agents condensed onto a surface can produce strong covalent bonding between the metal substrate and the organic adhesive. Coupling agent technology has been extensively reviewed.[iv]

Sol-gel chemistry is not new for application to adhesive bonding systems. Aluminum alkoxides[v] and silicon alkoxides[vi] have been employed to coat aluminum substrates in the past. In all cases, coatings have been applied by immersion of the aluminum substrate in either an alcoholic or aqueous solution of the metal alkoxide. Sufficient time is allowed for the hydrolysis and condensation of the metal alkoxide species onto the aluminum substrate. This application method will produce a thin, perhaps a monolayer, coating on the substrate surface. Coupling agent precursors are typically used in these processes.

Coatings may also be applied by spin or dip coating.[iii,vii] Dip and spin coating solutions are typically more concentrated than immersion coatings. These coatings can be significantly thicker than immersion applied coatings since some hydrolysis and condensation occurs within the sol solution prior to application on the substrate. In addition, the entrained solution layer dries on the surface.

We investigated three sol-gel systems for their viability as surface treatments for adhesive bonding. The first sol-gel system used organically modified silanes as coupling agents for the aluminum. The second sol-gel system combined metal alkoxides, such as zirconium and titanium, together with organic network modifiers (such as oxalic acid or 1-(2-aminoethyl)-piperazine) to yield coatings. The third sol-gel system used aspects of both systems 1 and 2, combining them to produce a polymetallosiloxane coating. This third sol system, combining a coupling agent with an inorganic network to produce a microstructured surface, gave the best results in the crack extension tests. Details of this system are described in this report.

Sols were applied by "drench" coating panels with the ultimate goal of developing a sprayable sol-gel process. The drench coating process approximates both spin coating and spraying application of film-forming solutions. The sol is mixed metal alkoxide solution containing zirconium isopropoxide and a silane coupling agent. The zirconate should condense rapidly on the aluminum surface. The zirconium surface then reacts with the slower hydrolyzing silane coupling agent to produce a layered coating with the coupling agent oriented toward the adhesive. The coating is dried on the surface with no rinsing required. While the alcohol solvent is a volatile organic compound (VOC), we are using isopropyl alcohol which is not on the EPA Hazardous Air Pollutant (HAP) list.

A clean and chemically active surface is required to bond the sol-gel coating to the aluminum. A bare, pure aluminum surface will oxidize in air or dry oxygen to form a barrier aluminum oxide film that has a limiting thickness of 2-4 nm (20-40A).[viii] In moist air or water, this oxide layer will react with water to form a variety of hydrolysis products. The most prevalent on the aluminum oxide surface is probably an aluminum oxyhydroxide, $AlO(OH)$ or Boehmite. This hydrolysis reaction is fairly slow on the alumina surface. Further hydrolysis is pH dependent with aluminum oxide being soluble in both strong acids and strong bases.

Sol-gel condensation reactions are affected by the acid-base character of the metal-hydroxide surface. Condensation reactions are favored by the basic aluminum surface. The isoelectric point (IEP, a measure of surface acidity) for aluminum oxide in water is 9.2. Both silicon dioxide and titanium dioxide are acidic with an IEP of 3.0 and 6.0, respectively. Zirconium dioxide is expected to be acidic as well.

Hydration, or activation, of the aluminum surface can be accomplished in several ways. Aluminum will self-anodize in hot water producing a hydrated oxide surface. After an initial latent period, the immersed panel evolves gas and darkens. This reaction is used as the basis of

several nonchromated conversion coating processes. Dilute acidic solutions should also protonate the native aluminum oxide surface producing the required surface reactivity.

The possibility of including recently identified nonchromate corrosion inhibitors is an advantage of the sol-gel chemistry approach. Several of the candidates, the cerates, borates, and vanadates, are also known to have some characteristics of sol-gel chemistry.

4.2 Test Methods

Screening level tests were conducted using the ASTM D 3762 Wedge Test. Test panels of 2024-T3 aluminum (6 in x 8 in x 0.25 in) were prepared by first solvent wiping and then etch deoxidizing in a nitric/sulfuric/hydrofluoric acid deoxidizer solution (Boeclene) followed by thorough rinsing. The panels were either dip-coated or drench-coated with the sol-gel preparations, depending on the solution used. After drying under ambient conditions for 15 to 30 minutes, the panels were dried in a 212°F oven for at least 1 hour.

The dried panels were primed with BMS 5-89 chromated adhesive primer (American Cyanamid BR 127) and bonded using BMS 5-101 Type II Grade 10 (Dexter-Hysol EA 9628) 250°F curing adhesive. After bonding, the panels were cut into five 1 in x 8 in strip specimens and wedges were driven into the bondline. Progress of the crack along the bondline was measured after driving the wedge, after an 18-hour ambient soak, and after exposure to 140°F and greater than 95% relative humidity for 1 hour.

5. Results and Discussion

5.1 Surface Preparation

5.1.1 Absorbent Cleaning

Surface preparation using absorbent cleaning was investigated as a process to eliminate some rinse water requirement. Abrasive blasting was tested using both wheat starch and corn cob media. A range of pressures from 10 to 50 psi was evaluated to determine the balance between effective cleaning and unacceptable surface damage. Blasting using a pressure of 40 psi was deemed sufficient to remove the surface oils, mill stamp ink, and particulates without unduly etching the surface. Even at 50 psi, the wheat starch blasting caused minimal surface roughening (Ra = 16 μin versus 10 μin for mill finish).

The 6 in x 8 in test panels for the ASTM D 3762 Wedge Test were absorbent cleaned over their entire surface for approximately one minute on each side. Blasting produced a smooth lustrous

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surface, free of visible contaminants. The surface was water-break free after immersion in deionized (DI) water. Wiping the panel with cheese cloth and DI water resulted in increased metallic luster.

Wheat starch blasting leaves residual material on the aluminum surface. Figure 2 shows infrared reflectance spectra for a panel which was blasted, cleaned with DI water, and then blasted again. Spectrum *a* is the panel after the first wheat starch blast. Absorptions due to the starch are clearly present. The broad absorption between 2950 and 3600 cm^{-1} is due to O-H stretching in water that is hydrogen bonded to the starch. Carbon-hydrogen stretching in the starch absorbs at about 2950 cm^{-1}. Water bending modes occur between 1750 and 1300 cm^{-1}. Vibrations from the starch backbone absorb in the 1200 to 950 cm^{-1} region.

