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Comparison of Electrochemical Impedance Spectroscopy (EIS) Results for Accelerated Exposures versus Outdoor Exposure

by Christopher Miller

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by Christopher Miller

Weapons and Materials Research Directorate, ARL

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14. ABSTRACT Cold-rolled steel and aluminum 2024 T3 panels were coated with 4 combinations of the chemical agent-resistant coating system (CARC) and exposed to 4 accelerated environments and outdoor environments at Cape Canaveral. The accelerated exposures included ASTM B117, ASTM D5894, and ASTM D5894 modified with 1 week of ASTM B117 or SAE J2334 in lieu of 1 week of ASTM G85. Electrochemical Impedance Spectroscopy (EIS), color, and gloss measurements were taken initially and at regular intervals during exposure. It was found that failure of these coating systems due to creep from scribe occurred before significant degradation was noticed using EIS, in part due to poor signal-to-noise in the electrochemical measurement. For systems where this was the case, samples were recoated and subjected to the accelerated environment with EIS measurements taken at regular intervals within the exposure. It was found that certain combinations of approved primer/topcoat demonstrate consistently better corrosion performance than other approved combinations. The choice of topcoat appears to have a greater impact than the choice of primer. Further, this testing validated the pretreatment and coating approval procedures that require outdoor exposure. This report compares the results of the outdoor exposures and accelerated corrosion. Also, EIS measurements generated from a second set of laboratory-accelerated corrosion panels were compared to the EIS measurements from the original outdoor set.					
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1. Introduction

ASTM B117, *Standard Practice for Operating Salt Spray (Fog) Apparatus*,¹ is an effective screening tool that allows formulators and applicators to quickly detect when there are problems with surface preparation, incompatibility, or application processes. All 3 military services cite and use this standard when specifying coating performance criteria for their materiel. As the performance of the coatings has improved, the length of exposure requirement for static salt fog and cyclic corrosion methods has been extended to accommodate that performance. A screening tool that could quickly check for compatibility of a coating system or determine if it had been applied correctly became an extended exposure that no longer provided this information within the coating application cycle. Improved methods are necessary for assessing corrosion/degradation that better replicate the actual environmental conditions under which fielded materiel is exposed. This study introduces a complementary method that allows one to detect degradation of a coating system before visual evidence of failure is available. If successful, the method will be placed into the coatings specifications.

If no action is taken, then the Army will continue to misuse a flawed standard that could, at worst, allow the Army to purchase and use coatings that provide little or no environmental performance benefit beyond the barrier protection afforded by the coating thickness. Alternatively, the ASTM B117 test could also drive maintenance costs higher by excluding coatings that provide superior real-world performance but fail under the constant conditions of salt fog. Finally, without reliable protocol and methodology that more accurately predicts outdoor exposure, research and development within the Department of Defense will remain hampered and flawed in providing enhanced and improved coating solutions to its soldiers and the equipment to support them.

Industry has developed several tests such as ASTM G85,² GMW14872³ (updated from GM 9540), and SAE J2334⁴ that better replicate outdoor performance in terms of appearance and progression in an accelerated manner than ASTM B117. Also available are ASTM G154⁵ and ASTM G 155⁶ that replicate outdoor degradation of coatings through accelerated ultraviolet (UV) exposure.

The testing performed in this work assessed cyclic weathering tests that combined accelerated corrosion and accelerated UV degradation, such as that described in ASTM D5894.⁷ Test results obtained were then compared and correlated to those generated through normal outdoor exposure. The ultimate goal, upon confirmation that correlation is better than ASTM B117, would be to include the accelerated corrosion/degradation test in the Army's paint specifications. A secondary benefit

is the improvement in the reliability of the currently used 4 rating criteria for assessing corrosion correlation.

In this study a complementary analytical technique, electrochemical impedance spectroscopy (EIS), was incorporated into the analyses. EIS measures the response of a coating system to a perturbation over a range of frequencies. The data are often modeled using an equivalent circuit, usually resistors and capacitors, which emulates the performance of the coating system to provide better understanding of material behavior and predict performance of new systems. EIS data are presented here using Bode plots that graph frequency along the x-axis and resistivity or phase shift along the y-axis. They are used because they present the absolute resistivity over the entire frequency range tested. A well-formed nonconductive coating often acts as a capacitor that is exhibited as a straight line on the Bode plot. Corrosion of the metal surface and degradation of the coating itself will introduce additional capacitive and resistive effects. For example, interface and solution interactions can create capacitive effects that lower the resistivity at higher frequencies.^{8–11} The Bode plot for a good coating is a nearly straight line with the highest resistivity at the lower frequency end of the plot. As the coating degrades, the line will shift down and the lower frequency end of the curve will become nearly horizontal. Individual EIS curves are overlaid to produce composite graphs that track the performance of coating systems through a test exposure. As there was no corrosion in the field portion of these panels, this procedure demonstrated that the technique can show degradation of a coating well in advance of any visible evidence of failure. EIS can provide a repeatable quantitative value that indicates coating degradation long before the currently used qualitative evaluations that rely solely upon visual examination.

The initial experimental plan for this work sought to compare 2 substrates, aluminum (2024) and steel (cold-rolled steel), coated with several combinations of the chemical agent-resistant coating (CARC) system. A complete set of panels were exposed at an outdoor site, Cape Canaveral. Evaluations were performed every 3 months to capture digital images, corrosion ratings, color, gloss, and make EIS measurements. A second complete set of panels were exposed to ASTM B117 for up to 4000 h or to failure. Specimen images, corrosion ratings, color, gloss, and EIS would be captured every 336 h. One set each were exposed to 10 complete cycles of ASTM D5894, ASTM B117, or SAE J2334–modified ASTM D5894 where a complete cycle is defined as 7 cycles (1 week) of ASTM B117, ASTM G85, or SAE J2334 followed by 1 week of ASTM G154. Images, corrosion ratings, color, gloss, and EIS were captured following every complete cycle. The coatings' performance was evaluated and ranked, followed by the development of a correlation factor between the outdoor exposure and the 3 accelerated exposures.

2. Procedure

A series of 132 steel panels pretreated with the Henkel Bonderite zinc phosphate and 132 2024 T6 aluminum panels pretreated with Alodine 600 were coated robotically by Pratt & Whitney Automation with MIL-DTL-53022¹² or MIL-DTL-53030¹³ primers and topcoated with MIL-DTL-53039¹⁴ or MIL-DTL-64159.¹⁵ Panels of each coating system were randomly assigned to make up sets of 24 that would be subjected to the following exposures: Florida outdoor exposure at NASA Kennedy Space Center (KSC), ASTM B117, ASTM D5894, ASTM B117 alternating with ASTM G154, and SAE J2334 alternating with ASTM G154. The latter 3 tests were chosen so that exposures would have an accelerated corrosion component and a weathering component.

NASA KSC was chosen as an aggressive outdoor site that had the capability to perform the required tests on site. ASTM B117 was chosen to reflect the current laboratory testing.

Before any exposure took place, half of each panel set had initial EIS, color, and gloss readings taken, and the spots used for these readings were marked. Future readings taken during exposure were performed on the same areas so that changes reflected changes in coating performance rather than minor variations in coating thickness or continuity. The other half of each panel set was scribed through the coatings with an “X” running from corner to corner.

The panel set sent to NASA had initial values remeasured using their equipment before exposure. Panels were placed in racks facing the beach 100 yd from the ocean (Figs. 1 and 2). Non-scribed panels had color, gloss, and EIS measurements taken while scribed panels were rated using ASTM D1654¹⁶ and images scanned following every 3 months of exposure. A rating of below 7 in ASTM D1654 was considered failing, although panels were run for a set period of time or until a rating of 0 was achieved. EIS measurements were taken using a Gamry 600 series instrument with impedance measured over a frequency range of 0.01 to 100,000 Hz. For EIS measurements, low-frequency impedance below $1 \times 10^9 \Omega$ was considered failure, and individual panel performance comparisons were made with respect to measurements taken of those same panels prior to exposure.



Fig. 1 Panels at Kennedy Space Center beach exposure site

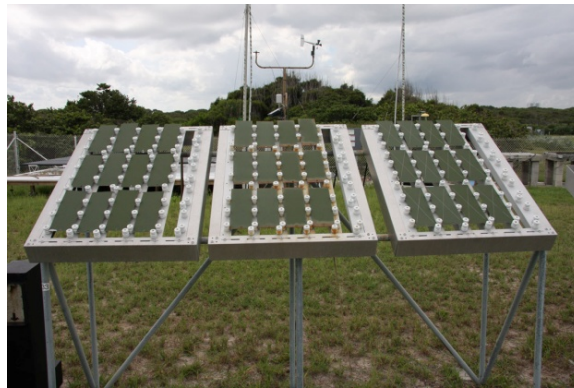


Fig. 2 Panels at Kennedy Space Center beach exposure site

Panels in the ASTM B117 set were placed in a water-jacketed Harshaw unit (Fig. 3) and exposed to 5% salt fog with measurements taken every 168-h intervals initially and 504-h intervals following 1008 h of exposure. Following each exposure period, panels were rinsed in deionized water prior to evaluation. As with the NASA panels, non-scribed panels had color, gloss, and EIS readings taken while the scribed panels were rated with ASTM D1654 and their images scanned. Panels were run through 4032 h except for the MIL-DTL-53030/MIL-DTL-64159 set, which was terminated after 2016 h.



Fig. 3 Harshaw salt fog chamber for ASTM B117 exposure

The modified ASTM B117 panel set was exposed in the same water-jacketed Harshaw unit for 168 h at a time. Panels were rinsed with deionized water and removed to a Q-Lab QUV machine (Fig. 4) and exposed per ASTM G154 to 168 h of an alternating 8-h UV, 4-h condensation cycle. For clarity, the combination of 168 h of accelerated corrosion exposure and 168 h of alternating UV/humidity exposure will now be referred to as one phase. After each phase, non-scribed panels in the modified ASTM B117 set had color, gloss, and EIS readings taken while scribed panels were rated per ASTM D1654 and their images scanned. This exposure was terminated after 14 phases for steel and 17 phases for aluminum.



Fig. 4 QUV accelerated weathering chambers for ASTM G154 exposure

The ASTM D5894 panel set was exposed to 168 h of alternating 1-h periods of low-concentration salt fog and higher-temperature dryoff per ASTM G85. The salt solution consists of 0.05% sodium chloride and 0.35% ammonium sulfate. An Autotechnology CCT-P chamber (Fig. 5) was used for this. Panels were rinsed with deionized water. Each phase was completed with 168 h of exposure to ASTM G154. Data gathering was accomplished as in the previous exposures at the completion of each phase. This exposure was terminated after 12 phases for steel and 15 phases for aluminum.



Fig. 5 Atotech cct-p chamber for ASTM G85 and SAE J2334 exposures

The SAE J2334 panel set was exposed to 7 cycles (168 h) of the steps outlined in SAE J2334. These included high-humidity, high-temperature dryoff, immersion in 0.9% salt, 0.1% calcium chloride, and 0.075% sodium bicarbonate, and ambient rest (Table 1). Following this exposure, panels were rinsed in deionized water with some rubbing to remove deposited calcium carbonate (Fig. 6). Each phase was completed with 168 h of exposure to ASTM G154. Data gathering was accomplished as in the previous exposures at the completion of each phase. This exposure was terminated after 12 phases for both substrates.

Table 1 Consolidated ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system. There is no correlation between the intervals of months for Florida outdoor, hours for ASTM B117, and the phases for the cyclic exposures.

Step	Description	Conditions	Duration (min)
1	Salt mist application	25±3°C, 45±10%RH	1
2	Ambient stage	25±3°C, 45±10%RH	59
3	Salt mist application	25±3°C, 45±10%RH	1
4	Ambient stage	25±3°C, 45±10%RH	59
5	Salt mist application	25±3°C, 45±10%RH	1
6	Ambient stage	25±3°C, 45±10%RH	59
7	Salt mist application	25±3°C, 45±10%RH	1
8	Ambient stage	25±3°C, 45±10%RH	59
9	Ambient stage	25±3°C, 45±10%RH	240
10	Humid stage	49±2°C, ~100%RH	480
11	Dry stage	60±2°C, 45±10%RH	480

Because of inconsistencies within the EIS data sets performed in the laboratory, it was decided to repeat 4 accelerated exposures for EIS only using a newly prepared panel set. The combinations of systems remained the same, but the specific manufacturers of the coatings used were different and were applied in-house. Non-scribed panel sets were exposed to ASTM B117, modified ASTM B117, GMW14872, and modified GMW14872 for 6 weeks of total accelerated corrosion exposure time. GMW14872 had replaced the GM 9540 accelerated corrosion test and is substantially similar to the older method except that one cycle is equal to 1 day, and the newer method has a more aggressive bare coupon corrosion rate. The GMW14872 exposure replaced the SAE J2334 in the repeated exposure because it is cited in the coatings specifications, and the corrosion produced is more similar to that formed in outdoor exposure. Cells were placed on the same location for each sample, filled with 3.5% sodium chloride (NaCl) solution, and allowed to equilibrate for 24 h. EIS measurements were taken before exposure and following every 168 h of accelerated corrosion chamber time.



Fig. 6 Calcium carbonate deposits from SAE J2334 exposure

3. Results

3.1 Steel: Scribed Samples

Tables 2–6 show the ASTM D1654 ratings for all of the scribed steel exposures. The first number represents the amount of creep from scribe. If present, the number following “BIF” represents the blistering away from the scribe. A value of below 7 (>2.0 mm) using ASTM D1654 is considered failing for creep from scribe. Scribed panels were scanned at every interval. A composite picture containing representative images of a steel panel following each exposure is presented in Fig. 7. Similar composites for each coating system are included in the Appendix. With the exception of the steel panels coated with MIL-DTL-53030 and MIL-DTL-64159 in the outdoor and ASTM B117 exposures, none of the non-scribed steel panels had any corrosion in the field apart from edge effects.

Table 2 ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system in Florida outdoor exposure

Substrate	Primer	Topcoat	Designation	3 Month	6 Month	9 Month	12 Month	15 Month	18 Month	21 Month	24 Month
Steel 1	MIL-P-53022	MIL-P-53039	Outdoor A1 Fe	7	5	6	5	3	3	3	3
Steel 2	MIL-P-53022	MIL-P-53039	Outdoor A2 Fe	7	5	5	5	3	3	3	3
Steel 3	MIL-P-53022	MIL-P-53039	Outdoor A3 Fe	7	5	5	5	3	3	3	3
Steel 1	MIL-P-53030	MIL-P-53039	Outdoor B1 Fe	5	4	3	3	2	1	0	
Steel 2	MIL-P-53030	MIL-P-53039	Outdoor B2 Fe	5	4	3	3	2	1	0	
Steel 3	MIL-P-53030	MIL-P-53039	Outdoor B3 Fe	6	4	3	3	2	2	1	0
Steel 1	MIL-P-53022	MIL-DTL-64159	Outdoor C1 Fe	6	4	4	3	2	2	2	0
Steel 2	MIL-P-53022	MIL-DTL-64159	Outdoor C2 F3	6	4	4	3	2	2	2	1
Steel 3	MIL-P-53022	MIL-DTL-64159	Outdoor C3 Fe	6	4	4	3	2	2	1	0
Steel 1	MIL-P-53030	MIL-DTL-64159	Outdoor D1 Fe	5	3	3	2	1	1	0	
Steel 2	MIL-P-53030	MIL-DTL-64159	Outdoor D2 Fe	5	3	3	1	1	1	0	
Steel 3	MIL-P-53030	MIL-DTL-64159	Outdoor D3 Fe	5	3	2	1	1	1	0	

Table 3 ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system in ASTM B117 exposure

Substrate	Primer	Topcoat	Designation	68 Hour	336 Hour	528 Hour	672 Hour	840 Hour	1008 Hour	1512 Hour	2016 Hour	2520 Hour	3024 Hour	3528 Hour	4032 Hour
Steel 1	MIL-P-53022	MIL-P-53039	B117 A1 Fe	8	8 BIF 9	7 BIF 7	7 BIF 7	7 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7
Steel 2	MIL-P-53022	MIL-P-53039	B117 A2 Fe	8	7	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	4 BIF 9	4 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8
Steel 3	MIL-P-53022	MIL-P-53039	B117 A3 Fe	8	7 BIF 9	7 BIF 8	7 BIF 7	6 BIF 7	6 BIF 7	5 BIF 7	5 BIF 6	5 BIF 6	4 BIF 6	4 BIF 6	4 BIF 6
Steel 1	MIL-P-53030	MIL-P-53039	B117 B1 Fe	8	7 BIF 9	7 BIF 8	7 BIF 8	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 3	5 BIF 1	5 BIF 1	5 BIF 0	5 BIF 0
Steel 2	MIL-P-53030	MIL-P-53039	B117 B2 Fe	8	7	7	6 BIF 9	6 BIF 9	6 BIF 9	5 BIF 9	5 BIF 7	5 BIF 6	5 BIF 5	5 BIF 5	5 BIF 5
Steel 3	MIL-P-53030	MIL-P-53039	B117 B3 Fe	8	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	5 BIF 9	5 BIF 9	5 BIF 6	5 BIF 5	4 BIF 4	4 BIF 4	3 BIF 4
Steel 1	MIL-P-53022	MIL-DTL-64159	B117 C1 Fe	8	7	7	7	7 BIF 8	7 BIF 8	6 BIF 8	5 BIF 6	5 BIF 6	4 BIF 6	4 BIF 6	4 BIF 6
Steel 2	MIL-P-53022	MIL-DTL-64159	B117 C2 F3	8	7	7	7	7 BIF 9	7 BIF 9	5 BIF 9	5 BIF 7	5 BIF 6	4 BIF 6	4 BIF 6	4 BIF 6
Steel 3	MIL-P-53022	MIL-DTL-64159	B117 C3 Fe	8	7	6	6 BIF 9	5 BIF 9	5 BIF 9	5 BIF 9	5 BIF 8	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7
Steel 1	MIL-P-53030	MIL-DTL-64159	B117 D1 Fe	8	7	7	6	6 BIF 9	5 BIF 9	4 BIF 3	4 BIF 2				
Steel 2	MIL-P-53030	MIL-DTL-64159	B117 D2 Fe	7	7	7	7	6	6	5 BIF 4	4 BIF 2				
Steel 3	MIL-P-53030	MIL-DTL-64159	B117 D3 Fe	8	7	6	6	6 BIF 9	5 BIF 9	4 BIF 3	3 BIF 2				

Table 4 ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system in modified ASTM B117 exposure

Substrate	Primer	Topcoat	Designation	1 Phase	2 Phase	3 Phase	4 Phase	5 Phase	6 Phase	7 Phase	8 Phase	9 Phase	10 Phase	11 Phase	12 Phase	13 Phase	14 Phase
Steel 1	MIL-P-53022	MIL-P-53039	Mod B117 A1 Fe	8	7 BIF 9	6 BIF 9	6 BIF 8	6 BIF 8	6 BIF 8	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8
Steel 2	MIL-P-53022	MIL-P-53039	Mod B117 A2 Fe	8	7	7	7	7	6	6 BIF 9	5 BIF 9	5 BIF 9	5 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8
Steel 3	MIL-P-53022	MIL-P-53039	Mod B117 A3 Fe	8	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8
Steel 1	MIL-P-53030	MIL-P-53039	Mod B117 B1 Fe	8	7 BIF 8	7 BIF 7	6 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	4 BIF 7	4 BIF 7	4 BIF 7	3 BIF 8	3 BIF 8	3 BIF 8
Steel 2	MIL-P-53030	MIL-P-53039	Mod B117 B2 Fe	8 BIF 9	7 BIF 9	7 BIF 6	6 BIF 6	6 BIF 6	6 BIF 6	5 BIF 6	4 BIF 6	4 BIF 6	3 BIF 7	3 BIF 7	2 BIF 7	2 BIF 7	2 BIF 7
Steel 3	MIL-P-53030	MIL-P-53039	Mod B117 B3 Fe	8	7	7 BIF 9	7 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8	3 BIF 8	3 BIF 8	3 BIF 8
Steel 1	MIL-P-53022	MIL-DTL-64159	Mod B117 C1 Fe	8	7	7 BIF 8	7 BIF 8	6 BIF 8	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7	5 BIF 7
Steel 2	MIL-P-53022	MIL-DTL-64159	Mod B117 C2 F3	8	7	7	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	5 BIF 9	5 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8
Steel 3	MIL-P-53022	MIL-DTL-64159	Mod B117 C3 Fe	8	7	7	6	6	6 BIF 8	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8	5 BIF 7	5 BIF 7
Steel 1	MIL-P-53030	MIL-DTL-64159	Mod B117 D1 Fe	8	6	5	5	5	4	4	3	2	2	2	1 BIF 8	1 BIF 8	1 BIF 8
Steel 2	MIL-P-53030	MIL-DTL-64159	Mod B117 D2 Fe	8	7	6	5	5	4	4	4	3	3	3	2	2	2
Steel 3	MIL-P-53030	MIL-DTL-64159	Mod B117 D3 Fe	8	7	6	6	5	4	4	3	3	3	3 BIF 8	2 BIF 7	2 BIF 7	2 BIF 7

Table 5 ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system in ASTM 5894 exposure

Substrate	Primer	Topcoat	Designation	1 Phase	2 Phase	3 Phase	4 Phase	5 Phase	6 Phase	7 Phase	8 Phase	9 Phase	10 Phase	11 Phase	12 Phase
Steel 1	MIL-P-53022	MIL-P-53039	G85 A1 Fe	9	8	7	7	7	6	6	5	5	5	5	5
Steel 2	MIL-P-53022	MIL-P-53039	G85 A2 Fe	9	8	8 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	6 BIF 9	5	5	5	5	5
Steel 3	MIL-P-53022	MIL-P-53039	G85 A3 Fe	9	8	7	7	7	6	6	5	5	5	5	5
Steel 1	MIL-P-53030	MIL-P-53039	G85 B1 Fe	8	7 BIF 8	6 BIF 8	6 BIF 8	5 BIF 9	5 BIF 9	5 BIF 9	4 BIF 9	4 BIF 9	4 BIF 9	4	4
Steel 2	MIL-P-53030	MIL-P-53039	G85 B2 Fe	8	7	6	6	5	5	4	4	3	3	3	3
Steel 3	MIL-P-53030	MIL-P-53039	G85 B3 Fe	8	7	7	7	6	6	5	5	5	4	4	4
Steel 1	MIL-P-53022	MIL-DTL-64159	G85 C1 Fe	9	8 BIF 9	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	6 BIF 8	6 BIF 9	5	5	5	5
Steel 2	MIL-P-53022	MIL-DTL-64159	G85 C2 F3	9	8 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	6	6	5	5	5
Steel 3	MIL-P-53022	MIL-DTL-64159	G85 C3 Fe	9	8	8	7	7	6	6	5	5	5	5	5
Steel 1	MIL-P-53030	MIL-DTL-64159	G85 D1 Fe	8	7	6	5	5	5	5	5	4	4	4	3
Steel 2	MIL-P-53030	MIL-DTL-64159	G85 D2 Fe	7	7 BIF 9	6 BIF 8	6 BIF 8	6 BIF 8	5 BIF 8	5 BIF 8	5 BIF 8	4 BIF 8	4 BIF 8	4 BIF 8	3 BIF 8
Steel 3	MIL-P-53030	MIL-DTL-64159	G85 D3 Fe	7	7	7 BIF 9	6 BIF 9	5 BIF 9	5 BIF 9	5 BIF 9	5 BIF 9	4 BIF 9	4 BIF 9	4 BIF 9	4 BIF 9

Table 6 ASTM D1654 ratings of scribed phosphated steel panels coated with the CARC system in modified SAE J2334 exposure

Substrate	Primer	Topcoat	Designation	1 Phase	2 Phase	3 Phase	4 Phase	5 Phase	6 Phase	7 Phase	8 Phase	9 Phase	10 Phase	11 Phase	12 Phase
Steel 1	MIL-P-53022	MIL-P-53039	J2334 A1 Fe	9	8	8	8	8	7	7	7	6	6	6	5
Steel 2	MIL-P-53022	MIL-P-53039	J2334 A2 Fe	9	9	9	8	8	8	7	7	7	7	7	7
Steel 3	MIL-P-53022	MIL-P-53039	J2334 A3 Fe	9	9	9	9	9	8	7	7	7	7	7	7
Steel 1	MIL-P-53030	MIL-P-53039	J2334 B1 Fe	9	8	7	7	7	7	6	6	6	6	5	5
Steel 2	MIL-P-53030	MIL-P-53039	J2334 B2 Fe	9	8	7	7	7	6	6	5	5	5	4	4
Steel 3	MIL-P-53030	MIL-P-53039	J2334 B3 Fe	9	8	8	8	6	6	6	5	5	5	5	5
Steel 1	MIL-P-53022	MIL-DTL-64159	J2334 C1 Fe	8	8	8	8	8	7	7	7	6	5	5	5
Steel 2	MIL-P-53022	MIL-DTL-64159	J2334 C2 F3	9	8	8	8	8	7	7	7	6	5	5	5
Steel 3	MIL-P-53022	MIL-DTL-64159	J2334 C3 Fe	9	9	9	8	8	8	7	7	7	6	6	6
Steel 1	MIL-P-53030	MIL-DTL-64159	J2334 D1 Fe	8	6	6	6	4	4	4	3	3	2	2	1
Steel 2	MIL-P-53030	MIL-DTL-64159	J2334 D2 Fe	8	7	6	5	4	4	4	3	3	2	2	1
Steel 3	MIL-P-53030	MIL-DTL-64159	J2334 D3 Fe	8	6	5	5	4	4	3	3	3	2	2	1



Fig. 7 Steel panels with coating System A following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

For steel samples coated with System A (MIL-DTL-53022/MIL-DTL-53039), the scribed panels corroded very rapidly at the outdoor site with failure occurring prior to 6 months. The ASTM B117 results showed failure by approximately 1000 h, and the modified ASTM B117 had all failed by the fifth phase (840 h of chamber time). For ASTM D5894, the samples failed by 6 phases (~1000 h of chamber time). For J2334, 2 of the 3 samples survived all 12 phases of exposure (~2000 h of chamber time).

