Nanostructured Silicon Sol-Gel Surface Treatments for Al 2024-T3 Protection

A.J. Vreugdenhil,† V.N. Balbyshev,** and M.S. Donley—Air Force Research Laboratories*

Current coatings for aircraft corrosion protection are based on chromate surface treatments, primers, and topcoats. One approach to developing a chromate-free surface treatment is through the use of sol-gel materials that interact strongly with both the substrate and the subsequent polymer layers. Results are reported here on a new sol-gel technique using a pre-formed, self-assembled, nano-phase particle (SNAP) sol-gel system. SNAP films have been investigated by infrared spectroscopy, atomic force microscopy, and electrochemical methods. Potentiodynamic polarization and electrochemical impedance spectroscopy demonstrated that the SNAP system generates high quality, defect-free, durable films. Formulation parameters, including crosslink density and coupling agent application, were optimized based on experimental results.

INTRODUCTION

Corrosion protection of aluminum-skinned aircraft and development of improved environmentally benign surface treatments for aluminum aerospace alloys are high priority topics for U.S. Air Force research. To date, the corrosion inhibition of aluminum alloys has relied extensively on hexavalent-chromium compounds included in both surface preparation, cleaning materials, and organic primers. However, the toxicity and carcinogenic properties of chromium has caused federal agencies, in particular the EPA, to impose severe restrictions on its use.[1] Changing federal regulations dictate the use of fundamentally new coating systems that are capable of meeting the new environmental standards. Much emphasis in recent years has been placed on modifying existing processes or developing new methods that are more environmentally acceptable than current practices.

The long-term goal of the U.S. Air Force, as expressed in its Coating Systems Strategy,[2] requires environmentally benign corrosion protection with the capability of performance over 30 years of service. This high performance corrosion protection requires a substantial basic research effort to establish materials and processing capable of meeting the life cycle requirements. The use of sol-gel based surface treatments and coatings for corrosion protection of aluminum alloys is being investigated by several researchers and offers great promise for meeting the above performance benchmark.[3-5] The results reported here describe a novel application of sol-gel chemistry to prepare nano-structured coatings that exhibit excellent barrier properties.

One factor that would contribute significantly to attaining a 30+ year coating stability is improving the hydrolytic stability of a coating system. Surface treatments that enable strong covalent bonding at the metal oxide/organic coating interface could dramatically improve the long-term hydrolytic stability.[6,7] One approach to such robust interface bonding is through the application of sol-gel coatings, which can provide inorganic functionality for bonding to the metal substrate and tailorable organic functionality for interaction with subsequent polymer layers. The thickness of sol-gel films used in these types of applications varies but is often on the order of 0.5 to 5 µm.[8,9] As well as providing tenacious adhesion, densified sol-gel coatings can also provide substrate protection in the form of anti-corrosion barriers.[10,11] Such environmentally benign surface treatment

Presented at the 78th Annual Meeting of the Federation of Societies for Coatings Technology, on October 18-20, 2000, in Chicago, IL.

*Materials and Manufacturing Directorate, Nonmetallic Materials Division, Coatings Research Group, Wright-Patterson AFB, OH 45433-7750.
†University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0168.
**Universal Technology Corp., 1270 N. Fairfield Rd., Dayton, OH 45432-2600.

Scheme 1

Scheme 2

coatings could replace the current chromate surface treatment, allowing chromate reduction. These surface treatments are intended to be used with primers containing corrosion inhibiting pigments to provide complete, high-performance, corrosion protection systems.

A large amount of sol-gel research, including the work presented here, is based on silicon precursors because of their balance of reactivity and ease of handling, as well as their ready availability.[12] Silane sol-gel chemistry consists primarily of hydrolysis and condensation reactions of alkoxysilane precursors that form nano-porous gels as the reactions proceed. The hydrolysis reactions are typically catalyzed by acid or base conditions, producing a hydrolyzed silanol of the general form $(RO)_xSi(OH)_{4-x}$ and an alcoholic by-product as shown in simplified form in *Scheme* 1. Subsequent condensation reactions occur to form siloxane bridges resulting in a substantial increase in molecular weight. One possible condensation reaction is shown in *Scheme* 2. It should be noted that a large number of similar hydrolysis and condensation reactions are possible.

The extent of hydrolysis that occurs before condensation is a function of the catalysis conditions, solvent, and water content.[13] As the condensation reactions proceed, an inorganic network polymer results from polysiloxane formation. The polycondensation reactions occur repeatedly, until the active silanol sites have formed a high density of siloxane bridges, usually slowing when a rigid gel is formed.

In both the hydrolysis and condensation reactions, a low molecular weight by-product is produced. The drying process for the sol-gel material requires that the alcohol and water escape as the gel solidifies. This evaporation process results in voids and channels throughout the solid gel so that the resulting porous material does not provide an optimal barrier to protect against substrate corrosion. High-temperature post-processing is often required to produce dense materials from sol-gel precursors.[12] However, in many applications, including the application of extended lifetime coating systems to existing aircraft, high-temperature processing is not possible.

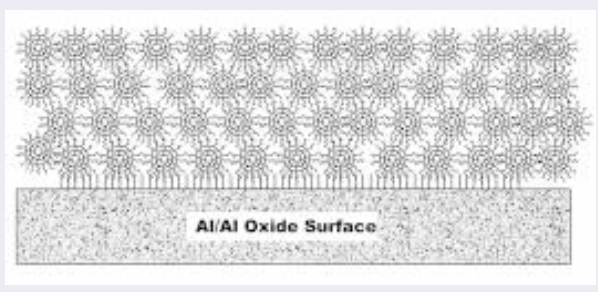

Figure 1—Proposed model of crosslinked SNAP films on an Al 2024-T3 substrate.