Thoroughly cleaning the panel with DI water and cheese cloth gives a surface with reflectance shown in spectrum *b*. All of the absorptions noted above for wheat starch have been removed. The weak broad absorption centered at about 3200 cm^{-1} and between 1750 and 1300 cm^{-1} result from adsorbed water on the aluminum surface. The slope of the spectrum is caused by surface roughness of the aluminum sample relative to the smooth reference mirror. Scattering due to surface roughness is wavelength dependent and is greatest at short wavelengths. Blasting this clean panel a second time with the wheat starch results in spectrum *c*, which again shows absorptions due to the starch.
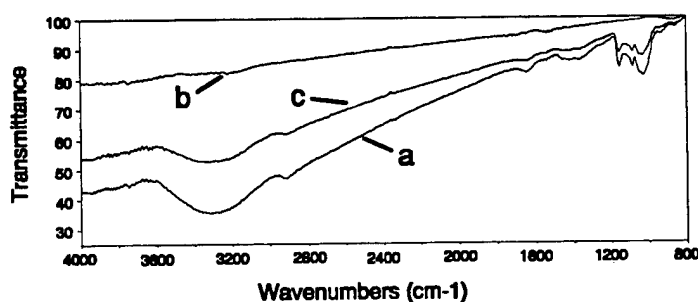
Figure 2 -- Specular Reflectance Spectroscopy of Wheat Starch Cleaned Test Panels.

These results show that wheat starch blasting does not leave a clean surface suitable for direct application of coatings. The friable nature of the wheat starch crystals and the adherence of the resulting extremely fine starch particles leaves an interfering residue on the aluminum surface. The starch residue must be removed by a DI water rinse and mechanical action.

Cleaning using corn cob media was investigated to determine if the surface contamination is unique to the wheat starch or is a common problem of media blasting. Corn cob media is much coarser than the wheat starch. It consists of pellets approximately 0.5 mm diameter. Blasting

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panels with this media leaves a visible residue that is removed by a water rinse. Panels contaminated with Apiezon N grease were not completely cleaned by 5 minutes of blasting with corn cob media. Surfaces were water-break free until the residue was rinsed away. Absorptions from the Apiezon N grease were observed in the infrared reflectance from the panel after the corn cob residue was removed.

Wedge tests showed significant variability when absorbent cleaning was used to prepare the panels. Owing to the contamination known to be present on the surface as discussed above, evaluation of absorbent cleaning was discontinued.

5.1.2 Surface Activation

A clean and chemically active surface is required to bond the sol-gel coating to the aluminum. We examined a hot water dip and a dilute acid dip as methods to produce a chemically active surface. Aluminum will self-anodize in hot water, producing a hydrated oxide surface. After an initial latent period, the immersed panel evolves gas and darkens. This reaction is used as the basis of several nonchromated conversion coating processes. Dilute acidic solutions should also protonate the native aluminum oxide surface producing the required surface reactivity.

Neither of these surface activation processes produced durable Wedge Test specimens. Surface activation testing was conducted early in the program before the best first round sol-gel system was identified.

5.1.3 Surface Preparation by Deoxidation

In order to ensure an active hydrated surface on the aluminum, a nonchromated etching deoxidizer (Boeclene) was used to clean test panels. Consistent results were obtained when panels are prepared using acid deoxidizing. All of the most successful tests described below used acid deoxidizing as the surface preparation prior to the sol-gel application.

5.2 Sol-Gel Screening Level Tests

Crack extension test results for the sol-gel solutions are compiled in Table 1. Both phosphoric acid anodize (PAA) and FPL etch control specimens were prepared for comparisons. As expected, the PAA specimens showed excellent bond durability. The FPL specimens (standard process, not optimized) showed excellent initial bond strength but poor bond durability, as expected.

The data in Table 1 show promising results with respect to bond strength of the sol-gel coating systems. Initial crack lengths, in many sol-gel samples, are equivalent to the PAA control and are cohesive in the adhesive layer. In all cases where the initial crack is less than about 1.6 inch the failure is cohesive in the BMS 5-101 adhesive layer. When the initial crack is greater than 1.6 inch, failure is predominantly adhesive at the sol-gel layer. Extension of the crack during ambient air soak and humidity exposure ranges from 0.5-0.7 inch in the best first round samples to essentially complete debonding. The failure mode of the first round samples is always adhesive at the sol-gel layer.

Analysis of the data in Table 1 is given in the following sections.

Table 1 -- Sol-Gel Screening Wedge Crack Extension Results

Sample #	Initial crack	Crack Extension (inch) (Average of 5 Specimens)		preparation*	volume ratio (ml) in 100ml isopropanol
		18 hour ambient	1 hour 140°F 100% Humidity		
control		1.36	1.37	PAA	
control		1.52	4.15	FPL etch	
G81-3	2.87	3.23	5.08	Zr/GlAc/APS	2:0.5:2
G83-1	3.03	3.27	3.43**	Zr/GlAc/GTMS	2:1:2
G83-2	2.52	2.52	2.52**	Zr/GlAc/GTMS/APS	2:1:2:2
G87-1	2.24	2.32	3.86	Zr/GlAc/APS	2:1:2
G87-2	2.60	2.68	3.23**	Zr/GlAc/GTMS	2:1:2
G89-1	1.65	1.69	2.95	Zr/APOH/GTMS	2:1:2
G89-2	2.64	2.72	3.30**	Zr/APOH/GTMS/APS	2:1:2:2
J19-1	1.34	1.34	2.16	Zr/HOAc/GTMS/stir 1 hr	2:1:2
J19-2	1.50	2.28	2.91	Zr/HOAc/APS/2 step	2:1:0.2
J19-3	1.38	1.65	2.99	Zr/APOH/APS/2 step	2:1.5:0.2
J21-1	1.30	1.69	2.28	Zr/HOAc/GTMS/ppt soln/3 hrs RT	2:1:2
J27-1	1.34	1.34	4.25	gelled Zr/APOH/ APS	2:1 sonicated 2% aq APS
J27-2	2.28	2.28	5.07	gelled Zr/APOH/ ECHS	2:1 sonicated 2% aq ECHS
J27-3	1.34	1.34	4.21	gelled Zr/APOH	2:1 sonicated
J29-1	1.26	1.26	1.97	Zr/HOAc/GTMS	2:1:1
J29-2	1.18	1.18	1.97	Zr/HOAc/GTMS/no primer	2:1:2
J29-3	1.30	2.32	2.56	Zr/HOAc/GTMS	2:1:4
J31-1	2.24	4.06	4.33	Zr/HOAc/ECHS	2:1:1.5
J31-2	2.44	4.13	4.72	Zr/HOAc/ECHS	2:1:3

