

Efficacy of Two Novel Anodic Coatings for Enhanced Corrosion Protection of Aluminum Armor Alloys

**by John V. Kelley, Elizabeth A. Charleton, Steven M. Kilczewski,
and Paul Huang**

ARL-TR-6796

January 2014

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT The purpose of this effort is to assess the efficacy of novel anodic coatings for military applications. The intent is to explore alternatives to hexavalent chromium pretreatments and sealing methods for anodizing. For this work, various sized Al A2024-T351 and Al A5083 substrates were subjected to the proprietary anodic coating process. The two coatings were designated "silicon" (Si) and "silver" (Ag) by the manufacturer. Each coating type was supplied to the U.S. Army Research Laboratory (ARL) in a range of thicknesses. The corrosion performance was characterized using electrochemical techniques, and ASTM B 117 salt fog exposure. The adhesion of an organic coating was determined using pull-off adhesion. All variations of the coatings provided some barrier protection, at least initially, and provided a good adhesive surface sufficient for military coatings.					
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1. Introduction

The use of aluminum armor alloys in the construction of armored vehicles is one of the most efficient ways for the Army to lighten the force in an effort to increase its mobility and deployability. Preventing corrosion of these aluminum alloys is typically done using chromate conversion coatings. These coatings are used to stabilize the native surface oxide of the metal, thereby promoting adhesion and inhibiting corrosion. Chemical treatments containing hexavalent chromium (Cr^{6+}) are risks to human health and the environment (1). In April of 2009, a memo was released from the Office of the Secretary of Defense (OSD) outlining a new policy for reducing the use of Cr^{6+} in Department of Defense (DOD) applications (2). The memo directs the military to approve the use of alternative Cr^{6+} coatings that perform adequately for the intended application and operating environment and to update relevant technical documents and specifications to authorize the use of qualified alternatives. It also requires the Program Executive Office (PEO) or equivalent in coordination with the Military Department's Corrosion Control and Prevention Executive (CCPE), to certify that there is no acceptable alternative to the use of Cr^{6+} on a new system. Effectively, the memo directs DOD Military Departments to restrict the use of Cr^{6+} unless a cost-effective alternative with satisfactory performance cannot be identified. The Army and private industry have been challenged to develop and evaluate environmentally benign pretreatments for aluminum armor alloys.

Anodic coatings are a viable option for aluminum structures. Aluminum anodizing for military applications is specified by MIL-A-8625F, Military Specification for Aluminum and Aluminum Alloys (3), which outlines the requirements for six types and two classes of electrolytically formed anodic coatings on aluminum and aluminum alloys. On monolithic aluminum, an anodic coating consists of a thin continuous barrier layer beneath a thicker porous columnar-structured layer (figure 1).

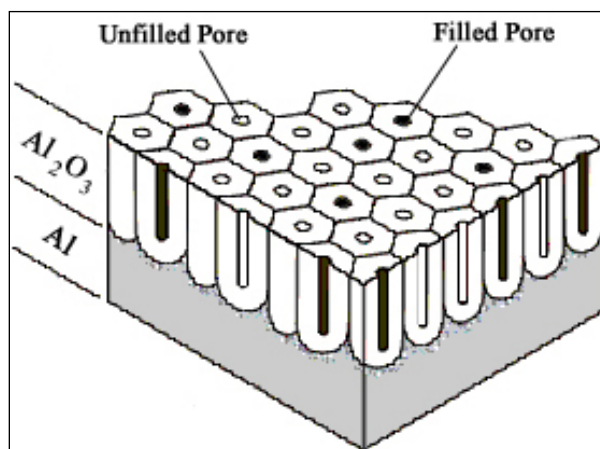


Figure 1. Cross section of an anodic coating.

This porous layer has been characterized as a closely packed array of columnar hexagonal cells that contain a central pore (4). The columns are oriented normal to the substrate surface. The pores are typically filled with a subsequent coating or sealing process. The process for forming these novel anodized coatings first uses conventional means to form the oxide. Then, an alternating voltage is applied to the part while immersed in a sulfate or nitrate solution of a given metal electrolytically impregnating the porous oxide with the desired metal (5)—for example, silicon (Si) and silver (Ag).

For conventional coatings, the most effective sealing methods contain Cr^{6+} . Since the military is actively trying to reduce the use of chromate coatings, novel alternatives are being explored. The objective here is to explore the efficacy of novel anodic coatings as alternatives to Cr^{6+} containing pretreatments currently used on aluminum armor alloys.

2. Experimental Procedure

Various sized samples of Al A2024-T351 and Al A5083 were coated with proprietary anodic coatings that were designated Si and Ag. The details of the coating process and the subsequent sealer used were not known prior to testing. For the purposes of sample identification, the designation for each type of coating in this report are, Silver = Ag, and Silicon = Si, Aluminum A5083 = A, and Aluminum A2024-T351 = B. The coating thicknesses ranged from 15 and 80 micrometers (μm) for the Si coating, and between 30 and 100 μm for Ag coating. A summary of the specific alloys, number of samples, coating types, and coating thicknesses can be found in table 1.

Table 1. Total number of each sample received.

Total Number of 101 mm × 101 mm Panels							
Alloy	Coating Type and Thickness						
	Ag				Si		
	30 μm	50 μm	75–80 μm	90–100 μm	15–20 μm	50 μm	80 μm
AA5083	1	9	9	0	0	1	2
AA2024-T351	2	9	0	9	5	0	0

3. Electrochemical Evaluation

Electrochemical impedance spectroscopy (EIS) was employed to measure coating integrity over time while exposed to an electrolyte. The apparatus used consists of a Gamry Instruments Reference 600 Potentiostat/Galvanostat and a Hewlett Packard (HP Compaq) laptop computer shown in figure 2. Background noise was minimized by placing the electrochemical cell in a

metal Faraday cage (figure 2). The electrochemical cell was comprised of the aluminum substrate (test sample) as the working electrode, a platinum coated 0.75-inch (in) round wire mesh as the counter electrode, and a calomel reference electrode in a 5% sodium chloride (NaCl) solution. The cell was allowed to equilibrate for at least 1 hour (h) prior to running the scans. Periodic measurements were taken at 0, 24, 192, 288, 336, 432, and 816 h of continuous exposure using the cell configuration illustrated in figure 3. Gamry Framework and Gamry Analysis software packages were used to acquire and analyze data, respectively.