This paper describes the coating formation, barrier properties, performance, and morphology of silicon-based sol-gel coatings that are formulated to provide thin, dense films utilizing only ambient temperature processing. These systems are based on nano-scale sol-gel particles, which are pre-formed in solution. This self-assembled nano-scale particle (SNAP) system relies on standard organic crosslinking reactions to form the film after application. An idealized model of the films formed by this process is shown in *Figure* 1. By pre-forming the sol-gel particles, the SNAP system does not rely on the pore forming hydrolysis and condensation reactions for curing. This results in improved film density and barrier properties. In this work, the barrier properties of the SNAP coating are investigated as a function of the crosslink density and the coupling agent. A study of the solution chemistry and formation processes of the SNAP particles is beyond the scope of this paper and will be published separately.[14]

EXPERIMENTAL

Coupons of Al 2024-T3 (2 in. × 3 in.) were cleaned in a standard four-bath cleaning process. The first step was a 10-minute immersion in Oakite® Aluminum Cleaner 164 (alkaline detergent, Oakite Products, Detroit, MI) with moderate air agitation at 55-60°C. The second step is a two-minute immersion in distilled water at 50°C. The third step is a 10-minute, room-temperature immersion in Turco Smut-Go NC-B deoxidizer (Turco Products, Westminster, CA) with moderate nitrogen agitation. The final step is an immersion in room-temperature distilled water for two minutes. To reduce bath contamination, the substrates are rinsed with flowing distilled water briefly before the second and fourth steps. Finally, the substrates are blown dry with compressed air and stored covered until use, typically one week or less.

The chemical structures of the major species used in the SNAP system are shown in *Figure* 2. SNAP solutions were made by drop-wise addition of glycidoxypropyltrimethoxysilane (GPTMS) and tetramethoxysilane (TMOS) in a 3:1 ratio to a dilute solution of acetic acid in doubly distilled deionized water. The solution was continuously stirred during the addition. After all of the silanes had been added, the solution was aged in a covered container while still stirring for a given length of time. After the aging period, the SNAP solution was ready for addition of the coupling agent solution, crosslinking agent (diethylenetriamine, DETA), surfactant (3M FC-430 and FC-171), and diluent (water). Upon

addition of these materials, the solution was immediately applied to the substrate. SNAP solution was applied to cleaned aluminum alloy panels by dip-coater at a speed of 0.2 cm s^{-1}. Coated panels were air dried overnight before any analysis was performed.

Concentrations of the crosslinking agent were varied to ascertain their optimum concentration and role within the SNAP system. The amount of amine crosslinking agent was studied based on the stoichiometry between the epoxide functionality present in the SNAP and the amount of diethylenetriamine (DETA) on a molar basis. Stoichiometries of 33, 16, 6.7, and 3.3 moles of epoxide per mole of DETA were investigated for the SNAP system using a pre-applied coupling agent. These ratios were chosen based on the five reactive hydrogens present on each DETA molecule and correspond to epoxide:reactive H ratios of 6.6, 3.2, 1.3, and 0.66 respectively.

Three types of SNAP coated aluminum panels were prepared. The nomenclature used for these samples is presented in *Table* 1. Samples labeled NA were prepared without any coupling agent and represent a baseline for the SNAP system. The GA samples included a coupling agent prewash on the aluminum alloy substrate. The prewash coupling agent solution was made by hydrolyzing 4.4 mL glycid-oxypropyltrimethoxysilane (GPTMS) in 72 mL of 0.05 M acetic acid for 30 min. The GA samples were prewashed with the coupling agent by immersing the aluminum alloy substrate in prewash solution for two minutes. The coupling agent provides a strong chemical interaction between the SNAP system and the substrate, which should enhance the hydrolytic stability of the coating system. The treated panels were then allowed to dry for an hour before application of the SNAP solution. The GG system incorporates the coupling agent directly into the SNAP solution just prior to coating application. This simplifies the application process.

Infrared spectra of the SNAP coatings on aluminum alloy 2024-T3 panels were obtained using a Bruker Equinox 55 Fourier transform infrared spectrometer equipped with a liquid-nitrogen cooled, mercury cadmium telluride (MCT) detector. Spectra of SNAP films were acquired with a resolution of 4 cm^{-1} using a variable angle specular reflectance accessory set to 30° and are presented as log(1/Reflectance) versus a gold mirror background. Spectra of the coupling agent on the substrate were acquired using the same accessory at a grazing angle of 80° and a wire grid polarizer. The spectral resolution of these measurements was 2.0 cm^{-1}. These spectra were ratioed against a background of polished Al 2024-T3 substrate cleaned by sonication in methanol to minimize background differences.

Potentiodynamic scan (PDS) and electrochemical impedance spectroscopy (EIS) were used for evaluation of the protective properties of SNAP films. Detailed descriptions of these electrochemical techniques can be found elsewhere.[15,16] These methods are widely used for evaluating the corrosion protection provided by coatings. Each coating system was evaluated in triplicate for corrosion protection using the PDS technique. Experiments were performed on a Gamry PC3/300 potentiostat coupled with Gamry corrosion measurement system

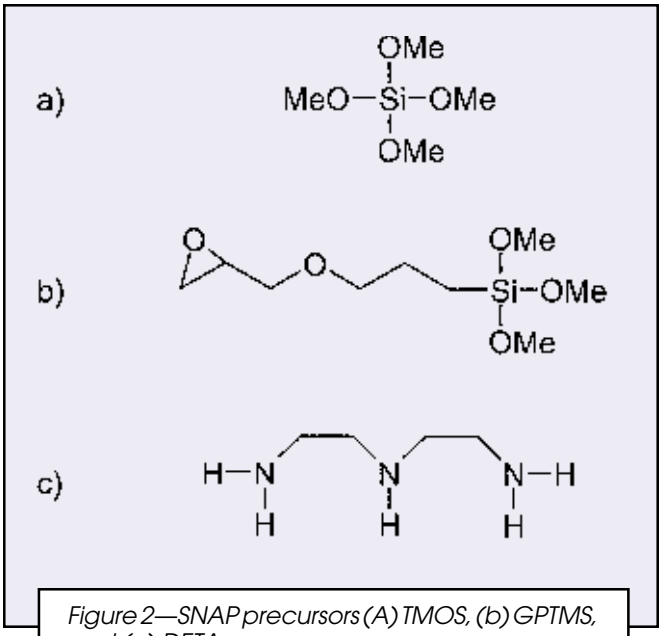

Figure 2—SNAP precursors (A) TMOS, (b) GPTMS, and (c) DETA.