* Zr = Zr(OPr)4; GlAc = Glacial Acetic Acid; HOAc = 80% Acetic Acid;
APS = γ-aminopropyltriethoxysilane; GTMS = glycidoxypropyltrimethoxysilane;
APOH = γ-aminopropanol;

ECHS = epoxycyclohexylpropyltrimethoxysilane

** Two or more of five crack test specimens did not extend after humidity exposure.

Figures 3 and 4 are photographs of the best first round crack extension panels. The crack specimen to the left of each photo is the PAA control. Sample J29-1, Figure 3, was prepared with chromated BR 127 bond primer. Sample J29-2, Figure 4, was prepared without the primer and shows nearly equivalent crack lengths. These two samples, along with J19-1, have nearly identical preparation and are close in Wedge Test performance. This leads confidence to our ability to prepare test specimens with consistent properties.
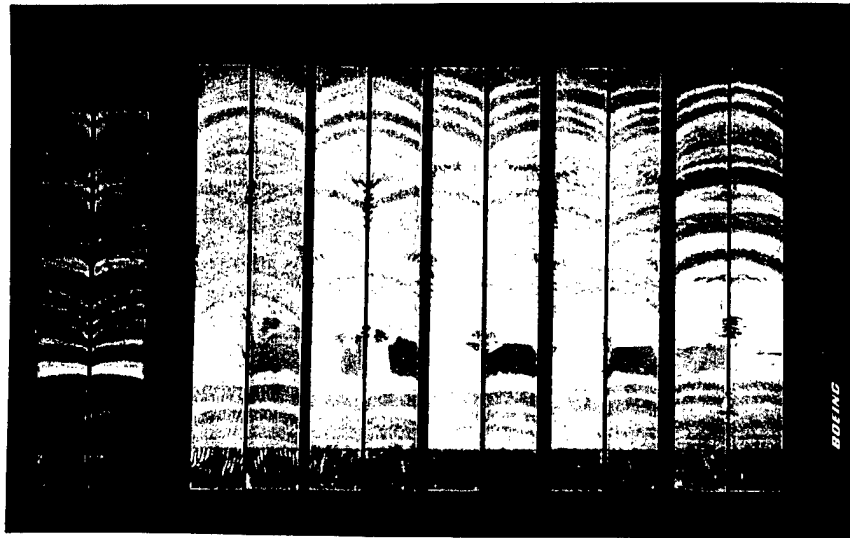

Figure 3 -- Sample J29-1 - Zr/1ml GTMS/80% HOAc - BR127 Primer.
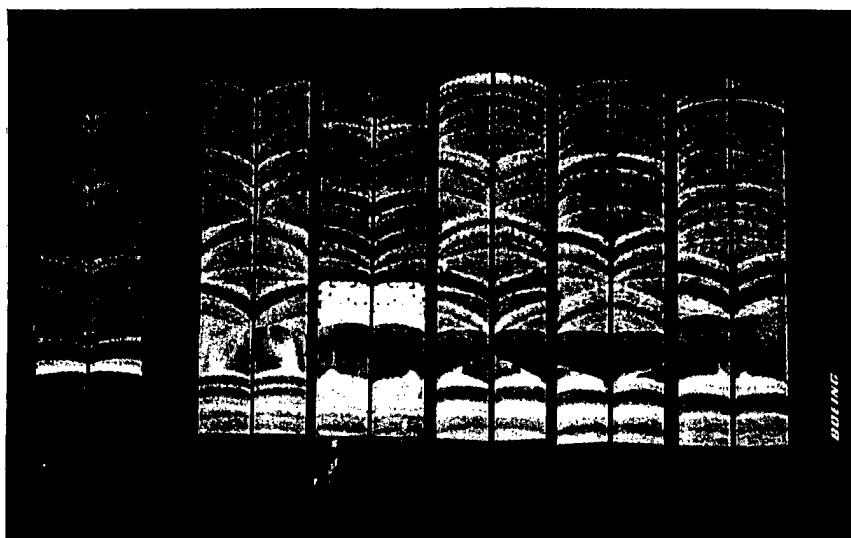

Figure 4 -- Sample J29-2 - Zr/2ml GTMS/80% HOAc - No Primer

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5.3 Effect of Sol Aging on Bond Strength

The importance of surface preparation and processing parameters was evaluated. The panels were prepared as described in Table 2 and drench-coated with the sol solution composed of zirconium isopropoxide, aminopropyltriethoxysilane (APS), aminopropanol, and isopropanol at 1:1:5:100 v/v. After solvent flash for 15 to 30 minutes, the panels were aged as indicated and then dried at 212°F for 2 hours. The panels were primed, bonded, and tested as usual.

Table 2 -- Surface Preparation Study Results

Sample #	Initial crack	Crack Extension (inch) (Average of 5 Specimens)		preparation	Age time before drying
		18 hour ambient	1 hour 140°F 100% Humidity		
control		1.36	1.37	PAA	
control		1.52	4.15	FPL etch	
G39		1.73	cd	wheat starch/water wipe	none
G39-3		1.26	5.51	wheat starch/water wipe	none
G47-1		3.03	cd	wheat starch/water wipe	none
G47-2		1.30	3.82	wheat starch/water wipe	none
G63-1		3.23	cd	solvent wipe	24 hours
G63-2		2.09	2.68	5min/200°F water	24 hours
G63-3		2.64	5.00	2% Acetic	24 hours
G71-1	2.76	3.27	cd	corn cob/water wipe	24 hours
G71-2	2.36	2.72	cd	scotch brite	24 hours
G71-3	1.42	1.46	4.17	Boeclene deox	none
G71-4	2.83	2.91	cd	Boeclene deox	24 hours

cd = complete debond

These data show that the most important processing factor is aging the coating before oven curing. Samples aged at ambient temperature for 24 hours before curing showed nearly twice the initial crack length as unaged specimens. Samples that are oven dried soon after coating show initial crack lengths comparable to the FPL and PAA controls. The variability in the wheat starch blasted samples is most likely due to incomplete removal of the wheat starch residue or incomplete cleaning.