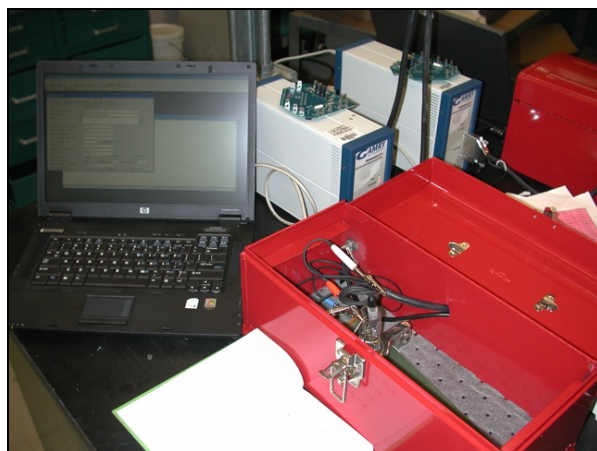


Figure 2. Electrochemical test setup showing the Faraday cage.

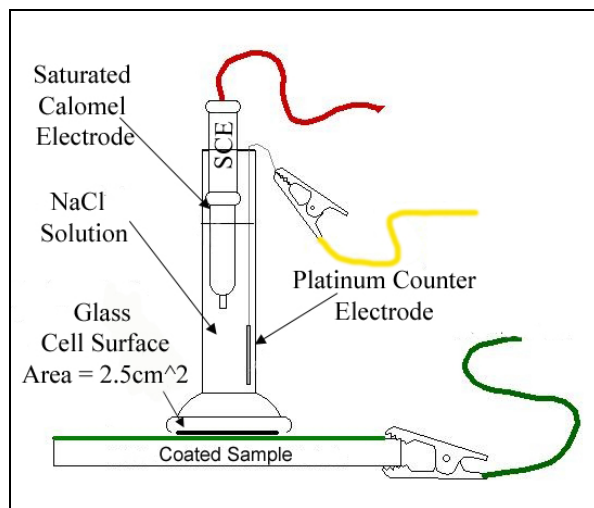


Figure 3. Electrochemical cell configuration.

Measurements were recorded at the corrosion potential of the sample over the frequency range of 100 kHz–0.01 Hz. A single sine technique was used with an applied amplitude of 10 mV. EIS data were then plotted and evaluated for low frequency over time and final Bode format. Low-frequency plots were made by taking the impedance value measured at 0.01 Hz and plotted versus time for each sample. Bode plots display the magnitude ($\log Z$) and the phase angle (θ) of

the impedance as a function of applied frequency (log f). The total impedance of the specimen, defined as the log value at 10 mHz in the Bode plot was also plotted as a function of exposure time for comparison.

Table 2. Test matrix for electrochemical evaluation.

Electrochemical Impedance Spectroscopy (EIS) Test Matrix							
Alloy	Coating Type and Thickness						
	Ag				Si		
	30 μm	50 μm	75–80 μ	90–100 μ	15–20 μ	50 μm	80 μm
A5083	1	1	1	0	0	1	1
A2024-T351	1	1	0	1	1	0	0

Potentiodynamic Polarization—Potentiodynamic polarization was performed using the same equipment and data acquisition program previously described. Cells were filled with a 3.5% sodium chloride solution and the potential was ramped from -0.4 V of the open circuit potential (OCP) to 0.4 V above the OCP at a rate of 5 mV/s.

4. Accelerated Corrosion Testing

Salt fog testing, in accordance with ASTM B117-03 (6), was used to evaluate corrosion resistance of the anodic coatings. Samples were placed into the salt fog chamber, figure 4, for a total duration of 1024 h. Samples were periodically removed for observation and photo documentation following 48, 168, 336, 480, 552, 696, 840, and 1032 h of exposure. Each sample was rated based on ASTM D 1654-79A (7). Rating system and color codes were assigned based on the ranges of the percentage of area failed as shown in figure 5.



Figure 4. Salt fog chamber used for measurements described in ASTM-B117.

Rating of Unscribed Areas (Procedure B)	
Representative Mean Area	Rating
Area Failed, %	Number
No failure	10
0 to 1	9
2 to 3	8
4 to 6	7
7 to 10	6
11 to 20	5
21 to 30	4
31 to 40	3
41 to 55	2
56 to 75	1
Over 75	0

Figure 5. Color coded/numerical rating system for unscribed areas.

5. Adhesion Testing

The tensile strength at the interface between an organic top coat (chemical agent resistant coating [CARC]) to the anodic coating was assessed using pull-off adhesion in accordance with ASTM D 4541 (8). A set of aluminum coupons measuring $4 \times 4 \times 0.5625$ in and $4 \times 4 \times 0.3125$ in were coated with MIL-DTL-53022 (9) epoxy primer to a dry film thickness (DFT) of 1.5 mils. Elcometer Model 108 Hydraulic Adhesion Test Equipment (HATE) was used to evaluate adhesion. The pull-off adhesion tests were performed using a loading fixture commonly referred to as a “dolly.” The dolly is secured normal to the coating surface using a cyanoacrylate adhesive. After allowing the adhesive to cure for 24 h at 25 °C at 50% relative humidity, the attached dolly is inserted into the test apparatus. The load applied by the apparatus was gradually increased and monitored on the gauge until the dolly detached from the surface. The failure tension in pounds per square inch (psi) was recorded, and the failure mode and location within the coating system was recorded. The pull-off test apparatus and dolly configuration are illustrated in figure 6.

