

Electrochemical and Salt Spray Analysis of Multilayer Ormosil/Conversion Coating Systems for the Corrosion Resistance of 2024-T3 Aluminum Alloys

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INTRODUCTION

In recent years, there has been extensive research conducted toward the development of chromate-free coatings and surface pretreatments that are effective corrosion inhibitors for aluminum alloys. These research efforts have stemmed from the need to replace hexavalent chromium as the active ingredient in corrosion inhibition pretreatments. Despite excellent corrosion protection properties, hexavalent chromium is toxic, a suspected carcinogen, and poses serious human health and environmental risks.¹ For these reasons, the use of hexavalent chromium-based processes for corrosion protection has been increasingly regulated by government agencies.

A wide variety of novel coating processes have been developed as potential replacements for hexavalent chromium-based conversion coatings as described in various reviews.² These processes have relied on inorganic molecules that react with the oxidized aluminum surface to form mixed oxides, metal ions that are able to oxidize the metal surface during service life, organic polymers with a high complexing capacity for aluminum surfaces, and inorganic film-forming oxides.³ Recent developments have included rare earth-based conversion coatings,⁴ Co-rich oxide layers,⁵ Mn-based conversion coatings,⁶ Mo-based conversion coatings,⁷ Zr-based conversion coatings,⁸ silane-based surface treatments,⁹ and trivalent chromium conversion coatings.¹⁰ Generally, however, the performance of these surface treatments has been found to be inferior to that of the chromate conversion coating. Presently, a combination of these approaches has been suggested for increasing the corrosion resistance of alternative coating systems.

Cr⁶⁺-, Co³⁺-, and Cr³⁺-based conversion coatings were selected for this study based on their reported corrosion resistance characteristics. Hexavalent chromium conversion coating was chosen as a control system due to its use as the standard military and industrial pretreatment for aluminum alloys. While the composition, structure, and mechanism of corrosion protection provided by chromate

The corrosion resistance characteristics of multilayer coating systems comprised of a conversion coating base layer and an organically modified silicate (ormosil) topcoat have been analyzed using salt spray and potentiodynamic polarization curve analyses. The effectiveness of the multilayer coating systems was found to depend on the presence of an electrochemically active species in the conversion coating and on the presence of a curing agent in the ormosil system. Multilayer coatings systems comprised of conversion coatings that contain active corrosion inhibitors were found to provide high degrees of corrosion protection. In all cases, the presence of the ormosil was found to enhance the corrosion resistance of the underlying conversion coating. The use of multilayer ormosil/conversion coating systems enhances the corrosion protection of 2024-T3 aluminum alloy by combining previously developed corrosion protection methods with emerging sol-gel technology.

conversion coatings is not definitively known, extensive research in this area has provided insights into the unique aspects of these coating systems.¹¹ Briefly, hexavalent chromium conversion coatings are formed by immersing aluminum alloys in an acidic solution of chromate and fluoride ions.^{11d} Chromate conversion coatings participate in redox reactions on the aluminum alloy surface, precipitating an insoluble amorphous Cr(OH)₃ layer that provides the underlying metal with a passive corrosion barrier.¹² Soluble Cr⁶⁺ species present in the conversion coating

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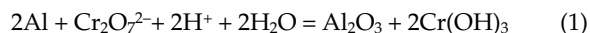
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Table 1—Electrochemical Characteristics Assessed from Potentiodynamic Polarization Curves for 2024-T3 Aluminum Alloy Substrates Coated with Various Conversion Coating/Ormosil Combinations

Conversion Coating	Immersion Time (min)	Ormosil	Mol % Curing Agent	$I_{\text{corr}} 10^7$, A/cm ²	E_{corr} , mV	E_{pit} , mV	R_{corr} , kΩcm ²
None		None	—	182	−719	−675	2
None		A ^a	—	5.25	−502	−460	48
None		B	50%	1.78	−406	−100	141
Cr ⁶⁺	2	None	—	1.74	−480	−439	143
Cr ⁶⁺	3	None	—	1.58	−516	−470	158
Cr ⁶⁺	2	A	—	1.41	−378	−227	177
Cr ⁶⁺	3	A	—	1.39	−420	−204	180
Cr ⁶⁺	2	B	50%	1.0	−199	+28	250
Cr ⁶⁺	3	B	50%	1.0	−230	+50	250
Co ³⁺	15	None	—	2.09	−518	−468	120
Co ³⁺	30	None	—	1.78	−493	−319	141
Co ³⁺	15	A	—	1.78	−427	−311	141
Co ³⁺	30	A	—	1.29	−429	−300	194
Co ³⁺	15	B	50%	1.26	−524	−200	198
Co ³⁺	30	B	50%	1.0	−477	−137	250
Cr ³⁺	10	None	—	28.1	−543	−511	9
Cr ³⁺	15	None	—	25.1	−565	−512	10
Cr ³⁺	10	A	—	17.8	−475	−230	141
Cr ³⁺	15	A	—	17	−461	−327	147
Cr ³⁺	10	B	50%	1.55	−307	−50	161
Cr ³⁺	15	B	50%	1.32	−413	−49	158

(a) A denotes a noncured ormosil; B denotes a cured ormosil.

impart active corrosion protection, as these ions can migrate on the metal surface, providing self-healing capabilities (i.e., throwing power) in the event that the integrity of the coating is breached.¹³ The overall reaction for the formation of chromate conversion coatings is shown in equation (1).^{11a}



The cobalt conversion coating developed by Schriever was chosen based on the reported excellent corrosion resistance characteristics, lower toxicity of cobalt (III) compared to hexavalent chromium, and reported good paint adhesion properties.¹⁴ The cobalt conversion coating is prepared from an aqueous solution of a cobalt (II) salt, an ammonium salt, an inorganic complexing agent, an organic complexing agent, and an oxidizing agent, leading to the formation of highly stable cobalt (III) complexes which are stored in the oxide conversion coating. The complexes are believed to be of the general formula $\text{Na}_3[\text{Co}(\text{NO}_2)_2(\text{X})_4]$ ($\text{X} = \text{OOCH}, \text{OOCCH}_3$, etc.), based on the reagents listed in the experimental portion of the patent. The soluble inhibitor complexes formed may migrate throughout the coating system and/or over the surface providing a self-healing repair process considered to be similar to that exhibited by the chromate conversion coating.²

Trivalent chromium conversion coatings developed by Pearlstein and Agarwala were selected due to their reported low toxicity and good corrosion resistance characteristics.¹⁵ Trivalent chromium conversion coatings are prepared from an aqueous solution of a water soluble trivalent chromium compound, a complex fluoride compound, and an alkaline reagent, the combination of which leads to the precipitation of hydrous chromic oxides on the aluminum surface.¹⁶ These aqueous, hexavalent chromium-free coatings are expected to provide barrier protection to the underlying metal substrate.