For steel samples coated with System B (MIL-DTL-53030/MIL-DTL-53039), the scribed steel panels failed before the first 3 month evaluation at the outdoor site. The ASTM B117 showed failure before 672 h, and all those samples had failed before 840 h. Additionally, blistering in the non-scribed regions of the scribed panels was also a factor for this exposure. The modified salt fog provided similar results to the salt fog for this system in that failures occurred prior to the fourth phase (672 h of accelerated corrosion exposure). However, blistering never progressed beyond a rating of 8 even after 14 phases. The ASTM D5894 panels failed before the fifth phase (840 h of corrosion exposure). The panels in SAE J2334 slightly outperformed the rest for scribed corrosion resistance by having one panel that was passing after 6 phases (1008 h of accelerated corrosion exposure).

Steel samples coated with System C (MIL-DTL-53022/MIL-DTL-64159) also failed prior to 3 months of outdoor exposure for scribed creep, although it had better

ratings at this point than either of the sets primed with MIL-P-53030. The ASTM B117 failed after 1512 h. The modified ASTM B117, ASTM D5894, and SAE lasted 4, 6, and 9 phases, respectively. The performances are similar to those provided by System A with the MIL-DTL-53039 having a slight performance edge over the MIL-DTL-64159.

System D (MIL-DTL-53030/MIL-DTL-64159) was a system comprising primer and topcoat that are both waterborne. The scribed corrosion performance for this system was the worst of the systems. The outdoor panels failed scribed corrosion prior to 3 months with ratings of 5. The salt fog panels failed before 1000 h and were terminated after 2000 h due to poor performance of the non-scribed regions of the panels. The modified ASTM B117 and ASTM D5894 failed prior to 3 and 4 phases, respectively. The modified SAE panels even failed after 2 phases.

3.2 Steel: Non-scribed Samples

Non-scribed panels were used to perform 3 nondestructive assessments on in-tact coatings: EIS, color, and gloss. The composite EIS curve for the MIL-DTL-53022/MIL-DTL-53039 system (System A, Fig. 8) shows that the low-frequency impedance of the outdoor panels began to degrade at between 6 and 9 months with significant degradation occurring at 18 months while the higher-frequency impedance essentially remained unchanged through the 2-year exposure. This is the expected result and is possibly due to a number of scenarios in which the barrier property of the coating system is reduced. The frequency dependence of this degradation is usually indicative of a diffusion-related phenomena. This can be due to osmotic diffusion through the coating, debonding at an interface, or development of porosity. Figures 9–12 show this same system's composite performance through 1000 h of accelerated corrosion chamber exposure time. There is the similar degradation in the low-frequency response but with no significant degradation in frequencies above 1 Hz. The GMW14872 exposure had the least degradation in the low-frequency response. The ASTM B117 exposure had the greatest degradation in this area, possibly because it also had the lowest starting values of impedance.

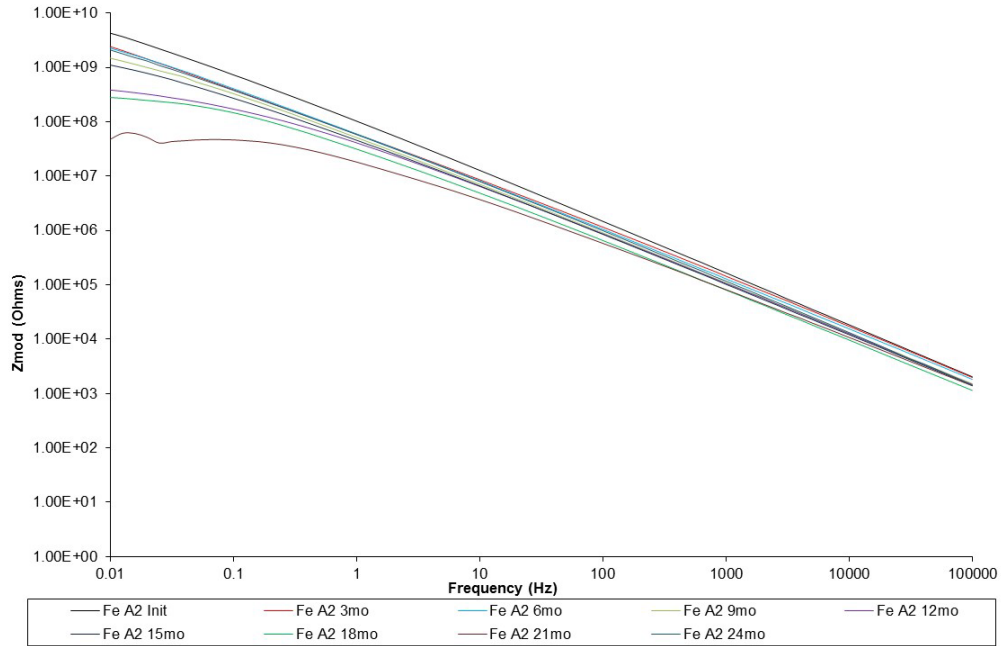


Fig. 8 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-53039 (System A) following exposure to Florida outdoor weathering

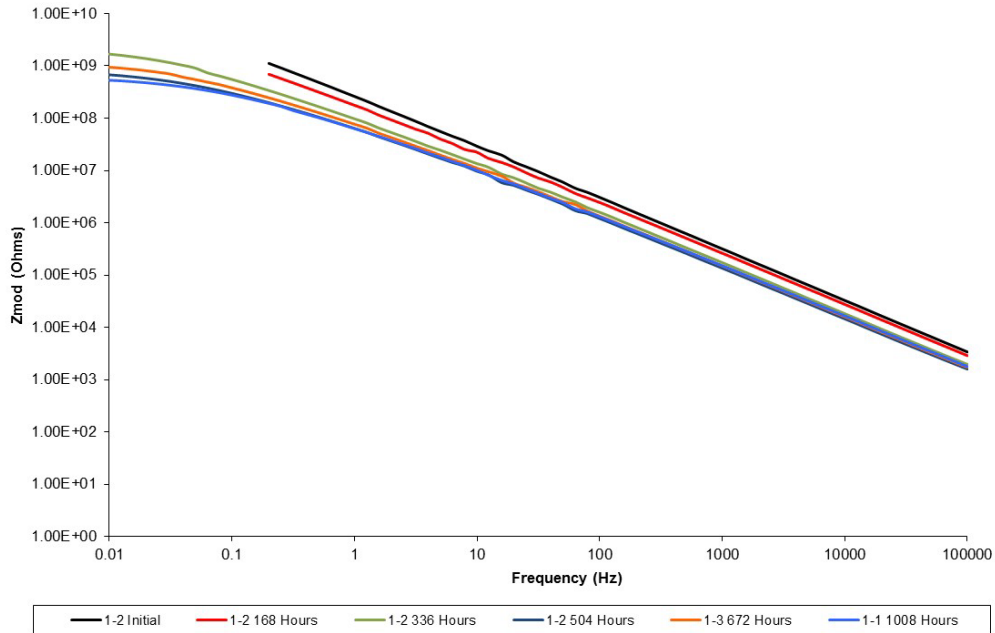


Fig. 9 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-53039 (System A) following ASTM B117 exposure

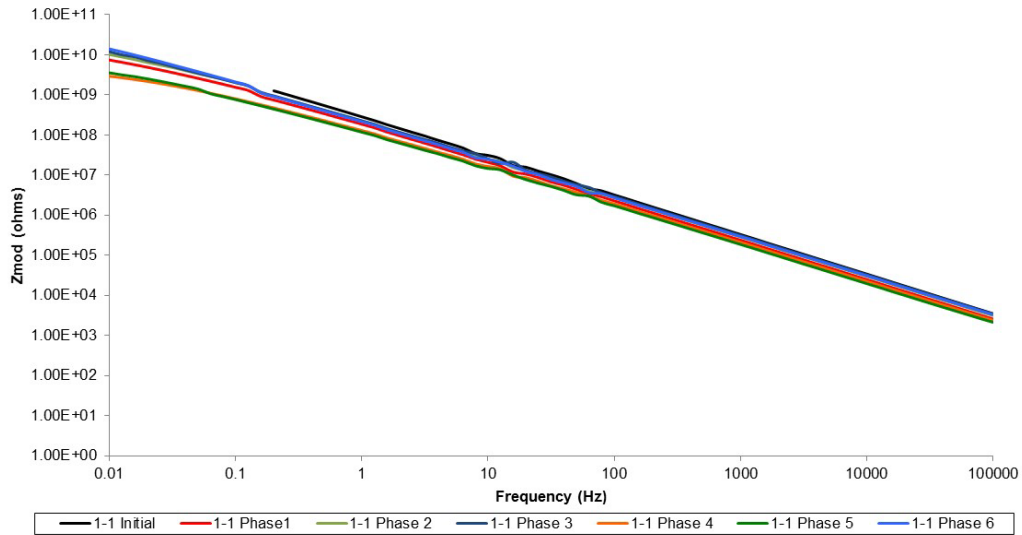


Fig. 10 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-53039 (System A) following modified ASTM B117 exposure

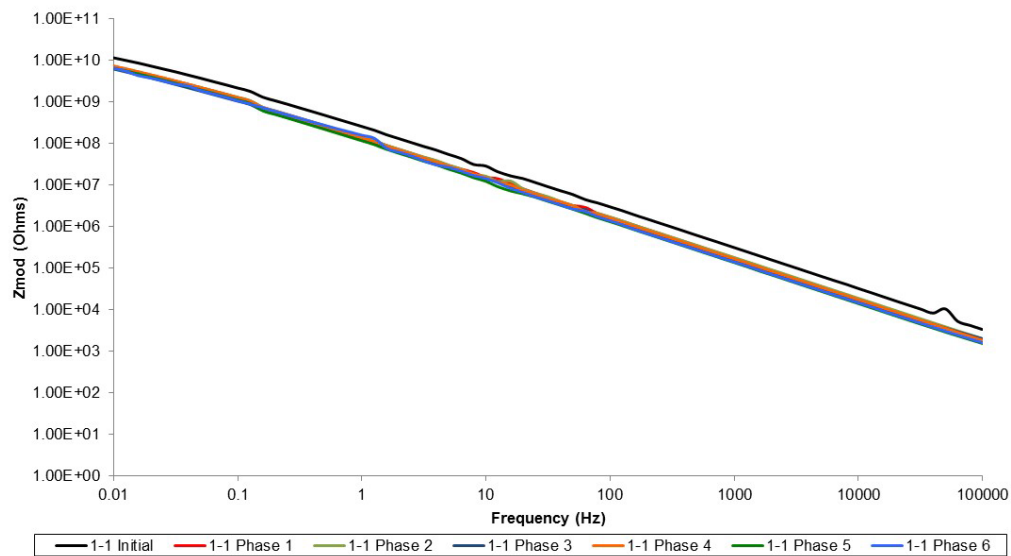


Fig. 11 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-53039 (System A) following GMW14872 exposure

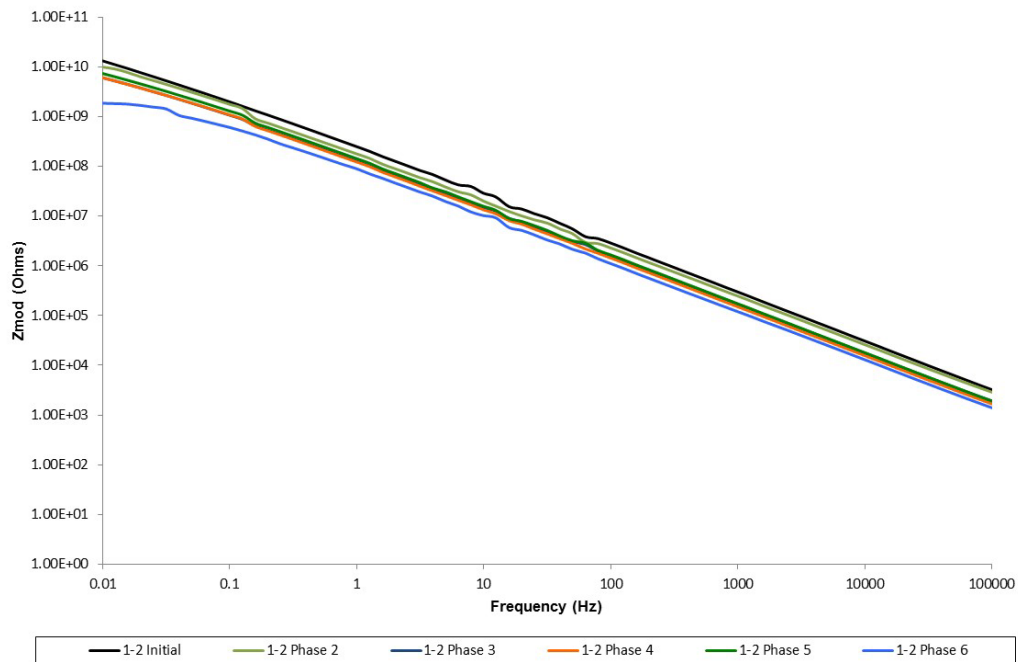


Fig. 12 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-53039 (System A) following modified GMW14872 exposure

Tracking color and gloss was more problematic. Although the Florida panels showed continual and relatively consistent changes from their original color spaces during their first year of exposure (Fig. 13), similar performance could not be attributed to the accelerated exposures. System A drifted from its original color within 3 months of exposure with a delta E of 0.75 units and by 1.5 units after 6 months. This measurement appears to be dependent upon the topcoat chosen. For Florida exposure, the 2 systems with MIL-DTL-53039 (Systems A and C) performed similarly.

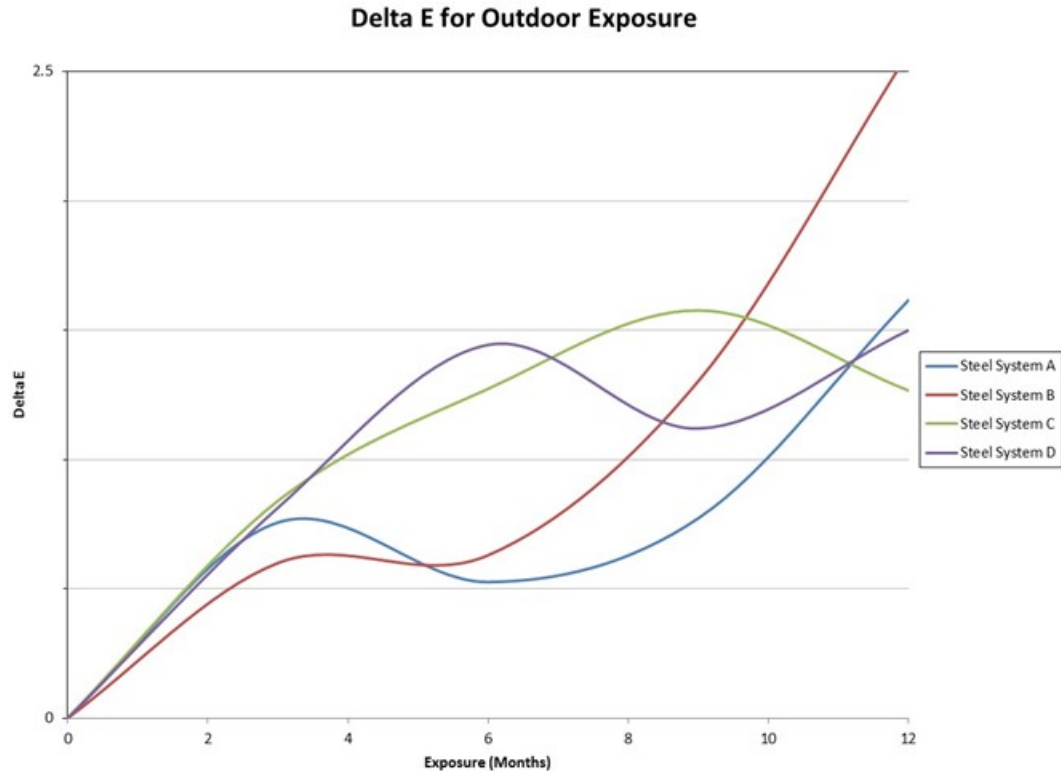


Fig. 13 ΔE for all outdoor systems. ΔE is expressed in terms of drift of the color from an initial value taken before exposure at the outdoor site.

Figure 14 shows the drift from the center of the color ellipse for those panels coated with System A and exposed to accelerated environments. Usually, it would be expected that the 3 exposures with the artificial weathering would show similar results. However, the modified ASTM B117 and ASTM D5894 were very much alike while the ASTM B117 paralleled these curves but was not taken out as far. The modified SAE J2334 did not show nearly as much change. The composite images contained in the Appendix show that the color change resulted more from rust contamination from the edges rather than from UV damage of the topcoat. For the ASTM B117 exposure and System A, a composite chart tracking the color change during the exposure was also generated (Fig. 15) to show color variation by wavelength and exposure length. This chart shows that the reflectance increases in the red, orange, and yellow portions of the spectrum as exposure time lengthens. Since much of the color change for salt fog exposures is probably due to edge effect corrosion staining of the evaluation site, the color change matches expectations. As this is a surface phenomenon, it would have little effect on impedance. The gloss results from this system and the others were not consistent enough to provide useful trends. The gloss measurements for these systems appeared to have been similarly impacted by edge corrosion staining.

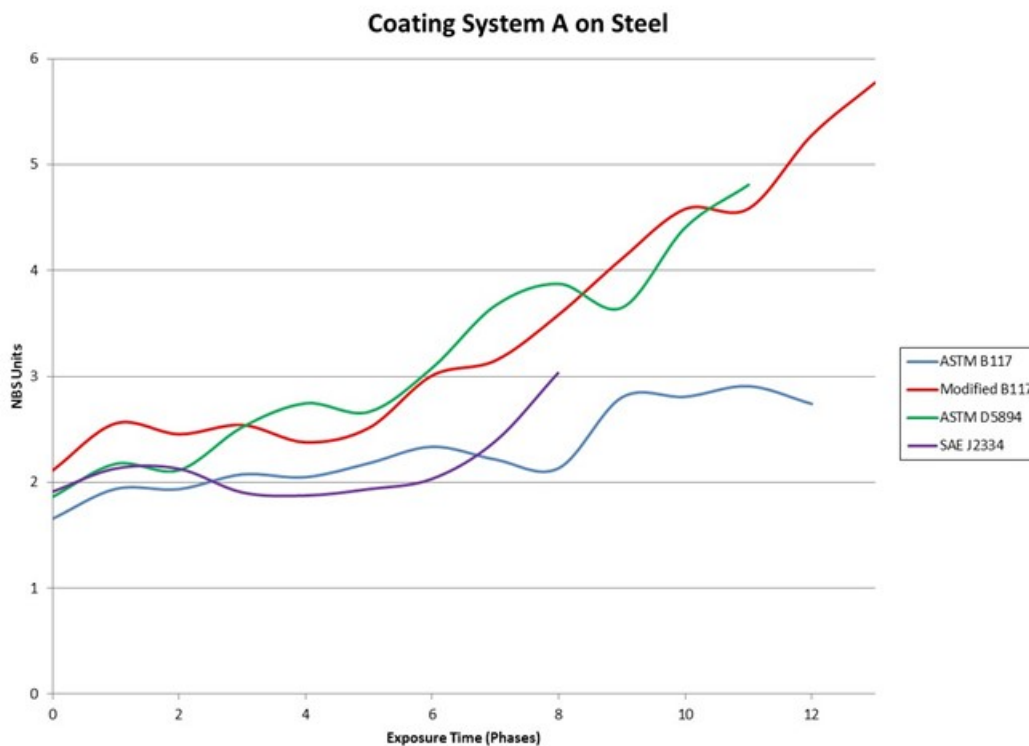


Fig. 14 National Bureau of Standards (NBS) change for all accelerated exposures of steel panel with MIL-DTL-53022 and MIL-DTL-53039 (System A)

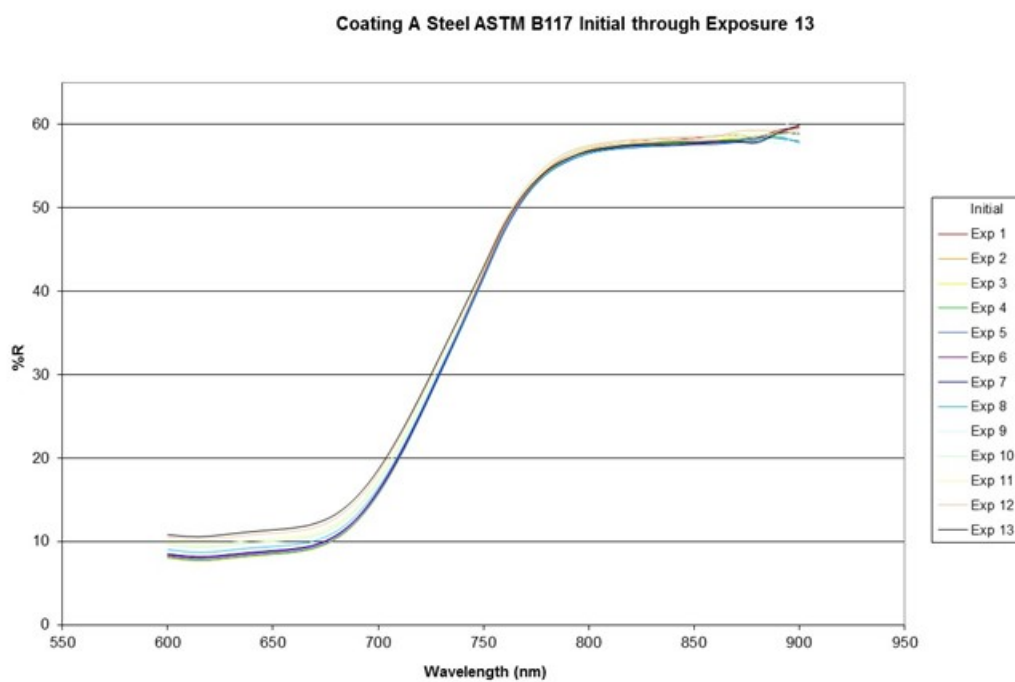


Fig. 15 Color curve composite for ASTM B117 modified with ASTM G154 for steel panel with MIL-DTL-53022 and MIL-DTL-53039 (System A)

Coating System B, MIL-DTL-53030/MIL-DTL-53039, showed consistent reduction of impedance through the first 9 months of outdoor exposure (Fig. 16). After this point, the low-frequency impedance experienced only slight changes with the exception of 2 outliers at 12 and 21 months. As seen in Fig. 17, the resistivity for the panel exposed to ASTM B117 degraded consistently during exposure and over a broad range of frequencies. It may have been that the primer was thinner and did not afford the same level of protection that the previous system did. Figure 18 shows that the System B panels in the modified ASTM B117 exposure experienced consistent impedance degradation that spread across the higher frequencies; the lower-frequency impedance performance dictated the ultimate impedance of the coating system. The impedance of the panels with MIL-DTL-53030 and MIL-DTL-53039 quickly deteriorated after a short exposure to GMW14872 or modified GMW14872 to a level at which it remained for the remainder of the exposure (Figs. 19 and 20). The performance of coating System B in color change (Fig. 21) is similar to that of System A.

