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Managing Water in the West

Preliminary Investigation of Corrosion Resistant Primers with Duplex Coatings Systems

Research and Development Office
Science and Technology Program
(Final Report) ST-2018-1850, 8540-2018-72

U.S. Department of the Interior
Bureau of Reclamation
Research and Development Office

December 2018

Mission Statements

Protecting America's Great Outdoors and Powering Our Future

The Department of the Interior protects and manages the Nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its trust responsibilities or special commitments to American Indians, Alaska Natives, and affiliated island communities.

REPORT DOCUMENTATION PAGE		*Form Approved* *OMB No. 0704-0188*
T1. REPORT DATE: DECEMBER 2018	**T2. REPORT TYPE:** RESEARCH	**T3. DATES COVERED**
T4. TITLE AND SUBTITLE Preliminary Investigation of Corrosion Resistant Primers with Duplex Coatings Systems		**5a. CONTRACT NUMBER** 18XR0680A1-RY15412018WI31850 **5b. GRANT NUMBER** **5c. PROGRAM ELEMENT NUMBER** 1541 (S&T)
6. AUTHOR(S) Dave Tordonato, 303-445-2394, dtordonato@usbr.gov		**5d. PROJECT NUMBER** ST-2018-1850 **5e. TASK NUMBER** **5f. WORK UNIT NUMBER** 86-68540
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials and Corrosion Lab, Technical Service Center U.S. Department of the Interior, Bureau of Reclamation, PO Box 25007, Denver CO 80225-0007		**8. PERFORMING ORGANIZATION REPORT NUMBER** 8540-2018-72
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Research and Development Office U.S. Department of the Interior, Bureau of Reclamation, PO Box 25007, Denver CO 80225-0007		**10. SPONSOR/MONITOR'S ACRONYM(S)** **R&D:** Research and Development Office **BOR/USBR:** Bureau of Reclamation DOI: Department of the Interior **11. SPONSOR/MONITOR'S REPORT NUMBER(S)** ST-2018-1850-01
12. DISTRIBUTION / AVAILABILITY STATEMENT **Final report can be downloaded from Reclamation's website: https://www.usbr.gov/research/**		
13. SUPPLEMENTARY NOTES		

14. ABSTRACT ***(Maximum 200 words)***

Recent research by Reclamation's Materials and Corrosion lab investigated vinyl resin coatings, a coating system traditionally used within Reclamation for severe service environments, with an aim of identifying potential replacements. To achieve the service life realized by vinyl coatings, replacements must not only provide outstanding barrier properties that do not diminish over time, but they must also provide excellent adhesion and disrupt the corrosion process at the substrate-coating interface. This prior research identified several materials, both thermoplastic and thermoset, that provided the desired barrier properties but failed to prevent interfacial corrosion. The next step is to create a system that combines a corrosion-resistant primer with a barrier coating to create a long-lasting solution for corrosion protection that is both non-toxic and low-VOC to meet modern day safety, health, and environmental standards. This year, initial research was performed on several materials which were previously tested in the vinyl study. The goal was to compare the laboratory results of the products tested both with and without corrosion inhibitors. The results of this scoping study were used to guide a research proposal for FY19-21.

15. SUBJECT TERMS Corrosion protection, barrier coatings, corrosion inhibitors, duplex coatings, coatings for severe atmospheric service, electrochemical impedance spectroscopy					
16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT** U	**18. NUMBER OF PAGES** 45	**19a. NAME OF RESPONSIBLE PERSON** David Tordonato
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U			**19b. TELEPHONE NUMBER**

BUREAU OF RECLAMATION

Research and Development Office
Science and Technology Program

Materials and Corrosion Laboratory, Technical Service Center,

86-68540

(Final Report) ST-2018-1850, 8540-2018-72

Preliminary Investigation of Corrosion Resistant Primers with Duplex Coatings Systems

Digitally signed by DAVID TORDONATO
Date: 2019.01.07 12:54:32 -07'00'

Prepared by: David Tordonato Ph.D.
Materials Engineer, Materials and Corrosion Laboratory, Technical Service Center, 86-68540

RICHARD PEPIN Digitally signed by RICHARD PEPIN
Date: 2019.01.07 14:34:41 -07'00'

Checked by: Richard Pepin, PCS
Materials Engineer, Materials and Corrosion Laboratory, Technical Service Center, 86-68540

ALLEN SKAJA Digitally signed by ALLEN SKAJA
Date: 2019.01.07 14:01:10 -07'00'

Technical Approval: Allen Skaja, Ph.D.
Chemist, Materials and Corrosion Laboratory, Technical Service Center, 86-68540

BOBBI JO MERTEN Digitally signed by BOBBI JO MERTEN
Date: 2019.01.07 13:17:46 -07'00'

Peer Review: Bobbi Jo Merten, Ph.D.
Civil Engineer, Materials and Corrosion Laboratory, Technical Service Center, 86-68540

Acknowledgements

The authors would like to acknowledge the coatings manufacturers in the study who provided coated test samples to Reclamation free of charge for testing evaluation purposes. Thank you to Blome International and Premier Coating Systems for their support and participation in this study.

Acronyms and Abbreviations

DI	deionized water
EIS	electrochemical impedance spectroscopy
HAR	dilute Harrison's solution
Reclamation	Bureau of Reclamation
S&T	Science and Technology Program
USACE	United States Army Corps of Engineers
VOC	volatile organic compounds

Executive Summary

Anticorrosion paints are a type of protective coating with the potential to increase service life and lower lifecycle costs on water infrastructure. Originally, many structures at Reclamation were coated with a lead or chromate-based primer. Equipment subject to this environment can see extended periods of moisture resulting from condensation, seepage past seals, or even intermittent immersion from reservoir fluctuations. Examples include radial gates, valves, gate stems, float weights, hoists equipment, handrails, tank exteriors and various piping systems in and around dam facilities. Lead and chromate act as corrosion inhibitors but have been largely phased out due to their toxicity. Most modern coatings designated for atmospheric service rely on barrier properties or sacrificial pigments to slow down corrosion by preventing the ingress of water to the metal substrate or galvanic protection of the steel. However, anti-corrosion additives can work in tandem with barrier coatings to further increase effectiveness and potentially extend service life. A literature review performed in FY 2017 identified several products now used as lead and chromate replacements for industrial maintenance painting. This report details the results of a scoping study intended to screen for effectiveness among several products:

Study 1: Aromatic polyurethane

1. Polyurethane control
2. Polyurethane with zinc-rich urethane primer

Study 2: Polysulfide epoxy

1. Anti-corrosion pigment - zinc phosphate
2. Anti-corrosion pigment - zinc phosphate & Raybo 85
3. Anti-corrosion pigment - Raybo 85
4. Control with no anti-corrosion - epoxy polysulfide barrier coating

Laboratory testing in both studies showed excellent rust creep resistance in immersion testing but no performance increase in prohesion testing when compared to the respective control. Barrier properties as measured by electrochemical impedance spectroscopy were not affected by the addition of an anti-corrosion additive or primer. Additional testing is needed to verify these results and expand the laboratory testing to include additional anti-corrosion additives such as pure zinc and other inhibitors as well as a system consisting of a zinc-rich primer, epoxy barrier coat and an aliphatic polyurethane topcoat to be used as a benchmark.

Subsequent research should expand the screening test into a full study to properly evaluate the materials for incorporation into Reclamation's Guide Specifications. In addition, a partnership with the U.S. Corps of Engineers (USACE) will allow for natural atmospheric testing in a real-world exposure test at USACE's Kwajalein Atoll test site. Results for this test site should be compared with accelerated laboratory test results.

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Background

Much of Reclamation's equipment is subject to variable conditions ranging from atmospheric service to fluctuating immersion. Equipment in this environment can see extended periods of moisture resulting from condensation, seepage past gate seals, or even intermittent immersion from reservoir fluctuations. Examples include radial gates, valves, gate stems, float weights, hoist equipment, handrails, tank exteriors, and various piping systems in and around dam facilities. To mitigate corrosion, increase service life, and lower lifecycle costs, the historical designs for these structures primarily included lead or chromate-based primers. Both act as corrosion inhibiting agents in paint by disrupting the corrosion reaction for water infrastructure but have been largely phased out due to their toxicity to humans and wildlife. Today, most modern coatings designated for atmospheric service rely on barrier or sacrificial pigments such as zinc to slow down corrosion. The former works by preventing the ingress of water to the metal substrate while the latter provides galvanic protection to the steel.

Zinc-rich Primers

Zinc is a well-known additive that provides cathodic protection to steel substrates in coatings intended for atmospheric service. In contrast to an inhibitor which disrupts the corrosion process, zinc acts as a sacrificial pigment by corroding preferentially to steel. A primary example of zinc use in coatings is the system commonly specified for bridge coatings which includes a zinc-rich organic epoxy, a solvent-borne epoxy barrier coating, and an aliphatic polyurethane topcoat. This system is sometimes used as a benchmark for the evaluation of new coating systems such as polysiloxanes. However, zinc is typically not recommended for immersion or fluctuating immersion service environments by manufacturers of crosslinked coatings. Reclamation has limited experience with laboratory testing of these systems.

Field experience has shown that solution vinyl resin coatings provide a long service life in a variety of immersion conditions. A recent laboratory study found that solution vinyl resin coatings retained high impedance levels during immersion but gave only "fair" rust creep resistance in cyclic "BOR" testing and prohesion testing [1]. Substituting zinc pigment into the vinyl system's primer layer enhanced performance in these tests by increasing resistance to rust creep and cathodic disbondment while maintaining a high impedance.

Previous Work

Anti-corrosion additives can also work in tandem with barrier coats to further increase effectiveness and potentially extend service life. A 2017 study funded by Reclamation's Science and Technology Program (S&T) surveyed the available literature on anti-corrosion coatings and identified several modern, commercially available anti-corrosion pigments being marketed for atmospheric service [inhibitor]. The report recommended performing laboratory evaluations on these products to determine their effectiveness and expected failure mechanisms.

Based on the findings of Reports ST-2017-8835-1 and ST-2017-1703 [1, 2], a new proposal was submitted to evaluate multi-coat systems that consist of a barrier coat in conjunction with a corrosion inhibitive primer i.e. a duplex system which could meet or exceed the performance of a three-coat benchmark system in atmospheric service or even splash zone environments. The rationale is that a duplex system may provide a long service life through a combination of barrier properties and undercutting (rust creep) resistance at coating defects. Another objective was to determine whether the performance of a 100% solids polyurethane coating could be improved by including a zinc-rich primer to facilitate increased adhesion and resistance to undercutting.

One product of interest was a 100% solids aromatic polyurethane that exhibited outstanding barrier properties in EIS, but performed poorly in the knife adhesion test and experienced high rust creep in the immersion and cyclic tests [1, 3]. An anti-corrosion primer could potentially address these shortcomings while retaining the high barrier properties.