Organically modified silicates (ormosils) are hybrid organic-inorganic materials formed through the hydrolysis and condensation of organically modified silanes with traditional alkoxide precursors. A variety of organic-inorganic composite materials, with widespread uses and properties, have been prepared using the sol-gel method.¹⁷ Precursors, which generally are di- and tri-functional silanes, span a wide range of sizes, chemical reactivities, and functionalities. The use of precursors containing nonhydrolyzable Si–C bonds introduces pendant organic groups directly bonded to the growing silica network, resulting in modification of the network structure, and subsequently, the physical and chemical properties of the resultant ormosil material.

Recent reviews, and the references presented therein, indicate that silane-based films are of interest for corrosion resistance of various substrates.¹⁸ For example, Kato studied inorganic SiO_2 films derived from $\text{Si}(\text{OC}_2\text{H}_5)_4$ – $\text{C}_2\text{H}_5\text{OH}$ – H_2O solutions for the corrosion resistance of aluminum.¹⁹ Van Ooij et al. investigated the use of silane-based pretreatments (aminopropyltrimethoxysilane, vinyltrimethoxysilane, 1,2-bis-triethoxysilyl ethane) for the corrosion protection of steel and aluminum alloy substrates.^{8a-e} Kasemann and Schmidt found that thermally cured epoxy silane/bisphenol A coatings exhibited high scratch, abrasion, and corrosion resistance on aluminum, magnesium, and silver.²⁰ Donley and Vreugdenhal prepared and investigated the use of self-assembled, nano-phase (SNAP) sol-gel derived coatings for the corrosion protection of 2024-T3 aluminum alloys.²¹ Our previous work has shown that organic concentration, hydrolysis water ratio, and curing agent have a dramatic effect on the corrosion resistance of ormosil thin films on 2024-T3 aluminum alloys.²²

In the present study, we have continued the investigation of multilayer ormosil/conversion coating systems for the corrosion protection of aluminum alloys.²³ Results of

electrochemical and accelerated salt spray analyses indicate that these coating systems significantly enhance the corrosion protection of the underlying aluminum alloy substrate. The magnitude of corrosion resistance enhancement was found to be dependent on the presence or absence of (a) an active corrosion inhibitor in the conversion coating and (b) a curing agent in the ormosil coating.

EXPERIMENTAL

Materials

Tetraethylorthosilicate (TEOS), 3-(trimethoxysilyl)propylmethacrylate (MEMO), vinyltrimethoxysilane (VTMOS), and mercaptopropyltrimethoxysilane (MTMO), were purchased from Aldrich or Gelest and were used as received. Sodium chloride (reagent A.C.S., Spectrum) and nitric acid (NF grade, Fisher) were used without further purification.

Coating Techniques

Aluminum 2024-T3 alloy substrates used for both polarization measurements and salt spray testing were freshly degreased and deoxidized using the following cleaning process. First, the aluminum alloy test coupons were wiped with hexanes and methanol. Subsequently, the aluminum alloy substrates were soaked in an aerated Oakite-164 alkaline cleaner solution (Oakite Products, Inc.) for 15 min at 65°C and then in Deoxalume 2310 deoxidizing solution (Henkel Surface Technologies) for 7-10 min at 25°C under rigorous air agitation. Each of these treatments was followed by thorough rinsing for two minutes using tap water at 50°C.

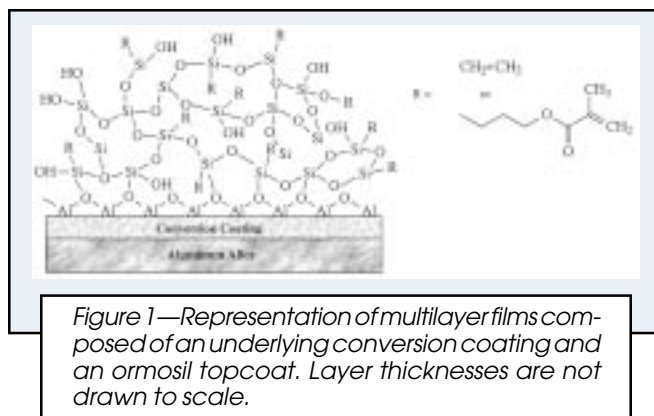
The ormosil solutions were subsequently applied onto a bare- or conversion-coated aluminum alloy by a spray coating technique using an airbrush setup. The coatings were allowed to dry at ambient conditions for at least 24 hr prior to their characterization.

Ormosil Preparation

Two series of ormosil films were prepared based on a TEOS/VTMOS/MEMO precursor mixture using 0.05 M HNO_3 as the catalyst. In the first series, noncured ormosils were prepared by mixing 5.6 ml TEOS, 7.6 ml VTMOS, and 2.0 ml MEMO with 9.8 ml 0.05 M HNO_3 . In the second series, cured ormosils were prepared by adding 4.5 ml MTMO as a curing agent to the above initial silane mixture prior to mixing with 0.05 M HNO_3 . The solutions were allowed to stir for one hour prior to film deposition. Ormosil film thicknesses were approximately 10-20 microns as measured using a digital DeFelsko Series 6000 coating thickness gage.