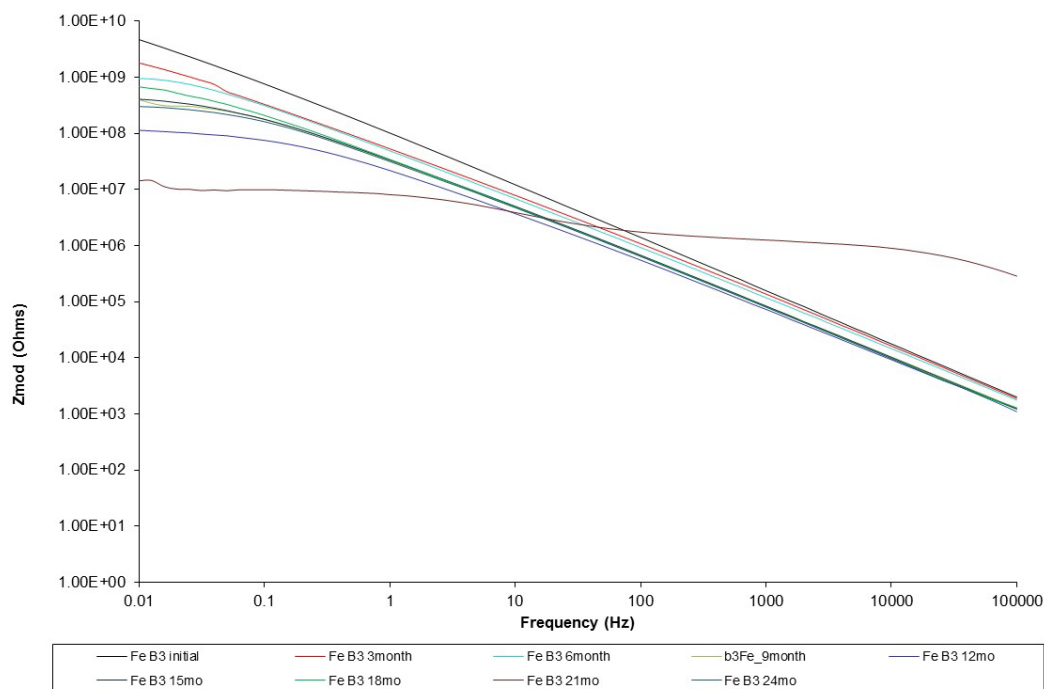


Fig. 16 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-53039 (System B) following exposure to Florida outdoor weathering

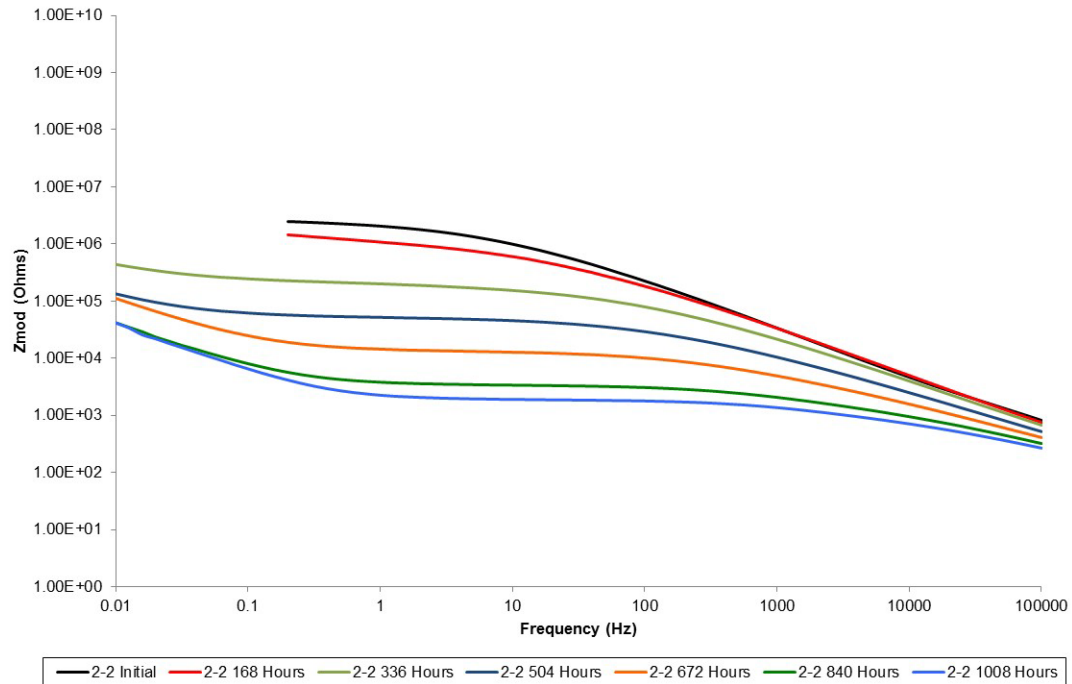


Fig. 17 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-53039 (System B) following ASTM B117 exposure

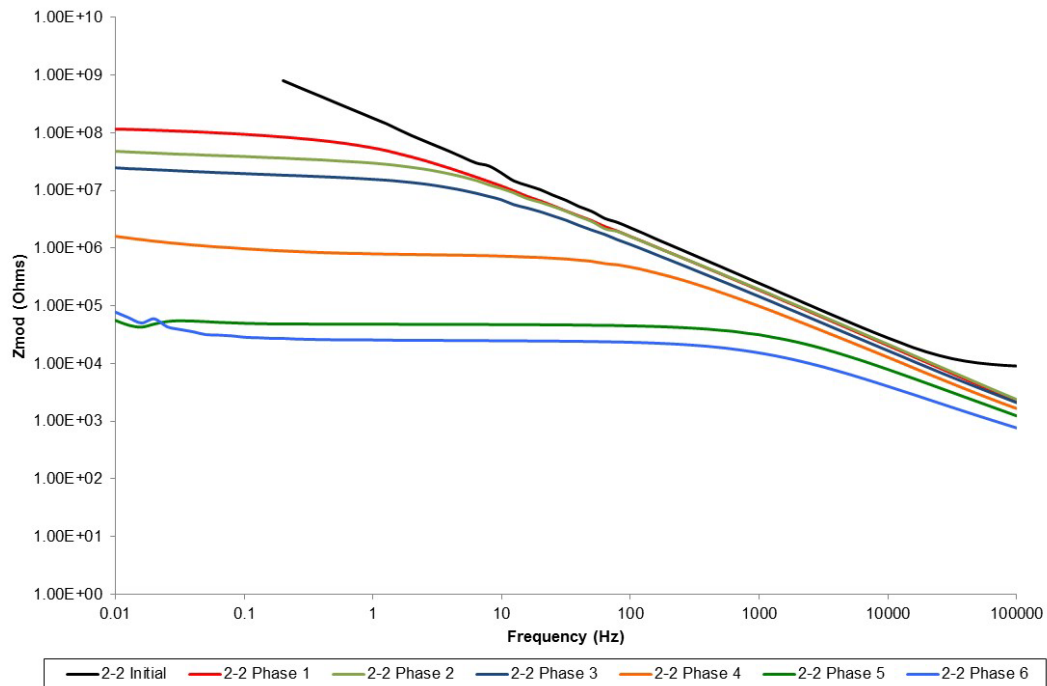


Fig. 18 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-53039 (System B) following modified ASTM B117 exposure

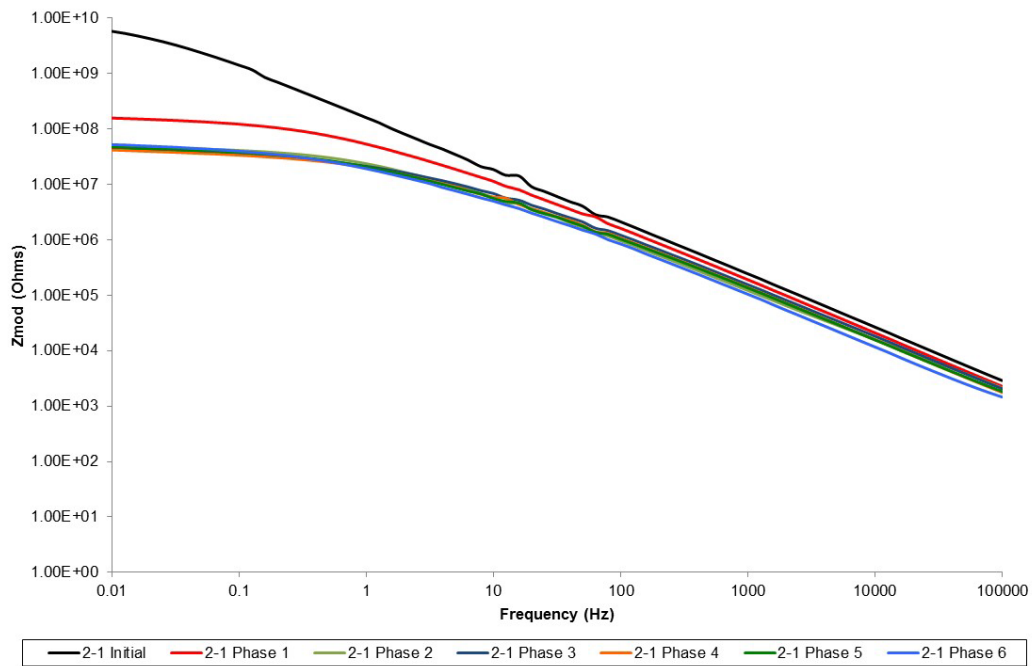


Fig. 19 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-53039 (System B) following GMW14872 exposure

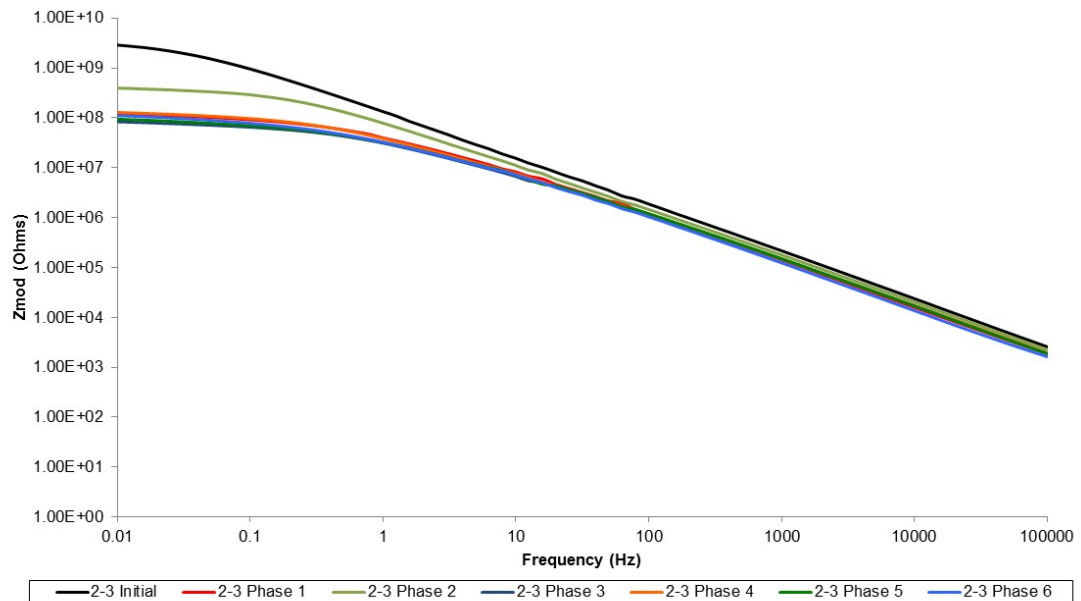


Fig. 20 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-53039 (System B) following modified GMW14872 exposure

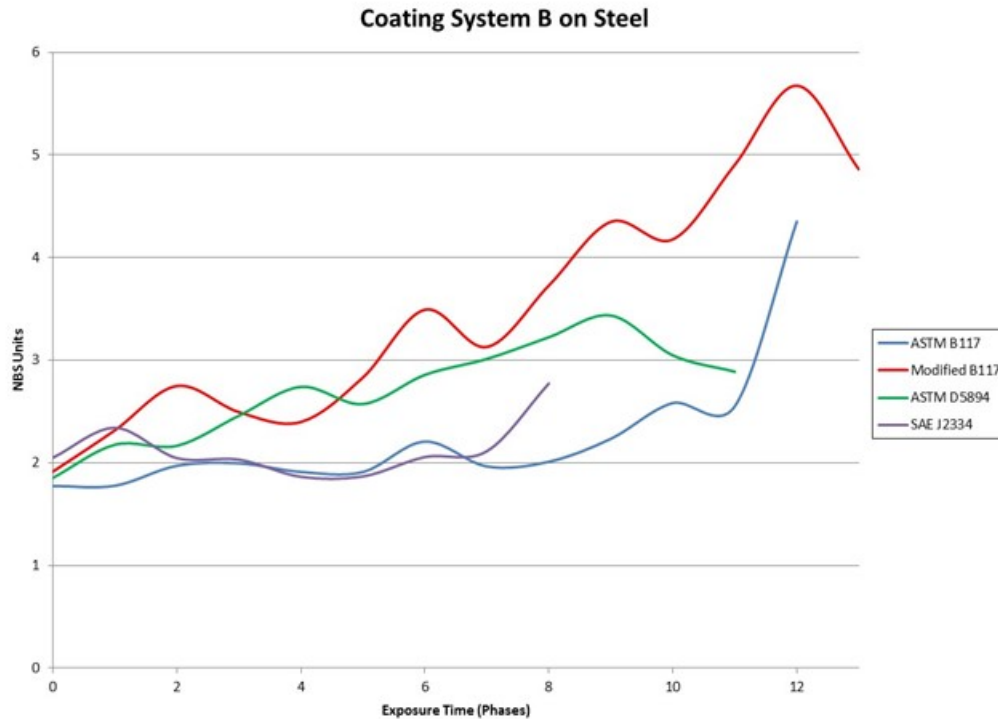


Fig. 21 NBS change for all accelerated exposures of steel panel with MIL-DTL-53030 and MIL-DTL-53039 (System B)

System C, MIL-DTL-53022/MIL-DTL-64159, displayed no significant degradation of the low-frequency response until between 21 and 24 months of exposure in Florida. As seen in Fig. 22, the higher-frequency response was unaffected for all exposure durations. The ASTM B117 exposure had consistent degradation for the low- and middle-frequency responses for each increasing length of exposure with little impact on the higher-frequency performance (Fig. 23). The curves were consistent with a thinner total coating thickness. Figure 24 shows that the modified ASTM B117 was not impacted by longer exposure times. The initial impedances of the panels exposed to GMW14872 and modified GMW14872 improved slightly during the first 168 h of exposure (Figs. 25 and 26). Additional exposure had little impact on the GMW14872 impedance. The modified GMW14872 exposure had consistent, minor degradation in the low-frequency regions. The color results for the outdoor panels were similar to those of System A: failure after 6 months. However, ASTM B117 failed after 2016 h and the modified ASTM B117 at 10 phases while the ASTM D5894 and modified SAE J2334 did not fail color change. It is suspected that the panels from ASTM B117 had severe staining at that point in its exposure that precipitated the failure (Fig. 27).

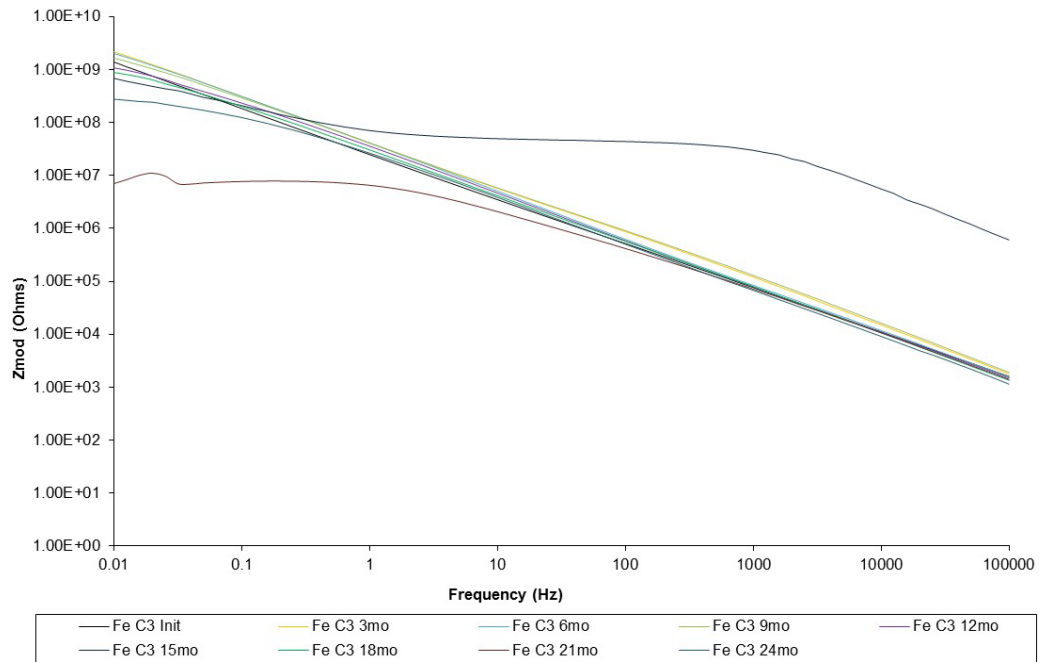


Fig. 22 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-64159 (System C) following exposure to Florida outdoor weathering

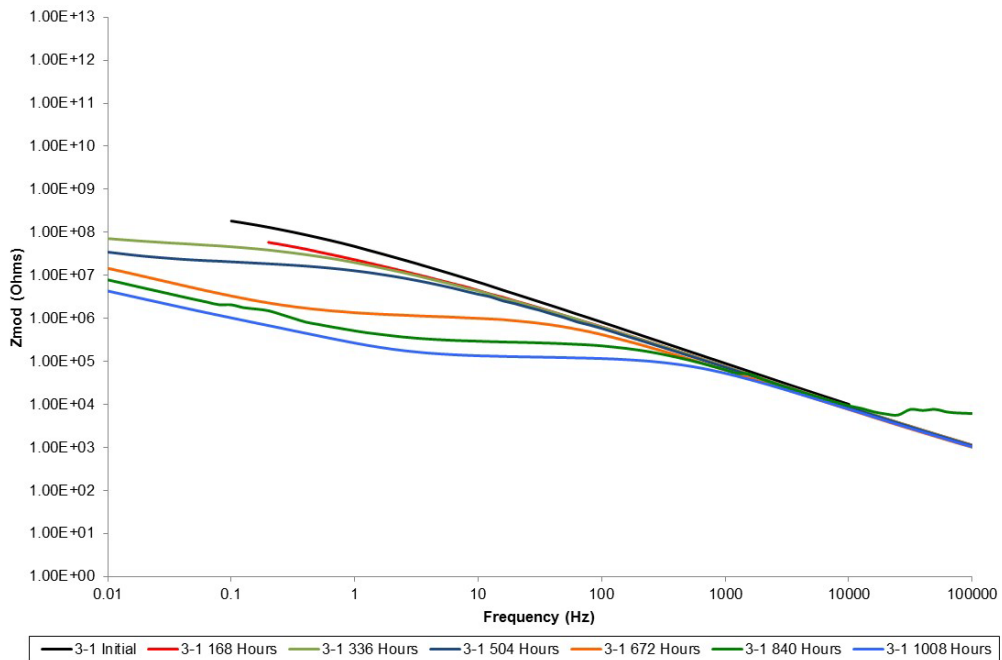


Fig. 23 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-64159 (System C) following ASTM B117 exposure

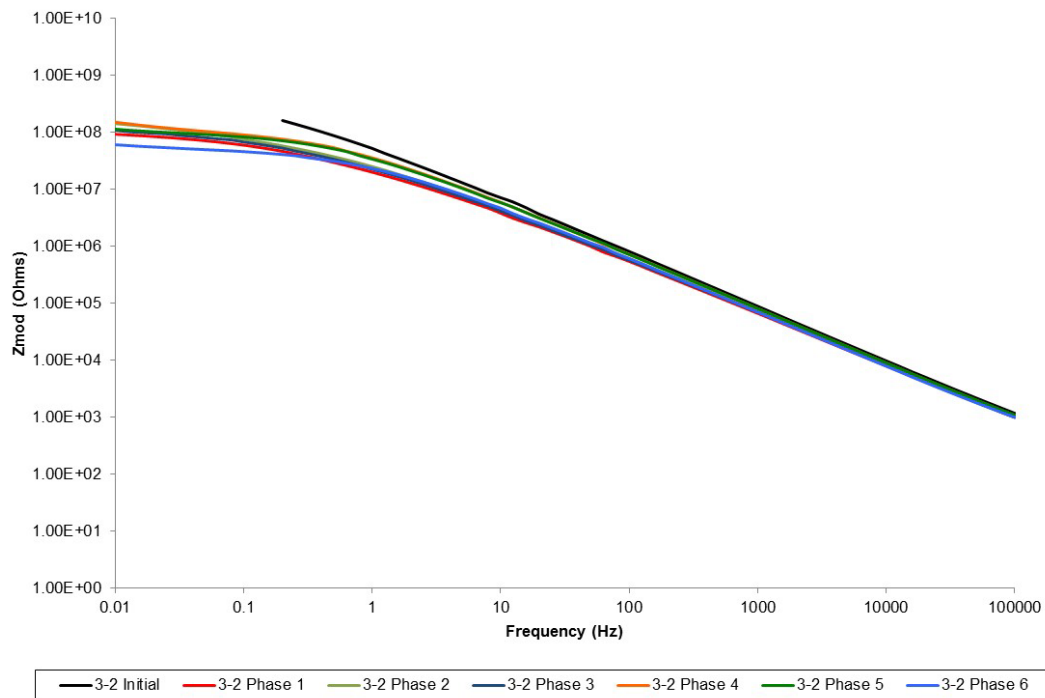


Fig. 24 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-64159 (System C) following modified ASTM B117 exposure

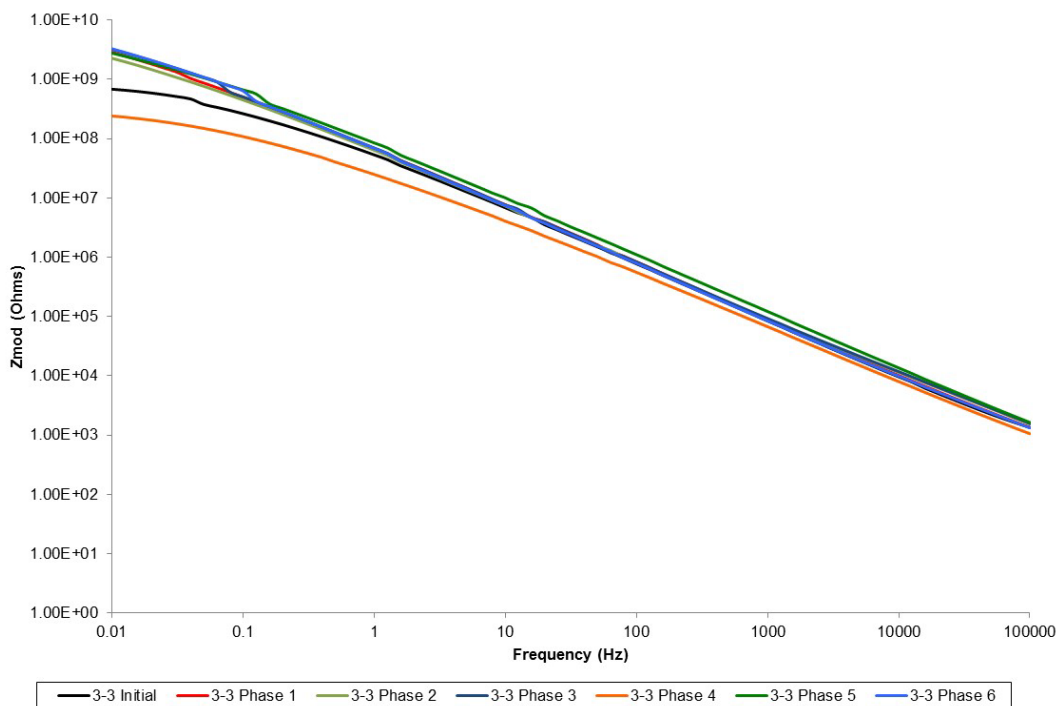


Fig. 25 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-64159 (System C) following GMW14872 exposure

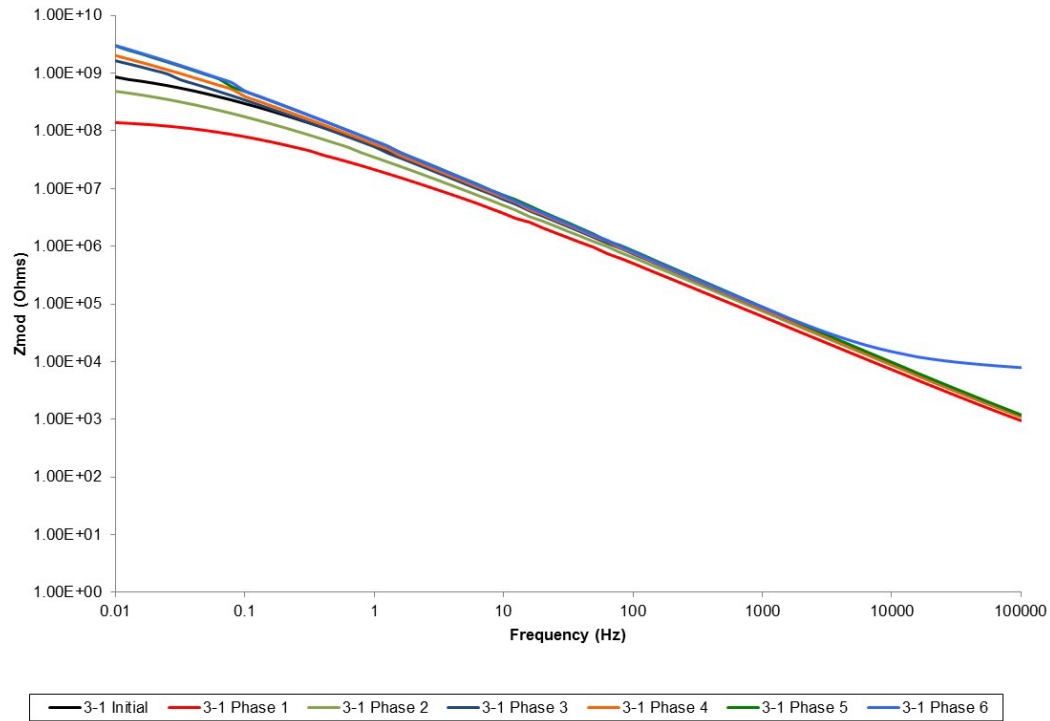


Fig. 26 EIS Bode plots for steel with MIL-DTL-53022 and MIL-DTL-64159 (System C) following modified GMW14872 exposure