The effect of aging on adhesion is probably due to differential rates of reaction between the zirconium alkoxide and the siloxane. In our model for this coating system, the rapidly hydrolyzable zirconium alkoxide reacts first with the aluminum oxide surface to form a

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zirconia-rich layer. The slower reacting aminopropylsiloxane then bonds to the zirconia-rich layer. The aminopropanol is present as a pH controller, modifying the hydrolysis and condensation rates of the two alkoxide species. In this model, the surface of the coating is predominantly amine which chemically bonds with the adhesive as shown in Figure 5.
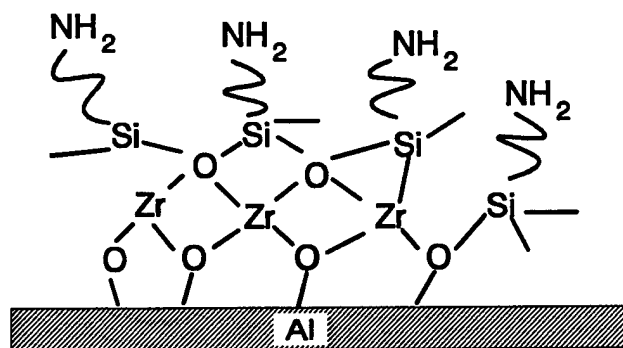
Figure 5 -- Zirconia-aminopropylsiloxane Coating System.

Amines are known to interact with aluminum oxide surfaces.[ix] When the coating is aged at room temperature before oven curing, hydrogen bonding interactions orient the amine end of both the aminopropanol and the aminopropylsiloxane toward the aluminum oxide surface. This hinders bonding of the zirconia to the substrate. Instead, condensation reactions occur at the surface of the coating between the hydrolyzed zirconium alkoxide and silicon alkoxide producing an upside down coating where weak alumina-amine hydrogen bonding holds the coating to the substrate. These weak hydrogen bonds are not nearly as strong as covalent bonds and are likely the cause of both the poor bonding observed in the crack extension tests. This upside down coating is shown in Figure 6.
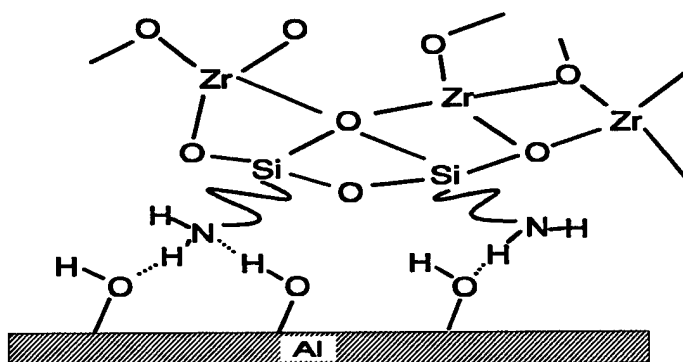
Figure 6 -- "Upside-down" Sol-Gel Coating.

Two samples, G63-2 and G63-3, tested surface activation processes. Exposure to hot water produced the must hydrolytically stable sample of the two. The 19-hour crack length showed moderate extension. The failure mode was adhesive at the sol-gel layer. Hot water is effective at increasing the concentration of hydroxyl groups on the surface of the aluminum substrate. This

surface should also retain significant amounts of adsorbed water. The zirconium isopropoxide will hydrolyze rapidly with the adsorbed water and condense on the aluminum hydroxide surface producing the stratified coating desired (APS on top of a zirconium dioxide layer). Later results, shown in Table 1, indicate that some amount of hydrolyzed zirconium alkoxide is necessary to develop a strong stable binder layer.

5.4 Effect of Catalyst

5.4.1 Acid versus base catalysis

The relative rates of the hydrolysis and condensation reactions that make up the sol-gel process are controlled by the catalyst (either acid or base) and the concentrations of the reagents in the reactions, the metal alkoxide, and water for hydrolysis. Acid catalysis promotes the hydrolysis reaction over condensation while base catalysis does the opposite. For reference, these reactions shown with zirconium and aluminum alkoxides as the sol-gel metals, are:

$$Zr(OR)_4 + 2\,H_2O ===> Zr(OH)_4 + 4\,ROH \qquad \text{Hydrolysis}$$

$$Zr(OH)_4 + Al(OH)_3 ===> (OH)_3Zr\text{-}O\text{-}Al(OH)_2 + H_2O \qquad \text{Condensation}$$

$$Zr(OR)_4 + Al(OH)_3 ===> (OR)_3Zr\text{-}O\text{-}Al(OH)_2 + ROH \qquad \text{Hydrolytic Condensation}$$

We chose γ-aminopropanol, APOH, as a catalyst since it is a nonaqueous, low volatility liquid similar in chemistry to the isopropanol being used as the solvent. The amine functionality makes it basic, promoting condensation reactions over hydrolysis. Zirconium isopropoxide reacts rapidly with water or other active hydrogens (i.e., aluminum hydroxyl groups). It should hydrolyze rapidly using ambient moisture and condense with itself and the aluminum surface, especially when the sol-gel coated panels are dried at 212°F. The zirconium alkoxide may also condense directly with the hydrated aluminum oxide substrate through the process known as hydrolytic condensation. In this process, unhydrolyzed zirconium alkoxide condenses directly with the hydrated aluminum surface producing the corresponding alcohol as the condensation product.

Even when catalyzed, the silane coupling agents hydrolyze more slowly than does the zirconium alkoxide. The presence of ambient moisture and heating is necessary to fully react the coupling agents with the zirconium oxide layer. A separate hydrolysis step is required before condensation will occur. Previous work has shown that siloxanes do not condense via the hydrolytic condensation process.[iii]

Acid catalysis enhances hydrolysis over condensation reactions. The data in Table 1 show that fast hydrolysis is important to hydrolytic stability. In all cases but one where acetic acid is the

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catalyst, at least two of the crack specimens did not extend after humidity exposure. The exception is a sol prepared with APS as the coupling agent where amine interaction with the aluminum substrate hinders the condensation reaction.

The coupling agent may also play a role in catalyzing hydrolysis and condensation reactions. Glycidoxytrimethoxysilane is acid-base neutral so its presence in the sol mixture will have no effect on the relative hydrolysis and condensation rates. Aminopropyltriethoxysilane, on the other hand, is basic due to the amine group. Using APS as the coupling agent may increase the alkoxide content of the coating.

Prehydrolysis of the sol-gel precursors is required for good initial bonding. When 80% acetic acid is used as the catalyst, initial crack length is equivalent to PAA controls. Initial crack lengths are significantly longer when glacial acetic acid is used as the catalyst. The 20% water allows some hydrolysis and condensation to occur in the sol and is required for good adhesion. Ambient atmospheric water is not adequate to fully hydrolyze the zirconium alkoxide and/or the silane coupling agent. The poor performance when using glacial acetic acid indicates that condensation reactions do not occur between aluminum hydroxyl and zirconium or silicon alkoxide groups. The hydrolytic condensation reaction is known in other systems to be slow or nonexistent.[iii]

Complete hydrolysis of the sol-gel precursors is important to develop a hydrolytically stable metal oxide film. The presence of hydrolyzable alkoxides in the film will have two effects. First, every residual alkoxide represents an incomplete condensation site that decreases the ultimate bond strength of the film. Second, in a humid environment these alkoxide residues can hydrolyze. The structural changes accompanying hydrolysis will cause stress in the film leading to failure in the sol-gel film or at one of the interfaces (metal/sol-gel or sol-gel/primer-adhesive).