Another previously tested product of interest was a 100% solids polysulfide-modified epoxy with a fluorinated polyurethane topcoat. This product also had excellent EIS properties and UV resistance but low impact resistance and somewhat poor rust creep resistance [1, 4]. An aluminum pigmented version of the same product with no topcoat showed better rust creep resistance but reduced barrier performance indicating the barrier properties are enhanced with the addition of an aliphatic polyurethane topcoat [1, 5]. The polysulfide epoxy is of interest because it possesses greater flexibility than a typical polyamide epoxy. Solution vinyl resin coatings also exhibit a high degree of flexibility due to its amorphous structure, which relies on chain entanglement instead of cross-linking for mechanical properties. One theory to explain the effectiveness of vinyl is that as a thermoplastic, it is better able to accommodate the repeated stresses to the polymer network caused by water molecule migration during wetting and drying cycles. Although a polysulfide epoxy is still a crosslinked material, perhaps the increased elongation could more effectively resist chain scission during intermittent immersion service. In addition, the material might be better able to accommodate dimensional changes associated with the oxidation of the zinc pigment during service in immersion. The polysulfide material warranted additional study for this reason.

The goal of the current scoping study was to further refine the scope of future testing and submit a more comprehensive conducting proposal for FY19. As such, a limited test program proceeded for the polyurethane and the polysulfide epoxy systems.

Method

This scoping study presents two separate laboratory evaluations. The first evaluation tested the inclusion of a zinc-rich primer for the polyurethane product originally tested in report 8540-2017-013 [3]. The second study expanded on the polysulfide epoxies whose results are detailed in reports 8540-2017-024 and 8540-2017-025 [4, 5]. Because four products were evaluated in the latter evaluation, a decision was made to abbreviate the testing into a screening test. The protocol for the screening test and full test are explained in detail in the proceeding section. In both evaluations, Reclamation supplied prepared steel substrates to the manufacturers who performed the product application. Surface preparation included solvent cleaning (SSPC SP-1) and abrasive blasting to white metal (SSPC SP-5) using steel grit to achieve an angular surface profile of 3 mils.

Zinc-rich polyurethane

A zinc-rich moisture-cured urethane primer, and 100% solids aromatic polyurethane topcoat were selected for this study. The goal was to determine whether the addition of a zinc-rich primer could prevent or reduce rust creep and improve knife adhesion performance. This system was applied in two coats with a target thickness of 1-2 mils for the primer (MCU1) and 35-40 mils for the aromatic polyurethane barrier coating (PU1).

Polysulfide epoxy

The goal of the polysulfide evaluation was to determine whether the addition of one or more anti-corrosion pigments to the polysulfide epoxy could increase rust creep resistance while retaining the barrier protection of the aliphatic polyurethane topcoat. The previously tested products are shown in Table 1.

Table 1: Description of the previously tested polysulfide-modified epoxy coating systems.

System ID	Anticorrosion additive (primer)	Primer	Topcoat	Report
EP5	Aluminum flake	Polysuflide-modified epoxy	N/A	8540-2017-025 [5]
EP+ALPU	None	Standard formula: Polysuflide-modified epoxy TiO_2, glass flake pigment.	Fluorinated polyurethane topcoat with aluminum flake pigment	8540-2017-024 [4]

The materials shown in Table 1 provided very low energy absorption in impact testing due to the soft polysulfide modified primer resin. The decision was made to slightly to reduce the polysulfide content to strike a balance between a rigid/brittle polyamide epoxy and a resin that is too soft to withstand mechanical damage. In addition, the aluminum flake pigments were replaced with traditional pigments (TiO_2 and glass flake) per manufacturer's standard formula at their suggestion. Table 2 provides designations and details for the coatings tested. The product manufacturer applied the coatings in December, 2017 with an average DFT of 14 mils for the system.

Table 2: Description of the experimental polysulfide epoxy coating products evaluated.

System ID	Anticorrosion additive (primer)	Barrier pigment (primer)	Topcoat
X1	Anti-corrosion pigment - zinc phosphate	Glass flake reduced by 5%, TiO_2 reduced by 50%	Fluorinated polyurethane topcoat (gray)
X2	Anti-corrosion pigments - zinc phosphate & Raybo 85	Glass flake reduced by 5%, TiO_2 reduced by 50%	
X3	organic anti-corrosion pigment - Raybo 85	TiO_2, glass flake. No change from standard formula	
X4	Control (polysulfide epoxy barrier coating with no anti-corrosion pigment)	TiO_2, glass flake. No change from standard formula	

Panels and Testing

A simplified screening protocol was utilized in evaluation of the polysulfide epoxies whereas the polyurethanes were subject to the full test program. Table 3 shows the screen test program compared to the traditional corrosion evaluation.

Table 3: Corrosion test protocol summary, number of 3"x6"x1/8" panels scribed/unscribed (denoted as "s" and "u" respectively) used for each test.

System ID	Immersion Exposure		Cyclic Exposure			
	Dilute Harrison (HAR)[1]	Deionized Water (DI)[2]	Prohesion (PRO)[3]	Immersion + Salt Fog + QUV (BOR)[4]	Salt Fog (FOG)[5]	UV + Condensation (QUV)[6]
PU1, MCU1 +PU1 (full)	2s/1u	2s/1u	2s/1u	2s/1u	1s/1u	2s/1u
X1, X2, X3, X4 (screen)	1s (backside)	1s (backside)	2s	N/A	N/A	N/A

[1] ASTM D870: Dilute Harrison's Solution (HAR) is water with 0.5 g/L NaCl, 3.5 g/L NH_42SO_4, testing performed at room temperature
[2] ASTM D870: DI water, testing performed at room temperature
[3] ASTM D5894: 1 week alternating exposure schedule in the following repeating order: QUV, FOG
[4] 1 week alternating exposure schedule in the following repeating order: QUV, FOG, HAR, FOG
[5] ASTM G85 Annex A5: 1 hr fog at ambient using HAR solution, 1 hr dry-off at 35 C.
[6] ASTM D 4587: Test condition "B" 4 h UV/60 C followed by 4 h Condensation/50C

For the polysulfide tests, Reclamation received five (5) coated panels for each system. A topcoat was only applied on one side of the panel. The number of samples and DFT measurements are provided in Appendix A. All corrosion testing was conducted for a duration of 30 weeks plus any makeup time needed for equipment downtime.

At the end of the test, panels were scraped from the scribe to remove loose coating out to the white metal. The rust creep for each panel was determined by measuring using a caliper after coating removal. For immersion samples, the maximum value was measured and reported. For cyclic testing, the full width of the rust area was measured on each panel at six predetermined locations along the scribe and averaged. The result is adjusted for the scribe width and divided by two.

In addition to corrosion testing, Table 4 shows the mechanical testing performed for the full and screening tests, respectively.

Table 4: Mechanical test protocol and substrates utilized for testing.

System ID	Cathodic Disbondment ASTM G8	Erosion Resistance USBR-5071-2015	Abrasion Resistance ASTM D 4060[1]	Impact Resistance ASTM D2794[2]	Pull-off Adhesion ASTM D4541	Pull-off Adhesion (wet) ASTM D4541	Knife adhesion test (wet) ASTM D6677[3]
PU1, MCU1+ PU1 (screen)	3-inch diam. pipe	2 – 11"diam. discs (PU1 only)	2 – 4" diam. discs	3"x6"x1/8" coupon(s)	3"x6"x1/8" coupon	3"x6"x1/8" coupon	DI and HAR
X1, X2, X3, X4 (full)	N/A	N/A	N/A	3"x6"x1/8" coupon	N/A	N/A	N/A

[1]ASTM D4060 weight loss measured after 1000 cycles, CS-17 wheels resurfaced after 500 cycles, 1 Kg load
[2]Test performed on 1/8-inch thick steel panels.
[3]Test performed on HAR and DI panels, post immersion.

Results

Zinc-rich polyurethane

Figure 1 and Figure 2 and show side by side comparisons of the HAR and DI immersion panels after coating removal. Note that coating removal beyond the rusted area was easily accomplished in both systems. There is notable rust creep on the DI panel in the case of the PU1 and none observed in the zinc rich system. Note that the PU1 was tested for 12 ½ months prior to coating removal and the creep values were prorated to 7 months. Therefore, there is less confidence in a direct comparison between these two systems, but it can be stated that the zinc does appear to reduce or eliminate rust creep in both cases.

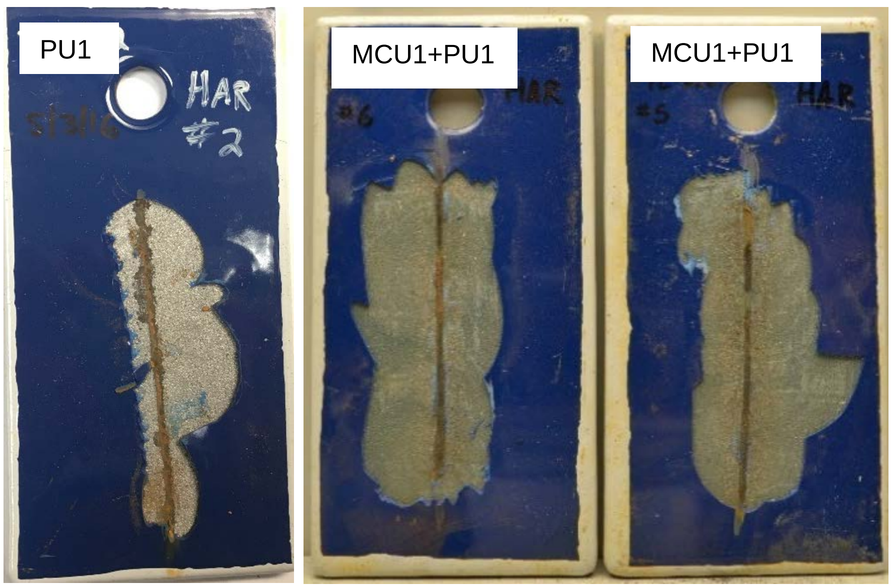

Figure 1: HAR rust creep results after coating removal for PU1, 12 ½ months (left) and MCU1+PU1, 7 months (right).

