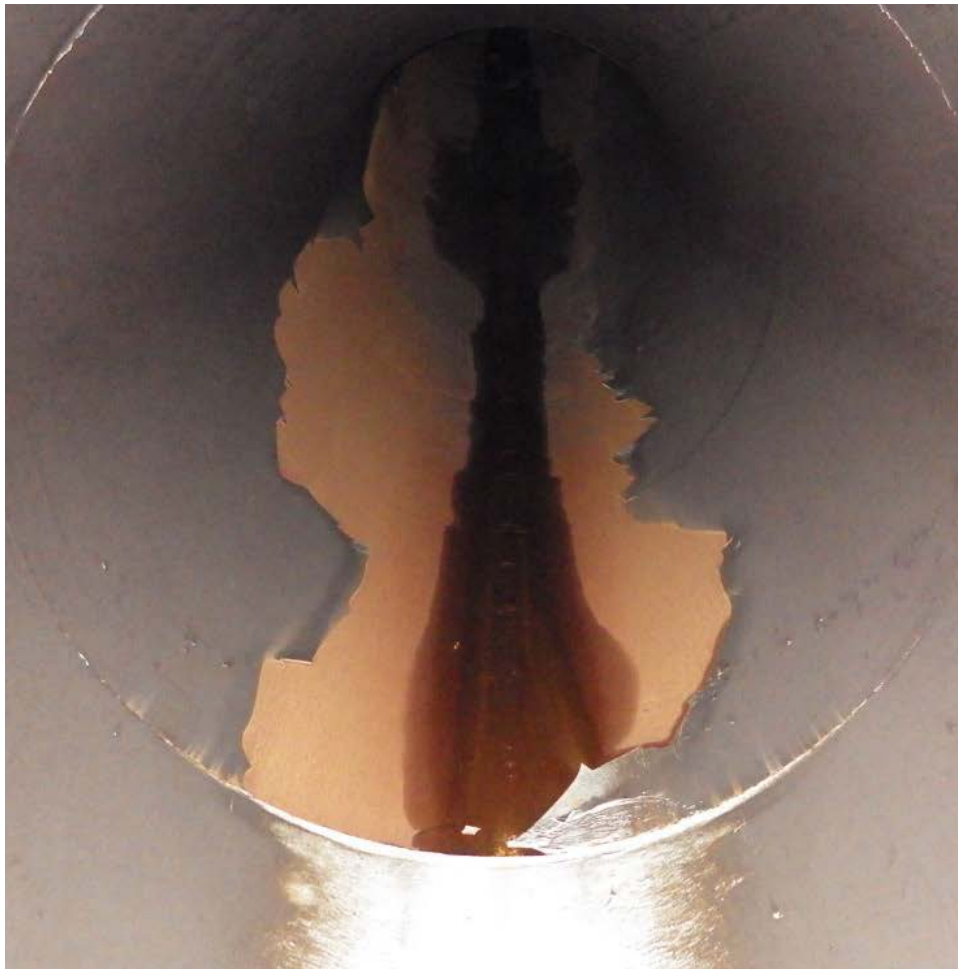


RECLAMATION

Managing Water in the West

Investigating Phosphoric Acid Pretreatments and Additives to Improve Polyurethane Adhesion

Research and Development Office
Science and Technology Program
Final Report ST-2018-1804-01, 8540-2018-49



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Bureau of Reclamation
Research and Development Office

September 2018

Mission Statements

Protecting America's Great Outdoors and Powering Our Future

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Materials and Corrosion Lab, 86-68540

Final Report ST-2018-1804-01

Investigating Phosphoric Acid Pretreatments and Additives to Improve Polyurethane Adhesion

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Acronyms and Abbreviations

CONTROL	control coupon
EIS	electrochemical impedance spectroscopy
EPA-A	amino ethyl phosphoric acid additive
EPA-P	amino ethyl phosphoric acid pretreated
MIBK	methyl isobutyl ketone
MPA-A	amino methyl phosphoric acid additive
MPA-P	amino methyl phosphoric acid pretreated
PA-A	phosphoric acid additive
PA-P	phosphoric acid pretreatment
PPA-A	amino propyl phosphoric acid additive
PPA-P	amino propyl phosphoric acid pretreated
Reclamation	Bureau of Reclamation
VOCs	volatile organic compounds
wt%	weight percent

Executive Summary

Polyurethane coatings have good abrasion and impact resistance, making them a good choice for use in the high flow, high pressure, and constant immersion environments of Reclamation's penstocks and outlet works. In addition, polyurethane application can occur in one coat, decreasing curing time and enabling faster return to service. Recent catastrophic failures in which the coating delaminated from the substrate, however, indicate that the adhesion properties need to be improved before specifying polyurethane for further use on these structures.

This research evaluated changes to polyurethane's adhesion strength following one of four phosphoric acid pretreatments (phosphating processes) to steel coupons before coating application. In addition, another set of coupons evaluated adhesion changes by mixing each phosphoric acid derivative into a component of the polyurethane coating as an additive. Adhesion was measured before and after a six week immersion period in dilute Harrison's solution.

The results showed that adhesion improved for all phosphated coupons compared to the control after the period of immersion. On average, adhesion strength increased by approximately 30 percent. The additive coupons performed worse or similarly to the control, but challenges in preparing the samples may have contributed to the poor results.