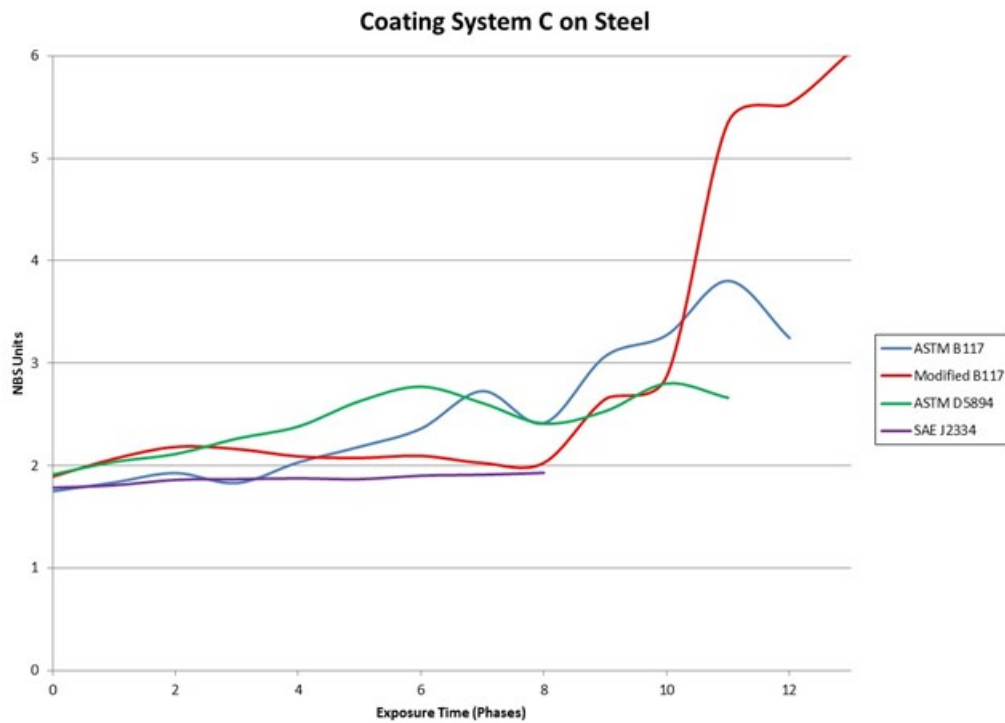


Fig. 27 NBS for accelerated exposures of steel panel with MIL-DTL-53022 and MIL-DTL-64159 (System C)

For System D, MIL-DTL-53030/MIL-DTL-64159, the impedance of the outdoor panels dropped prior to the 21-month evaluation for this system (Fig. 28). Again, the higher-frequency impedance values were unaffected by the duration of exposure. Figure 29 shows the constant stepwise degradation of impedance across most frequencies for increasing exposure duration in the ASTM B117. The modified ASTM B117 showed a similar, though more compact, impedance degradation that did not extend to the lower frequencies (Fig. 30). The GMW14872 and modified GMW14872, Figs. 31 and 32, displayed only minor degradation of impedance for increasing exposure length in spite of each having relatively low initial impedances. The color for the outdoor panels failed after 12 months at NASA KSC. As seen in Fig. 33, the modified ASTM B117 and ASTM D5894 failed color following 10 and 7 phases, respectively. System D did not fail color during exposure to standard salt fog and modified SAE J2334. Much of the change can be attributed to corrosion staining rather than UV degradation.

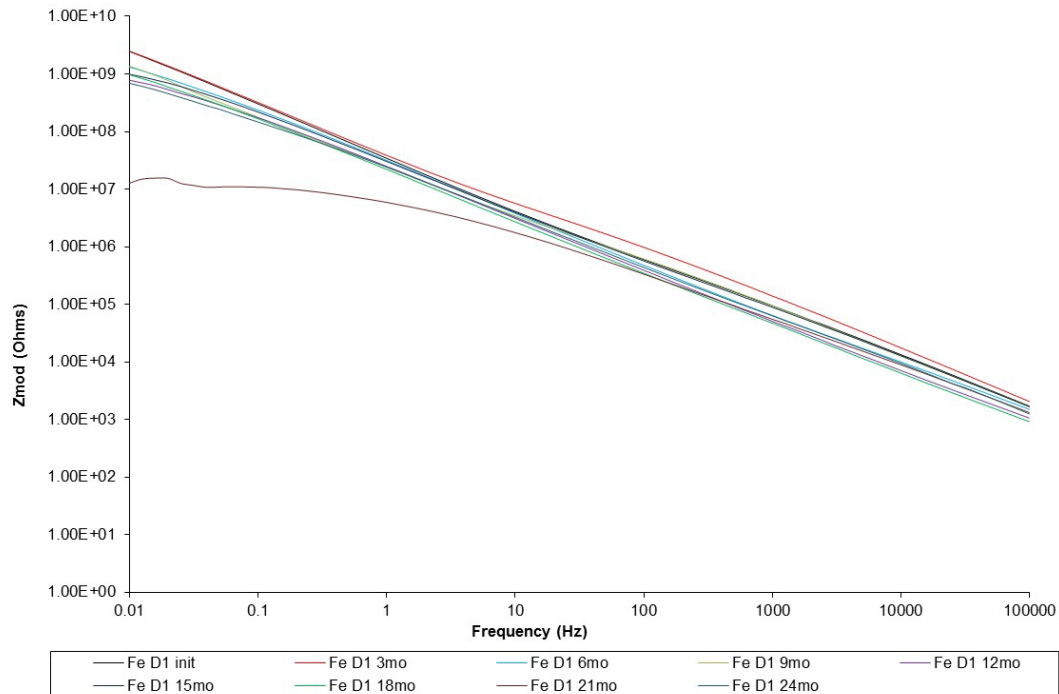


Fig. 28 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-64159 (System D) following exposure to outdoor exposure

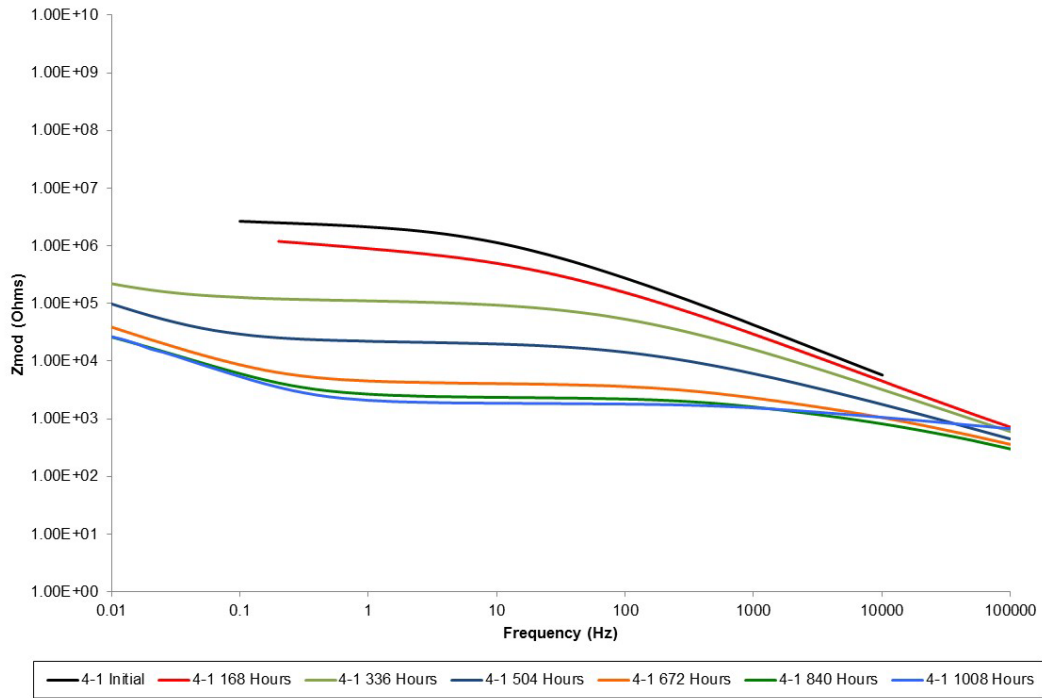


Fig. 29 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-64159 (System D) following ASTM B117 exposure

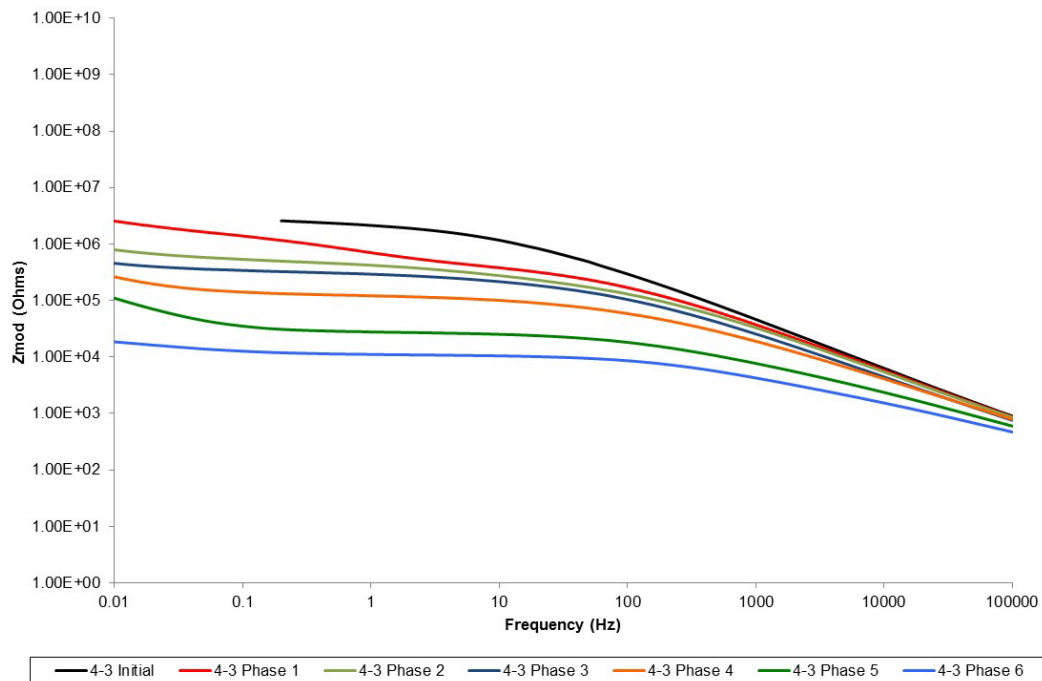


Fig. 30 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-64159 (System D) following modified ASTM B117 exposure

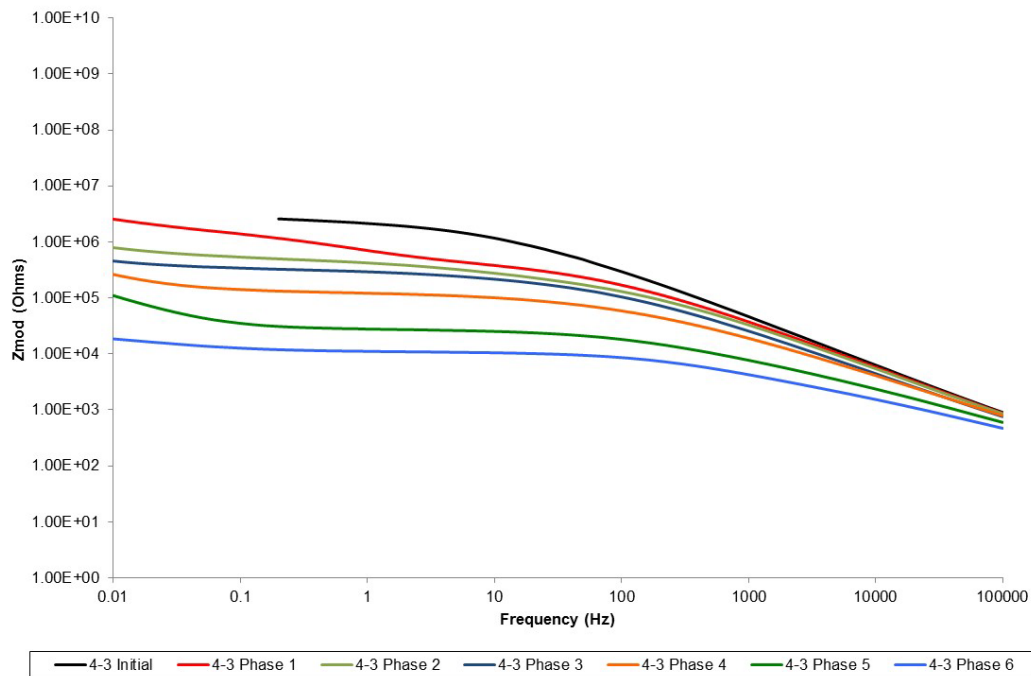


Fig. 31 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-64159 (System D) following GMW14872 exposure

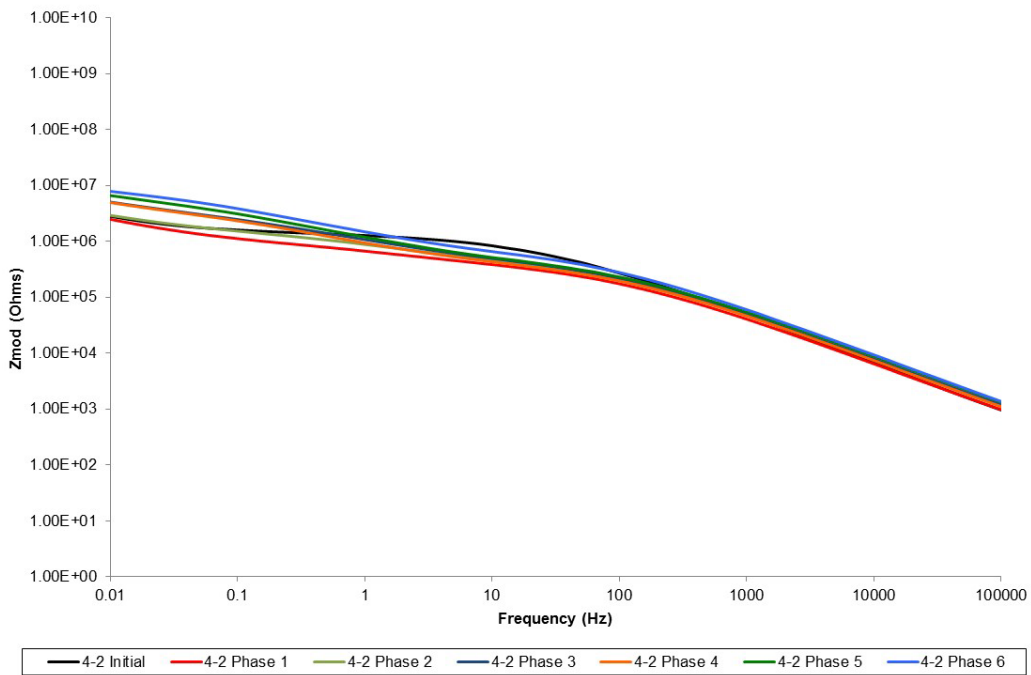


Fig. 32 EIS Bode plots for steel with MIL-DTL-53030 and MIL-DTL-64159 (System D) following modified GMW14872 exposure

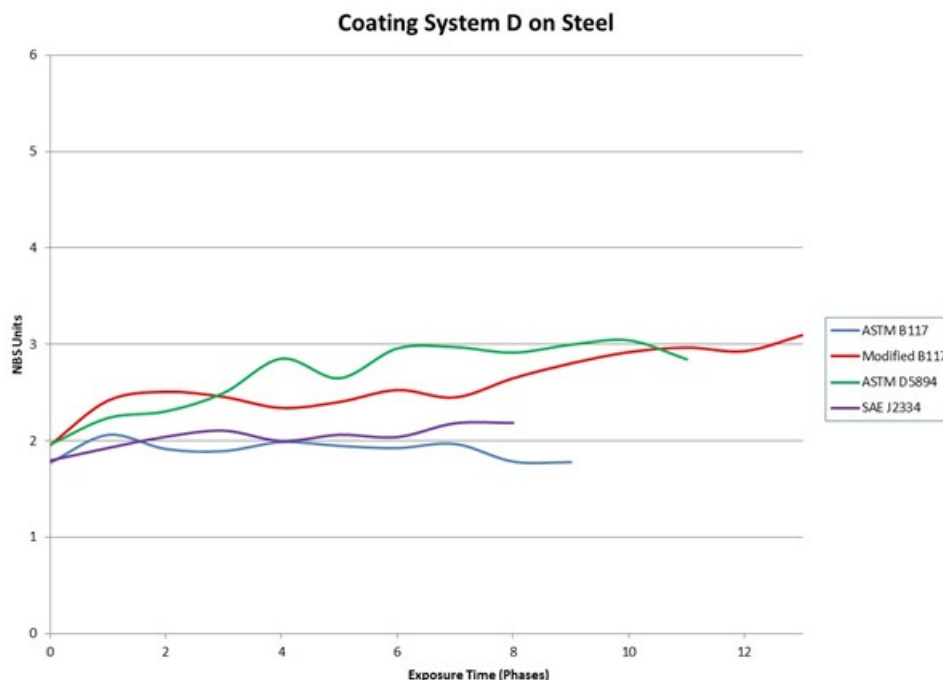


Fig. 33 NBS for accelerated exposures of steel panel with MIL-DTL-53030 and MIL-DTL-64159 (System D)

3.3 Aluminum: Scribed Samples

Tables 7–11 show the ASTM D1654 ratings for all the scribed aluminum exposures. In general, the aluminum performed much better than the steel with nearly half of the scribed samples having passing ratings at the end of exposure. A composite picture with representative images following exposure is presented in Fig. 34. Similar composite pictures for each of the other coatings systems can be found in the Appendix. Corrosion took 3 different forms along the aluminum scribes, as can be seen in Fig. 35. The first involved a slight discoloration of the scribe, which could degenerate into white corrosion products evolving within the scribe; the difference between a rating of a 9 and a 10. This occurred in the outdoor exposure panels, ASTM D5894, and modified SAE J2334. The second form occurred predominantly in the ASTM B117 exposures but was seen in most of them in which corrosion products formed and flowed out of the scribe, sometimes causing blisters to form adjacent to the scribe. Filiform corrosion, which occurred predominantly in the modified SAE J2334 exposures, was the final form seen on aluminum. There was also far less blistering in the non-scribed regions than was noted for the steel. In all cases, there were never more than 4 blisters scattered across the surface of any given scribed aluminum panel. The outdoor exposure for aluminum lasted for 3 years.

Table 7 ASTM D1654 ratings of scribed aluminum panels coated with the CARC system in Florida outdoor exposure

Substrate	Primer	Topcoat	Designation	3 Month	6 Month	9 Month	12 Month	15 Month	18 Month	21 Month	24 Month	27 Month	30 Month	33 Month	36 Month
Aluminum 1	MIL-P-53022	MIL-P-53039	Outdoor A1 Al	10	10	10	10	10	10	10	7	7	7	7	7
Aluminum 2	MIL-P-53022	MIL-P-53039	Outdoor A2 Al	10	10	10	10	10	10	10	10	9	9	9	9
Aluminum 3	MIL-P-53022	MIL-P-53039	Outdoor A3 Al	10	10	10	10	10	10	10	10	9	9	9	9
Aluminum 1	MIL-P-53030	MIL-P-53039	Outdoor B1 Al	10	10	10	10	10	7	7	6	6	6	6	6
Aluminum 2	MIL-P-53030	MIL-P-53039	Outdoor B2 Al	10	10	10	10	10	10	10	8	8	8	8	6
Aluminum 3	MIL-P-53030	MIL-P-53039	Outdoor B3 Al	10	10	10	10	10	10	10	10	9	9	9	9
Aluminum 1	MIL-P-53022	MIL-DTL-64159	Outdoor C1 Al	10	10	10	10	10	10	10	10	10	10	10	10
Aluminum 2	MIL-P-53022	MIL-DTL-64159	Outdoor C2 Al	10	10	10	10	10	10	10	10	10	10	10	10
Aluminum 3	MIL-P-53022	MIL-DTL-64159	Outdoor C3 Al	10	10	10	10	10	10	10	10	10	10	10	10
Aluminum 1	MIL-P-53030	MIL-DTL-64159	Outdoor D1 Al	10	10	10	10	10	10	10	10	10	10	9	8
Aluminum 2	MIL-P-53030	MIL-DTL-64159	Outdoor D2 Al	10	10	10	10	10	10	10	8	8	7	7	6
Aluminum 3	MIL-P-53030	MIL-DTL-64159	Outdoor D3 Al	10	10	7	7	6	6	5	5	5	5	5	5

Table 8 ASTM D1654 ratings of scribed aluminum panels coated with the CARC system in ASTM B117 exposure

Substrate	Primer	Topcoat	Designation	168 Hour	336 Hour	528 Hour	672 Hour	840 Hour	1008 Hour	1512 Hour	2016 Hour	2520 Hour	3024 Hour	3528 Hour	4032 Hour
Aluminum 1	MIL-P-53022	MIL-P-53039	B117 A1 Al	9	8	8	8	8	8	7	7	7	7	6	6
Aluminum 2	MIL-P-53022	MIL-P-53039	B117 A2 Al	8	8	8	8	8	8	7	7	7	6	6	6
Aluminum 3	MIL-P-53022	MIL-P-53039	B117 A3 Al	8	8	8	8	8	8	7	7	7	7	7	6
Aluminum 1	MIL-P-53030	MIL-P-53039	B117 B1 Al	8	8	8	8	8	8	7	7	7	7	7	7
Aluminum 2	MIL-P-53030	MIL-P-53039	B117 B2 Al	9	9	8	8	7	7	7	7	7	7	6	6
Aluminum 3	MIL-P-53030	MIL-P-53039	B117 B3 Al	9	9 BIF 9	8 BIF 9	8 BIF 8	8 BIF 8	8 BIF 8	7 BIF 7	7 BIF 7	7 BIF 7	7 BIF 7	6 BIF 7	6 BIF 7
Aluminum 1	MIL-P-53022	MIL-DTL-64159	B117 C1 Al	9	9	9	8	8	8	8	8	8	8	7	7
Aluminum 2	MIL-P-53022	MIL-DTL-64159	B117 C2 Al	9	9	9	9	9	8	8	7	7	7	7	7
Aluminum 3	MIL-P-53022	MIL-DTL-64159	B117 C3 Al	9	8	8	8	8	8	8	7	7	7	7	7
Aluminum 1	MIL-P-53030	MIL-DTL-64159	B117 D1 Al	8	8	8	8 BIF 8	8 BIF 8	8 BIF 8	8 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8
Aluminum 2	MIL-P-53030	MIL-DTL-64159	B117 D2 Al	8	8	8	8 BIF 8	8 BIF 8	8 BIF 8	8 BIF 8	8 BIF 8	8 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8
Aluminum 3	MIL-P-53030	MIL-DTL-64159	B117 D3 Al	9	8	8	8 BIF 9	8 BIF 9	8 BIF 9	8 BIF 9	8 BIF 9	7 BIF 9	7 BIF 8	7 BIF 8	7 BIF 8

Table 9 ASTM D1654 ratings of scribed aluminum panels coated with the CARC system in modified ASTM B117 exposure

