

INVESTIGATION OF THE CORROSION PROTECTION BEHAVIOR OF EXPERIMENTAL PRIMERLESS SILICONE COATINGS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

Space organizations face the difficult challenge of protecting launch pad structures from corrosion. Thin gauge steel and aluminum structures such as protective bellows around drive mechanisms flex repeatedly and thus require highly flexible and adherent coatings. The aerospace industry has traditionally used paints having high volatile organic compound (VOC) content for protecting vehicles and support structures. Flexible paints employ solvent borne rubber binder resins, which render the products highly viscous and difficult to apply by spraying.

Waterborne elastomeric anticorrosion coatings are being developed for the corrosion protection of metals such as aluminum and steel in corrosive environments. The ultimate goal in developing the coatings is to provide an effective and environmentally sound method for protecting the surfaces of aluminum and steel without introducing additional pretreatment and priming steps.

EIS, corrosion potential measurements, and visual observation were used to evaluate the corrosion protection properties of an experimental formulation of a primerless silicone coating on aluminum 2024-T3, stainless steel 316, and cold-rolled steel. EIS spectra as well as corrosion potential measurements were collected at 24-hour intervals for 168 hours in 3.5% aerated NaCl. Panels of the bare alloys, as well as panels of stainless steel 304 and aluminum 2024-T3, coated with an aluminum-filled nitrile rubber coating (AR-7) were also included in the investigation.

The newly developed primerless silicone coating was effective at the corrosion protection of stainless steel 316 but failed on aluminum 2024-T3 and cold-rolled steel. The failure was greater in the case of the cold-rolled steel. Corrosion potential as well as impedance measurements and visual observations indicate that the aluminum-filled nitrile rubber coating provides a superior degree of corrosion protection on aluminum 2024-T3 than on stainless steel 304.

Keywords: EIS, silicone coatings, corrosion, aluminum 2024-T3, stainless steel 304.

INTRODUCTION

Space organizations face the difficult challenge of protecting launch pad structures from corrosion.¹ Thin gauge stainless steel and aluminum structures such as protective bellows around drive mechanisms flex repeatedly and thus require highly flexible and adherent coatings. The aerospace industry has traditionally used paints having high volatile organic compound (VOC) content for protecting vehicles and support structures. Flexible paints employ highly solvated rubber binder resins, which render the products highly volatile and difficult to apply by spraying. Silicone-based paints are formulated to yield temperature- and weather-resistant coatings that prevent corrosion by forming effective electrolyte barriers. However, silicones are normally delivered from organic solvents and exhibit poor adhesion to unprimed metals.

Waterborne elastomeric anticorrosion coatings are being developed for the corrosion protection of metals such as aluminum and stainless steel in corrosive environments. These coatings consist of aqueous dispersions of silicone resins, stabilized with polymeric surfactants and pigmented with non-toxic anticorrosive additives. The latter silicone-modified polymers yield emulsions that adhere the coating to metal surfaces. By forming a topcoat-bound primer layer *in situ*, low VOC-coatings having simple application properties can be formulated.

Experimental VOC-compliant primerless silicone coatings² for corrosion control were available for characterization by Electrochemical Impedance Spectroscopy, EIS. The ultimate goal in developing the coatings is to provide an effective, environmentally sound method for protecting the surfaces of aluminum and stainless steel without introducing additional pretreatment and priming steps.

EXPERIMENTAL

Test Samples

Test panels (10 cm × 15 cm) were coated on one side with a formulation of the experimental primerless silicone coating. Panels of 2024-T3 aluminum alloy (with average composition of 4.4% Cu, 0.6% Mn, 1.5% Mg, and 93.5% Al), stainless steel 316 alloy (with average composition of 0.08% C, 17% Cr, 2% Mn, 2% Mo, 1% Si, 12% Ni, 0.045% P, 0.03% S, and balance Fe), and cold-rolled steel 1010 alloy (with average composition of 0.10% C, 0.45% Mn, 0.008% P, 0.025% S, and balance Fe) were coated twice by air assisted spraying with the waterborne anticorrosive paint and dried under ambient conditions. The formulation used in this study has a theoretical VOC content of 46 g/L and performed well in laboratory abrasion, flexibility and adhesion tests.