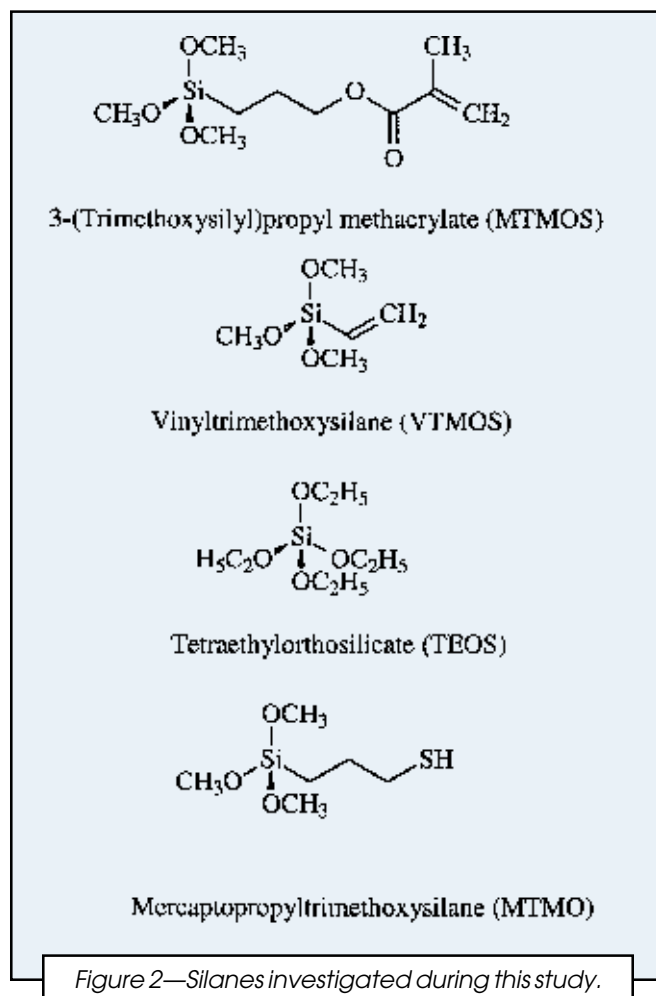
Conversion Coatings

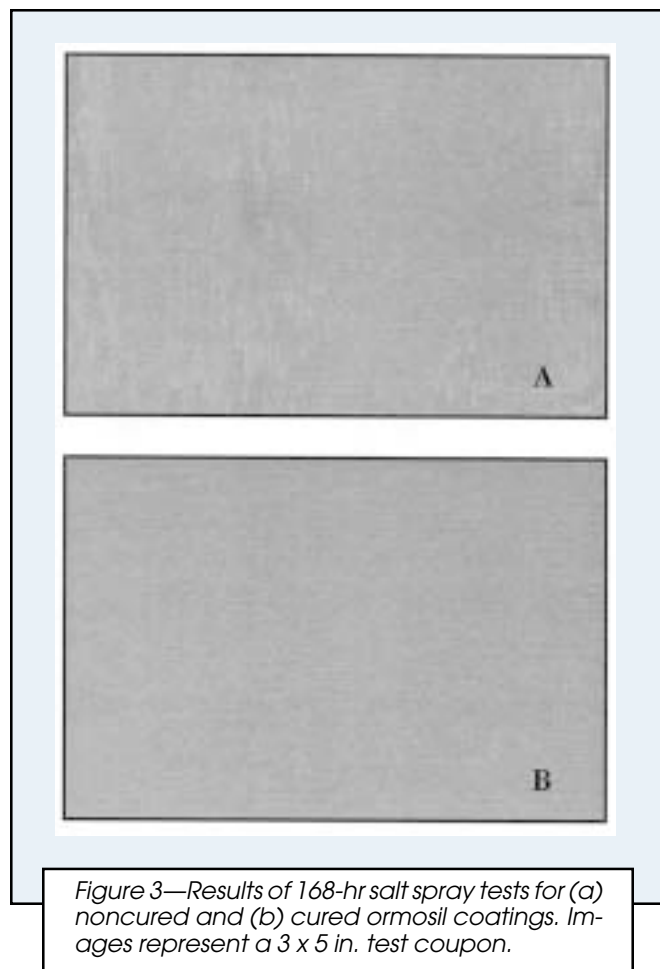
PREPARATION OF HEXAVALENT CHROMIUM CONVERSION COATINGS: Conversion coatings based on hexavalent chromium were prepared by immersing cleaned aluminum alloy



panels into commercial Alodine 1200S solution (Henkel Surface Technologies) for two or three minutes to yield a uniform, golden coating.

PREPARATION OF TRIVALENT COBALT-BASED CONVERSION COATINGS: A Co^{3+} -based solution was prepared as described by Schriever. A stock solution was prepared by mixing 55g/l NH_4NO_3 , 26 g/l $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 26.4 g/l formic acid in 750 ml H_2O . The pH of this solution was adjusted to 7.0-7.1 with concentrated NH_4OH . Subsequently, 3.5 ml/l H_2O_2 (30 wt%) and distilled H_2O were added to increase the volume to one liter. The stock solution was heated to 140°F





for 30-90 min. The final pH was adjusted to 6.8-7.0 using concentrated NH_4OH . Cleaned aluminum alloy test coupons were immersed in the conversion coating solution (140-150°F) for 15 or 30 min.

PREPARATION OF TRIVALENT CHROMIUM CONVERSION COATINGS: A trivalent chromium solution was prepared according to the procedure developed by Pearlstein and Agarwala. The solution was prepared by adding 0.6 g of $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ (26% Cr_2O_3 and 23-24% Na_2SO_4) and 0.8 g of K_2ZrF_6 to one liter of deionized water under continuous stirring for several hours. This solution was then allowed to stand for one week. The pH of the solution was found to decrease from 5.0 in the freshly prepared to about 3.7 in the “aged” solution. Immediately prior to coating deposition, the pH of the trivalent chromium conversion coating solution was adjusted to 4.1-5.1. In order to produce the trivalent chromium conversion coating, aluminum alloy substrates were immersed into the trivalent chromium solution for 10 or 15 min.

Potentiodynamic Polarization Measurements

Electrochemical measurements were performed using a BAS CV-50-W unit and a three-electrode cell equipped with a platinum counter electrode, an $\text{Ag}/\text{AgCl}/\text{Cl}^-$ (3M KCl) reference electrode and a coated or noncoated 2024-T3 aluminum alloy panel as the working electrode. Aluminum alloy working electrode panels, including un-

coated control and coated test specimens, had an exposed area of 0.36 cm^2 . All measurements were conducted in an aqueous 1M NaCl working solution at $25 \pm 1^\circ\text{C}$. The reported values of potentials shown both in the polarization curves and listed in Table 1 are given relative to the $\text{Ag}/\text{AgCl}/\text{Cl}^-$ reference electrode. Oxygen was removed by purging the solution with purified nitrogen for approximately 30 min prior to the polarization measurements.

In order to reach steady potential, the electrodes were kept in the working solution for 30 min prior to electrochemical measurements with the electrical circuit open. Then, the acquisition of polarization curves was started from this open circuit potential, with a constant sweep of 1 mV/sec . Corrosion current values, I_{corr} , reported herein correspond to a 50 mV stretch between the cathodic and anodic parts of the polarization curve. Corrosion resistance was calculated using the equation $R_{\text{corr}} = 50 \text{ mV} / 2I_{\text{corr}}$. This differs from the previously described definition of corrosion resistance²⁴; however, it allows for the derivation of the parameter R_{corr} for the entire pool of polarization curves collected in this study, regardless of their shift along the abscissa. Pitting potentials, E_{pit} , were determined using the criterion described by Kelly et al. wherein pitting would have occurred by the time the anodic current density of the specimen reached $3 \times 10^{-5} \text{ A/cm}^2$.^{11a}

Accelerated Salt Spray Testing

Corrosion protection properties of the coated aluminum alloy substrates were evaluated by exposing the substrates to a salt fog atmosphere generated by spraying 5 wt% aqueous NaCl solution at $35 \pm 1.7^\circ\text{C}$ for 168 hr in accordance with ASTM B117 specifications.