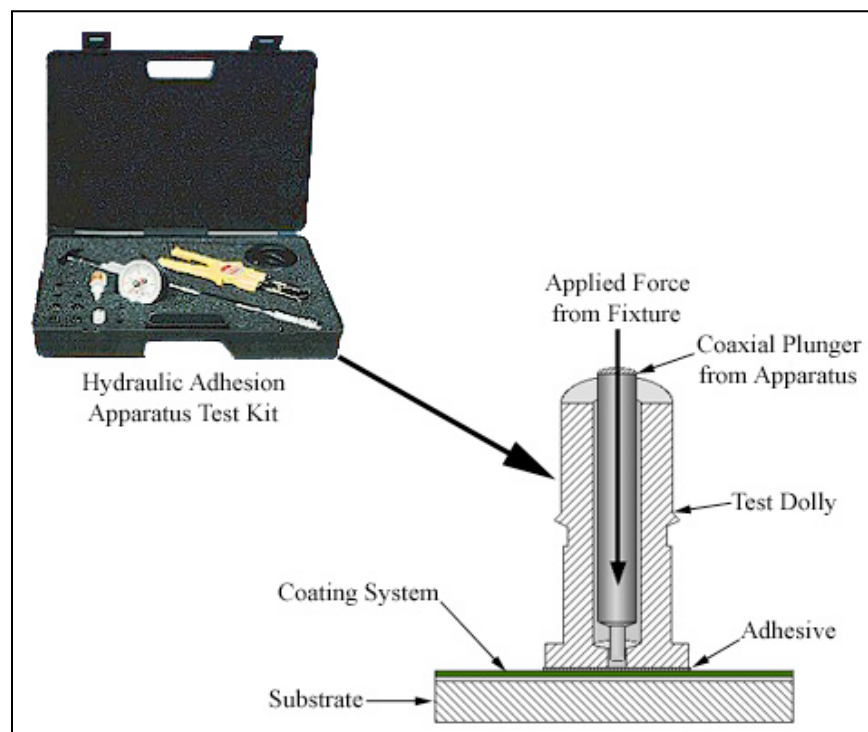


Figure 6. Pull-off test apparatus for ASTM D 4541.

6. Results and Discussion

6.1 Electrochemical Evaluation

EIS and direct current (DC) potentiodynamic polarization techniques were used to compare and characterize the relative performance of the anodic coatings on two aluminum alloys: AA5083 and AA2024-T351. Series 2000 aluminum contains copper, which makes it susceptible to pitting corrosion, and makes protecting this alloy series from corrosion particularly challenging. Conversely, AA5083 has historically been a relatively corrosion resistant alloy. A comparison of the performance of the anodic coatings on these two alloys was selected as best- and worst-case scenarios.

EIS was used to monitor the dielectric response of the coatings as they degrade over time while potentiodynamic polarization techniques were used to evaluate the corrosion resistance. The results of the EIS measurements can be seen in figures 7–10. Figure 7 is a plot of the log Z (log of the impedance) versus time in hours of exposure for the various anodic coatings on aluminum AA5083 while figure 8 is the Bode plot showing the initial and final impedance measurements of the same substrate and coating systems.

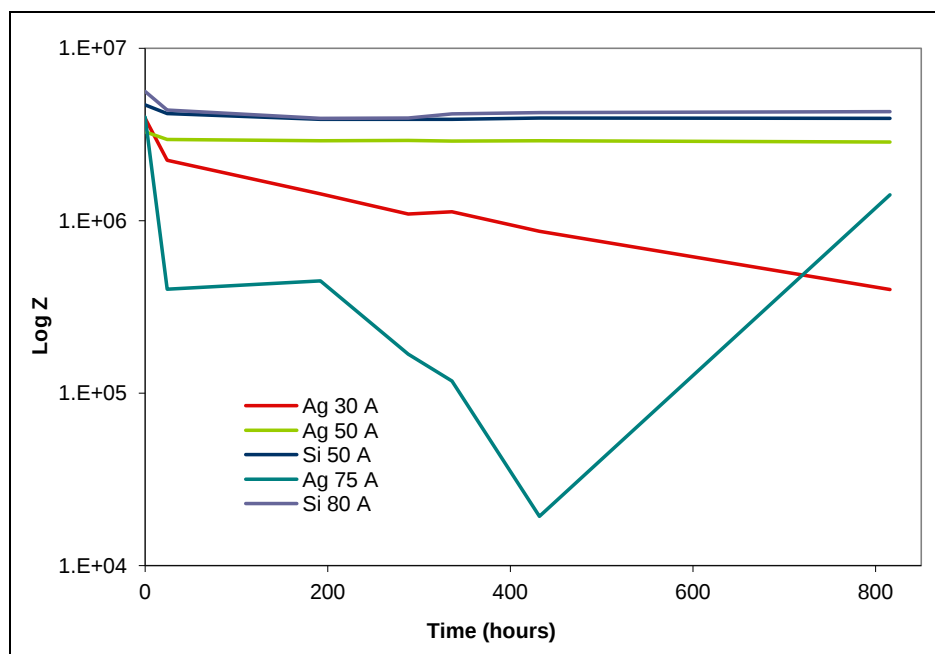


Figure 7. Low-frequency impedance vs. time for coated AA5083 samples.

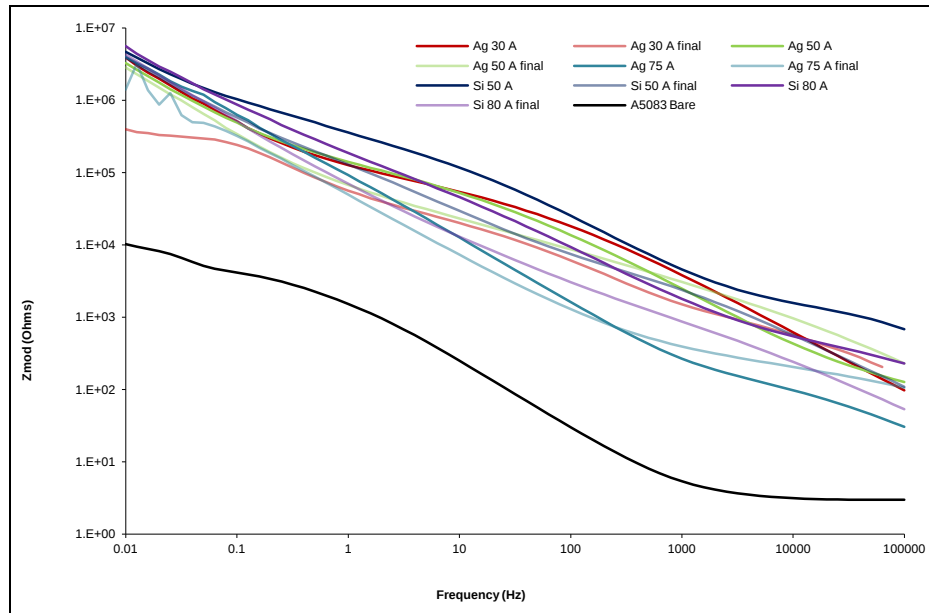


Figure 8. Initial and final Bode plots of AA5083 samples.