CMS100 and CMS105 software. Coatings were immersed in dilute Harrison's solution (0.35 wt% $(NH_4)_2SO_4$ and 0.05 wt% NaCl) five minutes prior to the test. This mixture of electrolytes is considered to closely emulate atmospheric environment for aircraft.[17] An area of 1 cm^2 on the surface of the film was masked off with electrochemical tape, thus fixing the size of the exposed area. A removable glass cylinder (1″ ID) was attached to the panel using a metal clamp and a rubber o-ring. A platinum mesh counter electrode and saturated calomel reference electrode (SCE) were utilized in a three-electrode configuration. PDS was acquired in the region from –200 mV vs. E_{oc} (open circuit potential) to +400 mV vs. E_{oc}.

EIS tests were performed in triplicate on a Gamry PC3/300 potentiostat coupled with Gamry corrosion measurement system CMS100 and CMS300 software. Coatings were immersed in dilute Harrison's solution (0.35 wt% $(NH_4)_2SO_4$ and 0.05 wt% NaCl) 30 min before the data acquisition process started. An area of 1 cm^2 on the surface of the film was masked off with electrochemical tape, thus fixing the size of the exposed area. A piece of PVC pipe (1½ in. ID) was attached to the surface using Marine Goop™ adhesive (propylacetate and petroleum distillate). The glue was allowed to air dry for at least 24 hr before any solution was poured into the cell. A platinum mesh electrode and an SCE reference electrode were used in a three-electrode electrochemical cell. The electrode arrangement is identical to the PDS cell setup. EIS spectra were acquired in the frequency range

Table 1—Sample Composition

Label	Coupling Agent	Crosslinker
NA	None	DETA
GA	Prewash	DETA
GG	Added to SNAP	DETA

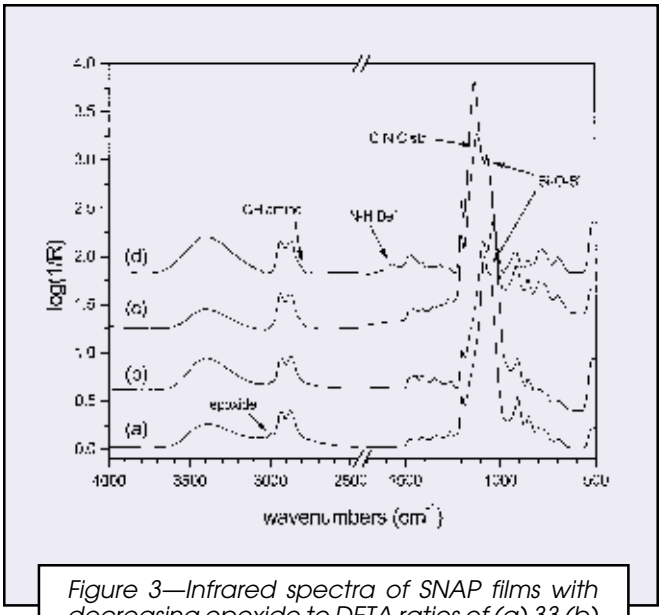

Figure 3—Infrared spectra of SNAP films with decreasing epoxide to DETA ratios of (a) 33 (b) 16 (c) 6.7 and (d) 3.3.

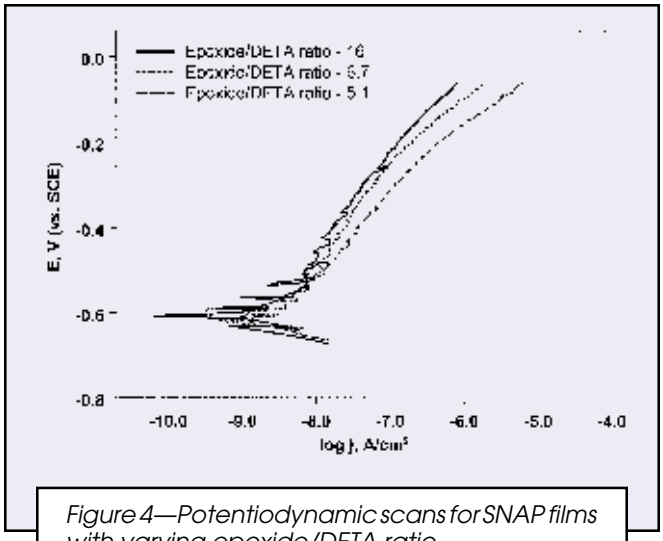

Figure 4—Potentiodynamic scans for SNAP films with varying epoxide/DETA ratio.

from 5 kHz to 10 mHz with 10 mV applied ac potential (vs. E_{oc}). The standard criteria were used for evaluating the EIS results.[18] Impedance values of above 1×10^9 Ω cm^2 are indicative of coating systems affording excellent barrier protection. Coatings with modulus values below 1×10^6 Ω cm^2 are considered poor, and $|Z|$ values between 1×10^6 and 1×10^9 Ω cm^2 indicate a good coating.

The atomic force microscope (AFM) images were acquired on a Digital Instruments Multimode Nanoscope III AFM in tapping mode. The J scanning mode was used with a maximum scan range of 125 μm^2. Images were acquired in soft and hard tapping modes. In soft tapping mode, the ratio of the tapping amplitude during scanning, A, to the free tapping amplitude, A_o, is 0.9. In hard tapping mode, (A/A_o) is equal to 0.5.