RESULTS AND DISCUSSION

Various multilayer coatings were prepared by depositing an ormosil film over a conversion coating base layer. These films may provide two passivation mechanisms as shown in Figure 1. The ormosil film, which contains no active corrosion inhibitors, is postulated to act as a dense barrier

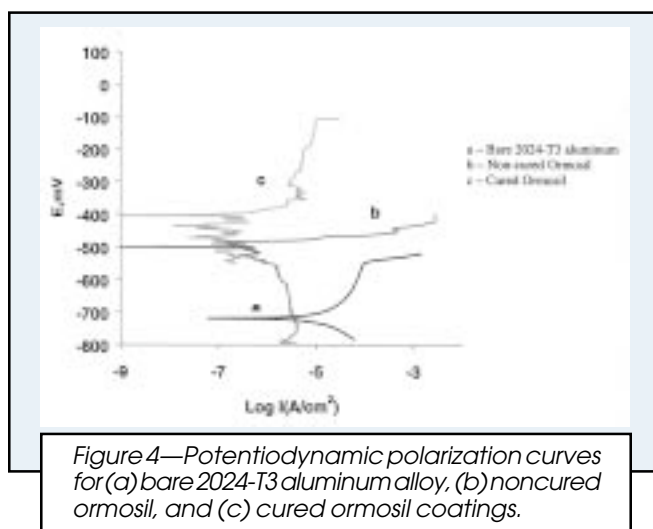
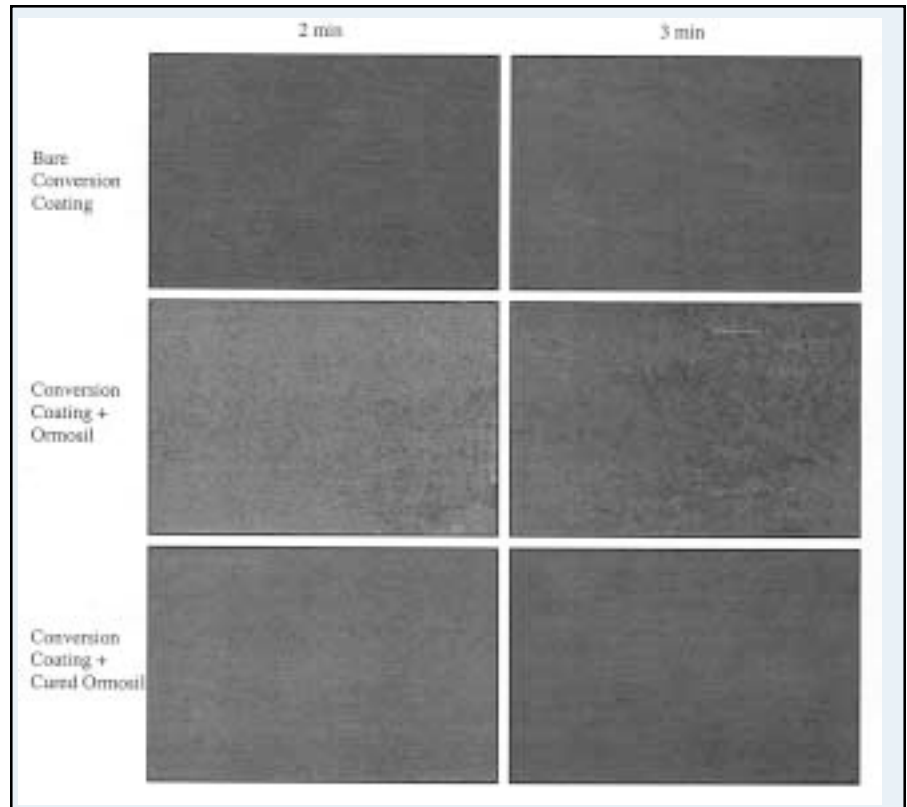


Figure 5—Results of 168-hr salt spray tests for test coupons prepared by immersion for two or three minutes in a hexavalent chromium conversion coatings solution. Images represent a 3 x 5 in. test coupon.



coating, slowing the mass transport of water and corrosion initiators to the underlying aluminum alloy surface.²⁵ In the event that the integrity of the sol-gel coating is compromised, the underlying conversion coating acts as an electrochemically active corrosion inhibitor.

Two types of ormosil films were compared in this study. Figure 2 shows the structures of the organically modified silanes investigated. The first ormosil coating is a mixture of TEOS, VTMO, and MEMO. The network structure of this ormosil contains pendant vinyl and methacrylate groups that may occupy pore space and surface positions. The presence of these groups is anticipated to make the ormosil coating hydrophobic, slowing the penetration of water and corrosion initiators. The second is a mixture of TEOS, VTMO, and MEMO, using MTMO as a room temperature curing agent for vinyl groups.²⁶ Pendant methacrylate and unreacted vinyl groups may increase the coating hydrophobicity. Figure 3 shows the results of 168-hr salt spray testing for both ormosil coatings investigated in this study. Noncured ormosil films failed the 168-hr salt spray test, as evidenced by the presence of localized pitting on the test panels. The cured ormosil film performed better in the salt spray test than did the noncured film as indicated by the lower concentration of visible pits observed on the test coupons.

Potentiodynamic polarization curves for (a) bare 2024-T3 aluminum alloy, (b) noncured ormosil coating, and (c) cured ormosil coatings are shown in Figure 4. Table 1 shows observed electrochemical characteristics for various coatings analyzed during this study. There is a significant increase in corrosion protection by coating the aluminum alloy with an ormosil film as indicated by the increase in corrosion resistance, R_{corr} , from 2 $\text{k}\Omega\text{cm}^2$ for bare aluminum to 48 $\text{k}\Omega\text{cm}^2$ for aluminum alloy coated with a noncured ormosil film. Addition of the curing agent to the ormosil led to a further increase in R_{corr} to 141 $\text{k}\Omega\text{cm}^2$, indicating the higher degree of corrosion protection provided by the cured ormosil film as compared to the noncured ormosil coating. The corrosion potentials for cured and noncured ormosil films are in the same range, (-502 to -406) mV. Conventional pitting is a measure of the stabilization of micropits that may have formed at potentials below the pitting potential. In this study, we observe an increase in E_{pit} values from -675 to -460 mV and further to -100 mV for noncoated aluminum alloy, aluminum alloy coated with a noncured ormosil film, and aluminum alloy coated with a cured ormosil film, respec-

tively. These results complement the trend observed in R_{corr} values and correlate with the 168-hr salt spray results presented in Figure 3.