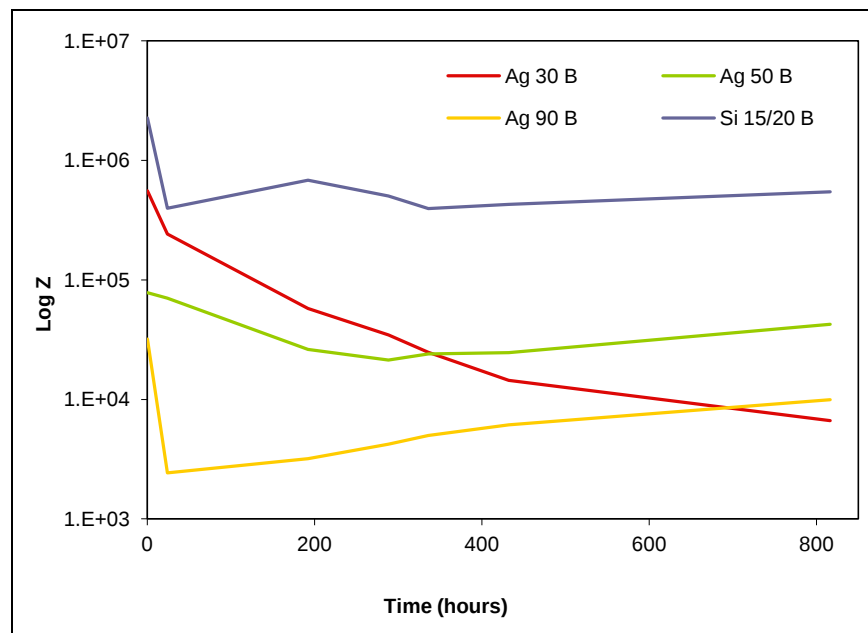


Figure 9. Low-frequency impedance vs. time for AA2024-T351 samples.

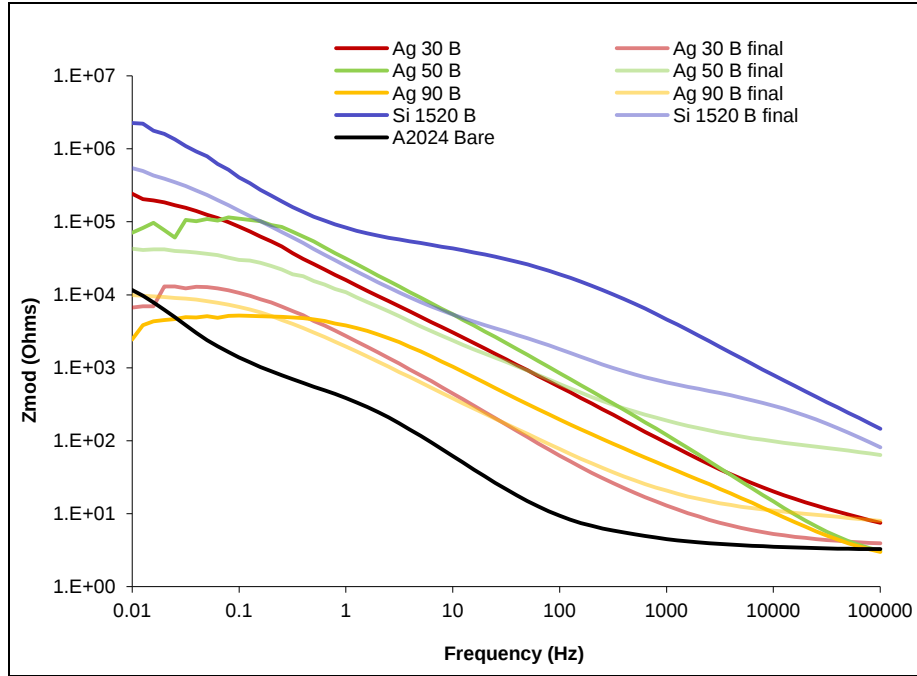


Figure 10. Initial and final Bode plots of AA2024-T351 samples.

Figure 7 shows that all of the coating variations on this alloy appear to provide at least some initial corrosion protection for the substrate. Two of the coating samples (Si80A, Si50A) provide nearly identical corrosion protection while the Ag50A curve shows a similar trend, although at a slightly lower value of impedance. These samples appear to display no major coating degradation over the 800-h test interval. Sample Ag30A showed steady decline over time indicating that the barrier properties are diminishing and that the coating is less robust than the two Si coatings and the Ag50A. Given that the Ag75A sample is a thicker coating than the Ag50A, it would be expected to behave similarly, but perhaps at a lower impedance. However, the inconsistency of the data indicates that Ag75A either may have had defects initially or there was some outside noise affecting the data.

Figure 8 shows the initial and final EIS measurements of the coatings on AA5083. The final Bode plot was taken following 1024 h of continuous static exposure to the 5% salt solution. The slopes show the relative performance of each coating sample versus bare AA5083 (black line) at the end of exposure—the higher the resistance the better the corrosion protection. Almost all maintained an impedance 2 orders of magnitude higher than bare AA5083 indicating good barrier protection was maintained throughout the exposure.