RESULTS AND DISCUSSION

Crosslinking Agent

Concentrations of the crosslinking agent and coupling agent were varied to ascertain their optimum concentration and role within the SNAP system. The amount of amine crosslinking agent was studied based on the stoichiometry between the epoxide functionality present in the SNAP and the amount of diethylenetriamine (DETA) on a molar basis. The amine should be the limiting reagent in the crosslinking reaction so that there is a residual epoxide concentration for reaction with subsequent paint layers.

Table 2—Electrochemical Test Results (GA Sample, PDS and Low-Frequency Limit EIS (10 mHz))

Epoxide: DETA Stoichiometry	16:1	6.7:1	5.1:1
Potentiodynamic (j_{corr}, nA/cm^2)	1-10	1-10	1-10
Initial EIS (Ω cm^2)	>1 x 10^6		>1 x 10^6
End of test EIS (Ω cm^2)	>1 x 10^5		<5 x 10^4

Figure 3 shows a series of infrared reflection spectra of SNAP films prepared with increasing amounts of crosslinking agent. Two spectral features due to the Si–O stretching motion of siloxane linkages in the SNAP coating are observed around 1086 and 1032 cm^{-1}. The C–H stretches of the organic component of the SNAP coating including the epoxide group appear between 3060 and 2800 cm^{-1}. The C–H stretches that identify the epoxide appear as weak peaks at 3056 and 2997 cm^{-1}. A third peak at 1255 cm^{-1} is assigned to the symmetric ring-breathing mode of the epoxide ring. These three bands show that there is residual epoxide present up to an epoxide to DETA mole ratio of 6.7 to 1. These spectroscopic results suggest that all five of the active hydrogen sites on the nitrogen atoms of the DETA undergo crosslinking reactions including the typically less reactive secondary amine.

As the amount of the amine crosslinking agent is increased in the SNAP formulation, bands characteristic of the C–N–C and N–H appear at 1132, 1580, and 2780 cm^{-1}. The very intense band at 1132 cm^{-1} is assigned to the C–N–C stretch and is partly due to the linkages that are formed during the curing process. The 1580 and 2780 cm^{-1} bands are due to molecular motions involving the N-H bands of the amine and are indicative of unreacted crosslinking agent.[19] These bands are most readily observed in *Figure* 3(d) which corresponds to the formulation with the largest excess of crosslinking agent.

Potentiodynamic screening tests did not detect differences in electrochemical behavior of the sol-gel films formulated at several stoichiometric ratios of the amine crosslinker. However, corrosion current densities on the order of 10^{-9}-10^{-8} A/cm^2 indicate the formation of resilient films with tenacious adhesion and good barrier properties, as shown in *Figure* 4.

EIS results show that films with low ratios of epoxide to DETA provide poor protection under continuous exposure to a corrosive environment. As summarized in *Table* 2, EIS values for the low-frequency modulus decrease significantly after two weeks of immersion. This is due to over crosslinking that results in brittle and cracked coatings. Improvement of the EIS results for films with higher ratios of epoxide to DETA is consistent with the IR results, as shown in *Figure* 3.

Based on these EIS and infrared results, the optimal range of concentrations for the amine crosslinker has been determined. The observed film properties are consistent with a well crosslinked, dense, reproducible film where the stoichiometry is 6.7 moles of epoxide per mole of DETA. This corresponds to an epoxide to amine active site ratio of 1.3. This is ideal for the projected role of the SNAP coating in that it forms an excellent barrier for a thin film while still retaining some epoxide functionality for binding to organic layers in the coating system. This stoichiometry of epoxide to crosslinking agent (6.7 to 1) was used in the following studies of the coupling agent in the SNAP system.

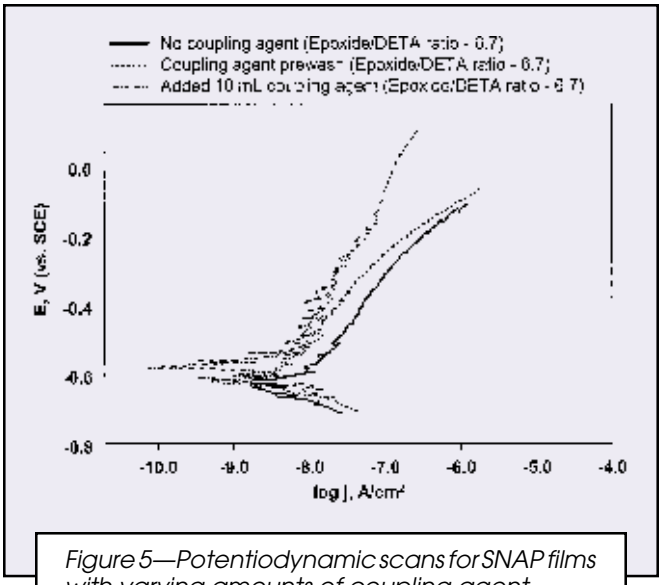

Figure 5—Potentiodynamic scans for SNAP films with varying amounts of coupling agent.

Coupling Agent

The three types of samples prepared for the investigation into the role of the coupling agent in the formation of the SNAP coatings are described in *Table* 1. The NA system should be capable of hydrogen bonding to the substrate via the epoxide functionality on the particles. However, there should be very little opportunity for direct bonding between the sol-gel and the substrate surface as the preformed SNAP particles are expected to be encapsulated by the organic component of the GPTMS.[14] The GA system has a silane-coupling agent pre-applied to the substrate. This generates a surface with epoxide functionality that bonds to the SNAP particles through the crosslinking agent. The GG system is formulated to include the coupling agent as an additive to the SNAP coating solution. This simplifies and shortens the SNAP coating process but assumes that the coupling agent is able to self assemble at the substrate-SNAP interface. Previous research with silane adhesion promoters has shown this to be a reasonable assumption.[20]

Potentiodynamic scans were performed to investigate the overall barrier properties of the SNAP films. All three sets of samples with epoxide/amine ratios of 16, 6.7, and 5.1 developed low corrosion currents ranging between 1 and 10 nA/cm^2, as shown in *Figure* 5. Considering that these SNAP coatings represent only a thin, primary treatment for metal protection, these values indicate an excellent anti-corrosion performance. More importantly, these highly reproducible results demonstrate that the SNAP system generates consistent, defect free films. This repeatability is critical for both the successful use of the coating and for the development of the SNAP system.