Substrate	Primer	Topcoat	Designation	1 Phase	2 Phase	3 Phase	4 Phase	5 Phase	6 Phase	7 Phase	8 Phase	9 Phase	10 Phase	11 Phase	12 Phase	13 Phase	14 Phase	15 Phase	16 Phase	17 Phase
Aluminum 1	MIL-P-53022	MIL-P-53039	Mod B117 A1 Al	8	8	7	7	7	7	7	7	7	7	7	7	7	6	6	6	6
Aluminum 2	MIL-P-53022	MIL-P-53039	Mod B117 A2 Al	9	8	7	7	7	7	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9
Aluminum 3	MIL-P-53022	MIL-P-53039	Mod B117 A3 Al	9	9	8	8	8	8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8	7 BIF 8
Aluminum 1	MIL-P-53030	MIL-P-53039	Mod B117 B1 Al	8	8	8	7	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9
Aluminum 2	MIL-P-53030	MIL-P-53039	Mod B117 B2 Al	8	8 BIF 9	8 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 8	6 BIF 8	6 BIF 8	6 BIF 8	6 BIF 8
Aluminum 3	MIL-P-53030	MIL-P-53039	Mod B117 B3 Al	8	8	8	8	7	7	7	7	6	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	5 BIF 9	5 BIF 9	5 BIF 9
Aluminum 1	MIL-P-53022	MIL-DTL-64159	Mod B117 C1 Al	9	9	8	8 BIF 9	8 BIF 9	8 BIF 9	8 BIF 9	8 BIF 9	8 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9
Aluminum 2	MIL-P-53022	MIL-DTL-64159	Mod B117 C2 Al	9	8	7	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6	6	5	5	4	4	3	3	3	3
Aluminum 3	MIL-P-53022	MIL-DTL-64159	Mod B117 C3 Al	9	8	8	8	7	7	7	7	7	6	6	6	5	5	5	5	5
Aluminum 1	MIL-P-53030	MIL-DTL-64159	Mod B117 D1 Al	10	8	8	8	7	7	7	7	7	6	6	5	5	5	5	5	5
Aluminum 2	MIL-P-53030	MIL-DTL-64159	Mod B117 D2 Al	10	8	8	7	7	7	7	6	6	6	5	5	5	5	5	5	5
Aluminum 3	MIL-P-53030	MIL-DTL-64159	Mod B117 D3 Al	10	9 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	7 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	6 BIF 9	5 BIF 9	5 BIF 9

Table 10 ASTM D1654 ratings of scribed aluminum panels coated with the CARC system in ASTM 5894 exposure

[illegible]

Table 11 ASTM D1654 ratings of scribed aluminum panels coated with the CARC system in modified SAE J2334 exposure

Substrate	Primer	Topcoat	Designation	1 Phase	2 Phase	3 Phase	4 Phase	5 Phase	6 Phase	7 Phase	8 Phase	9 Phase	10 Phase	11 Phase	12 Phase
Aluminum 1	MIL-P-53022	MIL-P-53039	J2334 A1 Al	10	10	10	10	9	9	8	8	8	7	7	7
Aluminum 2	MIL-P-53022	MIL-P-53039	J2334 A2 Al	10	10	9	9	9	9	9	9	9	8	8	8
Aluminum 3	MIL-P-53022	MIL-P-53039	J2334 A3 Al	10	10	10	9	9	8	8	8	8	8	8	8
Aluminum 1	MIL-P-53030	MIL-P-53039	J2334 B1 Al	10	10	10	10	10	10	8	8	8	7	7	6
Aluminum 2	MIL-P-53030	MIL-P-53039	J2334 B2 Al	10	10	9	9	9	7	7	7	5	5	5	5
Aluminum 3	MIL-P-53030	MIL-P-53039	J2334 B3 Al	10	9	9	9	8	8	8	8	8	8	7	6
Aluminum 1	MIL-P-53022	MIL-DTL-64159	J2334 C1 Al	9	9	9	9	9	9	9	8	8	8	7	7
Aluminum 2	MIL-P-53022	MIL-DTL-64159	J2334 C2 Al	8	8	8	8	8	8	8	8	8	8	8	8
Aluminum 3	MIL-P-53022	MIL-DTL-64159	J2334 C3 Al	9	9	9	9	9	9	8	8	7	7	7	7
Aluminum 1	MIL-P-53030	MIL-DTL-64159	J2334 D1 Al	10	10	8	8	7	7	7	7	7	7	6	6
Aluminum 2	MIL-P-53030	MIL-DTL-64159	J2334 D2 Al	10	10	7	7	7	6	6	6	6	5	5	5
Aluminum 3	MIL-P-53030	MIL-DTL-64159	J2334 D3 Al	10	10	9	8	7	7	7	7	7	6	6	6

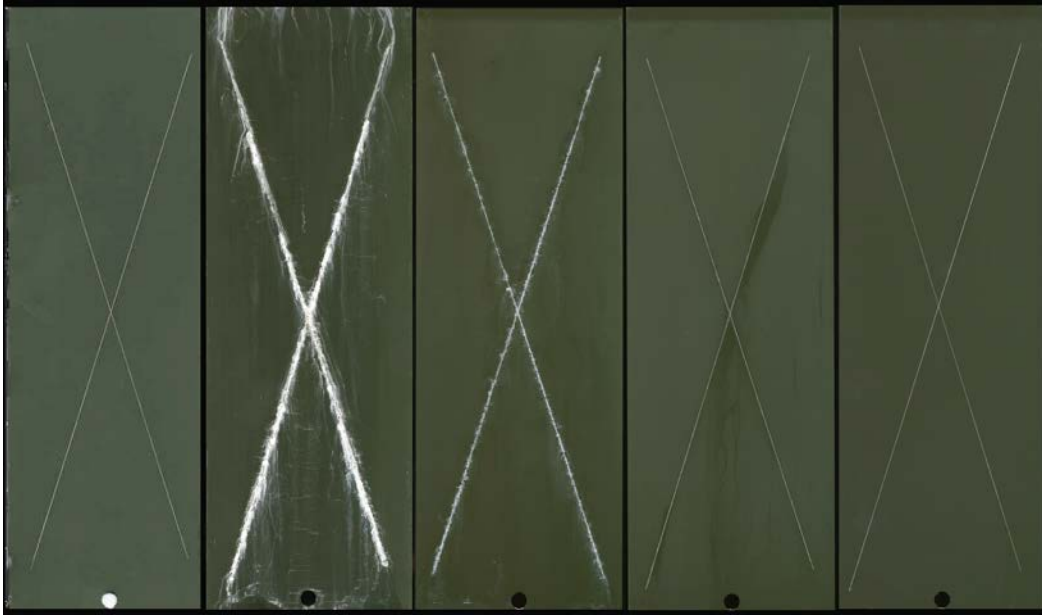


Fig. 34 Aluminum panels with coating System B following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

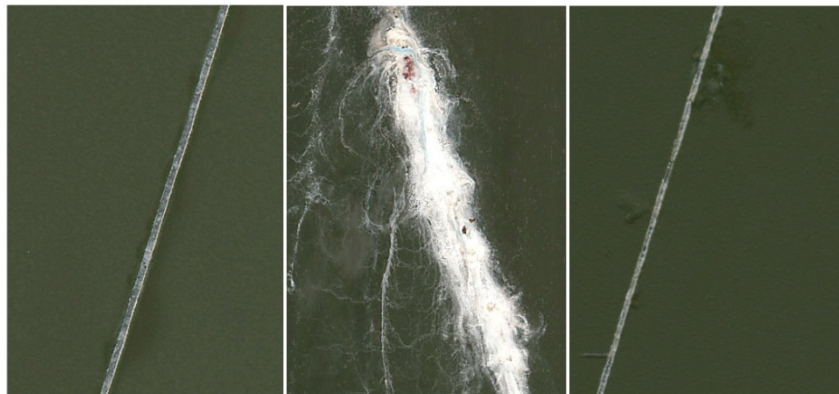


Fig. 35 Aluminum corrosion typical of outdoor and cyclic exposures, ASTM B117, and SAE J2334

Aluminum samples coated with System A (MIL-DTL-53022/MIL-DTL-53039) had only 4 panels fail by the end of their exposures: one modified ASTM B117 after 14 phases (2452 h of salt fog exposure) and all 3 salt fog panels at between 3024 and 4032 h. The outdoor exposure, ASTM D5894, and modified SAE J2334 exposures each had 1 of the 3 panels develop a blister along the scribe that negatively affected their ratings. The 2 salt fog exposures also provided similar results to one another except that the modified exposure had a blister or 2 to develop in the region away from the scribe.

For aluminum samples coated with System B (MIL-DTL-53022/MIL-DTL-53039), only one-third of the panels were passing at the end of their respective exposures. The best performance was turned in by the set in ASTM D5894 in which all panels passed. The 2 ASTM B117 exposures each had some blistering in the field away from the scribe. The Florida outdoor had creep from scribe ratings that were similar to the ASTM B117 panels, with 2 of 3 panels failing by the end of exposure, while the SAE J2334 and the modified ASTM B117 and SAE J2334 had all 3 panels fail scribed corrosion by the end of their exposures.

Aluminum samples coated with System C (MIL-PRF-53022/MIL-DTL-64159) performed best from a scribed corrosion standpoint. System C was the best-performing system on aluminum in Florida outdoor, ASTM B117, ASTM D5894, and SAE J2334. In fact, there was no visible corrosion on the Florida panels, although there was severe degradation of the color. Only the modified ASTM B117 panels had failed by the end of their exposure and were the worst-performing system in this exposure.

Performance of aluminum samples coated with System D (MIL-DTL-53030/MIL-DTL-64159) were similar to or a little worse than that of System B. The waterborne primer with waterborne topcoat performed significantly worse in modified ASTM B117 and slightly worse in outdoor exposure than when topcoated with a solvent-borne topcoat. Only 4 panels had passing ratings at the end of their exposures, and 3 of those were from ASTM D 5984 in which all coatings systems on aluminum passed. The final passing panel for System D was from the Florida exposure.

3.4 Aluminum: Non-scribed Samples

The outdoor aluminum panels with System A suffered a slight degradation in impedance following 3 months of exposure and then had consistent performance thereafter. There was also a slight degradation in low-frequency impedance at the 36-month mark (Fig. 36). The panels exposed to ASTM B117 showed a small but consistent degradation of the impedance in the low to middle frequency ranges as exposure time increased, as seen in Fig. 37, but with little effect on the very low- or high-frequency impedances. Increasing exposure time had little impact on the resistivity in the modified ASTM B117 exposure (Fig. 38). As seen in Figs. 39 and 40, the initial low-frequency impedance of the GMW14872 and modified GMW14872 improved during the early exposure and did not change with further exposure. Middle- and high-frequency impedances were not affected. Figures 41 and 42 show the 60° and 85° gloss performances for System A in salt fog and modified salt fog. Increased exposure to UV irradiation had no effect on the 60°

gloss readings and only minimal impact on the 85° gloss. It is likely that corrosion deposits had a larger impact on these readings than did coating degradation.

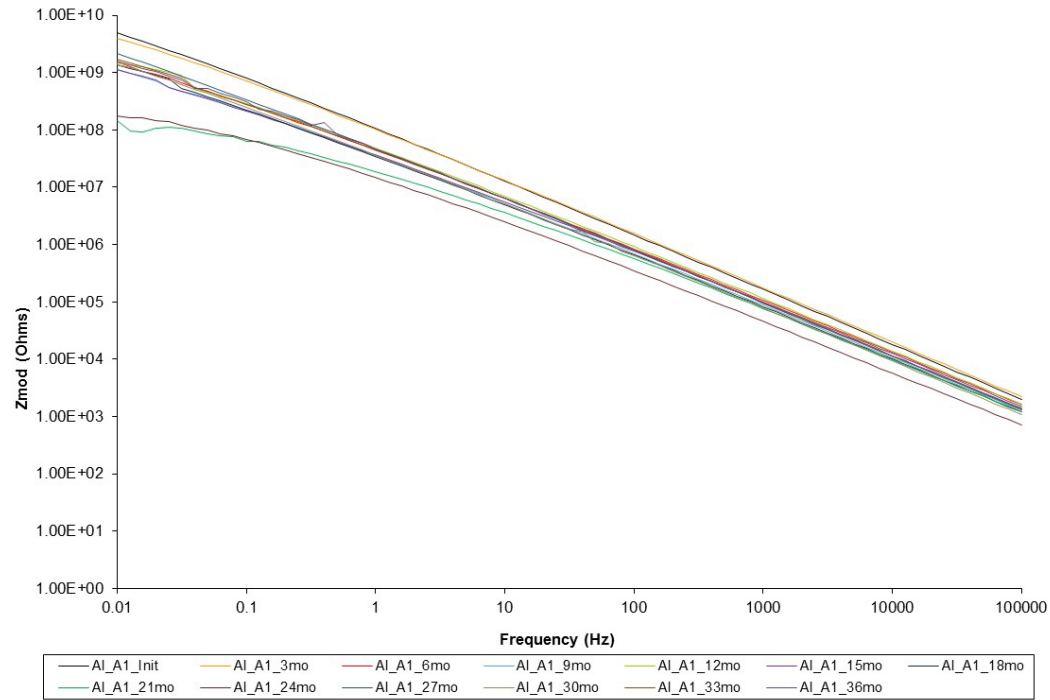


Fig. 36 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-53039 (System A) following exposure to Florida outdoor weathering

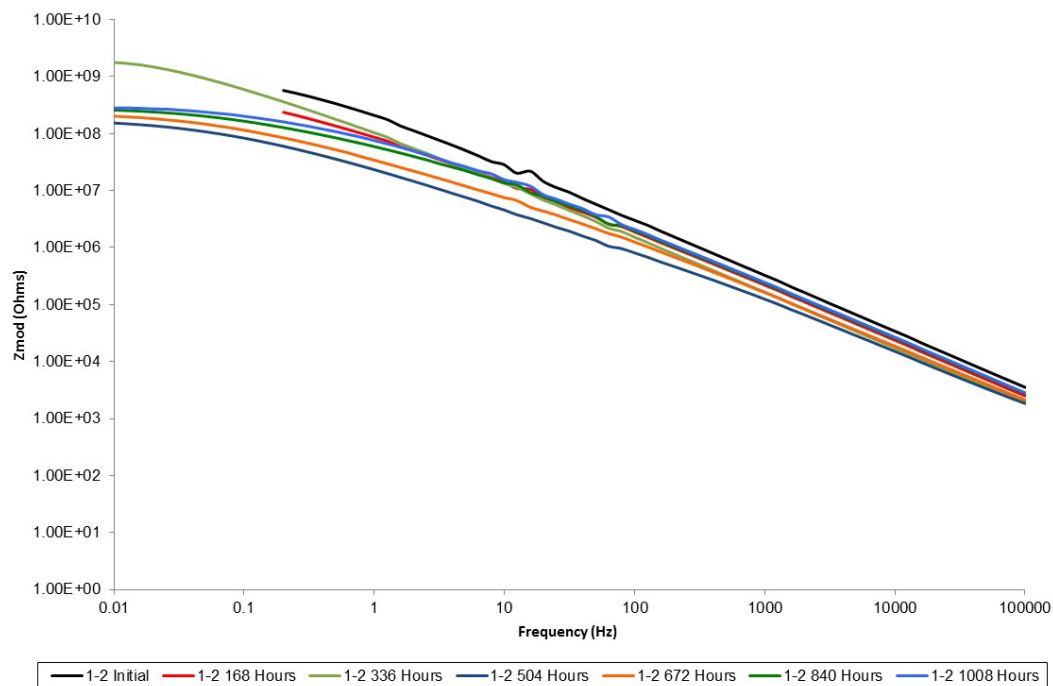


Fig. 37 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-53039 (System A) following ASTM B117 exposure

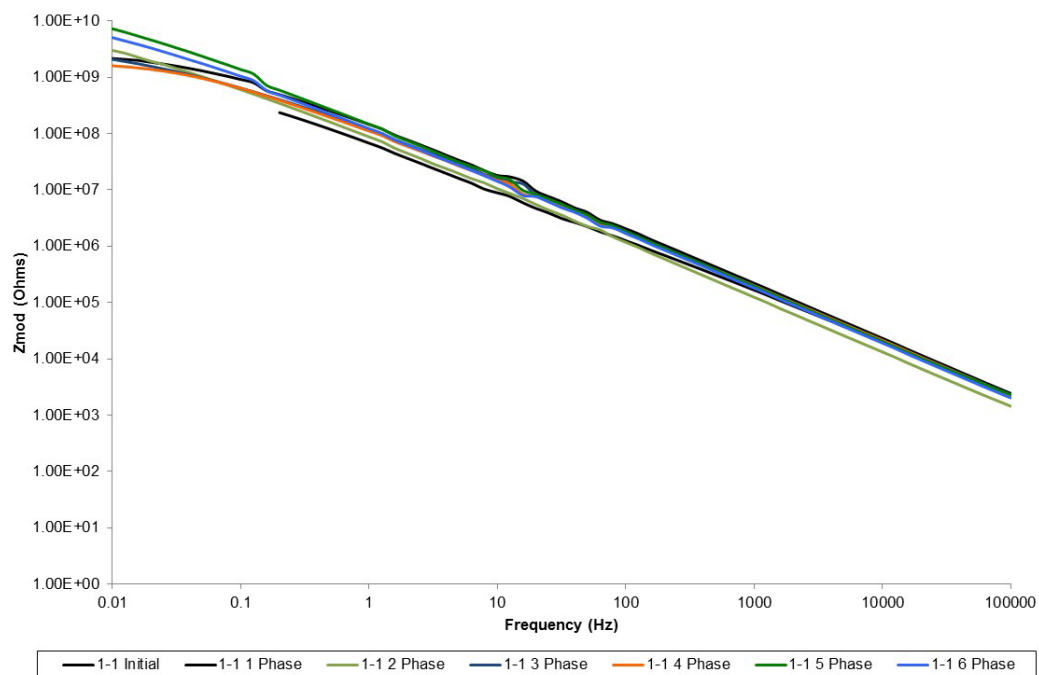


Fig. 38 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-53039 (System A) following modified ASTM B117 exposure

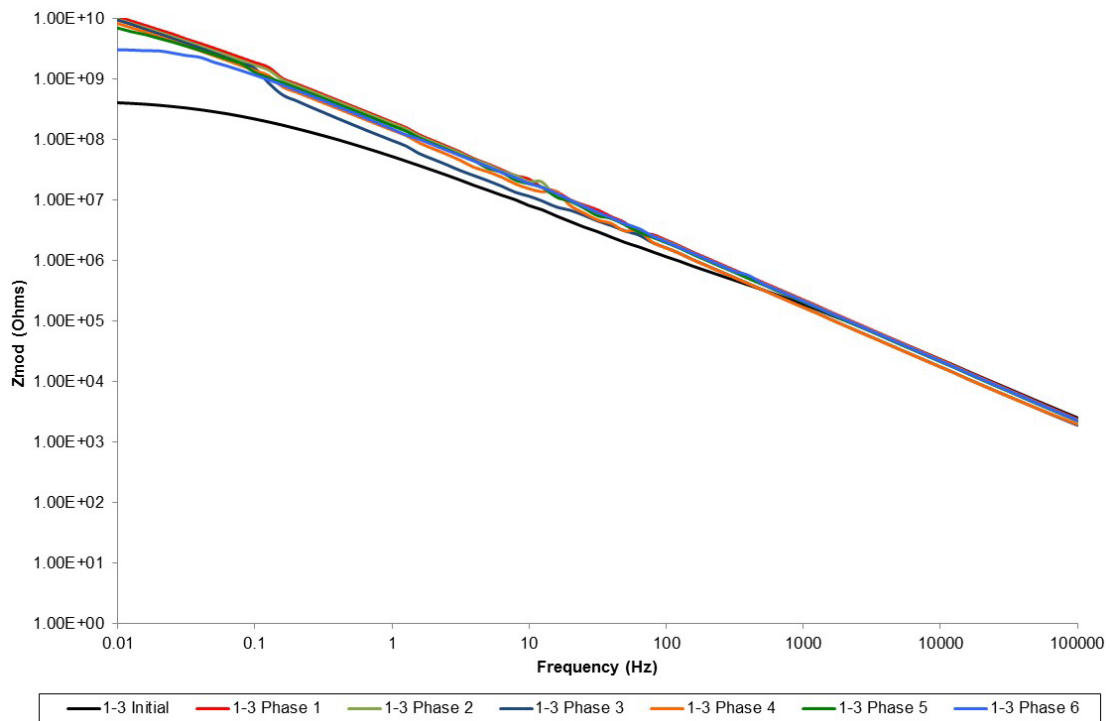


Fig. 39 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-53039 (System A) following GMW14872 exposure

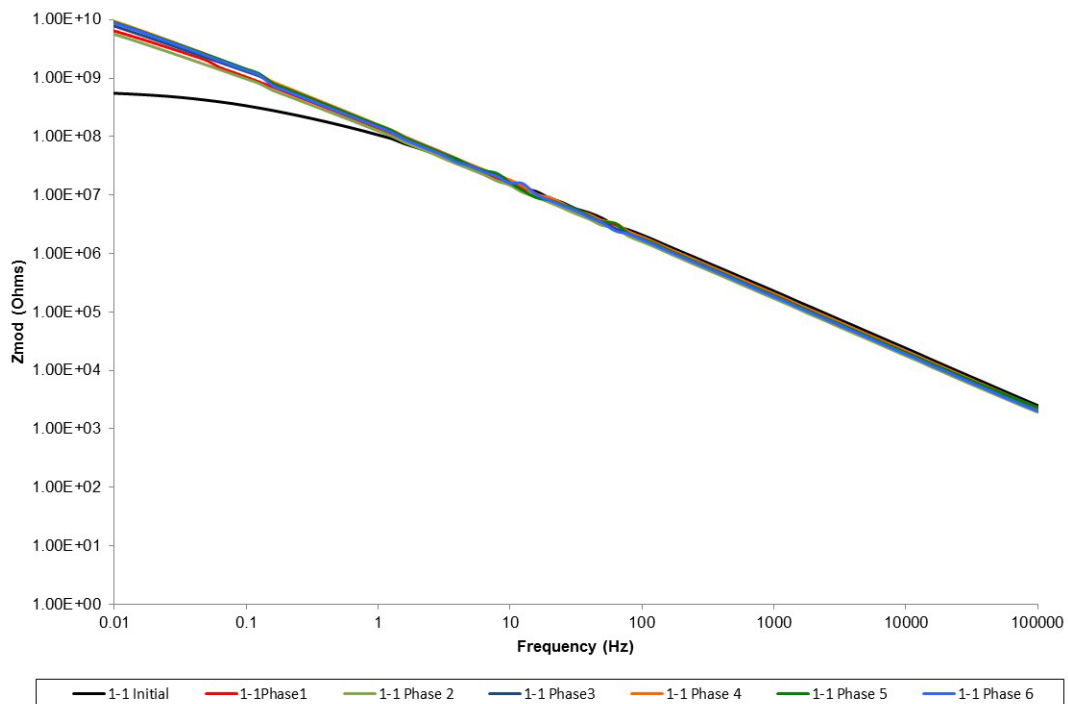


Fig. 40 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-53039 (System A) following modified GMW14872 exposure

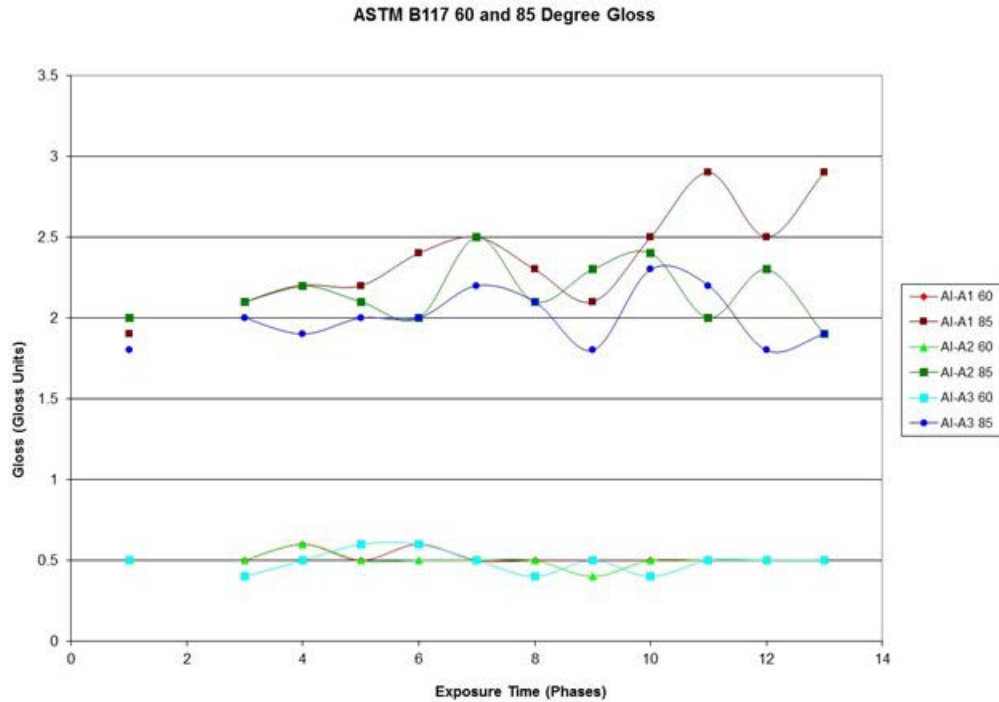


Fig. 41 60° and 85° gloss readings for MIL-DTL-53022 and MIL-DTL-53039 (System A) on aluminum in ASTM B117

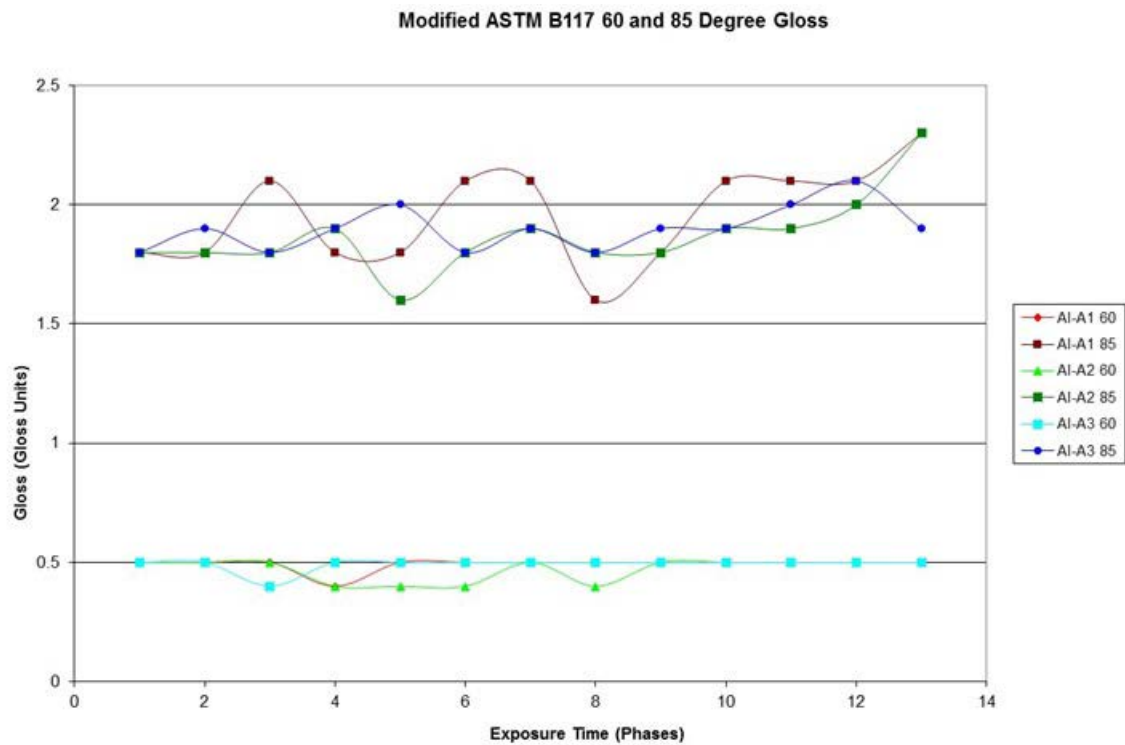


Fig. 42 60° and 85° gloss readings MIL-DTL-53022 and MIL-DTL-53039 (System A) on aluminum in modified ASTM B117

The Bode plot from the outdoor exposure of aluminum samples with System B, Fig. 43, shows consistent but minor degradation of the impedance across the frequency range for the duration of the test. For those panels exposed to continuous ASTM B117, the low-frequency impedance decreases initially within 336 h and then does not change for the duration of exposure (Fig. 44). The middle- and high-frequency impedances are unaffected for the duration of the exposure. The modified ASTM B117 Bode plot in Fig. 45 demonstrates similar behavior except there is minimal degradation of the low-frequency impedance with increased exposure time. The Bode plots for System B exposed to both GMW14872 and modified GMW14872, Figs. 46 and 47, show consistent minor degradation of the low-frequency impedance as exposure time increases. There is no significant degradation of the middle- and high-frequency impedances for these exposures. The 60° gloss is unaffected by the addition of a UV light exposure period, and the 85° gloss seems more stable with the UV degradation than without (Figs. 48 and 49). This indicates that the accelerated UV exposure provided by the QUV did not have any impact on these topcoats.