Figures 9 and 10 represent the EIS measurements for the anodic coatings on AA2024 aluminum. It is evident from comparing figures 7 and 8 with figures 9 and 10 that there is a significant difference in the corrosion inhibiting properties of the coatings on AA2024 versus the coatings on AA5083. Three of the four coatings on AA2024 are Ag. The Si 15/20B coating maintained the highest-impedance values throughout the test despite being the thinnest coating of the group.

Although the Ag50 on AA2024 showed the best performance of the Ag coatings, it was outperformed by the Si 15/20 B sample by nearly 1 order of magnitude. The Ag50 was the most consistent Ag coating on both substrates.

As with figure 8, the Bode plot in figure 10 represents data through 1024 h of static exposure to the 5% salt solution. The slopes here show the impedance of each coat sample variation at the beginning and end of exposure compared to bare initial AA2024. The Si 15/20 clearly maintained the highest-impedance levels. In fact, the impedance of this sample was nearly as high as some of the coatings on AA5083 (figure 8) indicating that it was providing a similar level of protection. This is supported by the results from the ASTM B 117 tests shown in table 3 and illustrated in figure 14.

The potentiodynamic polarization scans are shown in figures 11 and 12. Each of the samples was scanned from a cathodic polarization to an anodic polarization during polarization tests. It is known that when passivity forms on the metal surface the increasing rate of the anodic current density decreases dramatically (10). Thus, when the corrosion current density becomes stable (passivation current density) it indicates that a passivation film has formed on the surface of the sample. While the anodic current remains stable, the potential of the sample will increase continually until the potential reaches the breakdown potential where the passive film breaks down or dissolves into the electrolyte. At this point, the rate of the anodic-dissolution current rapidly increases. This trend can be clearly seen in the bare AA5083 sample in figure 11. Point (A) is the beginning of the passivation current density, and point (B) is where the anodic-dissolution current increase begins.

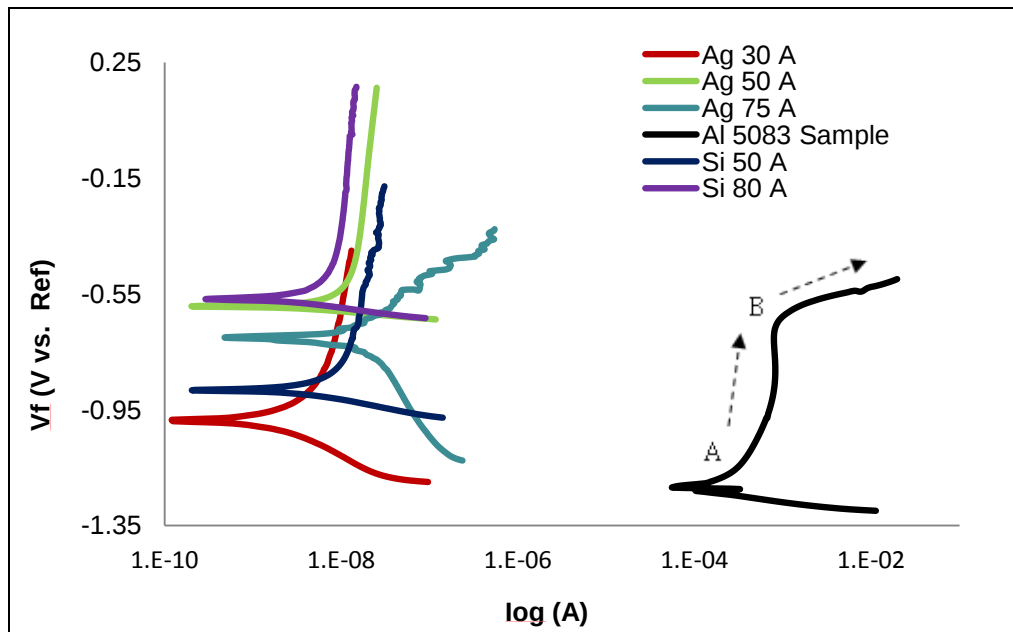


Figure 11. Potentiodynamic scan result for AA5083, voltage (vs. saturated calomel electrode [SCE]) vs. log current.

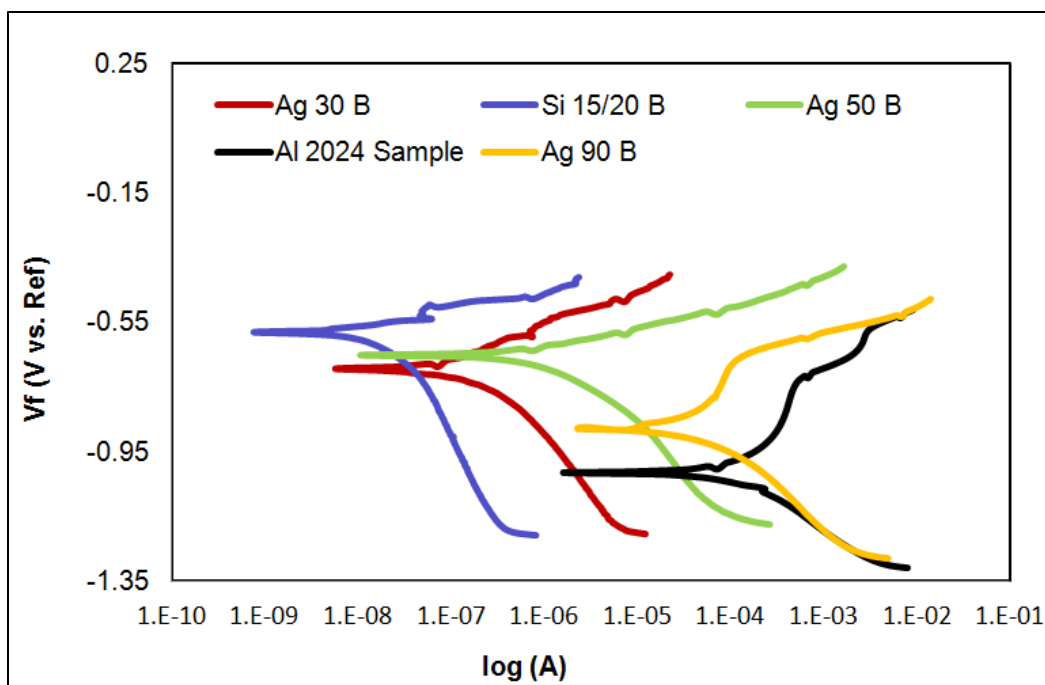


Figure 12. Potentiodynamic scan results for AA2024-T351, voltage (vs. SCE) vs. log current.