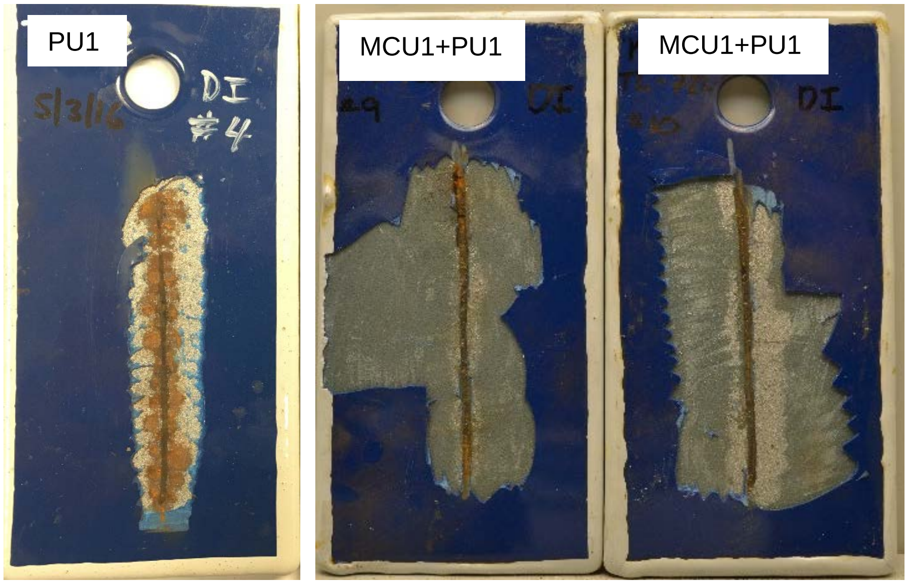

Figure 2: DI rust creep results after coating removal for PU1, 12 ½ months (left) and MCU1+PU1, 7 months (right),

Figure 3 and Figure 4 show a side by side comparison for the prohesion test and BOR test respectively. Note that coating removal beyond the rusted area was easily accomplished in both systems. The prohesion panels with a zinc primer showed a marked improvement but the BOR panels appear mostly unchanged.

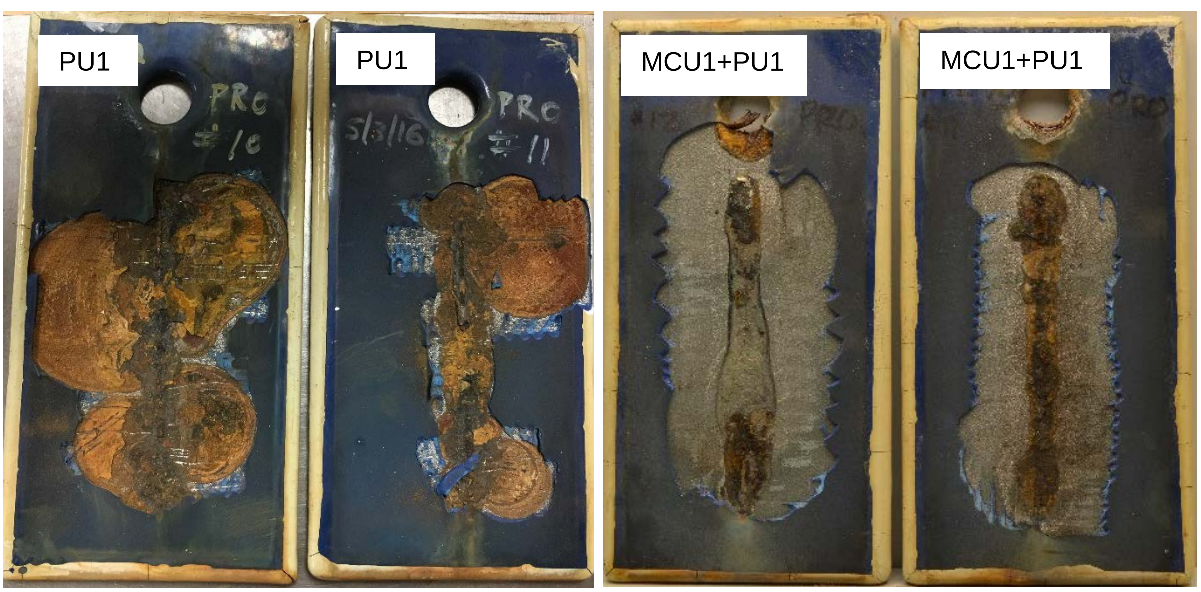

Figure 3: Prohesion rust creep after coating removal for PU1 (left) and MCU1+PU1 (right)

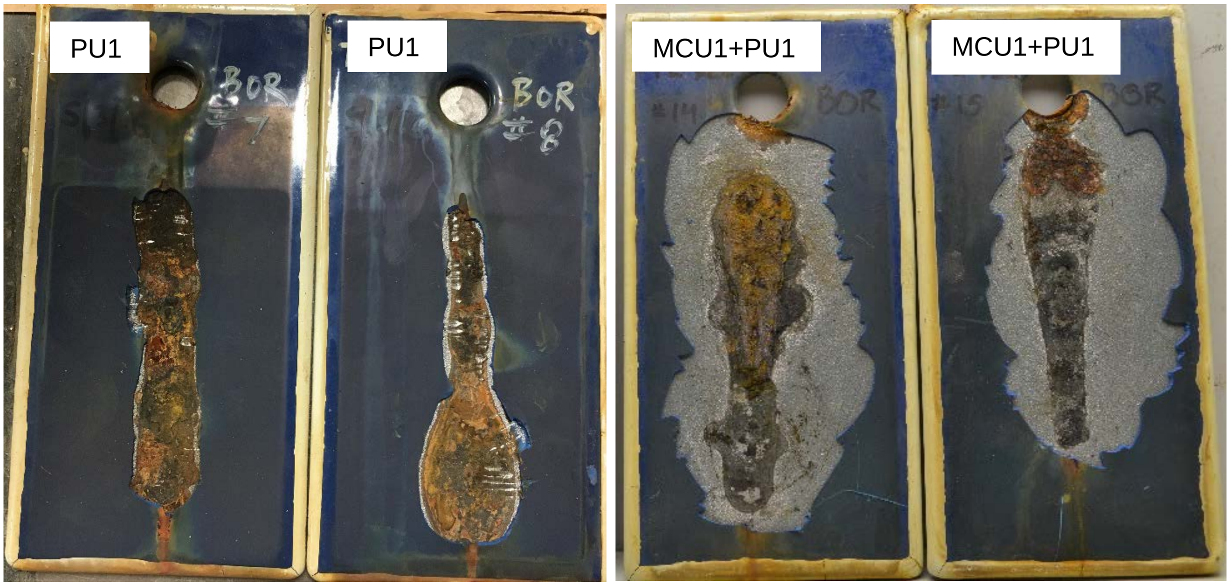

Figure 4: BOR rust creep results after coating removal for PU1 (left) and MCU1+PU1 (right)

Figure 5 and Figure 6 show the show a side by side comparison for the FOG and QUV exposure tests respectively. The FOG panels with a zinc primer showed an improvement but the QUV panels appear mostly unchanged with no rust creep observed on either system. Chalking and loss of gloss resulted in a “fair” rating for both panels in QUV testing.

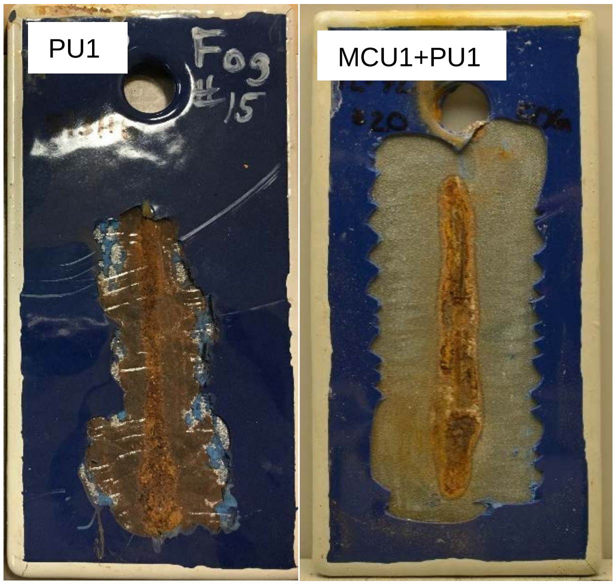

Figure 5: FOG rust creep results after coating removal for PU1 (left) and MCU1+PU1 (right)

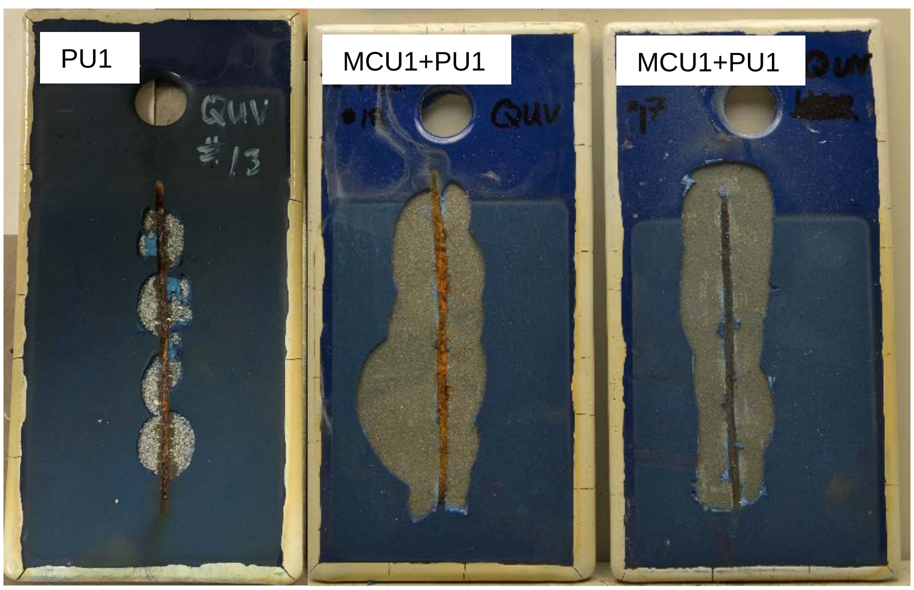

Figure 6: QUV rust creep results after coating removal for PU1 (left) and MCU1+PU1 (right)

The EIS results for PU1 were reported previously and were considered to excellent with final impedance of approximately $1x10^{10}$ ohms and the material experiencing no degradation after 11 months in immersion [6]. The EIS results for MCU1+PU1 are shown in Figure 7 and are also considered to be excellent.