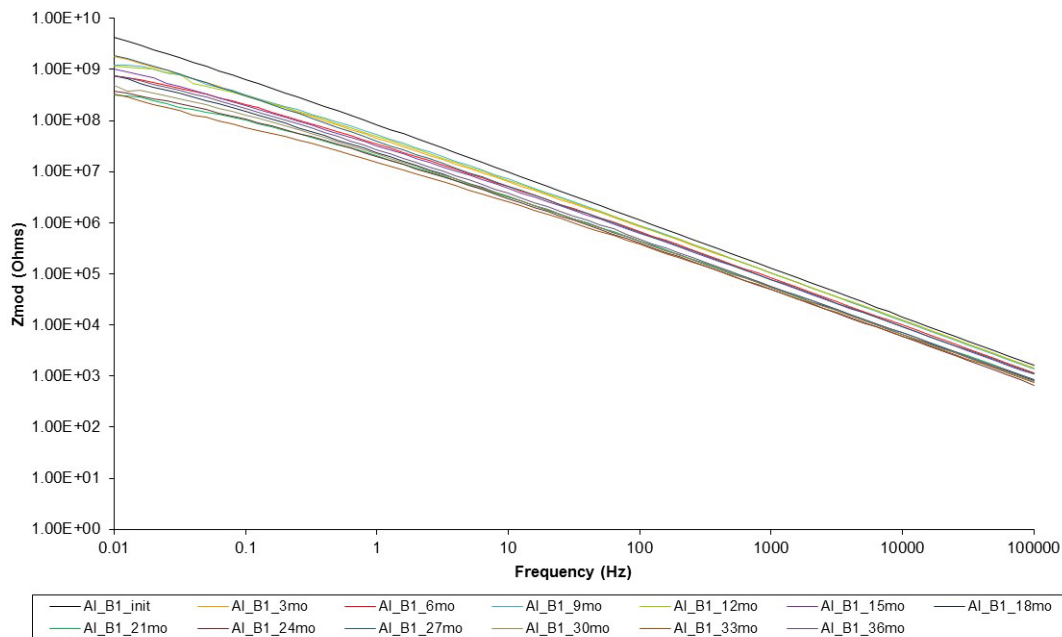


Fig. 43 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-53039 (System B) following exposure to Florida outdoor weathering

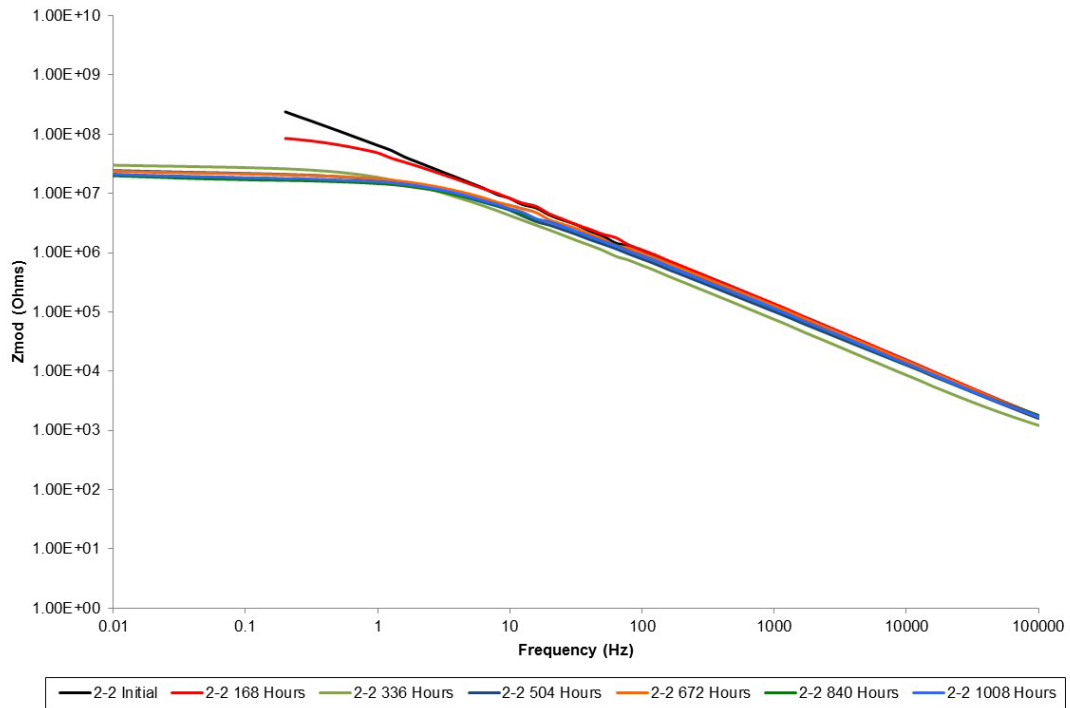


Fig. 44 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-53039 (System B) following ASTM B117 exposure

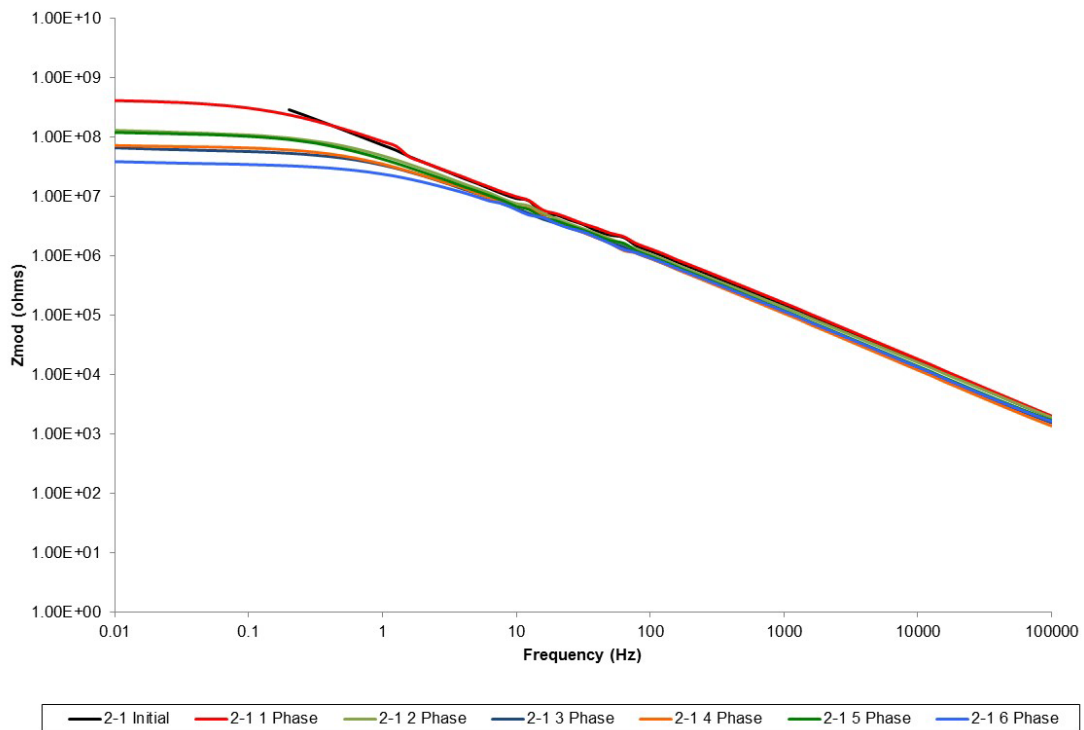


Fig. 45 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-53039 (System B) following modified ASTM B117 exposure

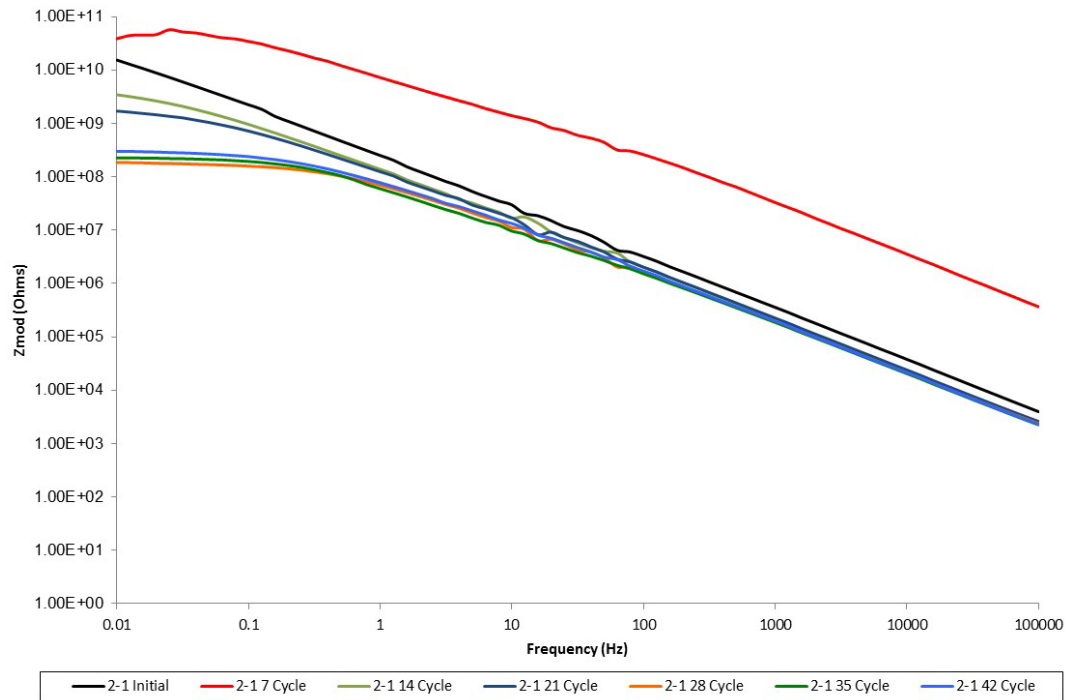


Fig. 46 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-53039 (System B) following GMW14872 exposure

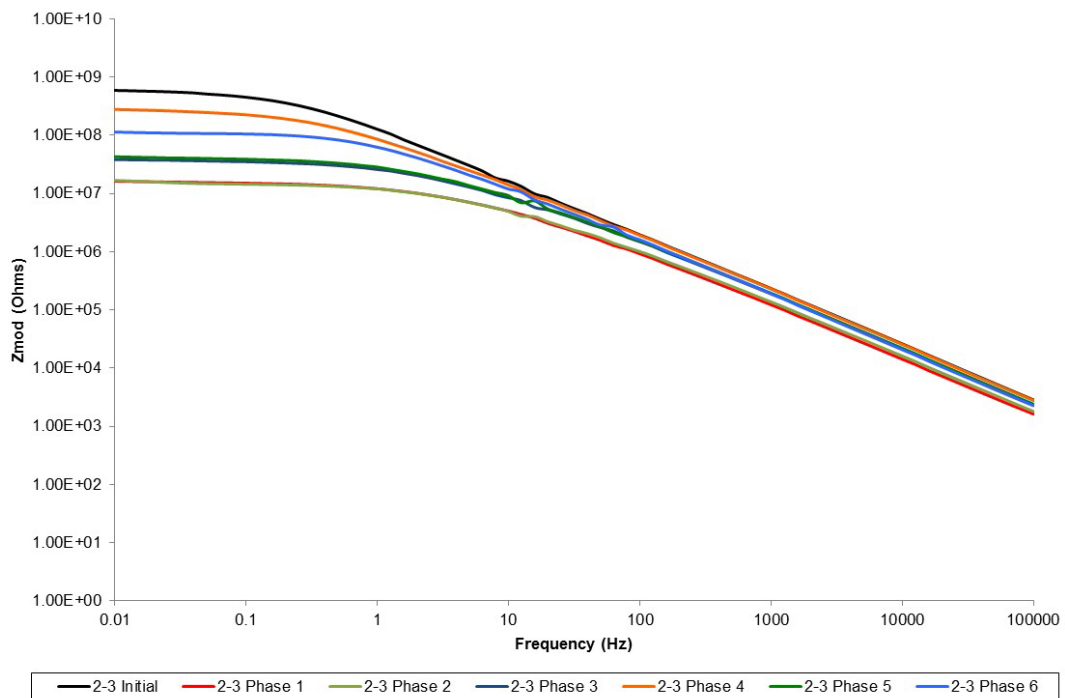


Fig. 47 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-53039 (System B) following modified GMW14872 exposure

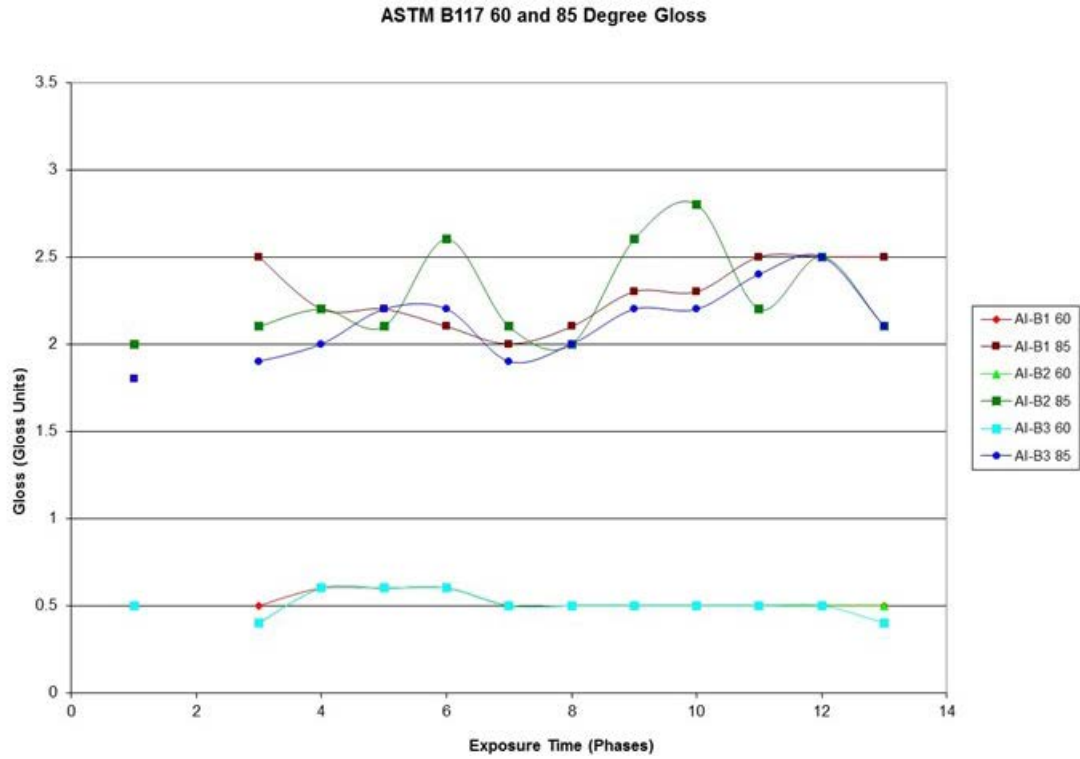


Fig. 48 60° and 85° gloss readings for MIL-DTL-53030 and MIL-DTL-53039 (System B) on aluminum in ASTM B117

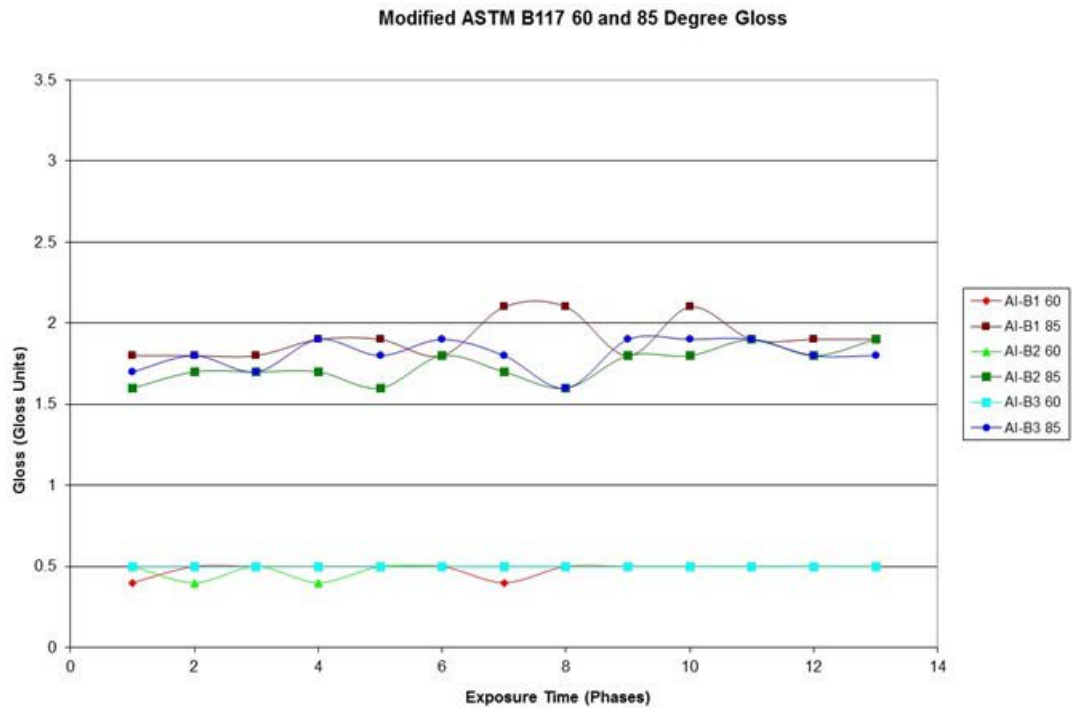


Fig. 49 60° and 85° gloss readings for MIL-DTL-53030 and MIL-DTL-53039 (System B) on aluminum in modified ASTM B117

As can be seen in Fig. 50, the Bode plots from 18 and 21 months of Florida exposure for aluminum samples with System C are the only 2 instances in which the impedance did not directly map over the previous plot, indicating that the coating had not degraded. Similarly, Figs. 51 and 52 demonstrate that System Cover aluminum was not degraded by exposure to either version of salt fog. Similarly, Figs. 53 and 54 demonstrate that there was a slight improvement in the low-frequency response for the System C coating immediately following introduction to GMW14872 and modified GMW14872. There was no further impact, positive or negative, on this system with increasing exposure. In examining the differences between salt fog and modified salt fog for coating System C, the 60° gloss did not change for either exposure while the 85° gloss increased more when exposed to the additional UV cycle (Figs. 55 and 56).