Multilayer Systems Containing Hexavalent Chromium Conversion Coatings

Hexavalent chromium conversion coatings were investigated as control specimens in this study. Figure 5 shows the results of 168-hr salt spray tests for single and multilayer hexavalent chromium conversion coated test coupons. When used without an ormosil coating, hexavalent chromium conversion coating films resisted corrosion well, though failure in the form of small, localized pitting was observed after the salt spray test, independent of immersion time in the hexavalent chromium conversion coating solution. The addition of the sol-gel overcoat enhanced corrosion protection, especially when the cured ormosil was used, as these test coupons were found to exhibit no noticeable film failure due to pitting after the 168-hr salt spray test. The ormosil films shown in Figure 5 were found to crack during drying after the 168-hr test, due to drying stresses induced by the low ambient humidity conditions. This behavior may be eliminated by the application of a complete paint system (primer/top-coat) onto the ormosil coating.

Figure 6a shows potentiodynamic polarization curves for coatings containing hexavalent chromium conversion coating. The conversion coatings significantly enhanced the corrosion protection of the underlying aluminum alloy, as indicated by the increase in the corrosion resistance, R_{corr} , from 2 $\text{k}\Omega\text{cm}^2$ for bare aluminum to 143-158 $\text{k}\Omega\text{cm}^2$ for aluminum alloy coated with hexavalent chromium conversion coating (two-or-three minute immer-

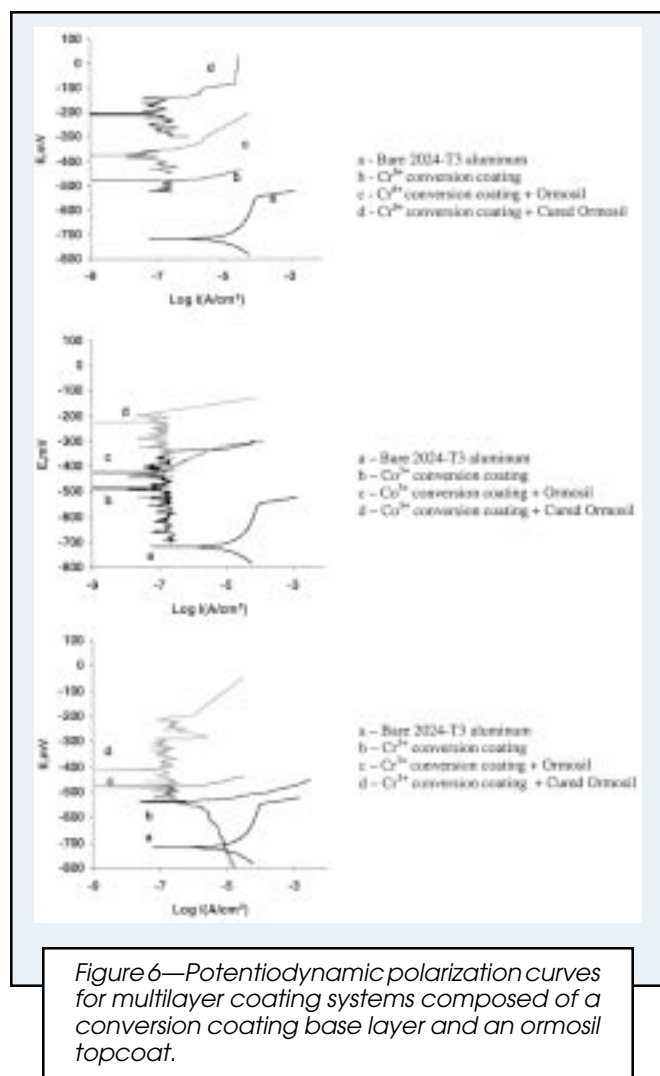


Figure 6—Potentiodynamic polarization curves for multilayer coating systems composed of a conversion coating base layer and an ormosil topcoat.

sion), as shown in Table 1. Addition of the ormosil (either cured or noncured) led to a further increase in R_{corr} to 177–250 $\text{k}\Omega\text{cm}^2$. A similar increase in corrosion protection may be inferred from corresponding changes in E_{corr} values from -719 mV for bare aluminum to -420 to -378 mV for a multilayer hexavalent chromium conversion coating/noncured ormosil coating and further to -230 to -199 mV for multilayer hexavalent chromium conversion coating/cured ormosil coating. A similar trend is observed for pitting potentials where E_{pit} changes from -675 mV for bare aluminum to -470 to -439 mV for Alodine 1200S treated alloys, -227 to -204 mV for a multilayer hexavalent chromium conversion coating/noncured ormosil coating, and further to $+28$ to $+50$ mV for multilayer hexavalent chromium conversion coating/cured ormosil films.

Multilayer Systems Containing Cobalt Conversion Coatings

Single layer cobalt conversion coatings developed by Schrieffer provided moderate corrosion protection independent of increasing the immersion time from 15 to 30 min as shown in Figures 6b and 7. When used in combination with the noncured ormosil, the corrosion resistance

of the cobalt conversion coating was enhanced, though film failure due to light, localized pitting was still observed. The most significant improvement in corrosion resistance, however, was observed for the multilayer cobalt conversion coating/cured ormosil coating system, as very few pits were observed after the 168-hr salt spray test.

The magnitude of enhancement of corrosion protection afforded by the cobalt conversion coatings was similar to that provided by the hexavalent chromium conversion coating. This is indicated by the increase in the corrosion resistance, R_{corr} , from 2 $\text{k}\Omega\text{cm}^2$ for bare aluminum to 143 $\text{k}\Omega\text{cm}^2$ and 141 $\text{k}\Omega\text{cm}^2$ for aluminum alloy coated with hexavalent chromium and cobalt conversion coatings, respectively (Table 1). Such reports are consistent with those previously reported,¹⁴ as Schrieffer's conversion coating comprises an active corrosion inhibitor that may migrate over the aluminum alloy surface in a manner similar to the mechanism of corrosion protection afforded by soluble hexavalent chromium ions. Addition of the ormosil topcoat leads to a further increase in R_{corr} values to 141–194 $\text{k}\Omega\text{cm}^2$ and 198–250 $\text{k}\Omega\text{cm}^2$ for multilayer coatings comprising noncured and cured ormosil films, respectively. A similar trend is observed for E_{pit} values, which were found to increase from -300 to -311 mV for multilayer cobalt conversion coating/noncured ormosil films to -200 to -137 mV for multilayer cobalt conversion coating/cured ormosil films. It is noteworthy to indicate that values of E_{pit} for multilayer hexavalent chromium conversion coating/orosil coatings lie in the more positive region compared to those observed for the cobalt conversion coating, consistent with the excellent corrosion-inhibitive characteristics of the hexavalent chromium conversion coating observed in the accelerated salt spray test.