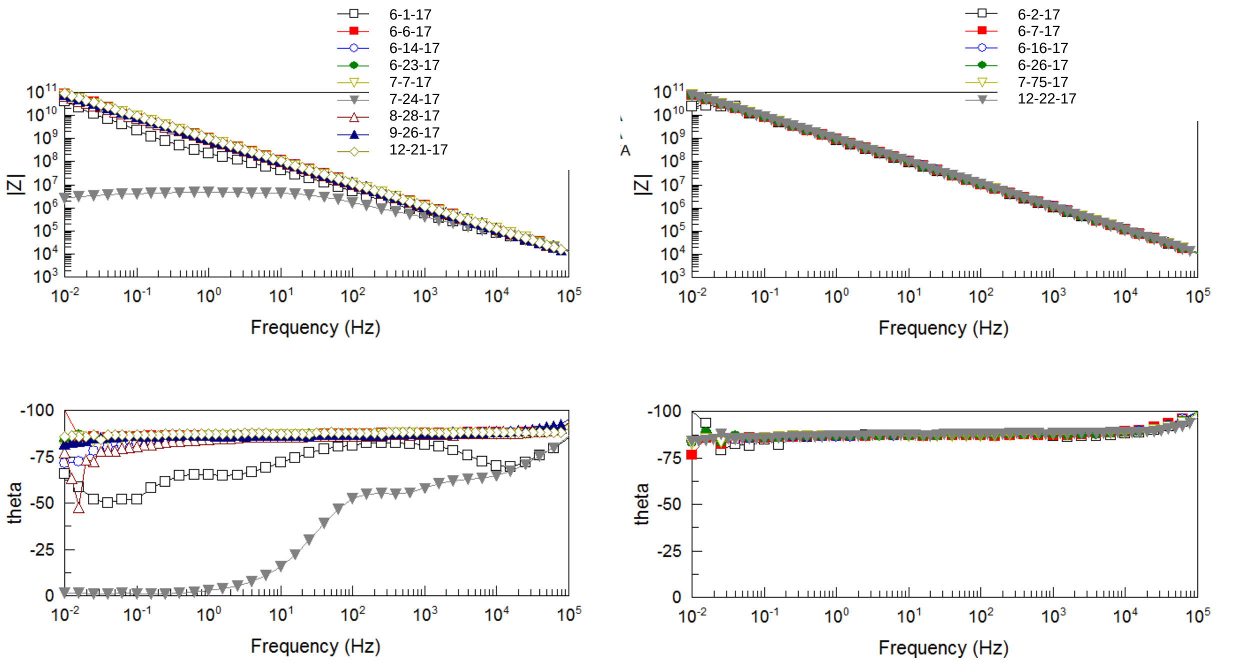

Figure 7: EIS data for MCU1+PU1 in HAR Immersion (left) and DI Immersion (right). Approximate degradation after 30 weeks: Both the HAR and DI panel increased around half an order of magnitude @ 10^{-2} Hz.

Both systems demonstrated excellent barrier properties that were maintained over a 30-week testing period so the inclusion of a zinc-rich primer did not appear to negatively affect the barrier properties of the polyurethane.

Table 5 summarizes the corrosion results for the polyurethane. Rust creep data for the two cyclic tests (prohesion and BOR) are listed as the average value measured over two panels at evenly spaced locations. There is typically a much lower amount of rust creep seen in immersion versus the cyclic exposure tests making the average difficult to report. For this reason, rust creep for the HAR and DI immersion tests are listed as the maximum measured value and the average value is reported for the cyclic tests. Note that because PU1 and MUC1+PU1 were tested for different durations, it was necessary to prorate the PU1 data using linear interpolation for comparison.

Table 5: Measured rust creep in inches and assigned score for polyurethane with and without a zinc-rich primer.

System ID	Immersion Exposure		Cyclic Exposure			
	Dilute Harrison (HAR)[1]	Deionized Water (DI)[2]	Prohesion (PRO)[3]	Immersion + Salt Fog + QUV (BOR)[4]	Salt Fog (FOG)[5]	UV + Condensation (QUV)[6]
PU1	0.08-inch* (good)	0.15-inch* (fair)	0.73-inch (poor)	0.24-inch (good)	0.40-inch (fair)	0.03-inch (fair)
MCU1+ PU1	0.03-inch (good)	0.00-inch (excellent)	0.17-inch (good)	0.34-inch (fair)	0.17-inch (fair)	None (fair)

[1] ASTM D870: Dilute Harrison's Solution (HAR) is water with 0.5 g/L NaCl, 3.5 g/L NH_42SO_4, testing performed at room temperature
[2] ASTM D870: DI water, testing performed at room temperature
[3] ASTM D5894: 1 week alternating exposure schedule in the following repeating order: QUV, FOG
[4] 1 week alternating exposure schedule in the following repeating order: QUV, FOG, HAR, FOG
[5] ASTM G85 Annex A5: 1 hr fog at ambient using HAR solution, 1 hr dry-off at 35 C.
[6] ASTM D 4587: Test condition "B" 4 h UV/60 C followed by 4 h Condensation/50C
* Prorated value from 12.5 to 7 months

Interestingly, the system with a zinc-rich primer (MCU1+PU1) showed much improved performance in the prohesion cyclic test but fared slightly worse in the BOR test.

Table 6 gives a comparison of the mechanical property-related test results for the two systems. Cathodic disbondment and knife adhesion both appeared to be similar, whereas abrasion and impact resistance were diminished. The latter two tests could be a result of variability between application conditions or technique. The adhesion comparison is somewhat inconclusive due to the glue failures observed in the direct to metal (PU1) application. A glue failure indicates that coating adhesion exceeds the strength of the dolly's adhesion to the coated surface. Therefore, it is inferred that coating adhesion in the direct-to-metal (PU1) wet adhesion test is at least 922 +/- 354 psi. Since the MCU1+PU1 averaged 1065 +/-132 psi in wet adhesion with an adhesive / cohesive failure, wet adhesion was not significantly increased with the addition of a zinc-rich primer.

Table 6: Mechanical properties test results for PU1 with and without a zinc-rich primer

Test	Test Metric	PU1		MCU1+PU1	
		Result	Score	Result	Score
Cathodic Disbondment ASTM G8	Disbondment radius, inches	0.56	Fair	0.5	Good
Erosion Resistance USBR-5071-2015	Stabilized weight loss rate, g/hr	0.005	Excellent	Not tested	N/A
Abrasion Resistance ASTM D 4060[1]	Total weight loss, mg	11.9	Excellent	61 mg	Fair
Impact Resistance ASTM D 2794[2]	Threshold with no cracking or holidays, inch-lbs	160	Excellent	80	Fair
Pull-off Adhesion ASTM D4541	Stress, Psi Failure Mode[4]	965 +/- 141 g	No score given	1614 +/- 313 adh	Good
Pull-off Adhesion (wet) ASTM D4541	Stress, Psi Failure Mode[4]	922 +/- 354 g	No score given	1065 +/- 132 g/adh/coh 0/73/27	Good
Knife Adhesion (wet) ASTM D6677[3]	ASTM Rating (0-10)	2	Poor	0	Poor

[1]ASTM D4060 weight loss measured after 1000 cycles, CS-17 wheels resurfaced after 500 cycles, 1 Kg load
[2]Test performed on 1/8-inch thick steel panels.
[3]Test performed on HAR and DI panels, post immersion.
[4] Adhesion (adh), cohesion (coh), intercoat (ic), glue (g). 20% > glue failure is not scored

Polysulfide epoxy

Figure 6 shows the panels after prohesion testing after coating removal for the previously tested materials (EP5 and EP+ALPU). Figure 7 shows the panels after prohesion testing and coating removal for the experimental coating systems. From these photographs, it is evident that EP5 had the least amount of rust creep of the previously tested panels while also outperforming the experimental coatings X1-X4.

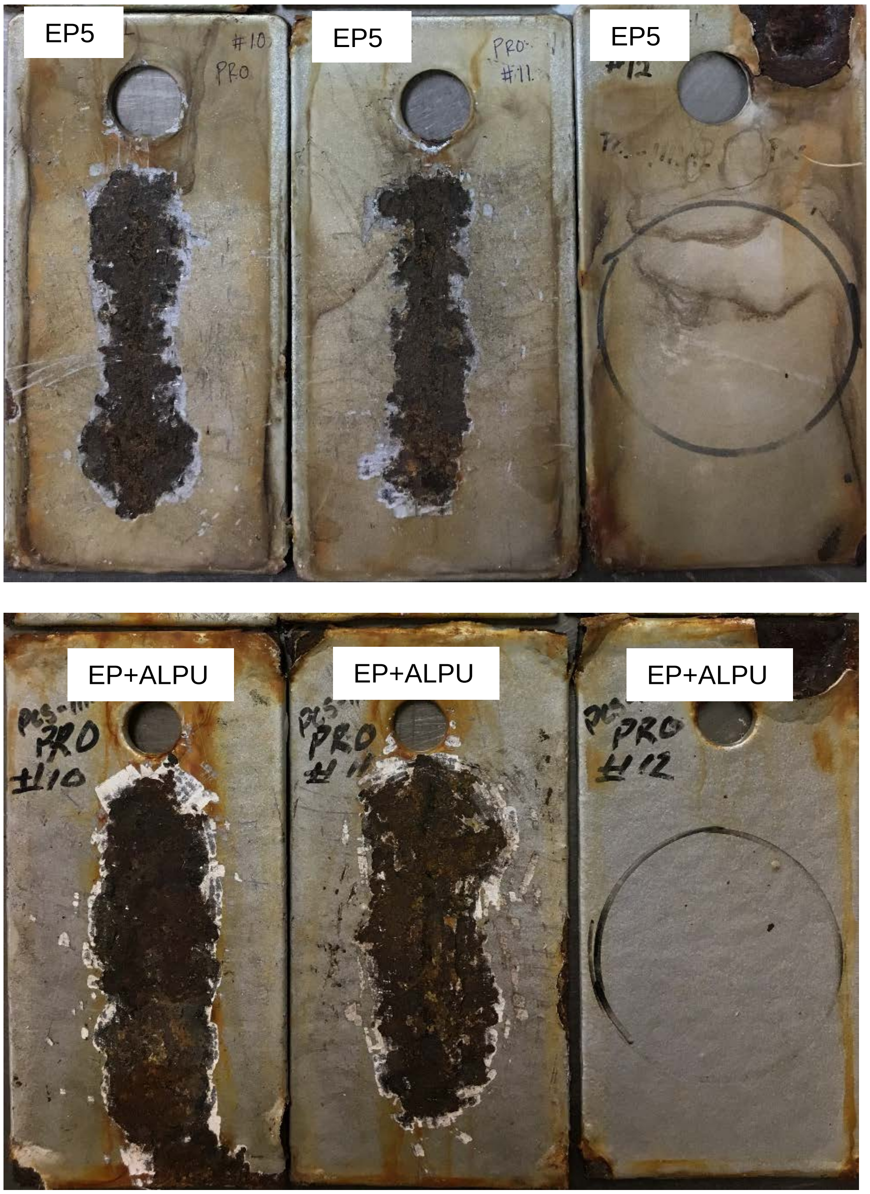

Figure 8: Previously tested polysulfide-modified epoxy panels EP5 and EP+ALPU following 30-week prohesion cycle after coating removal.