As for anodic samples in figure 11, it is evident that a dense passive layer exists on all but one of the samples. In the case of Ag75A, there does not appear to be a distinguishable point where the increasing rate of the anodic current density rapidly decreases, suggesting that the porous anodic coating has not been sealed properly. The impedance for the same coating shown in figure 7 suggests a similar trend. However, compared to the bare AA5083, all of the samples clearly have better corrosion resistance evidenced by their higher-corrosion potentials.

Very little if any passivation of the AA2024 samples can be seen in figure 12, indicating that there is active corrosion of the substrate occurring. That being said, it is also worth mentioning that the Si 15/20 coating has the highest-corrosion potential despite being the thinnest of all the anodic coatings on AA2024. Although it is well known that 2000 series aluminum alloys are susceptible to pitting, figure 14 shows that the Si 15/20 coating provided better protection against pitting than all the thicker Ag sealed anodic coatings. This is also consistent with what was seen in the impedance results in figures 9 and 10. The pitting of the 2000 series aluminum alloys is caused by the copper content, which is preventing a continuous anodic coating to grow on the surface of the substrate leaving behind many defects that contribute to the failure of the coating (11).

6.2 Accelerated Corrosion Testing

Accelerated corrosion tests were carried out according to ASTM B117 (6). Following ASTM D 1654-79A guidelines (7), table 3 shows the numerical value assigned to each sample based on the amount of corrosion formed. Si50A on AA5083 showed the best performance of all the coatings determined by the ratings shown in table 3. Conversely, Ag90B on AA2024 had the worst performance with over 40% of the surface area affected by corrosion.

Table 3. ASTM 1654 ratings for accelerated corrosion test ASTM B 117.

Panel Designation	Hours of Exposure				
	45	165	213	336	1024
AA5083 Substrate					
Ag30A	10	10	9	9	9
Ag50A	10	8	8	7	7
Ag75A	10	10	9	9	8
Si50A	10	10	10	10	10
Si80A	9	9	9	8	8
AA2024 Substrate					
Ag30B	9	8	7	7	6
Ag50B	8	7	7	7	7
Ag90B	6	5	4	3	2
Si15/20B	10	10	10	10	9

Figures 13 and 14 are photos of each sample taken at 0, 336, and 1032 h of ASTM B 117 exposure. The corners of each sample have been masked off in red Stop-Off sealant to cover bare substrate used to attach the leads for electrochemical testing.

It is well known that AA5083 is a more corrosion resistant alloy than the 2000 series aluminum. This is evident when comparing figures 13 and 14. All but the Si 15/20 coatings on AA2024 showed some pitting and corrosion products after only 336 h while the AA5083 samples showed only some minor staining following 1032 h of exposure.

The pitting caused by the copper-rich regions of AA2024 mentioned earlier is evident in the photographs of the samples in figure 14. There is significant pitting after only 336 h for all of the Ag sealed samples while the silicon-based sealant is only slightly affected after 1032 h. Again, this is in agreement with the previously discussed electrochemical results. After 1032 h of testing in ASTM B 117, the Si15/20B was the only coating that did not show noticeable corrosion on AA2024.

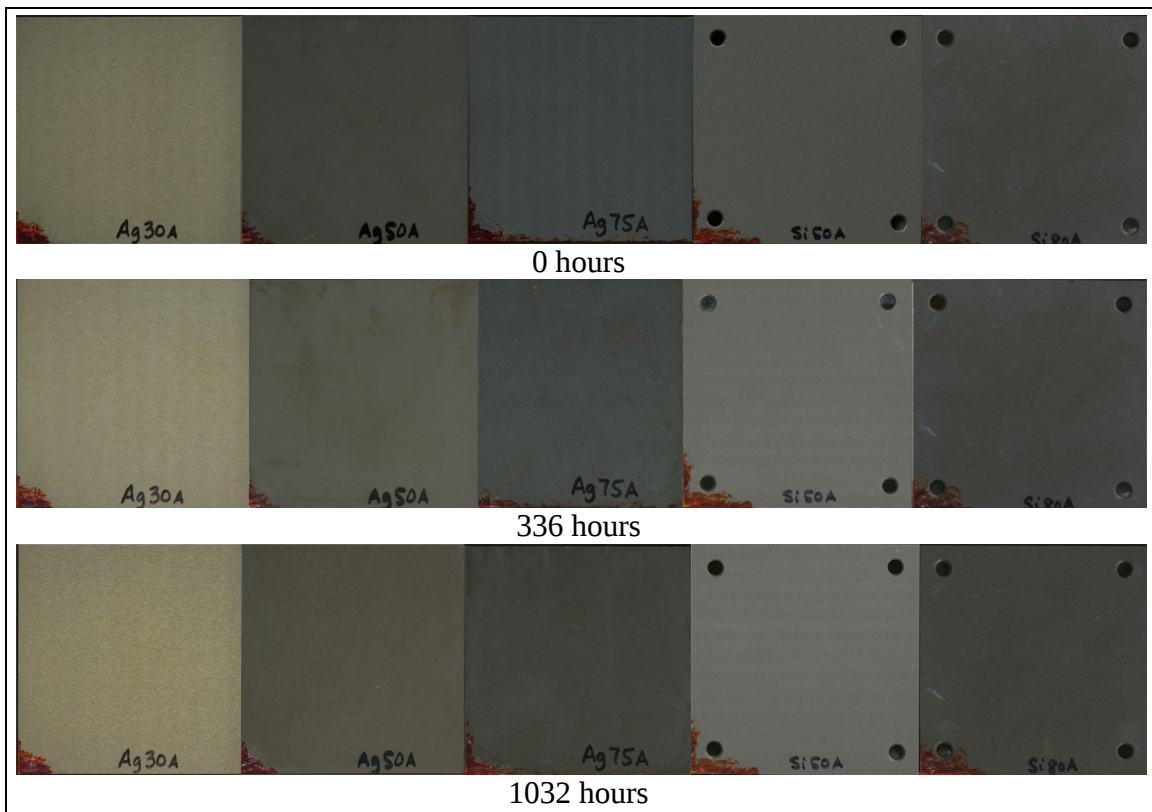


Figure 13. Coated AA5083 samples at three exposure intervals in the ASTM B117.