Grazing angle IR was used to ascertain that the coupling agent (GPTMS) has been successfully applied to the substrate surface in the GA series of samples. The results of the IR analysis are shown in *Figure* 6. The characteristic features of the coupling agent are found in the region from 1500-950 cm^{-1}. The largest peaks in this area are due to the Si-O stretches at 1095 and 1050 cm^{-1} and confirm that the hydrolyzed silane is present on the substrate. The absence of any strong Si–OH bands in the vicinity of 930 cm^{-1} suggests that the hydrolyzed coupling agent has undergone condensation to form a bonded monolayer on the surface.[21] The peak at 1253 cm^{-1} is due to the epoxide functionality of the coupling agent. The presence of this band demonstrates that the epoxide group has not been damaged in the coupling agent application and is available for subsequent bonding to the SNAP particle layer.[22]

EIS was used to assess the stability of the SNAP system as a function of exposure to a corrosive environment and the importance of a coupling agent in providing hydrolytic stability to the SNAP system. Upon initial

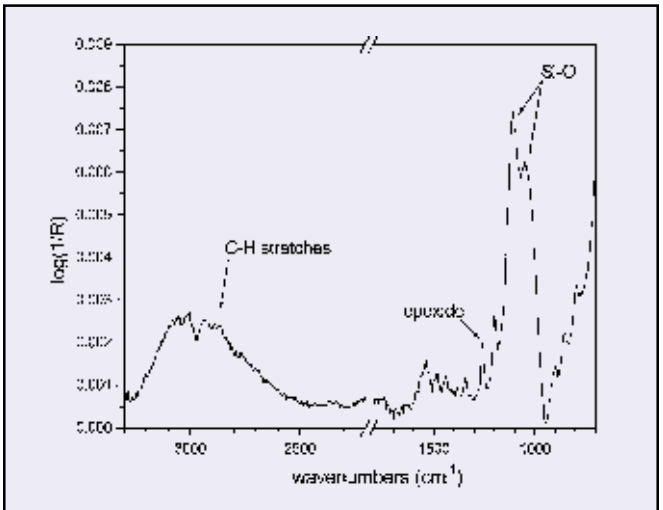

Figure 6—Grazing angle infrared spectrum of GPTMS coupling agent on an Al 2024-T3 substrate.

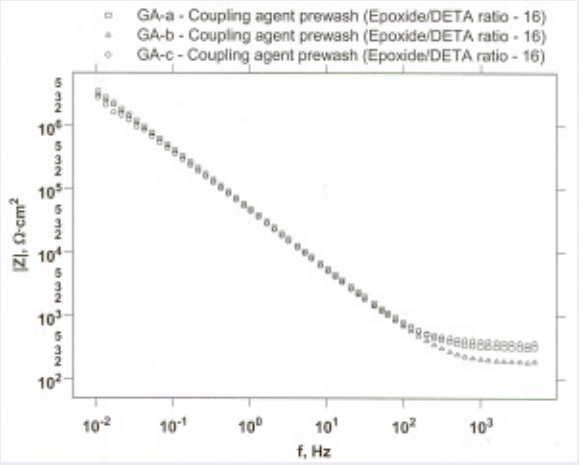

Figure 7—EIS Bode plots for GA triplicate samples at initial immersion.

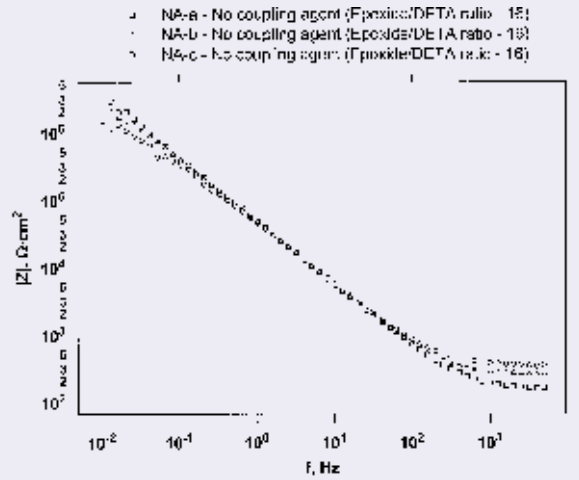

Figure 8—EIS Bode plots for NA triplicate samples at initial immersion.

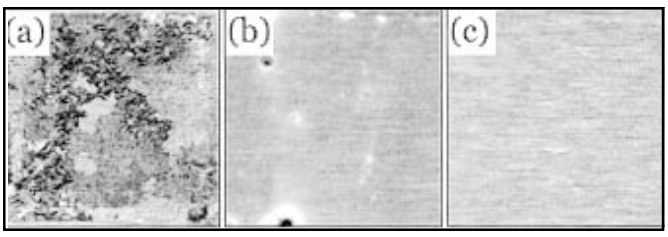

Figure 9—(a) NA (b) GA and (c) unexposed after two weeks of constant immersion.