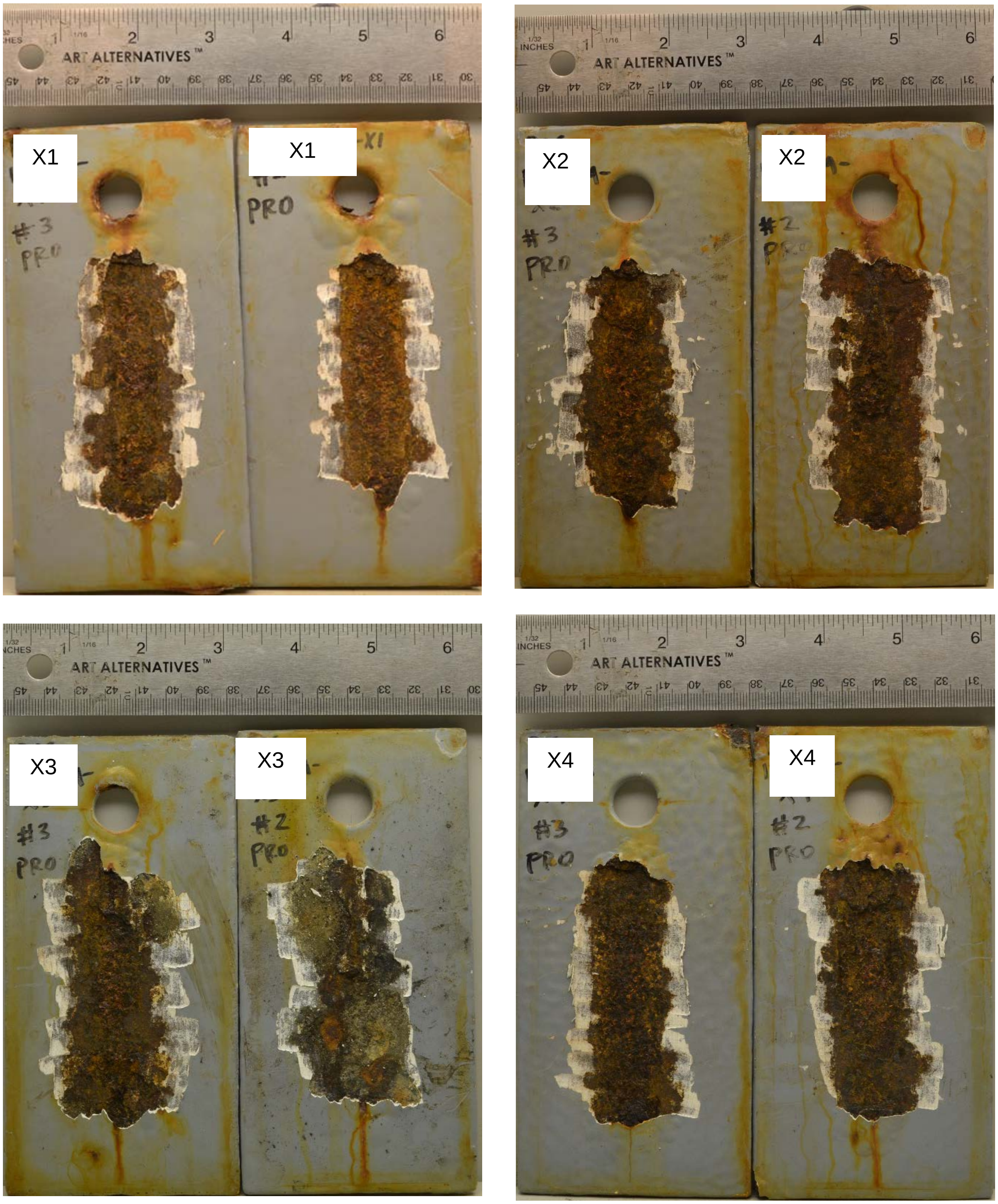

Figure 9: Experimental coatings X1, X2, X3 and X4 following 30-week prohesion cycle and after coating removal.

Photographs of the post-test immersion panels are shown in Figure 8 and Figure 9. The experimental test panels served a dual purpose as EIS test panels (frontside) and rust creep test panels (backside). Note that only the primer was applied to the backside whereas the front received a topcoat of fluorinated polyurethane. Hence, the rust creep on the experimental panels tested in immersion is best compared with EP5. None of the four of the experimental panels (including the control without an anticorrosive pigment) experienced any measurable undercutting whereas the EP5 performed poorly in DI immersion.

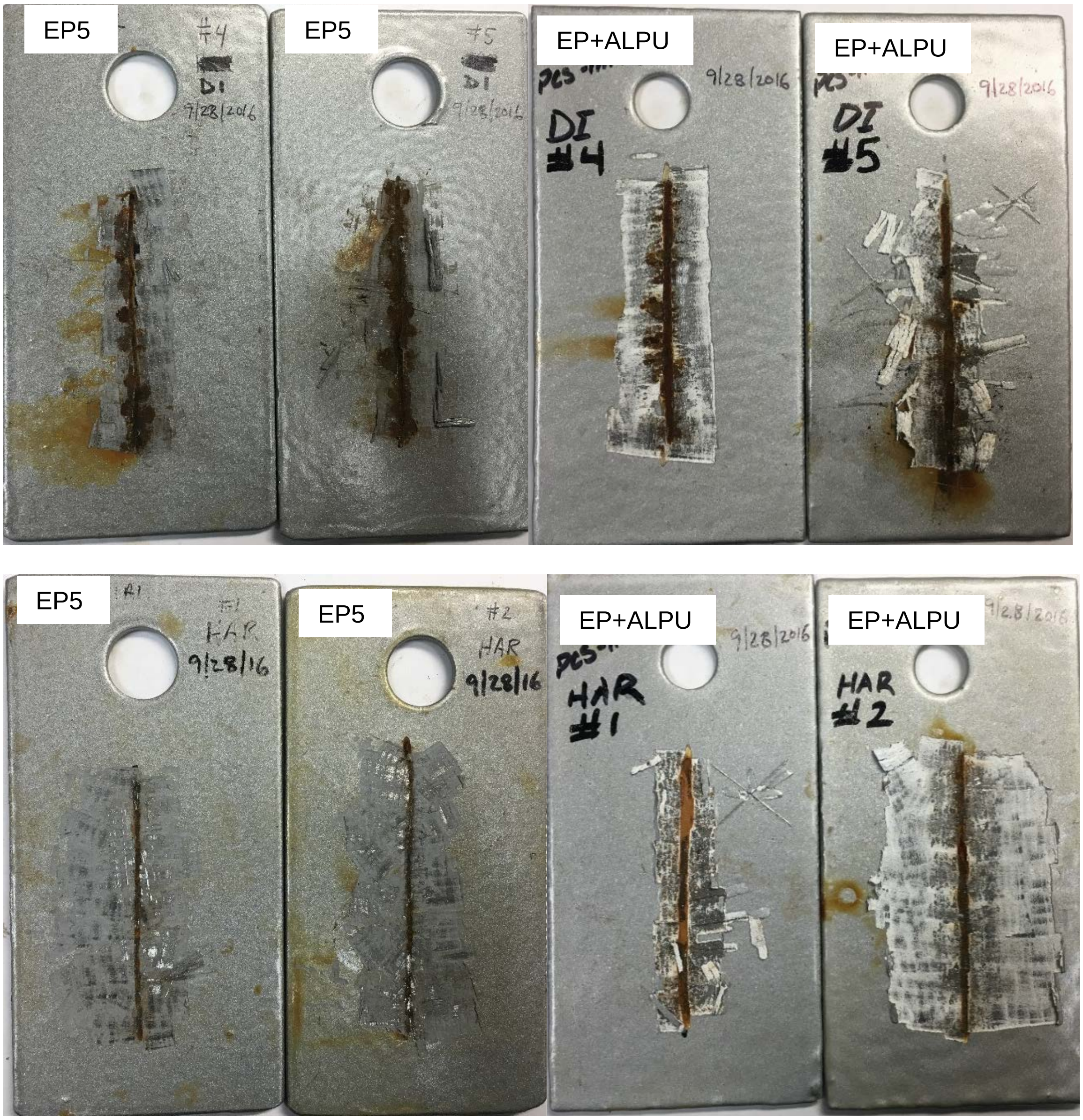

Figure 10: Immersion test panels (DI on top, HAR on bottom) after 7 months immersion for EP5 and EP+ALPU.

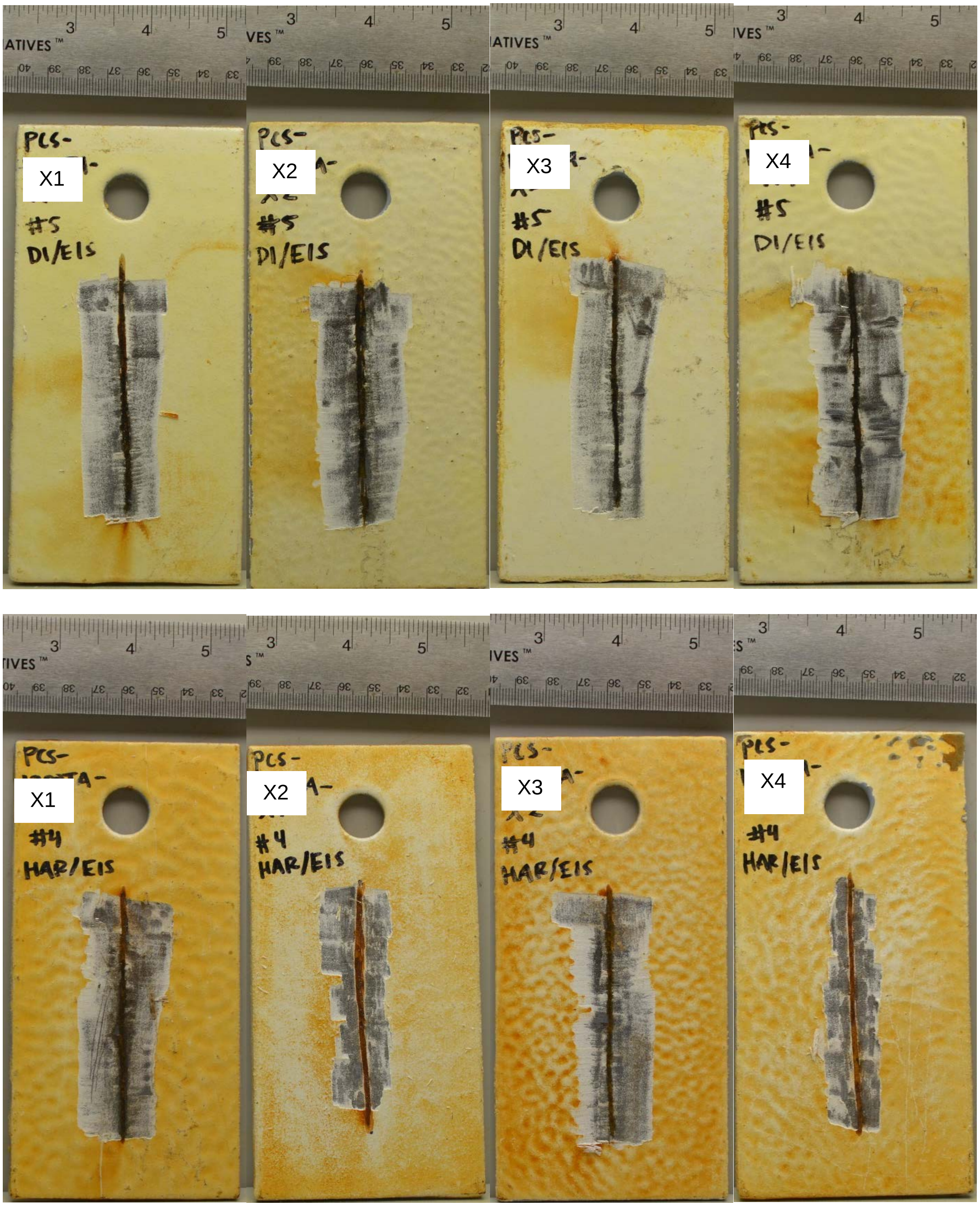

Figure 11: Immersion test panels (DI on top, HAR on bottom) after 7 months immersion for X1-X4.