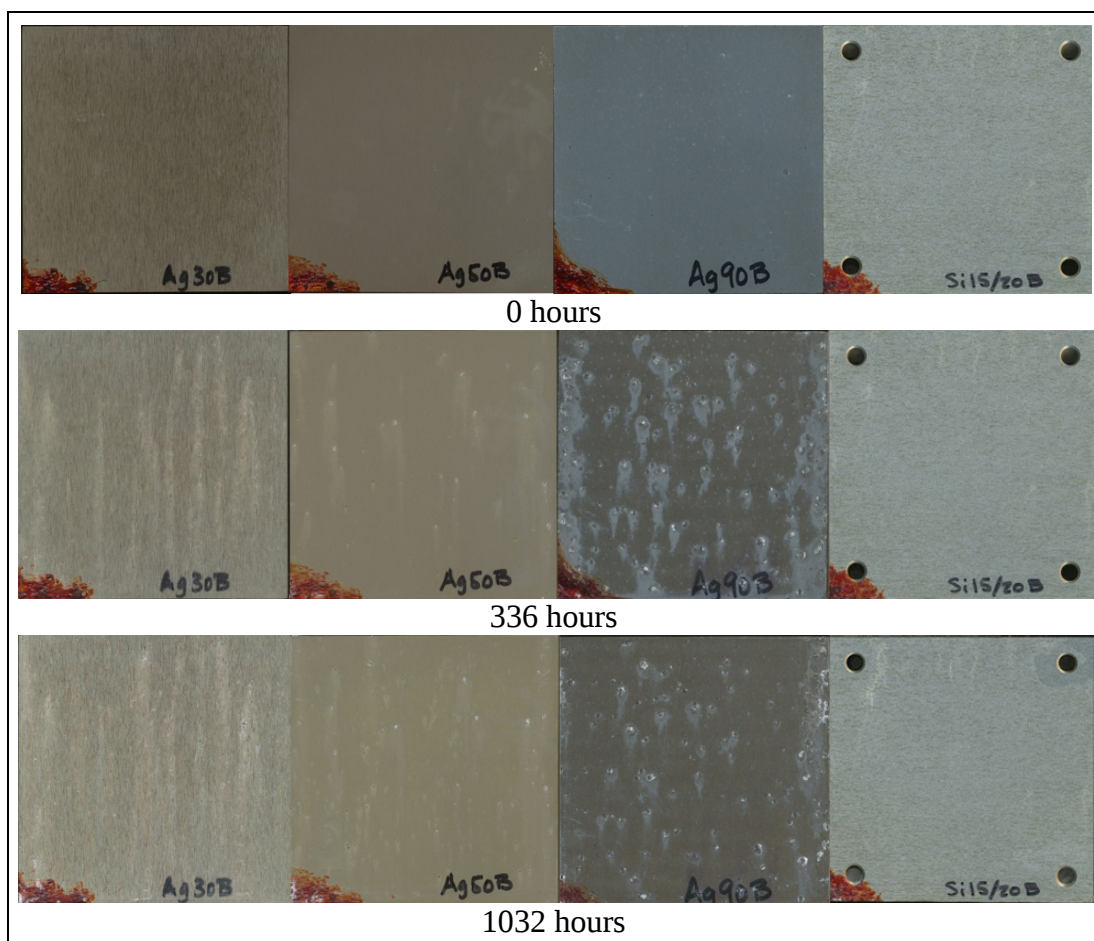


Figure 14. Coated AA2024-T351 samples at three exposure intervals in the ASTM B117.

6.3 Adhesion Testing

Finally, the paintability of the anodized samples was assessed by measuring the adhesion of an organic coating to the anodized substrate. In almost all cases, armor alloys are coated with CARCs; therefore, adequate adhesion of the organic coating to the substrate is critical to prevent premature coating delamination and subsequent corrosion. Figures 15 and 16 show two examples of the pull-off adhesion test results. The 3500 psi sample exceeded the range of the test apparatus. Figure 15 shows an adhesive failure of the coating at the substrate as well as cohesive failure within the coating itself. Figure 16 represents the coated anodic test sample and the pull-off adhesion dolly. On the left is the pull-off area of sample Ag90B (AA2024) and on the right is the dolly pulled off of that area at 1980 psi. The dolly represents a mirror image of the test sample on the left. In this case, it failed at 1980 psi at the anodic coating/aluminum substrate interface. The 1980-psi failure represents the lowest adhesion of all samples tested. Usually, the pull-off adhesion range of CARC primer to a typical chromate conversion coated substrate is between 1800 psi to 2400 psi. These samples are still well within that range.

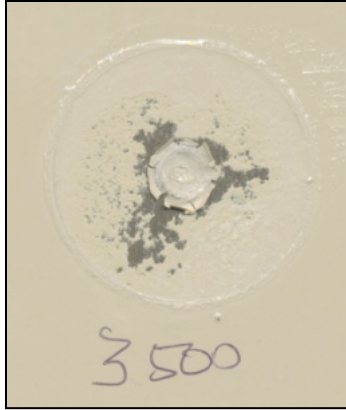


Figure 15. Pull-off area Ag30A (AA5083) sample pull off at 3500 psi.