immersion, samples treated with a coupling agent prewash (GA) and those without any coupling agent (NA) both showed high values of impedance modulus, $|Z|$, at low frequencies, indicating excellent corrosion properties with values on the order of 10^7 Ω cm^2. The impedance modulus for the GA system in *Figure* 7 shows very little variation in the low frequency region between the replicate samples of a triplicate set. In contrast, impedance modulus of the samples without coupling agent (NA), shown in *Figure* 8, had a wider range of impedances from 1×10^6 to 6×10^6 Ω cm^2 at 10 mHz. After only one day of immersion, all of the samples without the coupling agent pretreatment, NA, failed. This is indicated by the dramatic decrease in $|Z|$ value, some by as much as two orders of magnitude. At the same time, the GA series with the coupling agent pretreatment still had two out of three panels with impedance values of over 10^7 Ω cm^2. These results demonstrate that the SNAP system provides significant barrier protection when compared to the $|Z|$ value of less than 1×10^4 Ω cm^2, measured for a typical chromate surface treatment.[23]

After four to five days of immersion, the samples of SNAP coating without coupling agent (NA) showed visible signs of filiform corrosion, while those SNAP coatings with coupling agent (GA) developed no visible corrosion on the surface. This trend continued until the end of the test. Typical examples of the NA and GA samples after two weeks of immersion are shown in *Figure* 9. Significant amounts of corrosion can be observed over the entire surface of the NA sample. In contrast to this, only small spots of localized corrosion appear on the GA sample. These visual observations are consistent with the EIS results in that no specimen from the NA series maintained its modulus value above 5×10^4 W cm^2, while the GA coatings maintained $|Z|$ values above 5×10^5 Ω cm^2 at the low-frequency limit. After two weeks of constant immersion, all of the samples with the coupling agent prewash (GA) still had impedance values of over 2×10^5 Ω cm^2 shown in *Figure* 10, whereas all of the samples without coupling agent (NA) had failed by this time, as evident in *Figure* 11.

These results clearly demonstrate that the application of a coupling agent to the aluminum substrate prior to SNAP coating provides a dramatic enhancement to the stability of the film in a corrosive environment. This is consistent with the formation of strong chemical coupling between the substrate and the SNAP film via the GPTMS coupling agent.

A third system was investigated to consider an alternative method of application of the coupling agent. These samples, labeled GG, utilized a pre-hydrolyzed solution of GPTMS added directly to the SNAP coating solution just prior to dip-coating of the aluminum alloy panels as the only source of coupling agent material. In constant immersion EIS tests, samples generated with this method of coupling agent addition out-performed those samples prepared without coupling agent and those prepared with a coupling agent prewash. Because of the difficulty in determining the amount of coupling agent taken up by the substrate in the prewash step for the GA samples, a direct comparison of GG to GA samples based on

coupling agent content is not possible. For this reason, GG samples with four different, arbitrary levels of coupling agent additive were studied.

Initial EIS results for 0-1 days after immersion indicate capacitive behavior at frequencies down to 0.01 Hz for all four SNAP systems with coupling agent additive (GG) coated panels. These results are very similar to those observed for the SNAP samples with coupling agent prewash (GA) and even those SNAP samples without any coupling agent (NA). The EIS results for all three systems are compared in *Figure* 12. This observation is consistent with the PDS results indicating that all three systems initially afford effective corrosion protection. In contrast to the NA and GA systems, the high impedance values measured for these GG samples were unchanged for up to one and a half weeks of constant immersion. After two weeks, a gradual decrease in the low-frequency modulus values for the samples with the two lowest amounts of coupling agent additive (2 and 4 mL) was observed. Virtually no changes were recorded for the samples with the two higher amounts of coupling agent additive (8 and 10 mL) during this immersion period, as shown in *Figure* 13. Even after 80 days of constant immersion these GG samples showed modulus values of $3 \times 10^5\ \Omega\ cm^2$ and $8 \times 10^5\ \Omega\ cm^2$, respectively.

Both the GG and GA samples demonstrated significantly improved corrosion resistance over the NA samples. This improvement is due to the use of the GPTMS coupling agent in the GG and GA SNAP coatings. The action of the coupling agent at the interface is clear in the case of the GA samples. For these samples, the prewash of the coupling agent onto the substrate

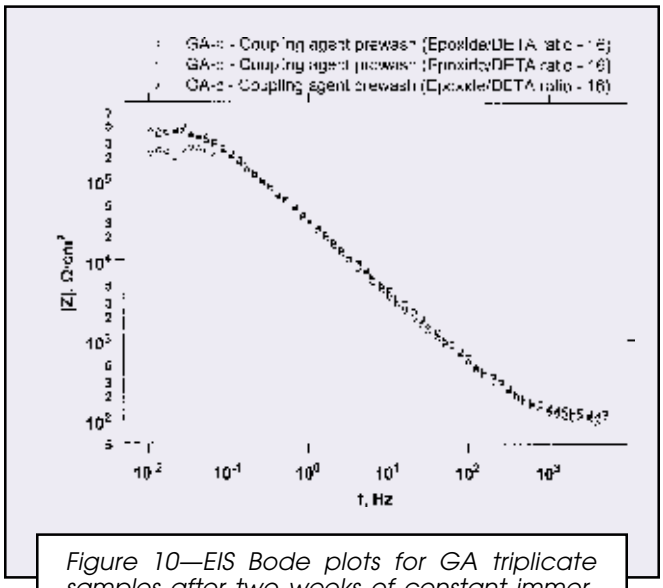

Figure 10—EIS Bode plots for GA triplicate samples after two weeks of constant immersion.