Figure 10 - Figure 13 show the EIS data collected for each test panel. The data show the approximate degradation after 30 weeks for all panels in HAR immersion was less than half an order of magnitude at 10^{-2} Hz. For DI immersion, the X1 also decreased by less than half an order of magnitude while X2, X3 and X4 experienced a slight increase at 10^{-2} Hz. Note that the graphs show a stable (likely) corrosion reaction. It is most obvious by the phase angle shape in the region of 1 Hz. EIS performance was either excellent or good/excellent for all experimental systems tested since none of the panels degraded more than half an order of magnitude from the initial test and some gained impedance slightly. The performance was similar to the EP+ALPU and exceeded that of EP5 which was the only system which did not include an aliphatic polyurethane topcoat.

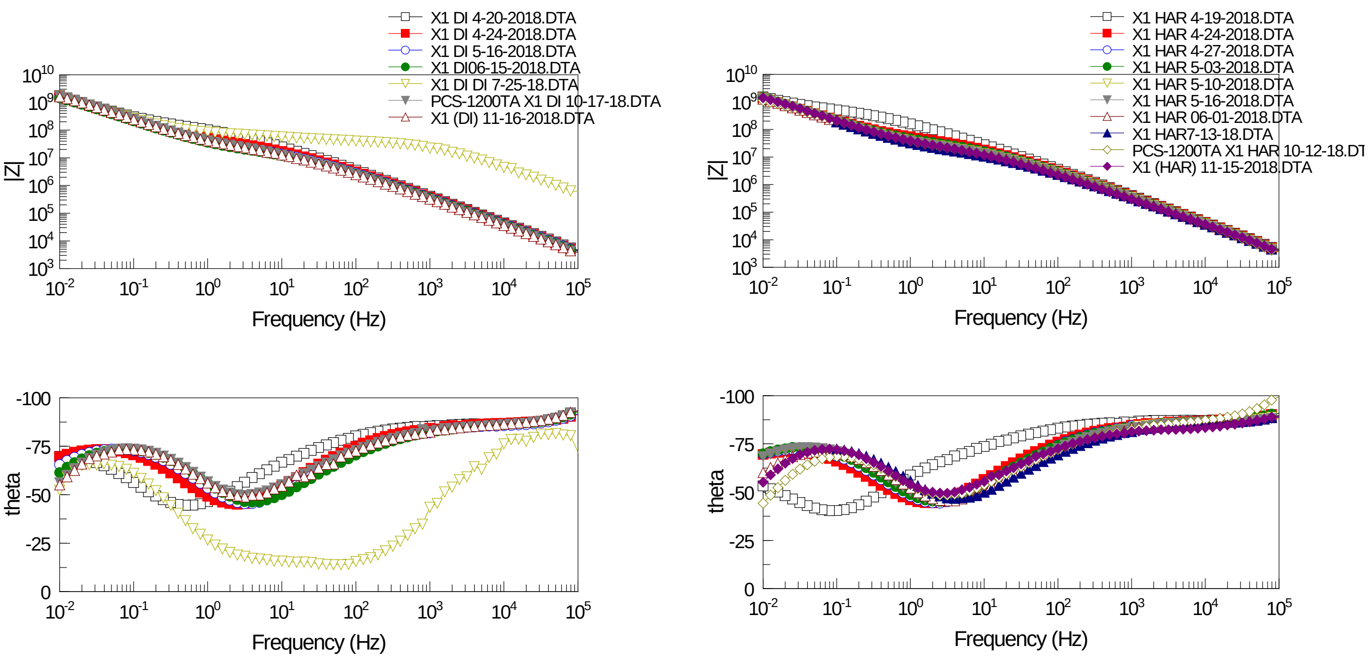

Figure 12: EIS data for X1 in DI Immersion (left) and HAR Immersion (right). Approximate degradation after 30 weeks: both the HAR and DI panel decreased by less than half an order of magnitude @ 10^{-2} Hz.

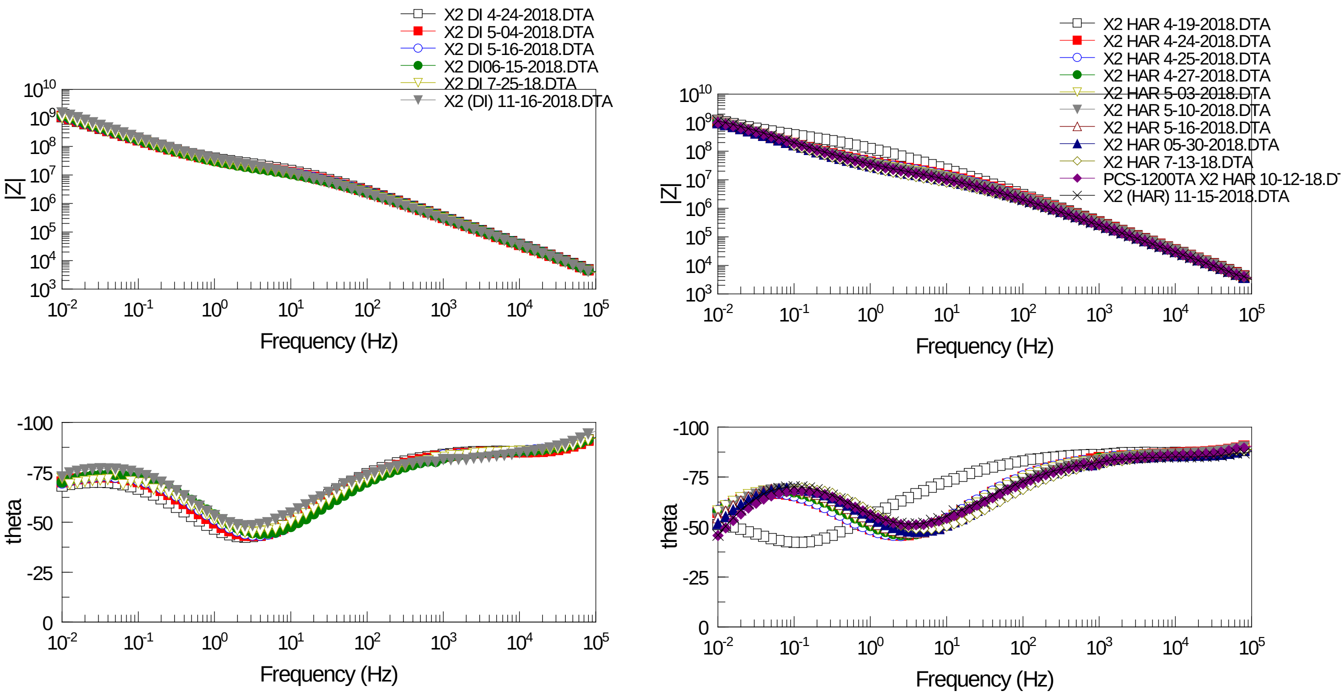

Figure 13: EIS data for X2 in DI Immersion (left) and HAR Immersion (right). Approximate degradation after 30 weeks: the HAR panel decreased by less than half an order of magnitude @ 10^{-2} Hz while the DI panel increased slightly.

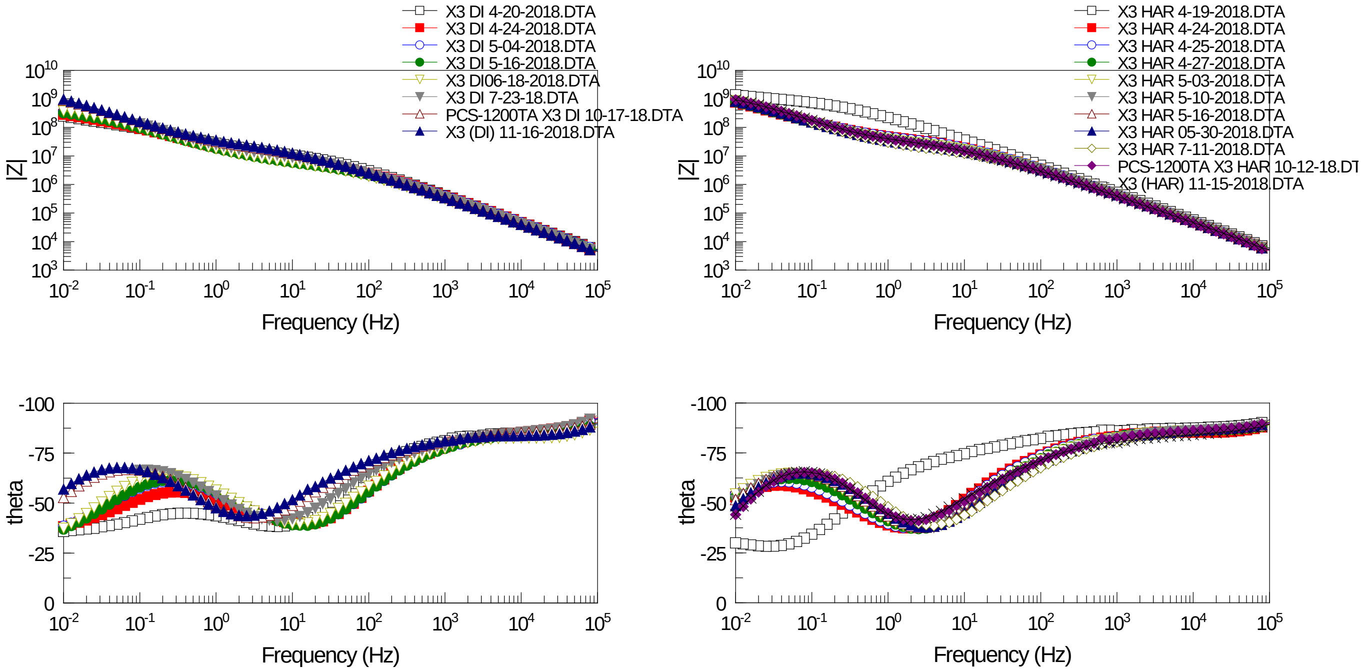

Figure 14: EIS data for X3 in DI Immersion (left) and HAR Immersion (right). Approximate degradation after 30 weeks: the HAR panel decreased by less than half an order of magnitude @ 10^{-2} Hz while the DI panel increased slightly.