Panels of the bare alloys as well as an aluminum panel and a 304 stainless steel panel (with average composition of 0.08% C, 2% Mn, 1% Si, 18-20% Cr, 8.0-10.5% Ni, 0.045% P, 0.03% S, and balance Fe) coated with Aerocoat 7 (AR-7)³ were also tested. AR-7 was used as a control coating because of its excellent corrosion protection performance during 18 months of seacoast exposure in which it obtained a rating of 9.5 (where 10 indicates no rusting or less than 0.01 percent of surface rusted and 9 indicates minute rusting with less than 0.03 percent of surface rusted as described in ASTM D-610).⁴ AR-7 consists of aluminum and zinc flake pigments in a

solvent borne, nitrile rubber matrix and is the coating that is to be replaced because of its high VOC content (700 g/l) and poor application properties. The silicone coating thickness on stainless steel and aluminum was measured with a Positector 6000-N4 thickness gage as 0.046 mm. An Elcometer 256FN T2 thickness gage was used to measure the coating thickness of the silicone-coated cold-rolled steel panel and the AR-7 coated aluminum and stainless steel panels. The thicknesses for these coatings were 0.064 mm, 0.15 mm and 0.12 mm respectively.

Open Circuit Potential Measurements

Open circuit potential measurements were performed using a system manufactured by EG&G Princeton Applied Research Corporation. The system used includes: (1) the Model 273A Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Model 352 SoftCorr™ III Corrosion Measurement Software. The electrochemical flat cell included a saturated Calomel electrode, SCE, a platinum counter electrode, the sample-working electrode, and a bubbler/vent tube. The flat specimen holder exposed a surface area of 1 cm². Open circuit potential values were gathered for one hour in aerated 3.5% (w/w) NaCl before the first set of EIS measurements was obtained. Subsequent open circuit potential values were collected before each set of EIS measurements, which were collected at several time intervals up to a maximum of 168 hours. All solutions were prepared using deionized water.

Electrochemical Impedance Measurements

A Model 378 Electrochemical Impedance system manufactured by EG&G Princeton Applied Research Corporation was used for all EIS measurements. The system includes: (1) the Model 273A Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Power Sine™ Electrochemical Impedance Software. Data were gathered in the frequency range from 100 kHz to 0.01 Hz. The AC amplitude used for the experiments was 10 mV. Each sample was studied at various immersion times in aerated 3.5% (w/w) NaCl for up to one week.

RESULTS AND DISCUSSION

Open Circuit Potential Measurements

Open circuit potential values were gathered during the hour immediately preceding each set of EIS measurements for each panel. Subsequent measurements were gathered at 24-hour intervals for up to a maximum of 168 hours. Fig. 1 shows the change in open circuit potential with immersion time for AR-7 on 304 stainless steel and on 2024-T3 aluminum. The large fluctuations in the open circuit potential that were observed during the first hour of measurements became smaller as immersion time progressed. The fluctuations were more pronounced for the coated stainless steel panel than for the coated aluminum panel. It can be hypothesized that these fluctuations are due to the galvanic activity of the metallic particles of aluminum and zinc in the coating. The corrosion potential of bare aluminum and bare stainless steel measured under the same conditions as those for the coated samples were -674 and -136

mV respectively. The plot shows the values of the open circuit potential obtained immediately before the EIS measurements were gathered.

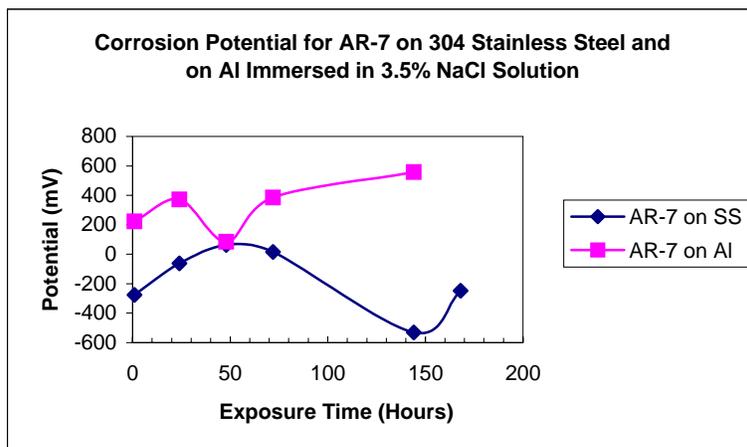


Figure 1. Open circuit potential as a function of immersion time in 3.5% NaCl for AR-7 on 304 stainless steel and on 2024-T3 aluminum.