Multilayer Systems Containing Trivalent Chromium Conversion Coatings

Deposition of an ormosil film on top of the trivalent chromium conversion coating was found to enhance the corrosion resistance characteristics of the underlying conversion coating, the most significant improvement being observed for coatings derived from trivalent chromium conversion coatings prepared from solutions of pH = 5.1. Figure 8 shows the results of the 168-hr salt spray testing for trivalent chromium conversion coatings formed from solutions (pH = 5.1) using immersion times of 10 and 15 min. For test coupons coated with a trivalent chromium conversion coating only, the corrosion resistance was considerably less effective than the hexavalent chromium conversion coatings, as significant concentrations of localized pitting were observed after the 168-hr salt spray test. Both ormosil compositions, when applied as an overcoat to trivalent chromium-based surface treatments, produced a significant enhancement of corrosion resistance as compared to the unprotected trivalent chromium conversion coating. Failure of corrosion inhibiting mechanisms for both ormosil coatings was in the form of very small, isolated localized pitting.

The application of trivalent chromium conversion coatings marginally enhanced the corrosion resistance of the underlying aluminum alloy, as R_{corr} increased to 9–10 $\text{k}\Omega\text{cm}^2$ as compared to 2 $\text{k}\Omega\text{cm}^2$ for bare aluminum as

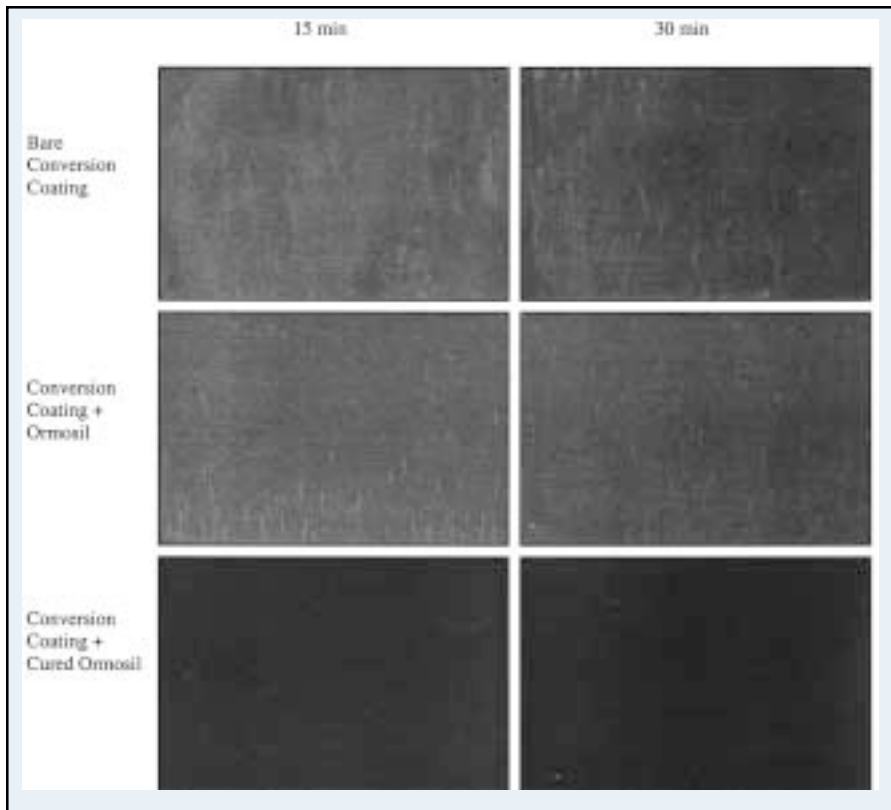


Figure 7—Results of 168-hr salt spray tests for test coupons prepared by immersion for 15 or 30 min in a trivalent cobalt conversion coating solution. Images represent a 3 x 5 in. test coupon.

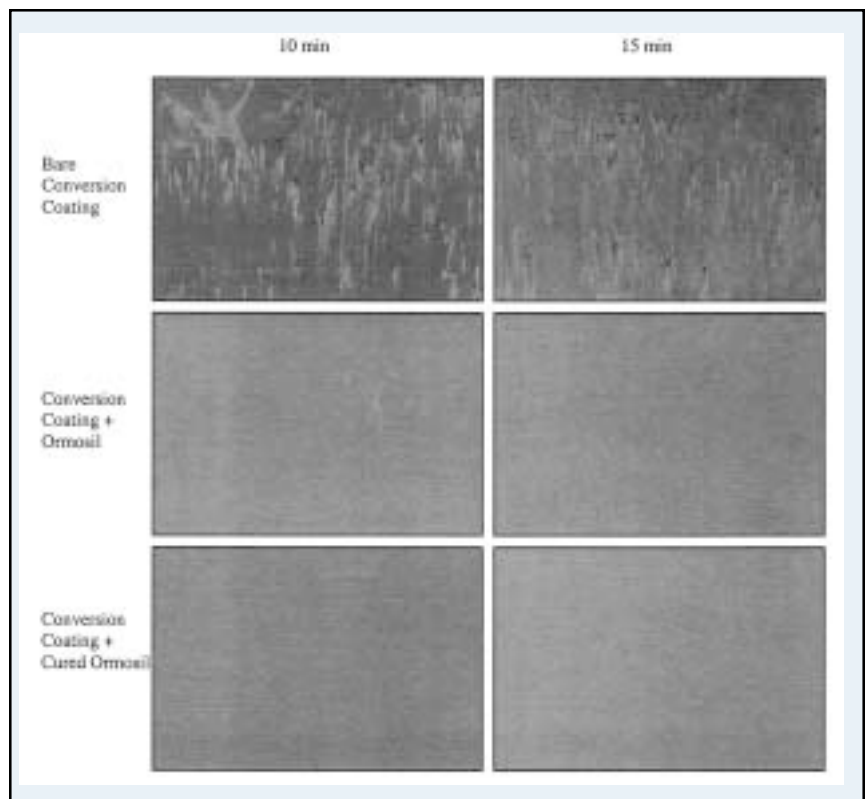


Figure 8—Results of 168-hr salt spray tests for test coupons prepared by immersion for 10 or 15 min in a trivalent chromium conversion coating solution at pH = 5.1. Images represent a 3 x 5 in. test coupon.

shown in Table 1 and Figure 6c. Multilayer trivalent chromium conversion coating/noncured ormosil coatings exhibited enhanced corrosion protection of the aluminum alloy as indicated by an increase in R_{corr} from 9–10 $\text{k}\Omega\text{cm}^2$ for single layer trivalent chromium conversion coatings to 141–147 $\text{k}\Omega\text{cm}^2$ for multilayer films containing noncured ormosil. Introduction of a curing agent into the ormosil coating increased R_{corr} values to 158–161 $\text{k}\Omega\text{cm}^2$, indicating the magnitude of corrosion protection afforded by these coatings is comparable to analogous multilayer cobalt- and chromium-based coatings.