5.5 Effect of Coupling Agent

Three coupling agents were studied in Phase I. They are shown schematically below.

γ-aminopropylsiloxane   glycidoxypropylsiloxane   3,4-epoxycyclohexylpropylsiloxane
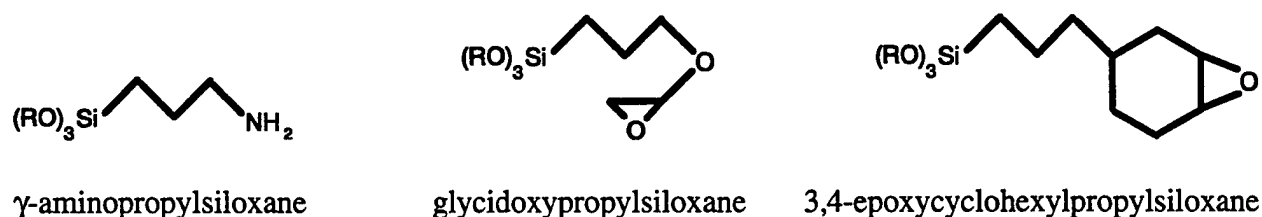
The data in Table 1 show that the choice of silane coupling agent is a significant factor leading to humidity stability of the bonding system. Glycidoxypropyltrimethoxysilane (GTMS) was present

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in all sols that produced hydrolytically stable crack specimens. The glycidoxy functionalized silane presents an epoxy group for reaction with the bond primer. GTMS is acid-base neutral and will not form strong Lewis acid-base interactions with the hydrated aluminum oxide substrate in a manner similar to APS. The aluminum oxide surface is more accessible to the zirconium alkoxide/hydroxide when GTMS is used allowing the desired stratification of the sol-gel coating with the epoxy groups oriented toward the primer. This orientation allows strong covalent metal-oxide bonding to develop between the aluminum oxide substrate and the zirconia and silica sol layer as well as orienting the epoxy moiety toward the adhesive.

Physical size of the coupling agent also has an effect on the bond performance. Both the initial adhesion and hydrolytic stability decrease when epoxycyclohexylpropyltrimethoxysilane is used as the coupling agent. This size effect is most likely the result of physical interference of both hydrolysis and condensation reactions by the bulky alkyl group attached directly to the silicon. Hydrolysis is incomplete and the silicon hydroxide cannot effectively condense with the zirconium surface.

These results suggest that the most effective coupling agents for a spray or drench coating application will be small so as not to sterically hinder hydrolysis and condensation reactions that must occur rapidly. Effective coupling agents for bond adhesion, regardless of application method (drench, spray, or immersion) should have minimal Lewis acid-base character so as to minimize interaction with the substrate surface.

5.6 Effect of Bond Primer

Crack extension results were found to be similar with or without the use of the bond primer. Samples J19-1 and J29-1 were prepared identically with the exception that J29-1 was not primed. Eliminating the primer requirement will result in considerable cost and time savings. Emissions and health risks from the chromated and very high VOC primer will also be eliminated.

5.7 ESCA Failure Surface Analysis

Crack surfaces of two samples were examined using Electron Spectroscopy for Chemical Analysis (ESCA) to determine the mode of failure. The results are shown in Table 3. Sample G98-2 shows adhesive failure in the initial crack with extension both during the 18-hour ambient soak and after humidity exposure. Interestingly, the data indicate failure at the adhesive-to-primer interface. Side 2, the side that appears to be bare metal, is the only side to show strontium and chromium, components of the adhesive primer. Perhaps the sol-gel layer is thick and porous

enough that the thin adhesive primer fully penetrated the sol-gel layer and became ineffective at bonding into the epoxy adhesive.

The carbon:oxygen ratio for side 1, the adhesive side, shows increased oxygen over that expected for the adhesive itself (approximately 8:1 C:O for the adhesive used here). This indicates that the surface has some metal oxide component. This sample used APS as the coupling agent and these results are consistent with an "upside down" coupling agent orientation of the sol-gel coating.

Sample J21-1 was prepared with a sol-gel solution composed of zirconium alkoxide, 80% acetic acid, and GTMS in a 2:1:2 volume ratio. The solution was stirred for 3 hours at which time extensive condensation had occurred as evidenced by the solution being cloudy. This sol was applied and bonded in the usual manner.

The ESCA data show that the failure mode in the initial crack is cohesive in the BMS 5-101 adhesive layer. In ambient and hot humid conditions, the failure is first cohesive in the sol-gel coating and then becomes adhesive at the primer/sol-gel interface. The key feature of cohesive failure in the sol-gel layer is a C:O ratio of about 2:1. Cohesion failure in the epoxy adhesive gives a C:O ratio of about 8:1.

In both samples studied, the sol-gel system is adhering to the aluminum substrate but is failing either inside the sol-gel layer or at the sol-gel-to-adhesive interface. Through mechanisms discussed above (e.g., incomplete hydrolysis and condensation) stresses can develop within the sol-gel film causing cohesive failure. Incorrect orientation of the coupling agent, to the extent that the coupling agent is important, will lead to adhesion failure at the sol-gel-to-adhesive interface. In order to achieve a strong stable binder, the sol-gel film must be thin enough to resist stress failure and the coupling agent must be oriented correctly on the surface. Developing a spray application to achieve consistent thin films and optimizing sol-gel constituents to achieve control of film orientation should improve the performance of these coatings.