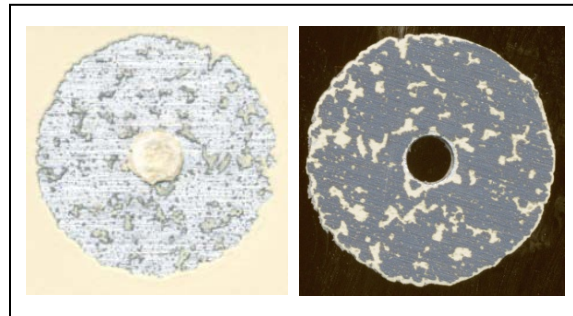


Figure 16. On the left is the pull-off area of sample Ag90B (AA2024). On the right is the dolly pulled off at 1980 psi.

All of the raw data for the ASTM D 4541 pull-off adhesion tests are listed in the appendix. The averages for each coating were plotted for comparison and are shown in figure 17. Ten data points per panel were obtained through HATE testing and averaged—these results are plotted along with a range of typical adhesion strength of chromate conversion coated aluminum. All adhesion values of the samples tested ranged from 1980 to approximately 3500 psi. The highest-adhesion values exceeded the limits of the HATE tester, which is 3500 psi. The adhesion of the organic coatings to the anodic coatings for all the tested samples fell within the range dictated by good adhesion of coatings to a typical chromate conversion coated aluminum sample represented by the gray shaded area on the bar chart.

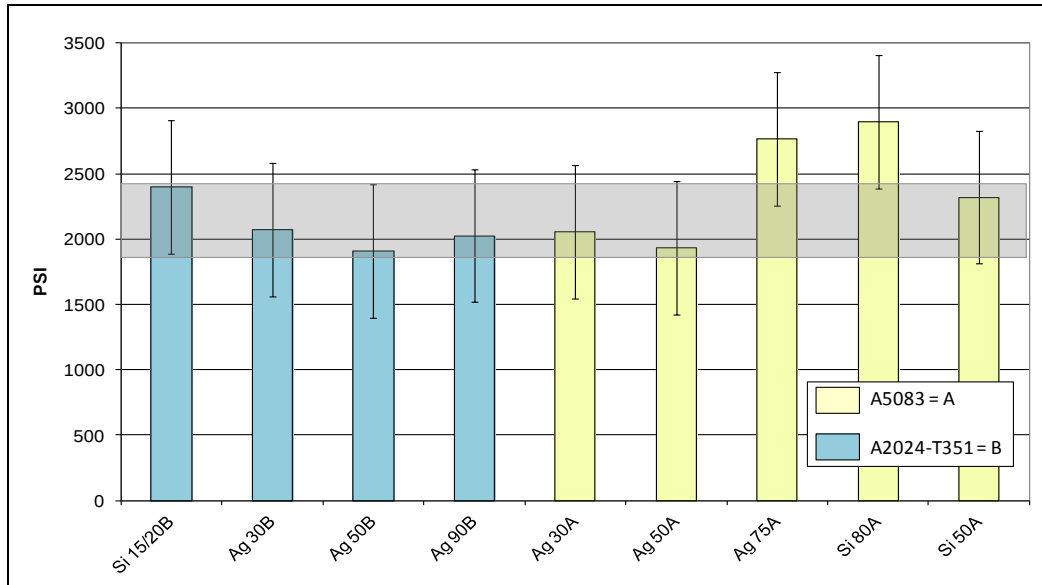


Figure 17. ASTM D 4541 average pull-off adhesion results. Shaded area represents the typical pull-off adhesion strength of chromate pretreated aluminum substrates.

7. Conclusions

- All coatings provided good barrier protection for AA5083 initially, however only Si80A, Si50A, and Ag50A proved to maintain good barrier protection beyond 800 h of exposure.
- There is no correlation between coating thickness and corrosion protection. The thicker coatings did not necessarily provide the best barrier protection. This was the case with both alloy substrates.
- The copper-rich phase of AA2024 likely affected proper growth of these particular anodic coatings and contributed to their poor performance. Of the coatings tested on AA2024, only the Si 15/20 coating performed adequately on this alloy.
- All of the coatings provided a good adhesive surface sufficient for military coatings. All met or exceeded historical values for the epoxy primer on conventional chromated conversion coated Al alloys.

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Appendix. Table of the Raw Data for Adhesion Test Results

This appendix appears in its original form, without editorial change.

Alloy	Designation	Pull-Off Strength (PSI)										Average (PSI)	STD DEV
		1	2	3	4	5	6	7	8	9	10		
2024	Ag30B	3000	2800	2520	2890	2200	1780	2600	2050	1950	2190	2398	422.68
2024	Ag50B	2780	3000	2090	2170	1790	2050	1400	1550	2200	1710	2074	508.14
2024	Ag90B	1980	2200	1980	1730	1680	1950	1800	1810	1700	2250	1908	200.71
2024	Si15/20B	2080	2500	2050	1420	1900	2700	1690	1320	2000	2600	2026	472.23
5083	Si50A	3100	2250	2300	2600	1000	1720	1600	1600	2750	1650	2057	647.51
5083	Ag50A	3500	2000	2000	2410	1520	1700	1510	1100	2400	1200	1934	710.64
5083	Ag30A	2700	2950	2830	2920	1050	3000	3000	2900	2790	3500	2764	639.22
5083	Si80A	3100	3100	2600	2900	2890	2550	2875	2550	3400	3000	2897	273.98
5083	Ag75A	3200	1950	2730	2300	1900	1610	1720	1600	3700	2500	2321	713.01
												avg stdev	509.79

List of Symbols, Abbreviations, and Acronyms

Ag	silver
CARC	chemical agent resistant coating
CCPE	Corrosion Control and Prevention Executive
Cr ⁶⁺	hexavalent chromium
DC	direct current
DFT	dry film thickness
DOD	Department of Defense
EIS	electrochemical impedance spectroscopy
h	hour
HATE	Hydraulic Adhesion Test Equipment
in	inch
NaCl	sodium chloride
OCP	open circuit potential
OSD	Office of the Secretary of Defense
PEO	Program Executive Office
psi	pounds per square inch
SCE	saturated calomel electrode
Si	silicon
μm	micrometers

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