Comparison of the Effectiveness of Single and Multilayer Coatings

Single layer hexavalent chromium and cobalt-based conversion coatings, which contain active corrosion inhibitors, provide substantially improved corrosion resistance compared to trivalent chromium conversion coatings. This trend is evidenced by comparing the corrosion resistance values, R_{corr} , for hexavalent chromium and cobalt conversion coatings. Values of 120–158 $\text{k}\Omega\text{cm}^2$ were observed for hexavalent chromium and cobalt conversion coatings; values of 9–10 $\text{k}\Omega\text{cm}^2$ were observed for trivalent chromium conversion coatings.

Overcoating surface pretreatments with an ormosil layer led to an increase in corrosion protection for all conversion coatings investigated. For example, the values of R_{corr} for multilayer coating systems composed of either hexavalent chromium-, trivalent cobalt-, or trivalent chromium-based conversion coatings with a noncured ormosil topcoat are in the range of 141–194 $\text{k}\Omega\text{cm}^2$, as compared to 48 $\text{k}\Omega\text{cm}^2$ for single layer noncured ormosil thin films. Similarly, the values of R_{corr} of multilayer coatings composed of a conversion coating and a cured ormosil are in the range of 161–250 $\text{k}\Omega\text{cm}^2$, as compared to 141 $\text{k}\Omega\text{cm}^2$ for single layer cured ormosil thin films. Similar changes were observed for E_{pit} and E_{corr} values for the coating systems under investigation. The results of this study indicate that both the presence of the underlying conversion coating and the curing agent in the ormosil film affect the corrosion resistance of the multilayer coating system.

CONCLUSIONS

Electrochemical and salt spray analyses indicate that single layer hexavalent chromium and cobalt conversion coatings containing active corrosion inhibitors provide enhanced corrosion protection of 2024-T3 aluminum alloy when compared to trivalent chromium conversion coatings. Multilayer ormosil/conversion coating systems exhibit enhanced corrosion protective properties as compared to single layer conversion coatings. R_{corr} values obtained for the investigated multilayer systems were 141–194 $\text{k}\Omega\text{cm}^2$ for noncured ormosil coatings and 161–250 $\text{k}\Omega\text{cm}^2$ for cured ormosil coatings. Implications of these findings present the option of using environmentally benign conversion coatings in place of hexavalent chromium. The use of multilayer coatings makes enhanced corrosion protection of 2024-T3 aluminum alloy possible

by combining previously developed corrosion protection methods with emerging technology.

ACKNOWLEDGMENT

This research was supported in part by the U.S. Department of Defense and by the Air Force Office of Scientific Research. The authors would like to thank Mr. Andy Anderton for his assistance with sample preparation.

References

- (1) Sax, N.J., *Dangerous Properties of Industrial Materials*, Fifth Ed., Van, New York, 1993.
- (2) (a) Nylund, A., "Chromium-Free Conversion Coatings for Aluminum Surfaces," *Aluminum Transactions*, 2, 121 (2000); (b) Smith, C.J.E., Baldwin, K.R., Garrett, S.A., Gibson, M.C., Hewins, M.A.H., and Lane, P.L., "The Development of Chromate-Free Treatments for the Protection of Aerospace Aluminum Alloys," *ATB Metallurgie*, 37, 266 (1997); (c) Puipe, J., "Surface Treatments of Aluminum for Space Applications," *Galvanotechnik*, 90, 3003 (1990); (d) Twite, R.L. and Bierwagen, G.P., "Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys," *Prog. Org. Coat.*, 33, 91 (1998).
- (3) Roland, W. and Kresse, J., "New Chromium-Free Processes for the Chemical Pretreatment of Aluminum Surfaces," *ATB Metallurgie*, 37, 89 (1997).
- (4) (a) Hinton, B.R.W., "Corrosion Inhibition with Rare Earth Metal Salts," *J. Alloys Compd.*, 180, 15 (1992); (b) Arnott, D.R., Ryan, N.E., Hinton, B.R.W., Sexton, B.A., and Hughes, A.E., "XPS Studies of Cerium Corrosion Inhibition on 7075 Aluminum Alloy," *Appl. Surf. Sci.*, 22, 236 (1985); (c) Morris, E., Stoffer, J.O., O'Keefe, T.J., Yu, P., and Lin, X., "Evaluation of Non-Chrome Inhibitors for Corrosion Protection of High-Strength Aluminum Alloys," *Polymeric Materials*, 81, 167 (1999); (d) Ramanathan, L.V., "Corrosion Control with Rare Earths," *Corrosion Prevention & Control*, 4, 87 (1998).
- (5) Schriever, M.P., U.S. Patent 5,551,994 (Sept. 3, 1996).
- (6) (a) Danilidis, I., Sykes, J.M., Hunter, J.A., and Scamans, G.M., "Manganese Based Conversion Treatment," *Surface Engineering*, 15, 401 (1999); (b) Srinivasan, P.B., Sathiyarayanan, S., Marikkannu, C., Balakrishnan, K., "A Non-Chromate Chemical Conversion Coating for Aluminum Alloys," *Corrosion Prevention & Control*, April, 35 (1995).
- (7) Rangel, C.M., Simões, A., and Newman, R.C., "The Formation of an Alternative Conversion Coating for Aluminum in Buffered Molybdate Solutions," *Portugalica Electrochimica Acta*, 15, 383 (1997).
- (8) Schram, T., Goeminne, G., Terry, H., Vanhoolst, W., and Van Espen, P., "Study of the Composition of Zirconium Based Chromium Free Conversion Layers on Aluminum," *Trans. I.M.F.*, 73, 91 (1995).
- (9) (a) van Ooij, W.J., Zhang, C., Zhang, J.W., and Yuan, W., "Pretreatment for Painting by Organofunctional and Non Functional Silanes," *Electrochemical Society Proceedings*, 97-41, 222 (1998); (b) van Ooij, W.J., Song, J., and Subramanian, V., "Silane-Based Pretreatments of Aluminum and Its Alloys as Chromate Alternatives," *ATB Metallurgie*, 37, 137 (1997); (c) Child, T.F. and van Ooij, W.J., "Application of Silane Technology to Prevent Corrosion of Metals and Improve Paint Adhesion," *Trans. IMF*, 77, 64 (1999); (d) Subramanian, V. and van Ooij, W.J., "Silane Based Metal Pretreatments as Alternatives to Chromating," *Surface Engineering*, 15, 168 (1999); (e) van Ooij, W.J. and Child, T., "Protecting Metals with Silane Coupling Agents," *ChemTech*, 28, 26 (1998); (f) Hinton, B.R., "Corrosion Prevention and Chromates: The End of an Era?" *Metal Finishing*, 89, 15 (1991).
- (10) Delaunois, F., Poulain, V., and Petitjean, J.P., "A Pretreatment Against Localized and Filiform Corrosion Applied to Aluminum Alloys: the Trivalent Chromium Pretreatment," *ATB Metallurgie*, 37, 106 (1997).