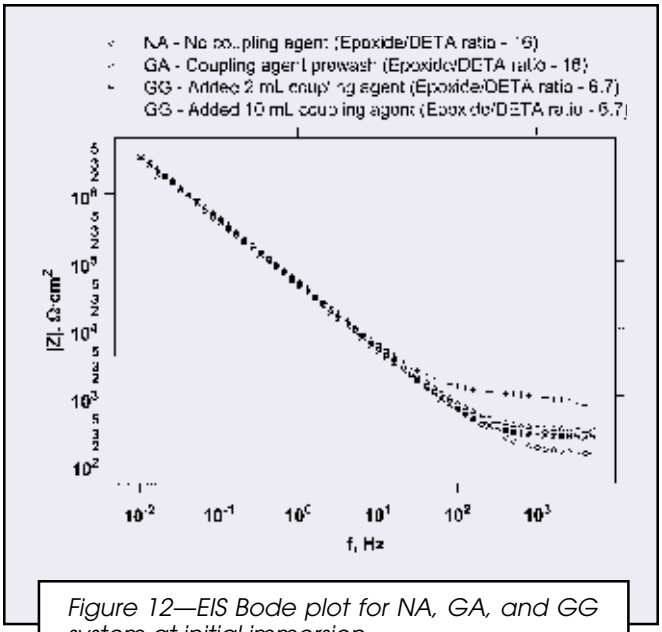

Figure 12—EIS Bode plot for NA, GA, and GG system at initial immersion.

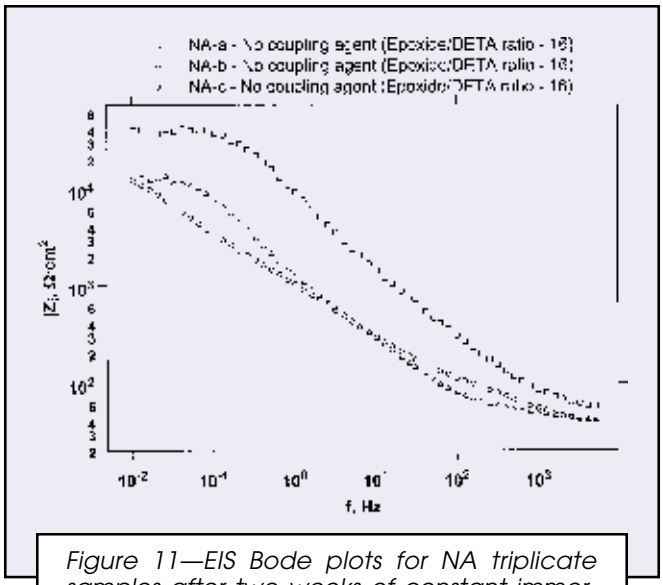

Figure 11—EIS Bode plots for NA triplicate samples after two weeks of constant immersion.

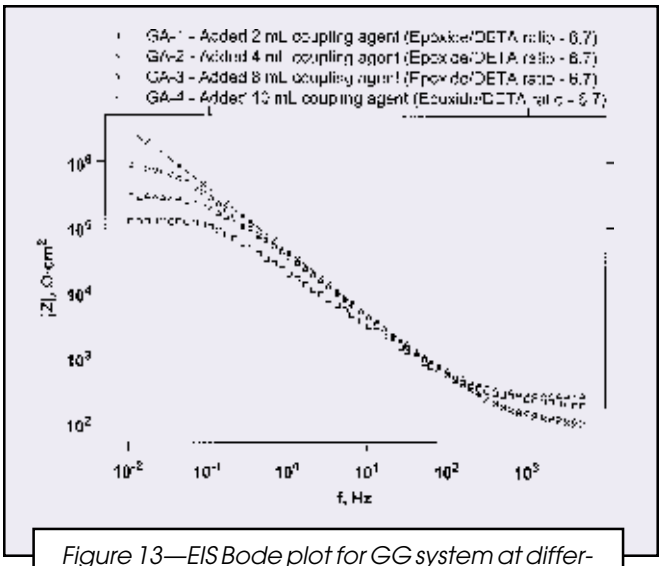

Figure 13—EIS Bode plot for GG system at different coupling agent concentrations after two weeks of constant immersion.

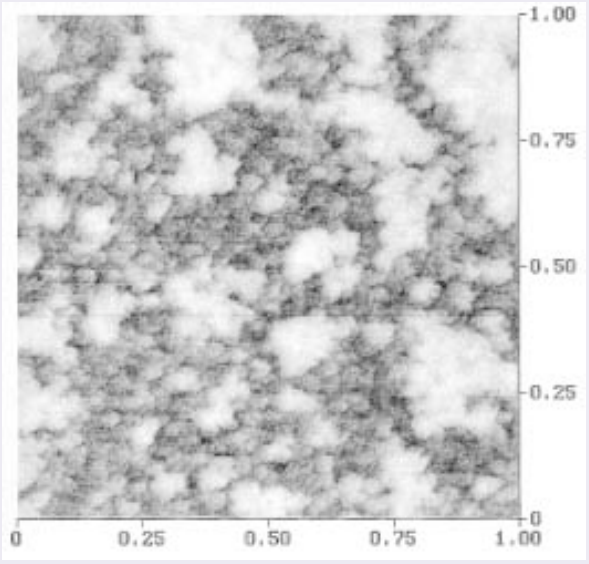

Figure 14—AFM phase image of SNAP-GG film.

generates an epoxide-functionalized surface that chemically bonds to the SNAP particles forming a durable and hydrolytically stable coating system.

In the GG samples, the coupling agent is not directly applied to the substrate but is included in the SNAP coating solution directly. Because of the chemical bonding capability of the coupling agent, some of it is expected to migrate to the substrate-coating interface. In this way, the coupling agent acts as hypothesized for the GA system. However, the significant improvement in stability observed for these samples in which the coupling agent is used as an additive is not explained by this mechanism. This improvement is thought to arise from an improved densification of the film. Some of the coupling agent additives can act as an extended crosslinker by dimerizing and reacting with available amine. This would have the effect of plugging any small cracks or defects present in the coating.[24] Furthermore, these extended crosslinks would form longer carbon chains than the amine crosslinks. These could effectively crosslink otherwise hindered sites and potentially reduce the stresses normally associated with excessive crosslinking within a coating.

Tapping mode AFM was used to relate the physical state of the coating surface with the observed film properties and proposed chemistry. A typical phase image of the SNAP system coatings is shown in *Figure* 14. The phase information suggests that there are small round features distributed throughout the film that could correspond to the SNAP particles. The observed size of approximately 10 nm in diameter is consistent with the preliminary results of tests performed on the SNAP system in solution.