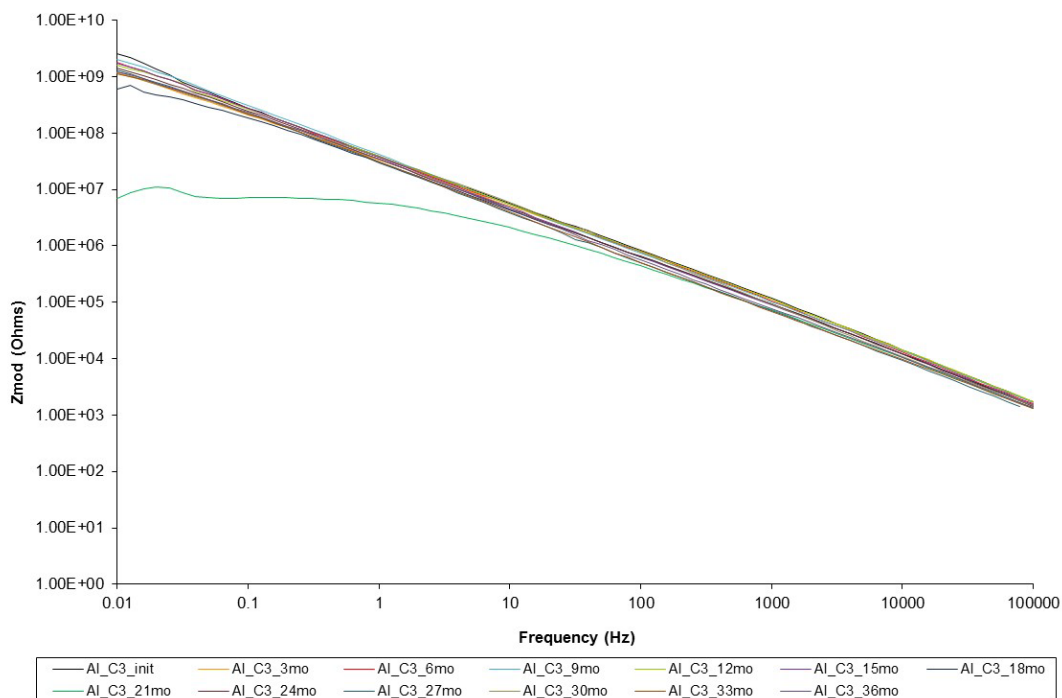


Fig. 50 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-64159 (System C) following exposure to Florida outdoor weathering

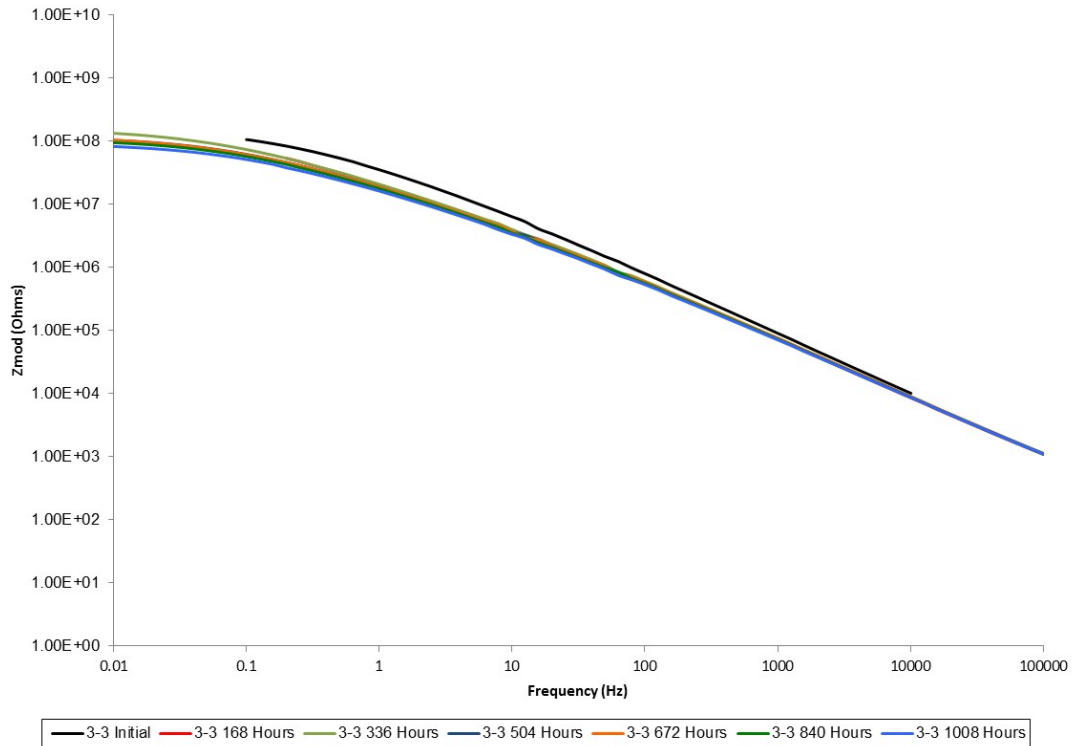


Fig. 51 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-64159 (System C) following ASTM B117 exposure

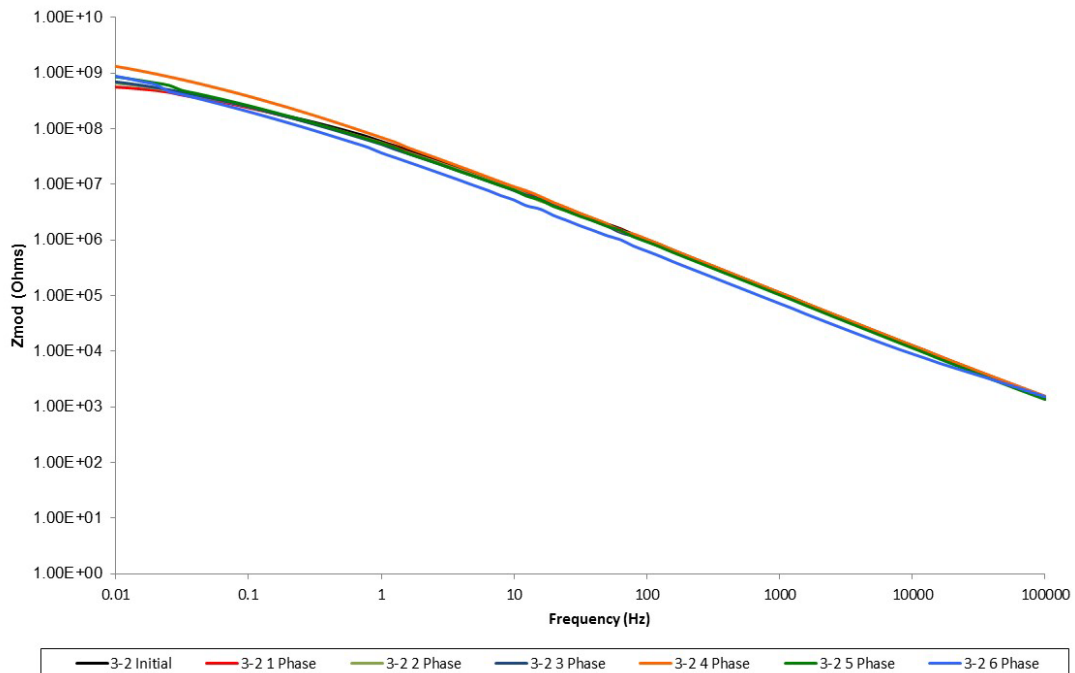


Fig. 52 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-64159 (System C) following modified ASTM B117 exposure

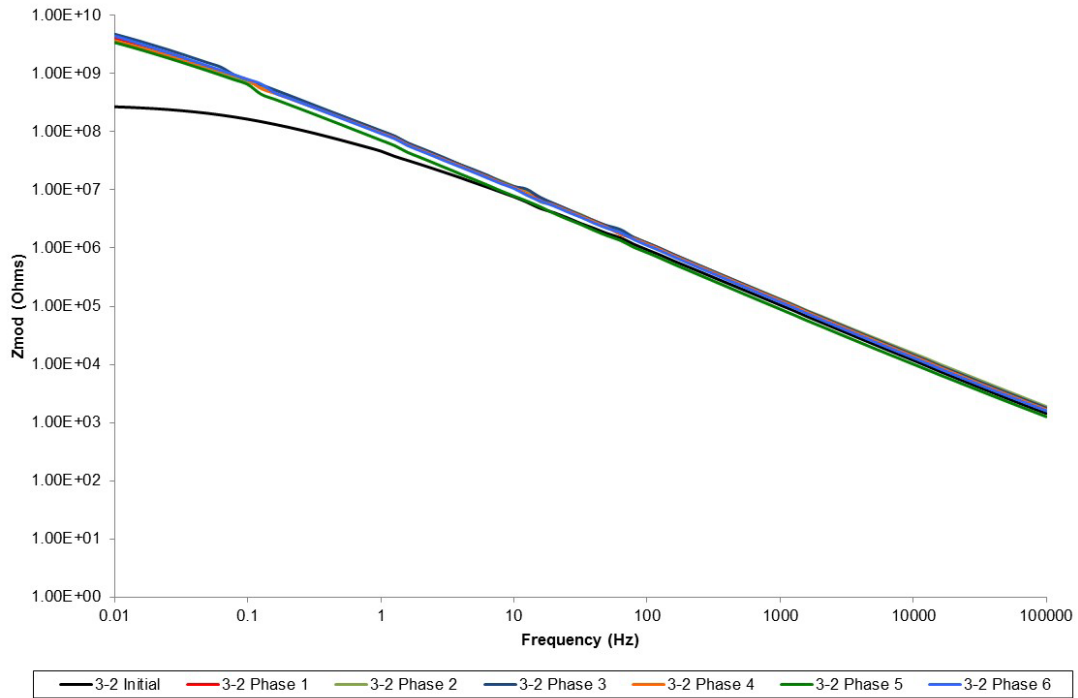


Fig. 53 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-64159 (System C) following GMW14872 exposure

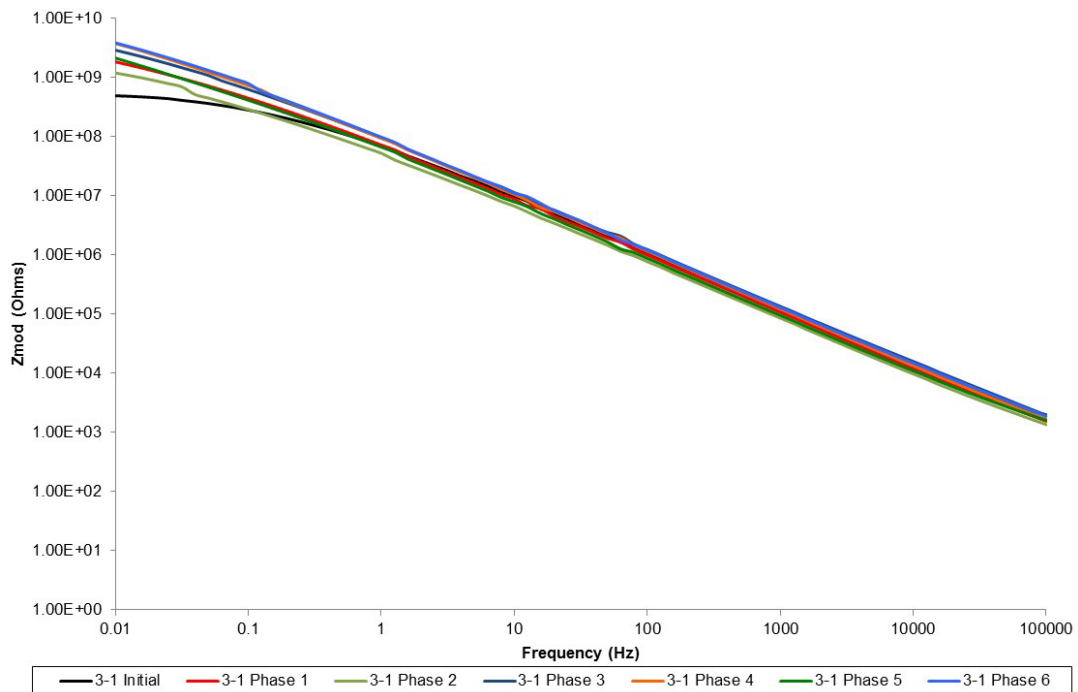


Fig. 54 EIS Bode plots for aluminum with MIL-DTL-53022 and MIL-DTL-64159 (System C) following modified GMW14872 exposure

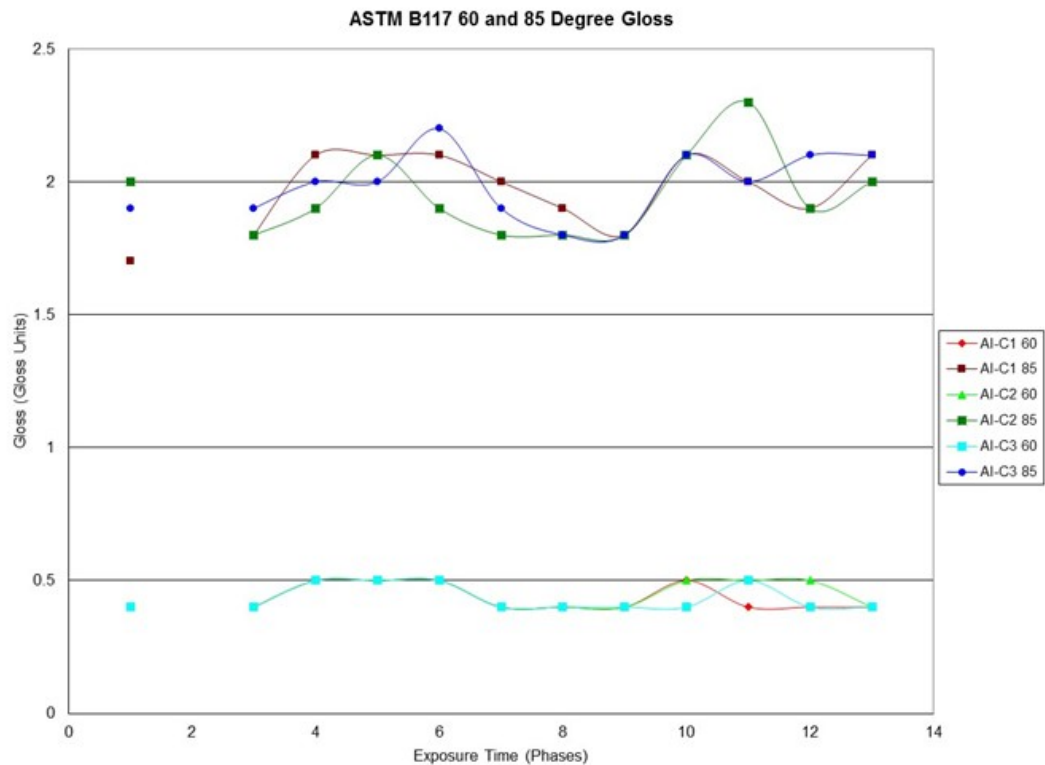


Fig. 55 60° and 85° gloss readings for MIL-DTL-53022 and MIL-DTL-64159 (System C) on aluminum in ASTM B117

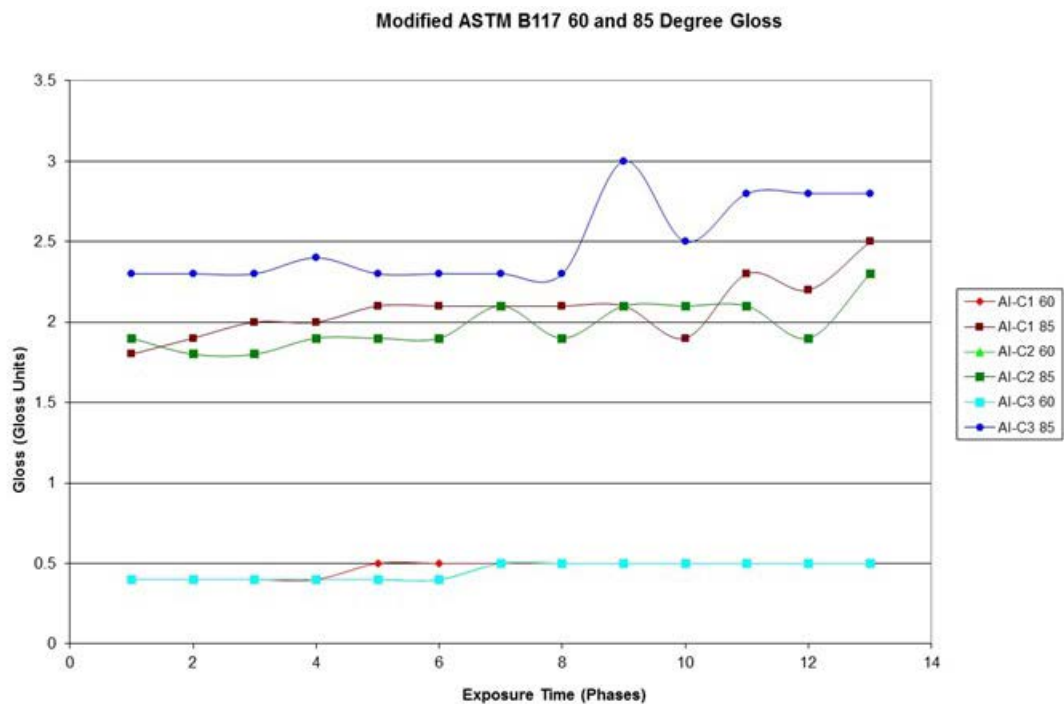


Fig. 56 60° and 85° gloss readings for MIL-DTL-53022 and MIL-DTL-64159 (System C) on aluminum in modified ASTM B117

The System D EIS results from the Florida exposure (Fig. 57) are similar to those for System C, which show minor and gradual degradation of coating impedance over time except for the curves at 12 and 21 months. In ASTM B117 (Fig. 58), the resistivity of the middle frequencies consistently degraded during the exposure for coating System D, while the low- and high-frequency responses were not affected. Figure 59 shows that there was similar performance in the modified version of this exposure, but the addition of a cyclic component to the exposure meant that there was some recovery. Figures 60 and 61 show that there may be slight improvement in the low- and mid-frequency impedance between initial and first phase reading. Subsequent measurements are nearly identical, indicating that there was little or no deterioration in the impedance for the duration of exposure. The gloss readings for the salt fog were not appreciably affected by exposure (Fig. 62).

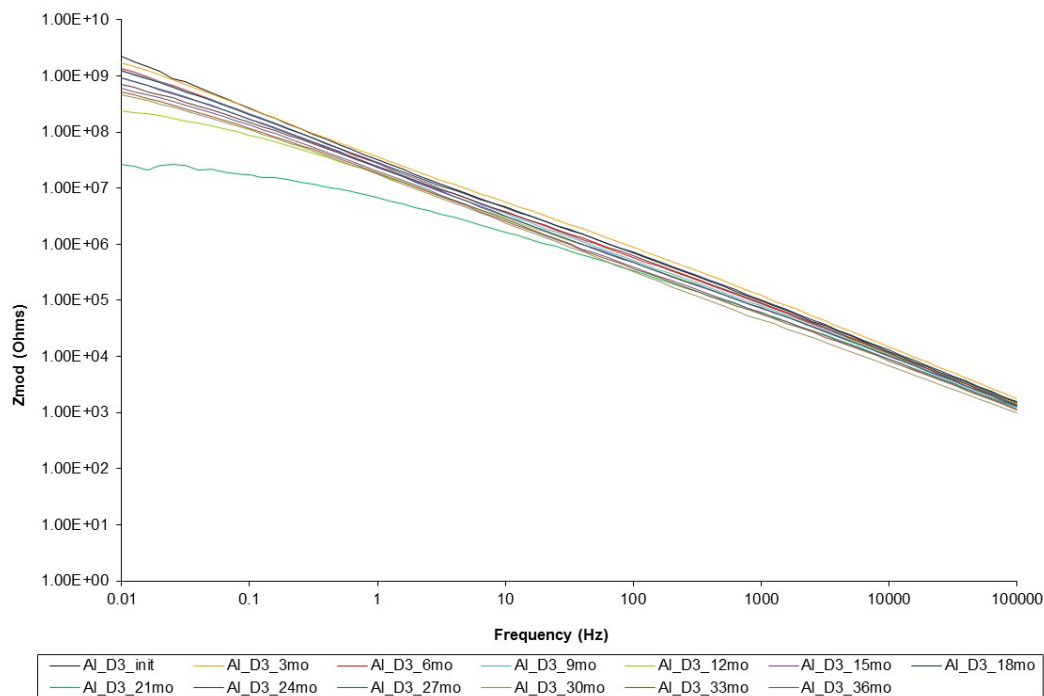


Fig. 57 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-64159 (System C) following exposure to Florida outdoor weathering

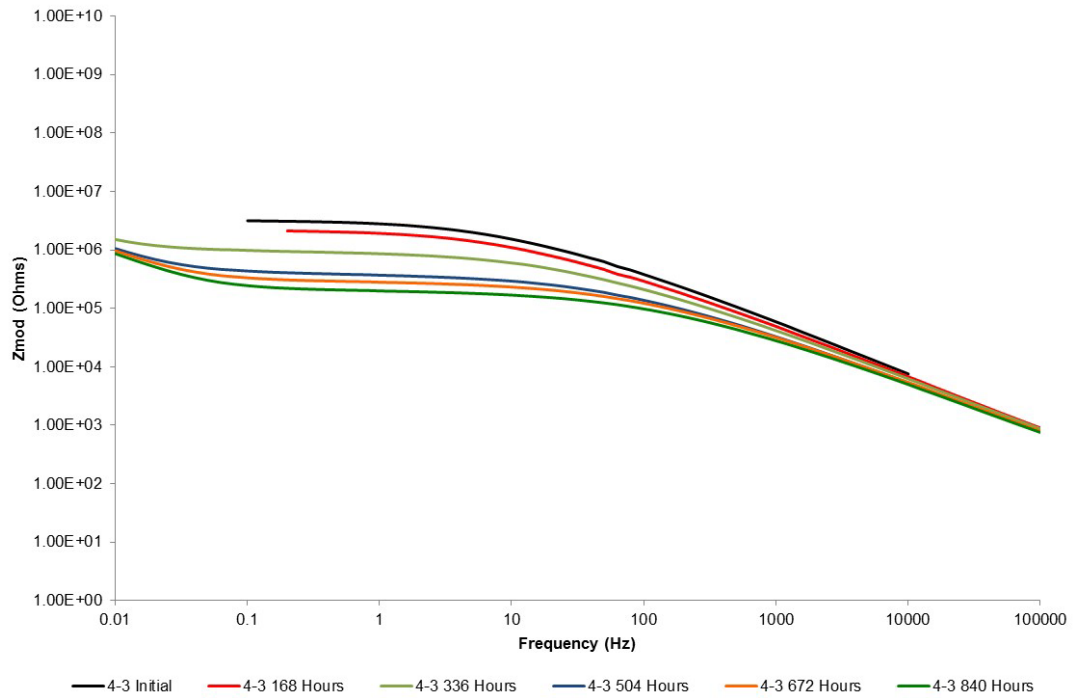


Fig. 58 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-64159 (System C) following ASTM B117 exposure

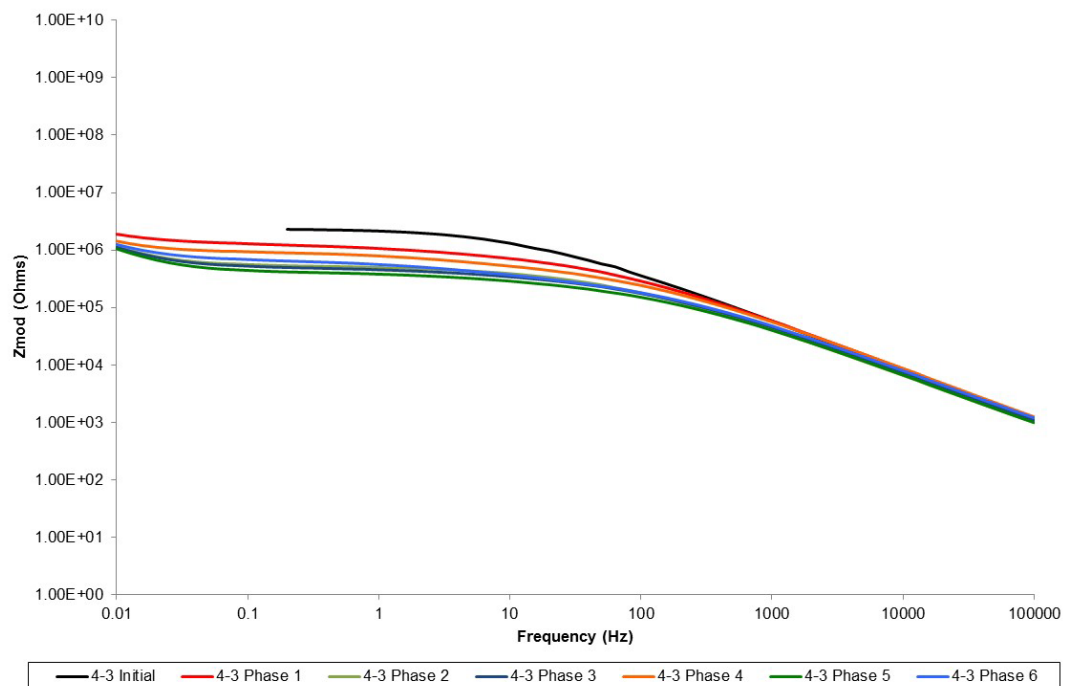


Fig. 59 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-64159 (System C) following modified ASTM B117 exposure

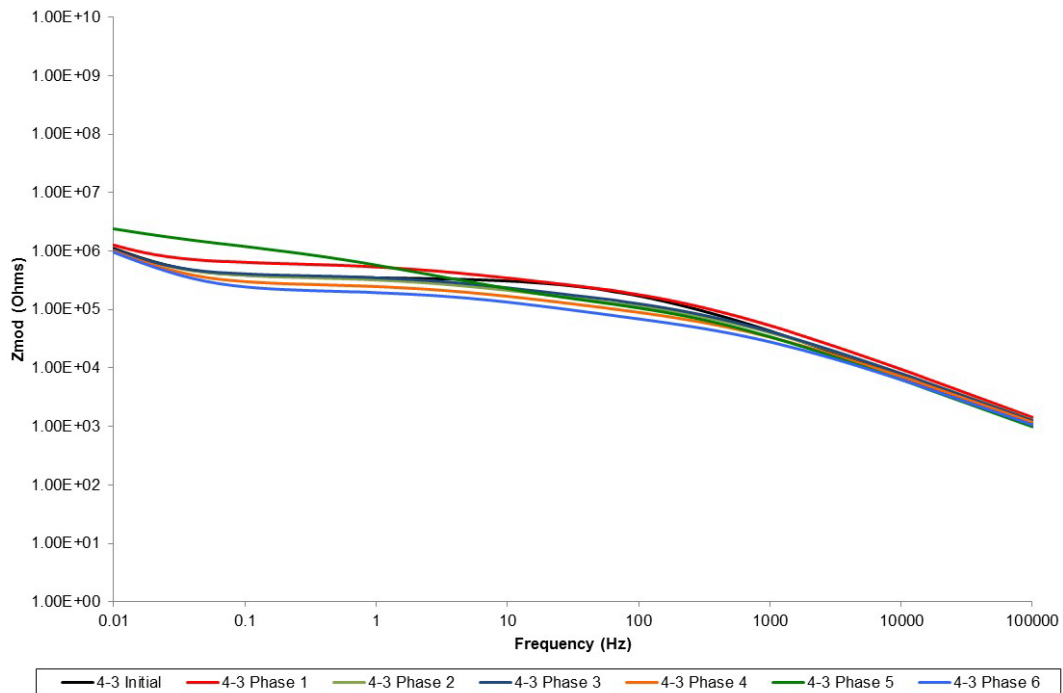


Fig. 60 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-64159 (System C) following GMW14872 exposure