- (11) (a) Ilevbare, G.O., Scully, J.R., Yuan, Y., and Kelly, R.G., "Inhibition of Pitting Corrosion on Aluminum Alloy 2024-T3: Effect of Soluble Chromate Additions vs. Chromate Conversion Coating," *Corrosion*, 56, 227 (2000); (b) Hughes, A.E., Taylor, R.J., and Hinton, B.R.W., "Chromate Conversion Coatings on 2024 Al Alloy," *Surface and Interface Analysis*, 25, 223 (1997); (c) Lytle, F.W., Greigor, R.B., Bibbins, G.L., Blohowiak, K.Y., Smith, R.E., and Tuss, G.D., "An Investigation of the Structure and Chemistry of Chromium Conversion Surface Layer on Aluminum," *Corrosion Science*, 37, 349 (1995); (d) Jeffcoate, S., Isaacs, H.S., Aldykiewicz, A.J., and Ryan, M.P., "Chromate in Conversion Coatings: a XANES Study of its Concentration and Mobility," *J. Electrochem. Soc.* 147, 540 (2000); (e) Xia, L., McCreery, R.L., "Chemistry of Chromate Conversion Coating of Aluminum Alloy AA2024-T3 Probed by Vibrational Spectroscopy," *J. Electrochem. Soc.* 15, 3083 (1998).
- (12) Waldrop, J.R. and Kendig, M.W., "Nucleation of Chromate Conversion Coatings on Aluminum 2024-T3 Investigated by Atomic Force Microscopy," *Electrochemical Society Proceedings*, 97-26, 557 (1998).
- (13) Laget, V., Jeffcoate, C., Isaacs, H.S., and Buchheit, R.G., *Electrochemical Society Proceedings*, 99-26, 173 (2000).
- (14) Schriever, M.P., U.S. Patent 5,873,953 (Feb. 2, 1999).
- (15) Pearlstein, F. and Agarwala, V.S., U.S. Patent 5,304,257 (Apr. 19, 1994).
- (16) Pearlstein, F. and Agarwala, V.S., "Trivalent Chromium Solutions for Applying Chemical Conversion Coatings to Aluminum Alloys or for Sealing Anodized Aluminum," *Plating and Surface Finishing*, 81, 50 (1994).
- (17) (a) Schmidt, H.K., "Aspects of Chemistry and Chemical Processing of Organically Modified Ceramics," *Mater. Res. Soc. Symp. Proc.*, 180, 961 (1990); (b) Mackenzie, J.D., "Structures and Properties of Ormosils," *J. Sol-Gel Sci. Technol.*, 2, 81 (1994); (c) Schubert, U., Hüsing, N., and Lorenz, A., "Hybrid Inorganic-Organic Materials by Sol-Gel Processing of Organofunctional Metal Alkoxide," *Chem. Mater.*, 7, 2010 (1995); (d) Sanchez, C. and Ribot, F., "Design of Hybrid Organic-Inorganic Materials Synthesized Via Sol-Gel Chemistry," *New J. Chem.*, 18, 1007 (1994); (e) Livage, L., "The Sol-Gel Route to Advanced Materials," *Mater. Sci. Forum*, 152-153, 43 (1994).
- (18) (a) Guglielmi, M., "Sol-Gel Coatings on Metals," *J. Sol-Gel Sci. Tech.*, 8, 443 (1997); (b) Metroke, T.L., Parkhill, R.L., and Knobbe, E.T., "Passivation of Metal Alloys using Sol-Gel-Derived Materials—A Review," *Prog. Org. Coat.*, 41, 233 (2001).
- (19) (a) Kato, K., "Preparation of SiO₂ Films from Si(OC₂H₅)₄-C₂H₅OH-H₂O Solutions Without Catalysts," *J. Mater. Sci.*, 28, 1445 (1992); (b) Kato, K., "Enhancement of the Corrosion Resistance of Substrates by Thin SiO₂ Coatings Prepared from Alkoxide Solutions Without Catalysts," *J. Mater. Sci.*, 28, 4033 (1993).
- (20) Kasemann, R. and Schmidt, H., "Coatings for Mechanical and Chemical Protection Based on Organic-Inorganic Sol-Gel Nanocomposites," *New J. Chem.*, 18, 1117 (1994).
- (21) Donley, M.S., Vreugdenhil, A.J., and Balbyshev, V.N., "Nanostructured Silicon Sol-Gel Surface Treatments for Al 2024-T3 Protection," *JOURNAL OF COATINGS TECHNOLOGY*, 73, No. 915, 35 (2001).
- (22) (a) Metroke, T.L., Parkhill, R.L., and Knobbe, E.T., "Synthesis of Hybrid Organic-Inorganic Sol-Gel Coatings for Corrosion Resistance," *Mater. Res. Soc. Symp. Proc.*, 576, 293 (1999); (b) Metroke, T.L., and Knobbe, E.T., "Crosslinked Organic-Inorganic Hybrid Thin Films for Corrosion Resistance: Spectroscopic and Salt Spray Characterization," *Mater. Res. Soc. Symp. Proc.*, 628, CC11.4.1 (2000).
- (23) Kachuri, O., Metroke, T.L., Stesikova, E., and Knobbe, E.T., "Comparison of Single and Multilayer Coatings Based on Ormosil and Conversion Layers for Aluminum Alloy Corrosion Inhibition," *JOURNAL OF COATINGS TECHNOLOGY*, 74, No. 926, 43 (2002).
- (24) Kabasakaloglu, M., Aydin, H., Aydin, H., and Aksu, M.L., "Inhibitors for the Protection of Aerospace Aluminum Alloy," *Materials and Corrosion*, 48, 744 (1997).
- (25) Parkhill, R.L., Knobbe, E.T., and Donley, M.S., "Application and Evaluation of Environmentally Compliant Spray-Coated Ormosil Films as Corrosion Resistant Treatments for Aluminum 2024-T3," *Prog. Org. Coat.*, 41, 261 (2001).
- (26) Carey, F.A. and Sundberg, R.J., *Advanced Organic Chemistry*, Plenum Press, New York, p. 540, 1977.