As the data on Fig. 1 shows, the variation of the open circuit potential with immersion time is very different for AR-7 on aluminum and on stainless steel. The open circuit potential of AR-7 on aluminum exhibited a general upward trend with all the values being at a potential significantly higher than the -674 mV for aluminum. On the other hand, the open circuit potential values for AR-7 on stainless steel fluctuated at values that were higher or lower than the -136 mV obtained for the bare metal. The AR-7 coated stainless steel panel showed the greatest variability in the open circuit potential. There seems to be a great deal of electrochemical activity taking place in this sample whose exact nature can be the subject of further investigation. Values of open circuit potential versus time for AR-7-coated cold-rolled steel were not collected due to the unavailability of an AR-7 coated sample.

Figs. 2-4 show the variation of open circuit potential with time for the silicone-coated samples of 2024-T3 aluminum, cold-rolled steel, and stainless steel 316. There was some protection of the aluminum by the silicone coating during the first hour of immersion. However, as shown in Fig. 2, the coating failed by the 24-hour period as indicated by the decay in the open circuit potential towards the -674 mV corrosion potential of aluminum. Visual observation of the area exposed to the electrolyte revealed the presence of blisters (Fig. 10). Fig. 3 shows the decline of the open circuit potential with immersion time for the silicone-coated cold-rolled steel sample. The open circuit potential for the coated sample decays towards the corrosion potential of the bare cold-rolled steel value of -628 mV measured under the same experimental conditions. Visual observation of the exposed area confirmed the complete failure of the coating as indicated by the degree of corrosion observed (Fig. 11). Fig. 4 shows the trend in the open circuit potential for silicone-coated stainless steel 316. The open circuit potential starts at a value that is indicative of corrosion protection and it declines gradually to -31 mV after 168 hours of immersion. This potential is higher than the -136 mV value obtained for the bare stainless steel 316 under similar conditions. Visual examination of the sample (Fig. 12) revealed no defects in the coating.

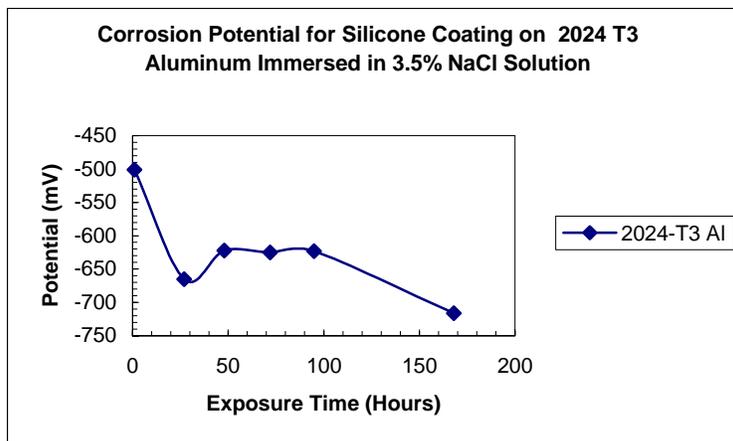


Figure 2. Open circuit potential as a function of immersion time in 3.5% NaCl for silicone-coated 2024-T3 aluminum.

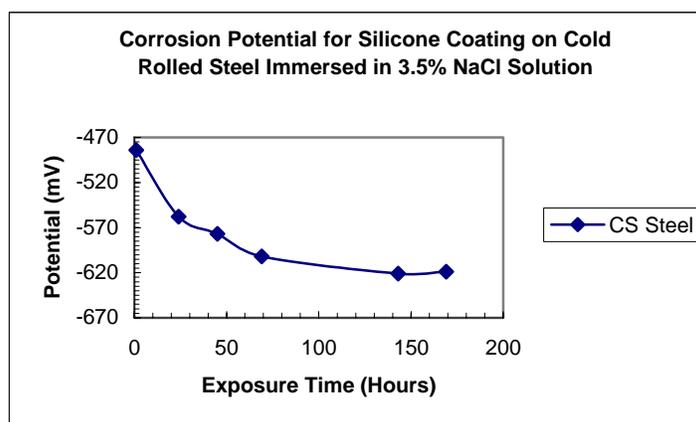


Figure 3. Open circuit potential as a function of immersion time in 3.5% NaCl for silicone-coated cold-rolled steel.