Table 3 -- ESCA Data

Sample G87-2	initial	18Hr soak	1 Hr humidity
Side 1 (keeps Adhesive)	78.5%C 17.3%O 2.8%N 1.1%Si 0.1%Sr	78.5%C 17.3%O 2.8%N 1.1%Si	75.0%C 18.5%O 2.4%N 4.1%Si 0.1%Zr
Side 2	56.8%C 25.6%O 3.4%N 10.7%Si 1.5%Zr 0.4%Cr 1.6%Al	56.1%C 27.4%O 3.9%N 8.7%Si 2.0%Zr 0.2%Sr 0.2%Cr 1.3%Al	56.1%C 27.4%O 3.9%N 8.7%Si 2.0%Zr 0.2%Sr 0.2%Cr
Failure Mode	Adhesive failure at the sol-gel/primer interface	Adhesive failure at the sol-gel/primer interface	Adhesive failure at the sol-gel/primer interface

Sample J21-1	initial	18Hr soak	1 Hr humidity
Side 1 (keeps Adhesive)	83.0%C 10.4%O 5.7%N	59.6%C 23.4%O 6.1%N 1.8%Si 0.24%Zr 0.74%Sr 2.0%Al	70.9%C 19.7%O 4.6%N 1.0%Si 1.6%Zr 0.25%Sr
Side 2	84.2%C 10.3%O 5.6%N	59.3%C 26.8%O 3.5%N 4.1%Si 2.4%Zr 1.9%Al	56.2%C 27.5%O 4.2%N 3.7%Si 2.1%Zr 1.2%Sr 3.0%Al
Failure Mode	Adhesive failure inside the adhesive layer	Adhesive failure in the sol-gel coating	Cohesive failure at the primer-sol-gel interface

5.8 Inhibitor Incorporation

A variety of nonchromate corrosion inhibitors were tested in a series of experiments using the selected sol-gel system. The inhibitors chosen were those that had initially done well in aqueous electrochemical impedance spectroscopy studies on aluminum specimens. The sol-gel was the zirconium isopropoxide with 3-aminopropyltriethoxysilane and aminopropanol in isopropanol. Aluminum panels were deoxidized with Boeclene prior to coating. Four individual inhibitors and three inhibitor mixtures as described in Table 4 were tested.

Table 4 -- Candidate Inhibitors Tested in Sol-Gels

Sample Number	Inhibitor
G69-1	Barium metaborate
G69-2	Sodium metavanadate
G69-3	Cerium oxalate
G69-4	Cerium acetate
G69-5	Barium metaborate Sodium metavanadate
G69-6	Cerium oxalate Cerium acetate
G69-7	Lanthanum acetate Cerium oxalate

The inhibitors were not entirely soluble in the alcoholic solutions, thus they were applied to the aluminum surface similar to a pigmented paint. The treated specimens were dried at 212°F as before, primed, and bonded as crack extension specimens. After the wedges were driven into the samples, most exhibited crack extension with cohesive failure occurring within the bondline of the adhesive (Table 5). Values were comparable with PAA and FPL controls. After 18 hours, some degradation had occurred, and after humidity exposure there was a larger increase in the crack length. In the crack extension region (after the initial crack), all samples failed adhesively at the sol-gel interface. Sample G69-2 was notably better than the others. The initial crack length is comparable to PAA and mostly cohesive. Degradation at ambient and in humidity was adhesive. Variations seen in the results shown in Table 5 are most likely due to sample preparation. The inhibitors may play a role as well, especially their relative insolubility in the alcohol solvents employed for these sols.

Samples were also prepared for salt spray exposure. After 1 day in salt spray, all of the samples had experienced some discoloration, some had striations throughout the specimen, and a few had small pit initiation. After 3 days in salt spray, striations and small pits were seen on all of the samples, Table 6. Sample G69-6, the cerium acetate/cerium oxalate sample exhibited slightly better corrosion resistance than the others. It is unknown at this point whether this increase in corrosion resistance is a result of the inhibitor used, sample preparation, or other factors. Cerium acetate was distinctly more soluble than the other inhibitors in the alcoholic sol-gel solution. It is possible that the combination of a more soluble and less soluble inhibitor provided the protection needed for the sample to survive salt spray conditions. After several days, this sample also experienced pitting.

Table 5 -- Crack Extension Results for Inhibitor Mixtures

Sample #	Initial	Crack Extension (mm) (Average of 5 Specimens)		inhibitor included
		18 hour ambient	1 hour 140°F 100% Humidity	
control		1.36	1.37	none - PAA control
control		1.52	4.15	none - FPL etch control
G69-1	2.56	2.20	3.62	Barium metaborate
G69-2	1.26	1.73	2.13	Sodium metavanadate
G69-3	1.54	3.46	3.94	Cerium oxalate
G69-5	1.42	2.09	3.62	Barium metaborate Sodium metavanadate
G69-6	1.65		4.33	Cerium oxalate Cerium acetate
G69-7	1.54		4.45	Lanthanum acetate Cerium oxalate

Table 6 -- Salt Spray Exposure Results

Filename	Exposure (days)	Observations
G69-1	3	Striations (color), small pit initiation
G69-2	3	Striations (color), small pit initiation
G69-4	3	Slightly better, fewer pit sites, less discoloration, but still technically a failure
G69-3	3	striations, initiation of pitting
G69-6	1	striations, no pitting
G69-7	1	striations, a few very small pit initiations
G69-5	1	striations, a few very small pit initiations
G71	1	some good and bad areas

Primers qualified to BMS 5-89 must pass a scribe corrosion test of 40 days in salt spray. It is unknown whether the nonchromate inhibitors have any chance of passing that test. Alternately, qualifying a sol-gel adhesive binder to BMS 5-89 may not be appropriate. A spray applied binder can be used immediately prior to bonding without the part storage requirement imposed by the logistics of an anodize or etch process.

6. Conclusions -- First Round Testing

Results from the survey studies lead to the following conclusions:

- **Polymetallosiloxane coatings produce strong bonds to aluminum.**

  The best first round zirconium/silicon coating yields initial adhesive bond performance that matches the initial performance of the phosphoric acid anodize and FPL etch controls.

- **Humidity exposure produces crack extension (~0.5 to 0.7 inch)**

  The initial crack for the best first round zirconium/silicon coating always shows cohesive failure. Failure during the 18-hour ambient soak and after humidity exposure was always adhesive. Improvement of environmental durability should be achievable by optimizing process and chemistry of the sol-gel system.

- **Surface preparation is vital to good adhesion performance. Inefficient surface cleaning and surface activation can negate a good sol-gel chemistry.**

  Absorbent cleaning techniques, such as wheat starch blasting of the aluminum surface, were efficient at removing most soils from the aluminum surface with minimal etching. However, this method left a residue on the surface and failed to produce a surface that was clean enough or active enough for direct application of the sol-gel coating. A clean and chemically active uniform surface was obtained using a nonchromated etching deoxidizer (Boeclene).

- **Initial results warrant further investigation**

  The initial results of this survey show that these sol-gel coatings show great promise as surface treatments for adhesive bonding and may eventually displace the use of the bonding primer as well.