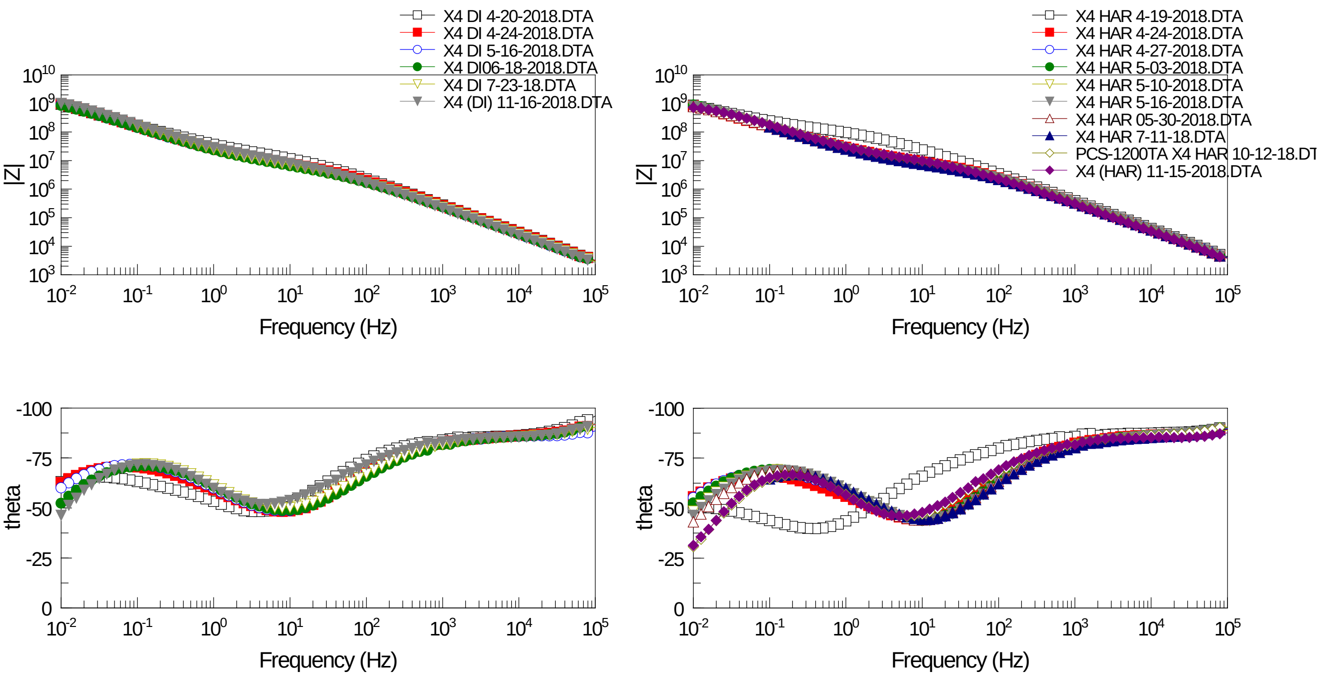

Figure 15: EIS data for X4 in DI Immersion (left) and HAR Immersion (right). Approximate degradation after 30 weeks: the HAR panel decreased by less than half an order of magnitude @ 10^{-2} Hz while the DI panel increased slightly.

Table 7 summarizes the results comparison for the polysulfide modified epoxies. The best performing coating in the prohesion test was EP5, the only coating system without a polyurethane topcoat. For the topcoated materials, X1 held a slight performance advantage with an average representative rust creep of 0.46 inches and a score of fair. Whereas the other products tested performed poorly with average rust creep exceeding 0.5 inches. All of the experimental products had greater impact resistance than the previously tested polysulfides; an improvement that likely stems from the reduction of polysulfide.

Table 7: Test results for polysulfide epoxy

	Immersion Exposure		Cyclic Exposure	EIS Score	Impact in-lbs (score)	Reference
System ID	Dilute Harrison (HAR)[1]	Deionized Water (DI)[2]	Prohesion (PRO)[5]			
EP5	0 (excellent)	0.25 (poor)	0.34 (fair)	Good	10 (poor)	8540-2017-025 [5]
EP+ALPU	0.04 (good)	0.28 (poor)	0.53 (poor)	Excellent	10 (poor)	8540-2017-025 [4]
X1	0 (excellent)	0 (excellent)	0.46 (fair)	Excellent	50 (fair)	N/A
X2	0 (excellent)	0 (excellent)	0.54 (poor)	Excellent	38 (poor)	N/A
X3	0 (excellent)	0 (excellent)	0.57 (poor)	Good / Excellent	76 (fair)	N/A
X4 (control)	0 (excellent)	0 (excellent)	0.51 (poor)	Good / Excellent	40 (fair)	N/A

Discussion and Conclusions

As shown with EIS testing, there were no adverse effects to barrier performance associated with the inclusion of an anti-corrosion primer coat in either the polyurethane or the polysulfide epoxy laboratory testing.

In immersion, all of the coating systems tested with anti-corrosion additives (inhibitive, sacrificial, or both) primers showed excellent rust creep resistance in steady state immersion testing in both HAR and DI solutions. This was clearly an improvement for the polyurethane but less clear for the polysulfide; while EP5 and EP+ALPU both experienced undercutting in previous testing, X4 (the control with no anti-corrosion pigments) also showed no undercutting. Further testing is needed to determine the effectiveness of anti-corrosion primers containing inhibitive and sacrificial pigments in immersion. In addition, pure zinc should also be tested in a polysulfide matrix as opposed to the zinc phosphate pigment.

The effects of the anticorrosion primer were also ambiguous in prohesion testing where there was no significant difference in rust creep between any of the experimental coating systems including the control. On the other hand, the polyurethane showed a large improvement when a zinc-rich primer was included (decreasing from 0.73 to 0.17 inches); a 77% reduction in rust creep. In the BOR test, rust creep increased slightly with the zinc-rich primer, but the increase was within the margin of experimental variation.

The best performing modified polysulfide epoxy in the prohesion test was the aluminum flake pigmented coating with no anti-corrosion primer and no topcoat. However, this system performed poorly in DI immersion as did the EP+ALPU system. The difference between the EP+ALPU and X4 is the reduction of polysufide content in the formulation and the fact that rust creep was measured on the backside (no topcoat). The immersion portion of the test is therefore inconclusive and additional testing would be needed to determine whether a topcoat impacts rust creep performance in the immersion tests.

The reduction of polysulfide levels did improve the impact resistance of the coating but it did not appear to affect the creep resistance during prohesion testing; EP-ALPU and X4 showed very similar values.

The screening approach was a good technique for testing multiple variations of formulations simultaneously. This allows a side-by-side comparison of the most properties determined to be significant. An expected improvement would be to coat both sides with both the primer and topcoat and provide for a third scribed panel to increase confidence in the test results.

Recommendations for Next Steps

A research proposal was submitted for FY19 and is now currently underway. In addition to incorporating these results, it is recommended to perform additional side-by-side testing on promising polysiloxane materials. The testing should also include a benchmark coating such as the zinc-rich epoxy, epoxy barrier and aliphatic polyurethane topcoat i.e. a bridge coating to provide a benchmark. Several additional products including corrosion inhibitor materials were also identified during the study which may be included in subsequent testing. Finally, it is also recommended to perform outdoor testing on each product to evaluate real-world performance and provide a contrast to laboratory testing procedures. A collaboration with USACE is anticipated to facilitate field testing for severe atmospheric service.

References

[1] Materials and Corrosion Laboratory, "Finding a Green Alternative of Vinyl Resin Coatings - Final Report," Bureau of Reclamation, Denver, CO, 2017.

[2] Materials and Corrosion Laboratory, "Review of Corrosion Inhibiting Mechanisms in Coatings," Bureau of Reclamation, Denver, CO, 2017.

[3] Materials and Corrosion Laboratory, "Coatings Test Report 8540-2017-013," Bureau of Reclamation, Denver, CO, 2017.

[4] Materials and Corrosion Laboratory, "Coatings Test Report 8540-2017-024," Bureau of Reclamation, Denver, CO, 2017.

[5] Materials and Corrosion Laboratory, "Coatings Test Report 8540-2017-025," Bureau of Reclamation, Denver, CO, 2017.

[6] Materials and Corrosion Laboratory, "Coatings Test Report 8540-2018-08," Bureau of Reclamation, Denver, CO, 2018.

Appendix A – Dry Film Thickness Readings

Table A-1: DFT readings for PU1

Panel Description	Panel ID	Scribed	Coating Thickness (mils)					
			1	2	3	4	5	Average
11" Disk 1A	1 Side A		47.8	45.4	57	53	42.4	49.12
11" Disk 1B	1 Side B		37.8	35.5	41.8	47.7	40.2	40.6
11" Disk 2A	2 Side A		55	47.5	53	55	51	52.3
11" Disk 2B	2 Side B		43.7	40.5	33	36.6	40.1	38.78
4" Disk 1A	1 Side A		55	55	57	56	54	55.4
4" Disk 1B	1 Side B		35.7	31.5	33.1	34.4	35.4	34.02
4" Disk 2A	2 Side A		52	51	51	52	53	51.8
4" Disk 2B	2 Side B		37.9	36.6	36.1	41.2	40.3	38.42
Pipe			60	54	52	42.4	58	53.28
3"x6"	1	X	37	38.9	40.7	40.9	42.5	40
3"x6"	2	X	43	44	42	41.1	40.3	42.08
3"x6"	3		41.5	42.6	39.9	41.9	40.7	41.32
3"x6"	4	X	42.9	42.7	41.2	42.2	43.3	42.46
3"x6"	5	X	40.4	48	43	40.1	43.3	42.96
3"x6"	6		40.3	40.5	38.4	41.3	42.3	40.56
3"x6"	7	X	34.6	38.1	38	43.1	39.6	38.68
3"x6"	8	X	43.5	41	40.3	40.4	39.8	41
3"x6"	9		37.5	35.6	36.3	38.8	39.7	37.58
3"x6"	10	X	36.2	37.1	37.5	39.3	40.9	38.2
3"x6"	11	X	40	38.8	39.2	39.1	41.3	39.68
3"x6"	12		42.1	44	40.1	38.7	40.8	41.14
3"x6"	13	X	39	44.4	41	42.1	41.5	41.6
3"x6"	14		36.3	38.8	37.9	37.1	37.1	37.44
3"x6"	15	X	45.2	44.3	44.3	42.4	44.3	44.1
3"x6"	16		44.4	41	41	37.4	40.8	40.92
3"x6"	17		37.8	37.8	38.8	37.5	39	38.18
3"x6"	18		50	53	54	48.3	47.6	50.58
3"x6"	19		41.4	42.2	45	43.7	43	43.06
3"x6"	20		39.7	37.3	40.7	47.4	46.3	42.28
3"x6"	21		36.2	36.5	36.8	38.8	38.6	37.38
3"x6"	22		41.7	37.1	38.9	39.7	36.5	38.78
					Average		42.7	42.4
					Standard Deviation		5.2	5.3