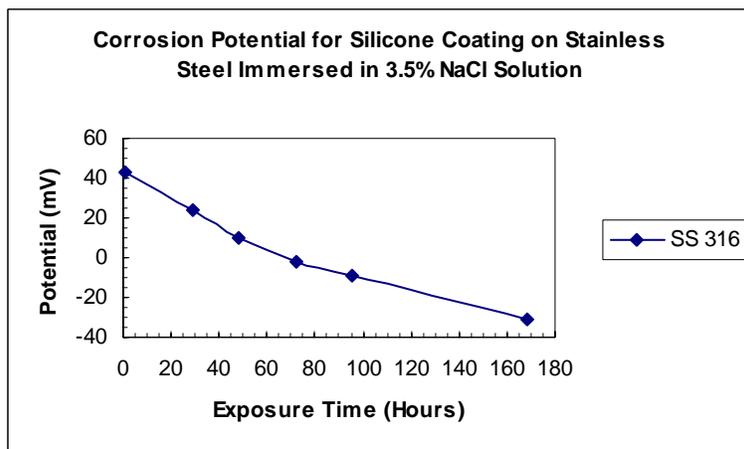


Figure 4. Open circuit potential as a function of immersion time in 3.5% NaCl for silicone-coated stainless steel 316.

Based on the open circuit potential measurements and visual observations, it was concluded that the silicone coating offered the best degree of corrosion protection to the stainless steel 316 and the poorest to the cold-rolled steel. The coating adhered well to the stainless steel, not so well to the aluminum, as indicated by the blistering, and very poorly to the cold-rolled steel sample.

Electrochemical Impedance Measurements

Bode magnitude plots for the AR-7 coated aluminum and stainless steel samples are shown in Figs. 5 and 6. The EIS spectra for the coated aluminum panel obtained at different immersion times (Fig. 5) shows sustained high impedance over the frequency range that did not decrease as the immersion time increased. This is indicative of the barrier properties of the AR-7 coating. Fig. 6 shows that the magnitude of the impedance over the frequency range for the AR-7 coated stainless steel 304 is lower than that of the aluminum and that it decreases with immersion time. The impedance data suggest that AR-7 exhibited a superior degree of corrosion protection on the aluminum than on the stainless steel.

Bode magnitude plots for the silicone-coated samples are shown in Figs. 7-9. A comparison between Figs. 5 and 7 would suggest a superior corrosion protection of aluminum by the AR-7 coating compared to the silicone coating. However, the fact that the thicknesses of the AR-7 coatings were 2-3 times greater than those of the silicone coatings precludes this conclusion. The impedance data shown on Fig. 8 shows the failure of the silicone coating in protecting the cold-rolled steel sample from corrosion. There was no AR-7 coated carbon steel sample available for comparison. A comparison of Figs. 6 and 9 indicates that, initially, the AR-7 coating provided a higher degree of corrosion protection to the stainless steel sample. However, the barrier properties of the coating decreased as the immersion time increased. This finding is not consistent with the excellent corrosion protection rating obtained for the AR-7 coating on steel in the seacoast exposure evaluation.⁴

Visual Observations

Figs. 10-12 show photographs of the silicone-coated aluminum, cold-rolled steel, and stainless steel panels. Fig. 10 shows blistering of the silicone coating after 168 hours of immersion in 3.5% NaCl. Fig. 11 shows that there were visible signs of coating failure on the cold-rolled steel panel. Fig. 12 shows the corrosion protection of the silicone coating for the 316 stainless steel panel. Fig. 13 shows the AR-7 coated aluminum panel with no visible signs of coating failure.

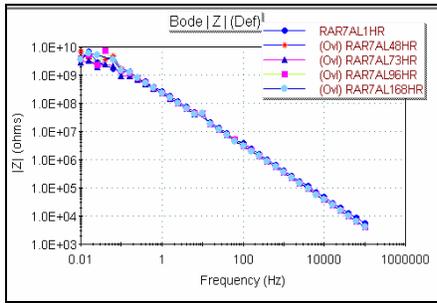


Figure 5. Bode magnitude plots for AR-7 coated aluminum 2024-T3 at different immersion times in 3.5 % NaCl.