7. APPENDIX -- Screening studies using Advanced Sol-Gel techniques.

Introduction

Significant progress has been recently made in water-based sol-gel coating systems and adhesive primers. A second round of screening level tests were conducted to evaluate these new technologies for their effectiveness as an adhesive bonding system for aluminum substrates. The test matrix was designed to accomplish four goals. The first goal was to determine whether the alloy substrate plays a role in the sol-gel bonding system. The second goal was to determine the effectiveness of spray applying the sol-gel as compared to immersing panels in the sol-gel solution. The third goal was to compare surface preparation techniques using acid etching and grit blasting with alumina as the candidates. The fourth goal was to compare the performance of solvent-based BR 127 primer to low volatile organic content (VOC) nonchromated XBR 6757 primer. The sol-gel formulation used was adapted from the process developed for use on titanium substrates. The wedge crack test (ASTM D 3762)was used for screening purposes.

Experimental

The sol-gel used for all specimens in the second round of testing was an aqueous mixture of glycidoxytriethoxysilane (GTMS) and tetra-n-propoxyzirconium (TPOZ) using an acetic acid catalyst. The preparation of the sol was adapted from a similar system successfully used for preparing titanium substrates for adhesive bonding. Volumes of reagents were chosen to achieve a 2:1 v:v ratio of GTMS to TPOZ and for total alkoxides to be 3% by volume of the final solution. This solution was further diluted to about 0.75% for some of the applications.

Test panels of 2024-T3 or 7075-T6 were prepared by alkaline cleaning (aqueous Alconox) and then either acid etching in Boeclene (nitric/sulfuric/ammonium bifluoride) or grit blasting using 180 grit aluminum oxide. The sol was applied to the panels by either immersing the panel in the sol for 10 minutes or by misting the sol onto the panel using a finger pump sprayer. The spray application was not so heavy as to cause runs or sags and one "coat" did not completely cover the surface. When multiple coats were applied, the sol was allowed to flash dry between coats. After drying in air, all panels were baked for 30 minutes at 250°F. The primer was applied and cured within 24 hours and the panels were bonded with EA 9628 adhesive in an autoclave. Wedge crack testing was accomplished in accordance with ASTM D 3762.

Results and Discussion: Sample preparation procedures, alloy, primer used, and wedge crack results are shown in Table A1. The crack extension data are the average values for the 5 "fingers"

cut from one bonded panel. Measurements were made by observing the edges of the specimens. Samples whose numbers start with "H" were prepared and tested at Boeing. Samples labeled "dayton" were prepared at Boeing (sol-gel and primer) but were bonded and tested at the University of Dayton Research Institute. All Boeing-prepared samples were allowed to soak at laboratory ambient conditions for 24 hours after driving the wedge. Only sample H139-8, prepared without the sol-gel, showed significant crack growth during the soak. Figure A1 graphs the cumulative crack extension as a function of time from first exposure to the hot humid environment. The failure mode appears to be cohesive in the better samples and a mixture of cohesive and adhesive for those samples which extend more than about 0.25 inch in 2 weeks exposure.

Specimen Description						Crack Extension Ambient	Cumulative crack extension (inches) Hours at 140 F & 95-100% RH			
Sample	alloy	prep	sol %	coats	primer	24 hr	24 hr	186 hr	336 hr	864 hr
H139-4-3	2024	grit	3%	1 spray	xbr6757	0.0	0.0	0.0	0.0	0.04
H139-2-3	7075	grit	3%	dip	xbr6757	0.0	0.0	0.03	0.03	0.11
H139-2-1	7075	etch	3%	dip	xbr6757	0.0	0.02	0.02	0.05	0.08
H139-5	7075	etch	3%	3 spray	xbr6757	0.0	0.02	0.04	0.06	0.11
H139-1	7075	etch	3%	dip	br127	0.0	0.01	0.06	0.08	0.08
H139-7-1	7075	etch	0.75%	4 spray	xbr6757	0.0	0.03	0.06	0.08	0.14
H139-6	7075	etch	0.75%	1 spray	xbr6757	0.01	0.02	0.07	0.1	0.15
dayton	7075	paa	---	---	control	---	0.038	0.078	0.104	
H139-2-2	2024	etch	3%	dip	xbr6757	0.0	0.04	0.09	0.11	0.19
H139-3	7075	etch	3%	1 spray	br127	0.0	0.05	0.08	0.11	0.17
H139-4-1	7075	etch	3%	1 spray	xbr6757	0.0	0.04	0.06	0.12	0.17
dayton	2024	paa	---	---	control	---	0.088	0.138	0.154	
H139-7-3	2024	grit	0.75%	4 spray	xbr6757	0.0	0.06	0.13	0.18	0.27
H139-7-2	2024	etch	0.75%	4 spray	xbr6757	0.02	0.15	0.26	0.28	0.52
dayton	7075	etch	3%	dip	xbr6757	---	0.238	0.288	0.385	
H139-4-2	2024	etch	3%	1 spray	xbr6757	0.0	0.08	0.33	0.46	0.61
dayton	2024	etch	3%	dip	br127	---	0.2	0.528	0.658	
dayton	2024	etch	3%	dip	xbr6757	---	0.466	0.754	0.824	
dayton	7075	etch	3%	dip	br127	---	1.316	1.364	1.52	
H139-8	2024	etch	0.00%	none	xbr6757	0.17	1.46	1.77	2.5	

Table A1 -- Sample preparation and Wedge Crack Results

The results from the second round of tests are significantly better than those described in the main body of this report. The success is primarily a result of the significant progress made in sol-