CONCLUSION

A new sol-gel approach using pre-formed, self-assembled, nano-phase particles (SNAP) has been reported. This SNAP system has been shown to produce a fully dense protective surface coating that could be used within a conventional coating system to provide improved corrosion protection. These water-based, environmentally benign coatings rely on aqueous solution processes to generate nanoscale particles with an inorganic core and an organic exterior. Organic reagents are used to crosslink the particles, forming a protective, thin coating on the substrate.

The required stoichiometry for generating dense but epoxide-functionalized films was investigated by EIS and infrared spectroscopy. The optimal molar ratio of epoxide to DETA was determined to be 6.7. This is consistent with each active site on the nitrogen atoms of the DETA reacting with epoxide. One of the most important features of the SNAP system is the coupling agent that provides strong chemical interactions between the substrate and SNAP coating. The effect of pre-applying the coupling agent or directly adding it to the SNAP coating has been studied. The coupling agent was found to be essential for providing effective stability under constant immersion in a corrosive environment. Furthermore, directly adding the coupling agent to the SNAP was found to generate greater stability than that observed for preapplication of the coupling agent to the substrate. This is thought to be due to a second role for the coupling agent. As well as generating strong substrate-coating interaction, some of the coupling agent additive could act to reinforce defects in the film, thus improving overall film performance. The SNAP coatings could be used as a substrate preparation component to replace the currently used chromate containing surface treatments and provide the basis for long-lived coating system for aluminum alloys.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of Dr. Robert Parkhill of CMS Technetronics for his advice on the silane chemistry and Dr. Xiaofan Yang at the department of Polymers and Coatings of North Dakota State University for her assistance with the AFM imaging. Funding from the Air Force Office of Scientific Research and the Air Force Research Laboratory supported this work.

Refences

(1) *Fed. Regist.*, 12.4, *60*, No. 170, 45947, 1995.
(2) Implemenation Plan–Air Force Coatings System Strategy, Department of the Air Force, United States of America, Washington, D.C., March 15, 1995.
(3) (a) Metroke, T.L., Parkhill, R.L., and Knobbe, E.T., *Mater. Res. Soc. Symp. Proc.*, *576*, 293-298, 1999 ; (b) Blohowiak, K.Y., Osborne,

J.H., Krienke, K.A., and Sekits, D.F., *Int. SAMPE Tech. Conf*., 28, 440-446,1996; (c) Blohowiak, K.Y., Osborne, J.H., and Krienke, K.A. U.S. Patent, 1998.
(4) Voevodin, N.N., et al., *Surf. Coat. Tech.*, in press.
(5) Dorogy, W.E., Jr., Tiano, T., Pan, M., and Jayaraj, K., *Tri-Serv. Conf. Corros, Proc*., 2, 4/1-4/16, 1997.
(6) Gettings, M. and Kinloch, A.J., *J. Mater. Sci.* 12, 2511 (1977).
(7) (a) Matienzo, L.J., Shaffer, D.K., Moshier, W.C., and Davis, G.D., *Polym. Mater. Sci. Eng*., *53*, 592 (1985); (b) Matienzo, L.J., Shaffer, D.K., Moshier, W.C., and Davis, G.D., *J. Mater. Sci.,* 21, No. 5, 1601 (1986).
(8) Khobaib, M., Reynolds, L.B., and Donley, M.S., *Surf. Coat. Tech*., in press.
(9) Parkhill, R.L., et al., *Tri-Serv. Conf. Corros, Proc.*, *2*, 1997.
(10) Subramanian, V. and Van Ooij, W.J., *Surf. Eng*., *15*, No. 2, 168 (1999).
(11) Van Ooij, W.J., Zhang, B.C., Conners, K.D., and Hornstrom, S.E., *AIP Conf. Proc.,* 354, 305, 1996.
(12) Brinker, C.J. and Scherer, G.W., *Sol Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York, NY, 1990.
(13) Schmidt, H., *J. Non-Cryst. Mat*., 100, 51 (1988).
(14) Vreugdenhil, A.J., Balbyshev, V.N., and Donley, M.S., to be sumbitted to *J. Non-Cryst. Mat*. for publication.
(15) Impedance Spectroscopy, MacDonald, J.R. (Ed.), Wiley-Interscience: New York, NY, p. 260-308, 1987.
(16) *Principles and Prevention of Corrosion*, Jones, D.A. (Ed.), Macmillian Publ. Comp., New York, pp. 122 and 161, 1992.
(17) Twite, R., Balbyshev, S., and Bierwagen, G., *Proc. Symp. Environ. Accept. Inh. Coat., Special Publication of the Electrochemical Society*, 95, Taylor, S.R., Isaacs, H.G., and Drooman, E.W. (Eds.), p. 202, 1997.
(18) Bacon, R.C., Smith, J.J., and Rugg, F.M., *Ind. Eng. Chem*., *40*, 161 (1948).
(19) Lin-Vien, D., Colthup, N.B., Fateley, W.G., and Grasselli, J.G., *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, New York, 1991.
(20) Hong, S.G. and Boerio, F.J., *Surf. Inter. Anal*., 21, No. 9, 650 (1994).
(21) Yan, Y. et al., *Chem. Mater*., 9, 2583 (1997).
(22) Brewis, D.M., et al., *Surf. Inter. Anal*., 6, No. 1, 40 (1984).
(23) Mansfeld, F. and Kendig, M.W., "Electrochemical Impedance Tests for Protective Coatings," in *Laboratory Corrosion Tests and Standards,* Haynes, G.S. and Baboian, R. (Eds.), ASTM, Philadelphia, 122, 1985.
(24) Chu, L., Daniels, M.W., and Francis, L.F., *Chem. Mater*., 9, 2577 (1997).