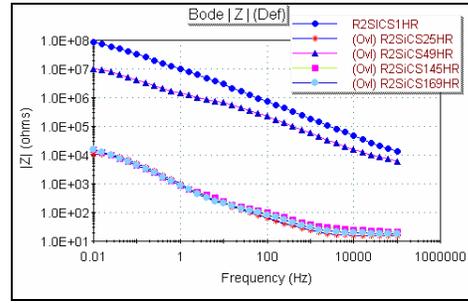


Figure 8. Bode magnitude plots for silicone coated cold-rolled steel at different immersion times in 3.5 % NaCl

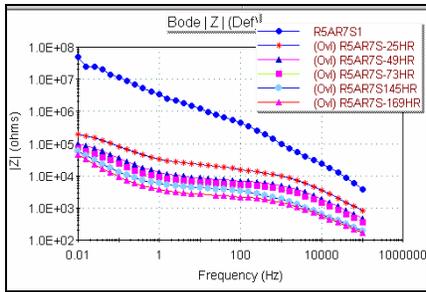


Figure 6. Bode magnitude plots for AR-7 coated stainless steel 304 at different immersion times in 3.5 % NaCl.

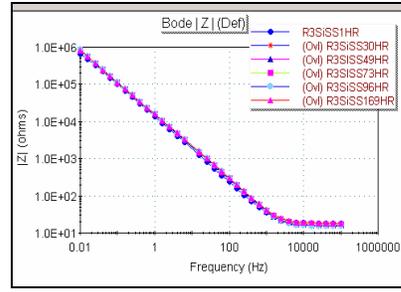


Figure 9. Bode magnitude plots for silicone coated stainless steel 316 at different immersion times in 3.5 % NaCl.

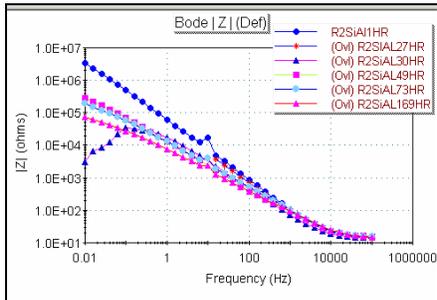


Figure 7. Bode magnitude plots for silicone coated aluminum 2024-T3 at different immersion times in 3.5 % NaCl.



Figure 10. Silicone-coated Al 2024-T3 panel after 168 hours of immersion in 3.5% NaCl

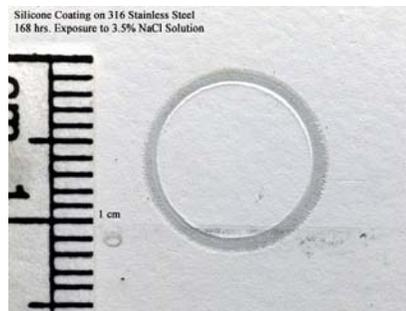


Figure 12. Silicone-coated 316 stainless steel panel after 168 hours of immersion in 3.5% NaCl

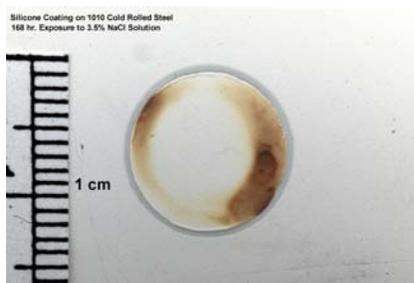


Figure 11. Silicone-coated cold-rolled steel panel after 168 hours of immersion in 3.5% NaCl.

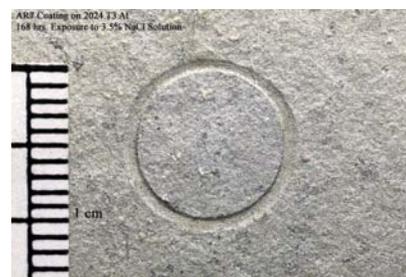


Figure 13. AR-7-coated 2024 T3 after 168 hours of immersion in 3.5% NaCl.

CONCLUSIONS

Open circuit potential as well as impedance measurements and visual observations indicate that AR-7 provides a superior degree of corrosion protection for aluminum 2024-T3 than for stainless steel 304.

The newly developed primerless silicone coating was effective at the corrosion protection of stainless steel 316 but it failed on aluminum 2024-T3 and on cold-rolled steel. The failure was greater in the case of the cold-rolled steel.

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