gel technology and techniques during the past 18 months. The aqueous sol-gel preparation is significantly better than the alcohol-based preparation used in the first round tests.
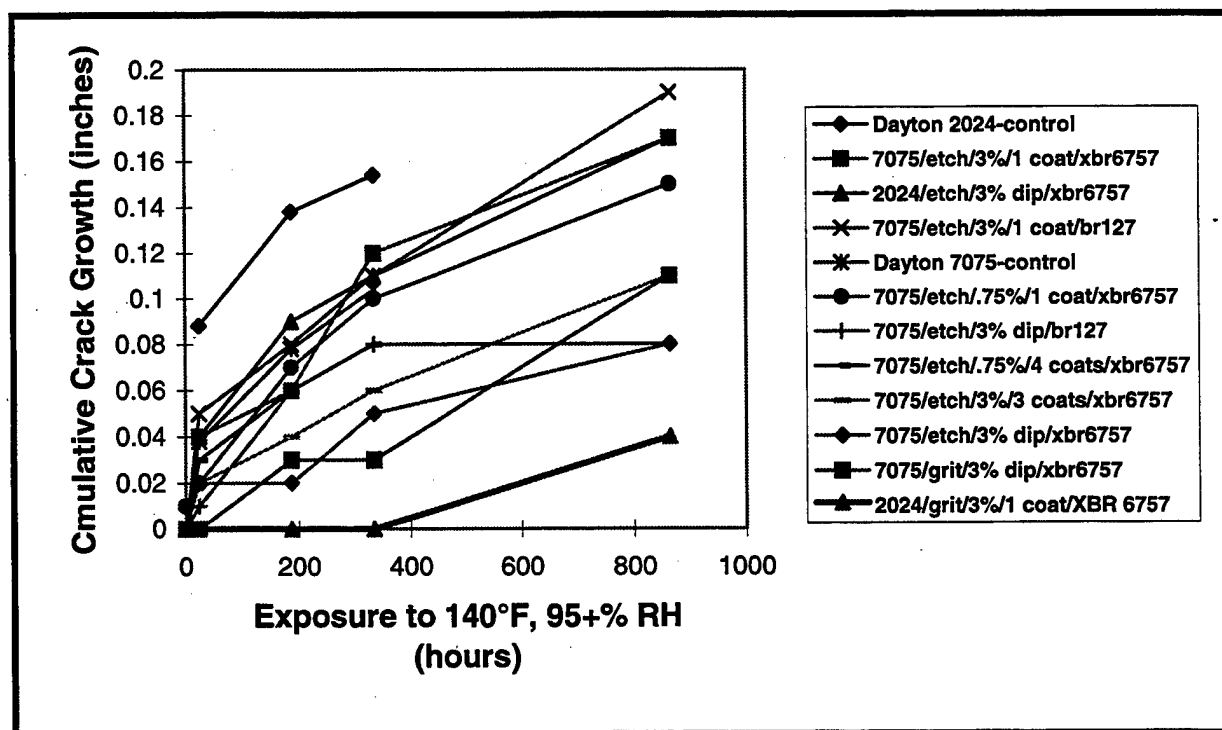

Figure A1 -- Wedge Crack Data for Advanced Sol-Gel Formulations

The results are discussed below relative to the goals of the second round of tests. All of the best specimens are strongly bonded as evidenced by the initial cohesive crack which does not extend in ambient conditions. Samples are compared primarily on the basis of their durability to humidity exposure.

Effect of Alloy. The 7075 alloy in general gives better results than does 2024. The model for sol-gel interaction with the substrate through condensation reactions is likely sensitive to alloy. The number of hydroxyl groups and their reactivity will depend on the alloy surface chemistry. It is these hydroxyl groups which condense with the sol-gel coating system. Surface preparation, discussed below, has a substantial effect on the alloy surface chemistry. The interaction between alloy and surface preparation needs further study.

Effect of Application Method. There is no clear indication that immersion ("dip") and spray application of the sol differ in producing a strong durably bonded system. This is a positive result as it implies that the sol-gel is not sensitive to application technique. The coating can be applied in a conventional immersion tank or as a sprayed coating. Immersion is likely better at coating

complex shaped parts. Spray application has the advantages of being transportable, uses a minimum volume of materials, and does not require rinsing.

The application process needs significantly more evaluation. Variations in technique (spray application in particular) may interact with substrate alloy, the surface preparation method, and the sol application procedure. For example, there is little difference between 7075 samples which are etched or grit blasted when the coating is applied by immersion (Table A1, samples H139-2-3 and H139-2-1). However, for 2024 substrates, coating by immersion or spraying does not seem as important as whether the surface was etched or grit blasted (c.f. samples H139-4-3, H139-2-2, and H139-4-2).

Effect of Surface Preparation. Grit blasting with alumina appears to produce a more durable system than etching although not enough specimens were prepared to show statistical significance. The two best specimens were grit blasted. The only other grit blasted was coated with the 0.75% sol-gel and is not comparable.

Further evaluation of surface preparation techniques is needed. Grit blasting is dependent on operator technique while etching is dependent on bath chemistry. Greater sample-to-sample variations are expected from the blasting process. Furthermore, it is likely that the surface preparation technique interacts with the substrate alloy. This interaction, if present, needs to be evaluated.

Effect of primer. The best results were most often obtained using the waterborne low VOC XBR 6757 primer. This is likely a function of better wetting of the primer to the hydrophilic sol-gel coating. Other testing has shown that the waterborne primer is also equal to or better than the solvent based BR 127 when applied to anodized surfaces.[x] As an added bonus, XBR 6757 is nonchromated as well as being low VOC.

Sol-Gel Coating Thickness. The data indicate that thicker application of the sol-gel gives more durable bonds. Comparing the data in Table A1 for specimens made using 2024 substrate, the best (sample H139-4-3) has a spray applied 3% coating. In the middle are samples with thinner coatings applied by immersion (H139-2-2) and 0.75% spray (H139-7-2 and H139-7-3). A specimen which was etched only (H139-8) with no sol-gel coating was the only sample which extended during the ambient soak. It failed adhesively in less than 24 hours of humidity exposure.

Conclusions:

The conclusions in the original report are substantiated by the second round test results. In particular, the substrate cleaning and surface preparation is critical. Also, the chemistry of the sol and its application technique play significant roles. The latest results show that sol-gel chemistry has considerable promise to produce a strong environmentally durable bonded system on aluminum. Follow-on work in several areas is warranted.

First, the sol-gel coating needs further characterization. The model discussed above for sol-gel coatings increasing bond strength and durability depend on forming an oriented film on the substrate surface. The inorganic end of the sol-gel interacts with the metallic substrate while the organic functional group is available to form covalent or entanglement bonds with the adhesive primer or adhesive. Little effort has been applied to the fundamental understanding of the sol-gel system. Techniques such as Electron Spectroscopy for Chemical Analysis (ESCA), Auger profiling, and Reflectance spectroscopy can be used to better characterize the coating.

A second focus of coating characterization is to understand the mechanism of film formation and the differences between immersion and spray application techniques. There are fundamental differences in the manner of film formation between the two processes. In immersion coating, slow reactions which are thermodynamically favored can dominate. With the part immersed in the solution, reactants can convect or diffuse to the metal surface and reaction products can leave. The most stable coating will develop. In the case of the spray on application, only a thin film of the reacting solution contacts the part surface. Depletion of reactants can and likely does occur. Reaction products can not escape and may influence the character of the sol-gel film. As the film evaporates, changes in concentration can alter the chemistry that occurs. In addition all reaction products remain on the surface when the film evaporates. In all, the film developed in the spray on application is dominated by kinetically accessible products. Those processes which occur fast are the ones which occur.

Third, the interaction of process parameters needs to be evaluated. For instance, the optimum surface preparation is likely to be alloy dependent. A particular alloy surface preparation procedure may be better for immersion application of the sol than spraying. An appropriately designed experiment should be able to sort out these secondary effects.

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