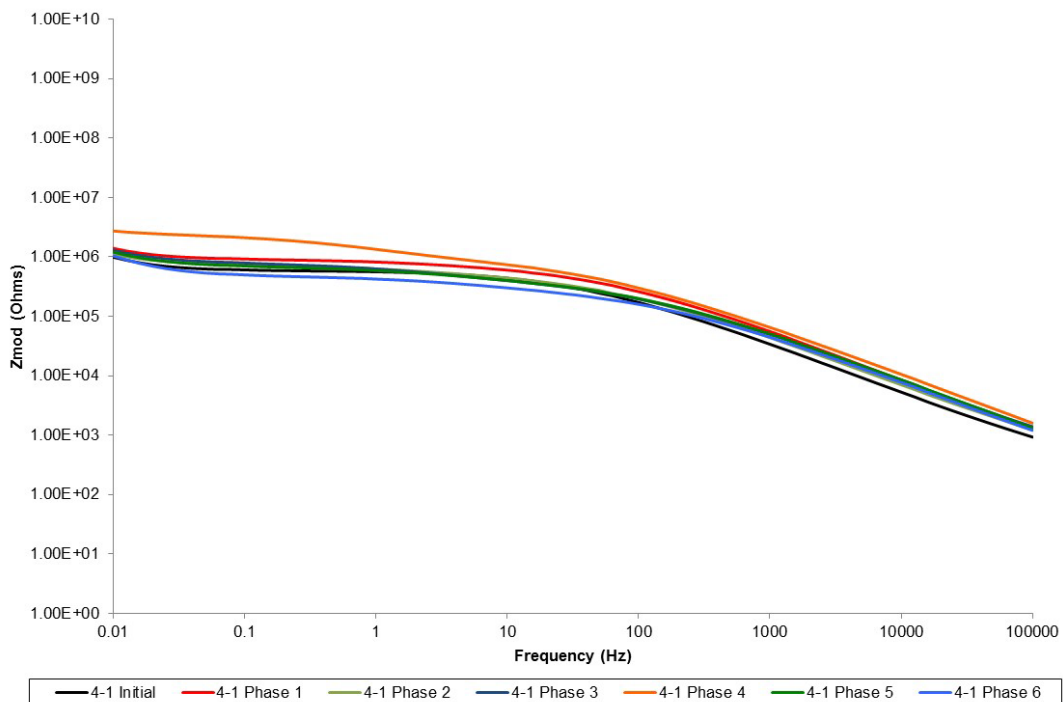


Fig. 61 EIS Bode plots for aluminum with MIL-DTL-53030 and MIL-DTL-64159 (System C) following modified GMW14872 exposure

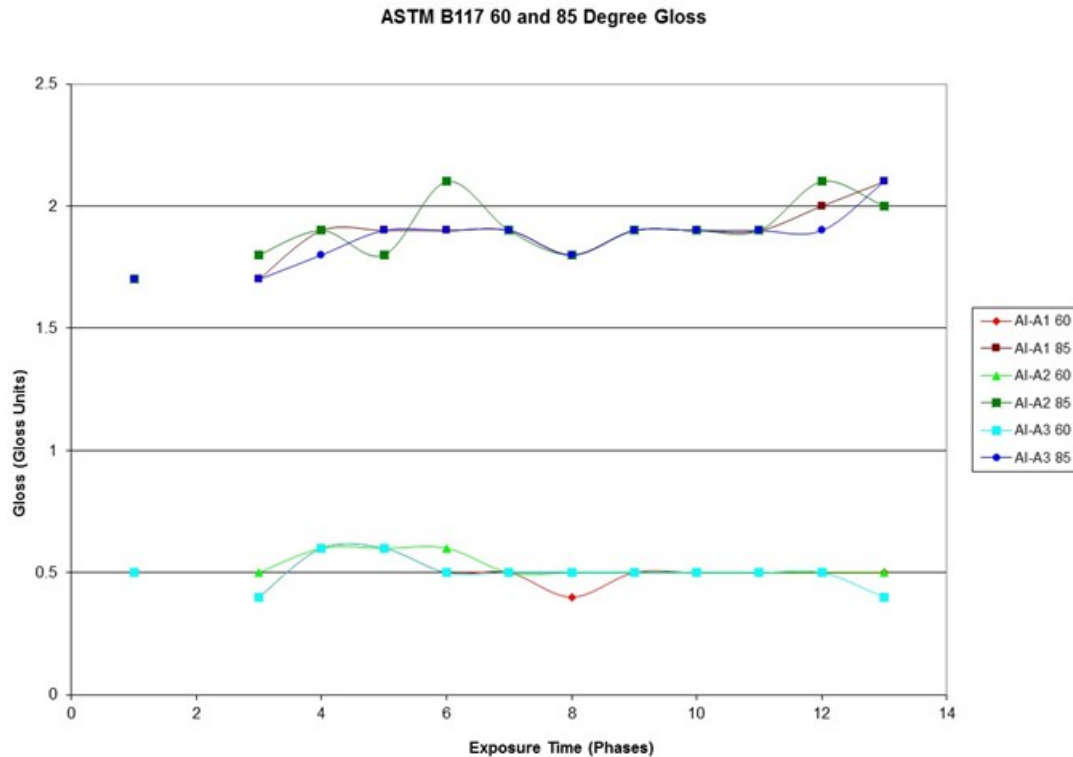


Fig. 62 60° and 85° gloss readings for MIL-DTL-53030 and MIL-DTL-64159 (System C) on aluminum in ASTM B117

4. Discussion of Results

The original intent of this project was to demonstrate that EIS could be used to identify the point at which a coating breaks down and that a qualitative value could be assigned as a pass/fail criteria for that coating system. To that end, ARL selected 2 primers and 2 topcoats whose performance has provided consistently good results. The coating systems were initially applied, robotically, to zinc-phosphated steel and conversion-coated aluminum panels from vendors with a reputation for consistency. The robotic coating application minimized thickness variation on each panel and across the set. Variability was minimized in an effort to ascertain how a consistently good coating would perform in EIS in outdoor versus the accelerated tests. Because of irregularities in the data generated in only the laboratory portion of the EIS study, 4 new sets of panels were sprayed locally to rerun the EIS in 4 accelerated corrosion environments. Legacy evaluations such as scribed corrosion resistance, color, and gloss were performed to provide context to the EIS measurements.

The different corrosion testing methods used in this study showed good agreement in the relative performance of each coating system. For scribed steel, all systems

failed prior to 6 months of outdoor exposure. For all accelerated tests, the solvent borne/solvent borne system (System A) did best, followed by the solvent borne/waterborne system (System C), waterborne/solvent borne (System B), and waterborne/waterborne (System D). Modified SAE J2334 was the only accelerated exposure in which multiple systems lasted an appreciable amount of time. The EIS evaluations from the outdoor site showed that MIL-DTL-53022 outperformed the MIL-DTL-53030, while the MIL-DTL-64159 did better than the MIL-DTL-53039 (in terms of systems, C>A>D>B) and that the degradation of the coating was delayed by at least 6 months as compared to the scribed panels. For the second set of panels exposed to salt fog, the System A panels had a higher initial impedance ($\sim 1.0 \times 10^{10} \Omega$) and suffered very little degradation over the exposure period. Systems B, C, and D had lower initial impedances (1.0×10^7 - $1.0 \times 10^8 \Omega$) and suffered significant degradation of impedance for increasing exposure, and the relative performance of each system was in line with expectations from the outdoor exposure. In modified ASTM B117, even though the initial impedance values were similar, impedance values of systems A and C were only minimally decreased with increasing exposure. Systems B and D continued to have stepwise degradation with increasing exposure, but the steps were smaller. The GMW14872 exposures had the greatest change in impedance between the initial and first reading; after that, there was not much degradation. It is believed that the cyclic nature of the UV exposures (whether programmed as in GMW14872 or within the UV exposure portion of the modified tests) allowed for some recovery of the coatings in all cases.

There was also good agreement between the relative performances of each coating system over an aluminum substrate. For scribed corrosion resistance, coating System C was best in all but modified ASTM B117 followed by System A, System B, and System D. A significant number of panels were passing creep from scribe following exposure to outdoor, ASTM B117, ASTM D5894, and modified SAE J2334 exposures. The EIS scans for aluminum may show better correlation to the scribed corrosion results simply because there was significantly less damage to the scribed panels. The outdoor panels produced Bode plots that only show minor decrease in impedance over the course of 3 years of exposure for each of the coating systems. The ASTM B117 Bode plots for the waterborne primers over aluminum show the same performance characteristics as occurred in the coated steel panels. The fact that System C did not exhibit this behavior could be that a minimum impedance threshold was not met for consistent degradation of impedance or that the solvent-borne primer provides slightly better protection. The cyclic exposures involving aluminum did not have much, if any, degradation in impedance except for System B. The low-frequency degradation is especially puzzling since the initial

impedance for System D is lower, and these panels did not degrade during the ensuing exposure.

Despite the confirmation of relative performance between coating system performance using traditional measurements and EIS evaluations, the second set of panels uncovered issues that make the method untenable as a quantitative metric to drive acceptance within a specification. Every effort was made with the first set of panels to ensure that there was little variability within each set. The thicknesses of each coating within the system were the same. For the second set, there was more variability between the thicknesses of each coating within the systems. As a result, the baseline resistivity within a single set of 3 panels could vary by 2 or 3 orders of magnitude. While the resistivities of the coatings varied greatly, the coating performance did not. The resistivity would degrade over time, but until a threshold was reached, which varied from system to system, corrosion did not occur.

5. Conclusions

Using EIS as a nondestructive evaluation method provides results that are similar to and consistent with the other scribed corrosion test methods. In all cases, there was significant degradation of the low-frequency impedance well before the first manifestation of corrosion on an undamaged coating. With the exception of coating System D on steel in ASTM B117, each of the non-scribed coatings survived to the end of exposure without developing blisters or other visible corrosion in the center of the panel where evaluations were made. The scribed corrosion has better-defined failure criteria, which most of the steel and about half of the aluminum panels exceeded by the end of their respective exposures.

The scribed corrosion performance, creep from scribe, appears to be largely dependent upon choice of primer and not topcoat. The solvent-borne MIL-DTL-53022 performs better than the waterborne MIL-DTL-53030. However, for an intact coating, there seems to be a synergistic effect between the waterborne and solvent-borne primers and topcoats. Better performance occurs when solvent-borne primer is used with MIL-DTL-64159 and when waterborne primer is used with MIL-DTL-53039 according to the EIS data.

The degradation of the color was more dependent upon the topcoat than on the type of accelerated exposure. The MIL-DTL-53039 failed at about 6 phases (1000 h of ASTM G154) for modified ASTM B117 or ASTM D5894 and 8 phases of modified SAE J2334. The MIL-DTL-64159 survived an additional 4–6 phases (600–1000 h). The color numbers for the outdoor panels seem to confirm this trend. Additionally, the steel panels produced corrosion products from edge effects, which

were generally not present on the aluminum panels. The gloss results from this were not consistent enough to provide useful trends.

EIS is an effective technique for tracking the degradation of a coating or a coating system. It can also show when that coating is no longer effective. In this study, however, it was not demonstrated to be useful for detecting corrosion before visible manifestation through a coating, and it would not be particularly adaptable for use in the field. At this time, it is not a test method that provides consistent, easily interpreted, reproducible results across the coating systems used by the Army and therefore will not be incorporated into the Army coatings specifications.

Finally, when testing an undamaged coating using any of the accelerated or outdoor tests, it would seem that color degradation would precede any marked deterioration in the corrosion performance. There are 2 caveats to this. First, the coatings used in this study were well made and well applied. The performance of other coatings that approach the edges of acceptability may provide less relative resistance to corrosion than to color degradation. And second, an undamaged coating may deliver spectacular performance; however, it is that same coating with a flaw whose performance we must be aware of.

6. Return on Investment

As it has been decided that EIS will not be incorporated into the Army coatings specifications, a return on investment calculation is not applicable. However, an analysis of the benefits of the study follows.

This project enabled several critical conclusions. Primarily, EIS as it was used was determined not to be a viable predictor of coating performance in the Military environment. First, there are differences between the corrosion behaviors of flawed and in-tact coatings. For the pretreatments, primers, and topcoats used in this study, visible degradation in the form of corrosion would not be expected in a continuous well-applied coating system for an extended period of time. However, the presence of an intentional flaw (a scribe) accelerates the process and provides pass/fail criteria within 6 weeks for ASTM B117 and 6 months for outdoor exposure. It was hoped that EIS measurements would be able to provide a nice transition point that could be used to identify the difference between a good coating and a poor one. Unfortunately, this did not occur. Second, the coating systems initially used in this study were consistent both in application and performance. For this testing, the bar was arbitrarily set at an impedance value below $1 \times 10^9 \Omega$, and comparisons were made with respect to initial measurements made prior to exposure. With poorer coatings, the criteria for failure may have to be defined as a system that has lost a

certain percentage of its original impedance. Further investigation would be required with a broader range of manufacturers before such a standard could be set. Finally, requirements for EIS performance will not be incorporated into the various coatings and pretreatment specifications due to the problems listed above.

However, this project was not without positive outcomes. First, the testing did validate the procedures that are currently in place for the qualification of pretreatments, primers, and topcoats. ASTM B117 and GMW14872 (formerly GM 9540) are used to demonstrate corrosion resistance of the candidates. Since passing these accelerated tests is a good indication that a coating will perform similarly in the field, candidates are granted “conditional approval” pending the results from the longer-term outdoor exposure. This allows accelerated testing to remove substandard submissions while making products available to the inventory that can help protect Army assets. Second, this testing illustrated a need to expand the range of materials tested using the EIS techniques. The 4 systems that were initially used were quite similar in performance and composition. Two chrome-free epoxy primers in combination with 2 low-gloss agent-resistant polyurethanes; all 4 coatings were known to well meet the requirements of their respective specifications when applied properly. The replacement set of coatings proved that having products that were closer to the margins for performance and application could provide information that would otherwise be missed in systems that exceed the requirements. Variation of coating thicknesses and the effect of pretreatments should also be approached. This testing demonstrated the synergistic effect of using a solvent-borne primer/topcoat with a waterborne topcoat/primer.

Finally, because of the second set of laboratory EIS specimens, there appears to be a minimum low-frequency impedance that provides consistent impedance degradation. For steel, we found that the threshold was below $1 \times 10^9 \Omega$ for the MIL-DTL-53022/MIL-DTL-53039 system, $1 \times 10^8 \Omega$ for the MIL-DTL-53030/MIL-DTL-53039 and MIL-DTL-53022/MIL-DTL-64159 systems, and $1 \times 10^7 \Omega$ for the MIL-DTL-53030/MIL-DTL-64159 system in ASTM B117 and $1 \times 10^7 \Omega$ for the MIL-DTL-53030/MIL-DTL-64159 system in GMW14872. For aluminum, that threshold was below $1 \times 10^8 \Omega$ and $1 \times 10^9 \Omega$ for the MIL-DTL-53030/MIL-DTL-53039 in ASTM B117 and GMW14872, respectively; and $1 \times 10^7 \Omega$ for the MIL-DTL-53030/MIL-DTL-64159 system in ASTM B117. Therefore, if EIS were to be used as a screening tool, any samples that had low-frequency impedance values of less than $1 \times 10^9 \Omega$ should be considered suspect as they probably will not meet the accelerated corrosion requirements of our specifications.

7. Reference

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Appendix. Composite Images of Exposed Panels



Fig. A-1 Steel panels with coating System A following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334



Fig. A-2 Steel panels with coating System B following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

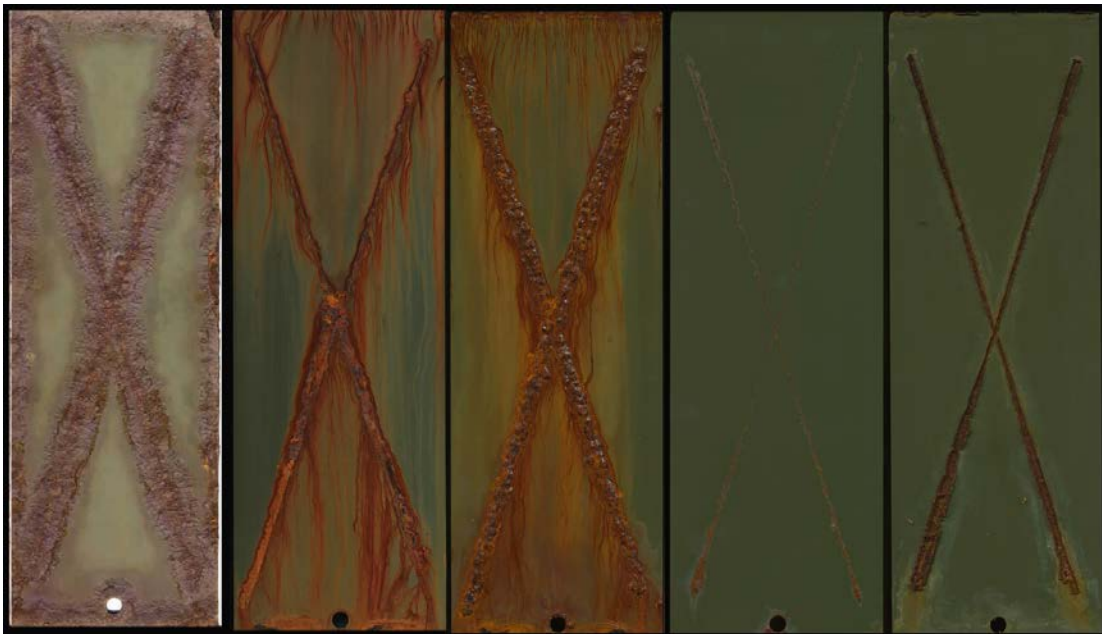


Fig. A-3 Panels with coating System C following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334



Fig. A-4 Panels with coating System D following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

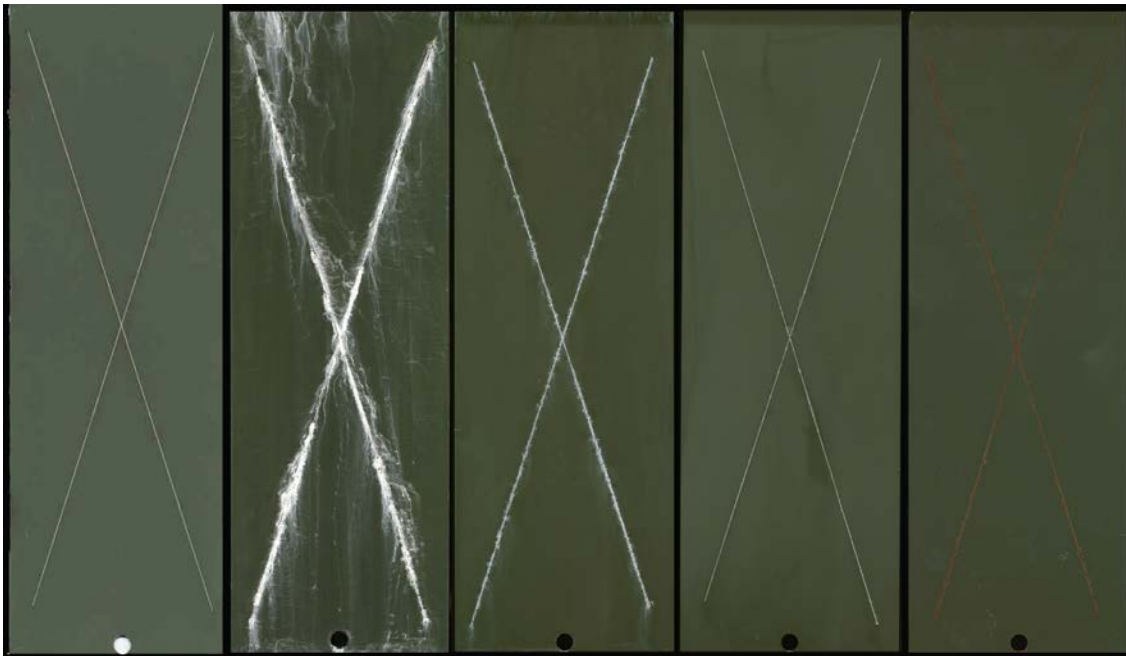


Fig. A-5 Aluminum panels with coating System A following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334



Fig. A-6 Aluminum panels with coating System B following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

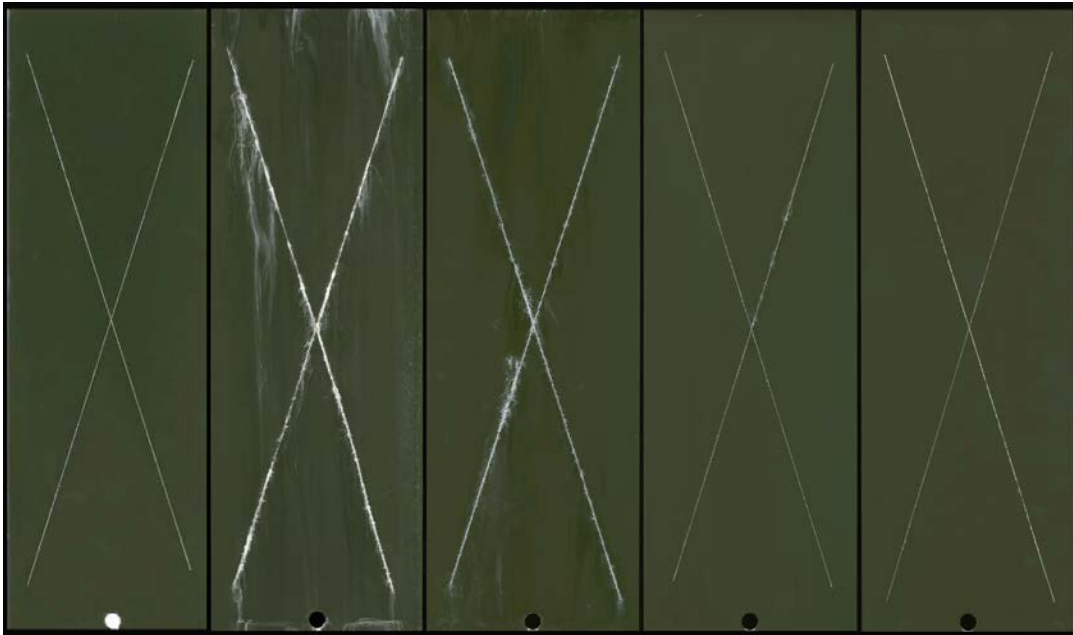


Fig. A-7 Aluminum panels with coating System C following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

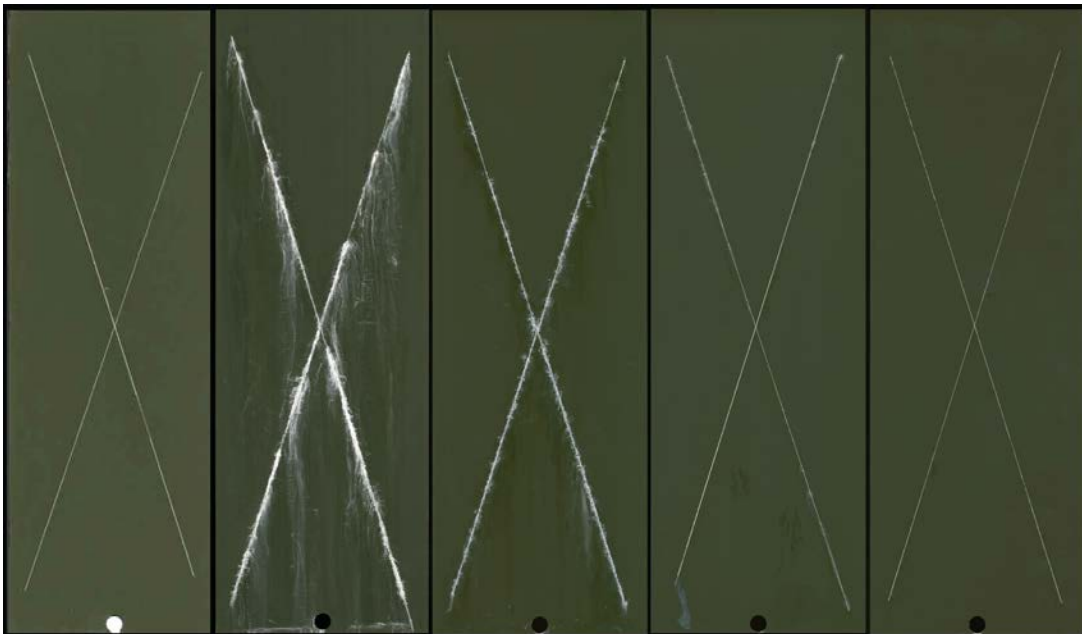


Fig. A-8 Aluminum panels with coating System D following 24 months Florida outdoor, 4032 h ASTM B117, 14 phases modified ASTM B117, 12 phases modified ASTM G85, and 12 phases modified SAE J2334

List of Symbols, Acronyms, and Abbreviations

CARC	chemical agent-resistant coating
EIS	electrochemical impedance spectroscopy
KSC	Kennedy Space Center
NBS	National Bureau of Standards
QUV	“Q” = Q-Lab Company; “UV” = type of exposure
UV	ultraviolet

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