Table A-2: DFT readings for MCU1+PU1

Panel Description	Panel ID	Scribed	Coating Thickness (mils)					
			1	2	3	4	5	Average
11" Disk 1A	1 Side A		23.8	24.2	28.4	32.7	23.1	26.44
11" Disk 2A	2 Side A		28.1	39.1	46	43.6	30	37.36
4" Disk 1A	1 Side A		29.5	33.8	32.8	31.2	28.5	31.16
4" Disk 2A	2 Side A		34.4	30.5	34.2	41.9	37.1	35.62
Pipe								
3"x6"	1		25	28.3	28.4	32.2	31	28.98
3"x6"	2		45.1	43	43.9	46.3	46.4	44.94
3"x6"	3		43.3	46.1	42.9	45.3	40.5	43.62
3"x6"	4		41.6	36.3	32.5	27.3	23.3	32.2
3"x6"	5	X	28.3	32.2	31.8	38.7	36	33.4
3"x6"	6	X	39.8	41.4	39	35.7	37.9	38.76
3"x6"	7		30.5	28.3	32	37.3	38.8	33.38
3"x6"	8		26.2	28.7	26.5	31	28.8	28.24
3"x6"	9	X	24.7	23.3	28.1	30.3	26.1	26.5
3"x6"	10	X	38.9	37.9	37.3	36	39.1	37.84
3"x6"	11	X	43.4	37.8	42.6	39.5	37.1	40.08
3"x6"	12	X	50.3	55.8	48.4	47.2	43.4	49.02
3"x6"	13		24.1	24.4	25.2	29.6	31.4	26.94
3"x6"	14	X	28.2	25.3	27.3	28.4	25.6	26.96
3"x6"	15	X	30.6	31.1	30.2	31.2	33.7	31.36
3"x6"	16		29.4	32.6	31.6	31.8	31.6	31.4
3"x6"	17	X	43.4	39.9	32	30	29.2	34.9
3"x6"	18	X	46.4	46.9	47.1	47.6	46.2	46.84
3"x6"	19		43.1	47.1	42.3	41.3	39.9	42.74
3"x6"	20	X	56	46.6	40.5	41.8	36.8	44.34
3"x6"	21		40.4	39.2	40.8	40.5	37.9	39.76
3"x6"	22		26.2	25.5	21.6	22.9	24.2	24.08
					Average		34.0	35.3
					Standard Deviation		6.8	7.1

Table A-3: DFT readings for Polysulfide epoxy 3”x6” panels

System ID	Panel ID	Side	Scribed	Coating Thickness (mils)					
				1	2	3	4	5	Average
X1	#1	Primer		9.2	9.9	9.6	9.3	10.1	9.62
X1	#1	Topcoat		12.9	12.7	12.4	12.5	12.7	12.64
X1	#2	Primer		7.3	8.2	8.1	8.5	6.5	7.72
X1	#2	Topcoat	X	12.6	12.8	12.1	14.3	13	12.96
X1	#3	Primer		11.9	10.9	7.9	7.3	9.5	9.5
X1	#3	Topcoat	X	15	16.1	14.6	15.4	15.6	15.34
X1	#4	Primer	X	11.8	15.2	13.8	16.4	15.4	14.52
X1	#4	Topcoat		14.9	15	13.2	12.1	12.5	13.54
X1	#5	Primer	X	14.5	13.9	11.6	11.6	14.4	13.2
X1	#5	Topcoat		15.8	13.9	13	14.7	13.8	14.24
X2	#1	Primer		12.4	13.2	13.2	13	12.2	12.8
X2	#1	Topcoat		16.4	12.2	13	12.8	10.5	12.98
X2	#2	Primer		10.6	12.6	10.9	11.7	13.5	11.86
X2	#2	Topcoat	X	13.8	12.2	13.3	16.2	17.5	14.6
X2	#3	Primer		11.2	11.1	11.2	10.8	10.4	10.94
X2	#3	Topcoat	X	13.6	13.6	14.3	12.8	13.6	13.58
X2	#4	Primer	X	10.3	9	10.3	8.1	9.8	9.5
X2	#4	Topcoat		12.5	9.2	10.8	9.6	10.9	10.6
X2	#5	Primer	X	6.4	8.2	8.5	7.4	8.9	7.88
X2	#5	Topcoat		15.1	9.9	10.1	11.3	11.4	11.56
X3	#1	Primer		15.7	14.8	12.3	14.2	12.5	13.9
X3	#1	Topcoat		19.6	20.1	17.4	17.3	18.8	18.64
X3	#2	Primer		11.6	15	14.2	15.5	14.8	14.22
X3	#2	Topcoat	X	20.2	15.2	15.2	15.8	18.2	16.92
X3	#3	Primer		15.1	15.5	14	12.3	12.1	13.8
X3	#3	Topcoat	X	13.1	13.5	16.3	17	17.3	15.44
X3	#4	Primer	X	15	13.4	13.8	15	13.4	14.12
X3	#4	Topcoat		24.2	17.6	16.6	15.6	15.9	17.98
X3	#5	Primer	X	10.3	10.6	12.9	12	13.5	11.86
X3	#5	Topcoat		15.7	14.6	16.4	16.2	15.6	15.7
X4	#1	Primer		10.3	10.7	7.8	8.7	8.1	9.12
X4	#1	Topcoat		11.3	11.1	12.9	11	10.2	11.3
X4	#2	Primer		7	7.4	7.2	8.4	8.1	7.62
X4	#2	Topcoat	X	10.2	10.2	13.4	11.1	10.8	11.14
X4	#3	Primer		10	10.1	9.6	12.7	8.9	10.26
X4	#3	Topcoat	X	10.8	14.2	13.1	11.4	11.8	12.26
X4	#4	Primer	X	11.9	12.8	11.7	12.4	12.5	12.26
X4	#4	Topcoat		12.9	13.9	13.4	14.1	12.8	13.42
X4	#5	Primer	X	13.7	13.5	11.8	12.4	12.1	12.7
X4	#5	Topcoat		14.6	15.6	13.6	13.4	13.6	14.16

Appendix B – Coatings Rating Criteria

Immersion Testing (Dilute Harrison, Deionized):

Excellent: No visual defects
Good: No blistering, minor rust creep ≤ 1/8”
Fair: No blistering, moderate rust creep ≤ ¼”
Poor: Blistering, delamination or rust creep over ¼”

Cyclic Weathering Testing (BOR, Prohesion, FOG):

Excellent: No blistering, minor rust creep ≤ 1/8”
Good: No blistering, minor-moderate rust creep ≤ ¼”
Fair: No blistering, moderate rust creep ≤ ½”
Poor: Blistering, delamination or rust creep > ½”

Accelerated Weathering (QUV)

Excellent: No visual defects
Good: No blistering, no rust creep, minor color change
Fair: No blistering, moderate color/gloss change, chalking, or undercut ≤ ⅛”
Poor: Any of the following: blistering, delamination, rust creep > ⅛”

EIS (immersion):

Excellent: After 5000 hrs - Minor degradation < 1 order of magnitude @ 0.01 Hz and ≥ 10^9 Ω
Good: Some degradation after 5000 hrs ≤ 2 order of magnitude @ 0.01 Hz and ≥ 10^8 Ω
Fair: Moderate degradation after 5000 hrs ≤ 3 orders of magnitude @ 0.01 Hz and ≥ 10^7 Ω
Poor: Signification degradation after 5000 hrs > 3 orders of magnitude @ 0.01 Hz

Adhesion (initial, dry):

Excellent: ≥ 2,500 psi
Good: ≥ 1,500 psi
Fair: ≥ 1,000 psi
Poor: < 1,000 psi

Wet Adhesion:

Excellent: ≥ 2,000 psi
Good: ≥ 1,000 psi
Fair: ≥ 500 psi
Poor: < 500 psi

Tabor Abrasion (ASTM D4060):

Excellent: < 30 mg loss
Good: < 40 mg loss
Fair: < 100 mg loss
Poor: ≥ 100 mg

Erosion (USBR-5071-2015):

Excellent: < 30 mg/hr average loss
Good: < 50 mg/hr average loss
Fair: < 100 mg/hr average loss
Poor: ≥ 100 mg/hr average loss

Impact:

Excellent: ≥ 160 in-lbs
Good: ≥ 100 in-lbs
Fair: ≥ 50 in-lbs
Poor: < 50 in-lbs

Cathodic Disbondment (ASTM G8)

Excellent: Disbondment radius ≤ 0.25"
Good: Disbondment radius ≤ 0.5"
Fair: Disbondment radius ≤ 1"
Poor: Disbondment radius > 1"

Knife Adhesion Testing (ASTM D6677)

Excellent: ASTM Rating 8.5-10 - Coatings is extremely difficult to remove. Chips up to 0.8 mm by 0.8 mm.
Good: ASTM Rating 6-8 - Coating is difficult or at least somewhat difficult to remove. Chips up to 6.3 mm by 6.3 mm.
Fair: ASTM Rating 3.5-5.5 - Coating chips in excess of 6.3 mm by 6.3 mm, can be remove with light pressure from a knife blade.
Poor: ASTM Rating 0-3 - Coating peels with fingers once started with a knife blade

Data Sets that Support the Final Report

- Share Drive folder name and path where data are stored: \\bor\do\TSC\Jobs\DO_NonFeature\Science and Technology\2018-PRG-Corrosion Resistant Primers, Barrier Topcoats, and Duplex System Investigation
- Dave Tordonato, dtordonato@usbr.gov, 303-445-2394:
- Short description of the data: (Raw EIS data, photos, DFT.)
- Keywords: Corrosion protection, barrier coatings, corrosion inhibitors, duplex coatings, coatings for severe atmospheric service, electrochemical impedance spectroscopy
- Approximate total size of all files: 260 Mb