The next steps should include the following:

- A long-term, comprehensive study of the effects of phosphating on adhesion including evaluation of undercutting resistance, electrochemical impedance spectroscopy (EIS), knife adhesion, and impact testing. The number of replicates should be increased so the dataset produces statistically significant results.
- Evaluation of phosphoric acid and its derivatives to determine the effect (if any) of carbon chain length on adhesion strength.
- Reevaluation of phosphoric acid and its derivatives as an additive component using improved preparation methods to ensure complete and uniform dispersion of the acids in the polyurethane.
- A small-scale field test to determine if the laboratory results are scalable and reproducible on field structures.

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Introduction

Polyurethane coatings are a rapidly-curing, abrasion resistant alternative for legacy coatings such as coal tar enamel and lead-based paints. Coatings specialists at the Bureau of Reclamation (Reclamation) began specifying polyurethanes for large diameter piping in 2010 [1]. However, the experimental practice ceased following several reports of large-scale coating delamination under high flowing water conditions. Refer to Appendix A for an account of Reclamation's history with using polyurethane to line penstocks and outlet works.

Despite having higher initial adhesion than epoxies and coal tar enamel, polyurethane's adhesion falters after time in immersion, in some cases resulting in catastrophic delamination of the lining. This research investigated the adhesion mechanisms of polyurethane to better understand the modes of failure. In addition, this work describes a preliminary experimental approach to promote better polyurethane adhesion to steel by using either a substrate pretreatment (phosphating) process, or by incorporating an additive into the liquid coating prior to application.

Polyurethane Compositions

Polyurethanes are not always pure polyurethanes. Over time, the term "polyurethane" evolved to also include materials that are an amalgam of polyurethane and polyurea linkages [2]. A traditional polyurethane film forms by a reaction between the hydroxyl group of a polyol and an isocyanate group (Figure 1) [2]. Polyurethane films can be rigid or flexible depending on the amount of cross-linking, and, in general, a higher ratio of hydroxyl groups to isocyanate results in an under-crosslinked polyurethane that is flexible and elastic [3]. Isocyanates, particularly when combined with polyol, react readily with water to form carbon dioxide, amines, and ultimately urea linkages [4].

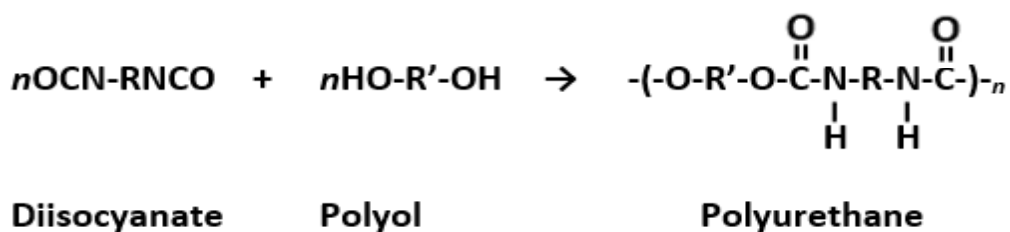


Figure 1: Polyurethane linkage chemical reaction.

Polyurethane coatings are low in volatile organic compounds (VOCs), have good water resistance, and are highly abrasion resistant [5]. The low VOC content is largely a result of the isocyanate components being very low molecular weight and low viscosity. They are also highly reactive, and as such, polyurethanes have pot lives that range from seconds to minutes.

A traditional polyurea film forms by a reaction between an amine group and an isocyanate group (Figure 2).

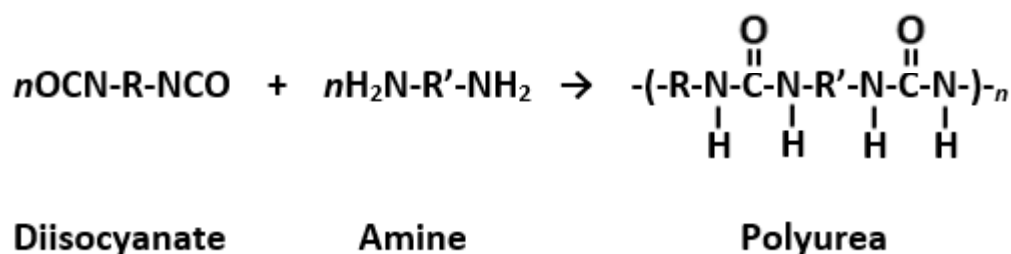


Figure 2: Polyurea linkage chemical reaction.

Polyureas can cure at very low temperatures (below 0°C), are durable, and are chemical resistant [6]. In addition, they conform to all VOC regulations because they are typically 100 percent solids. Polyureas set within 6 to 30 seconds.

The major advantage of polyurethane/polyurea hybrids is that they can be developed to exhibit the best properties of both polyurethanes and polyureas [7]. Therefore, these hybrids are tailored to take advantage of the individual components. For example, they can be formulated to have a longer cure time. This generally results in improved mechanical adhesion by increasing the amount of time that the coating has to wet the surface.

However, despite their longer cure times, polyurethane hybrids still concede to a decrease in adhesion strength that results in delamination. The “polyurethane” lining in the outlet works at Enders Dam that delaminated was a polyurethane/polyurea hybrid [8]. Aside from the truncated surface wetting, O’Donoghue and Datta attribute the poor adhesion to the inherent bonding mechanisms of polyurethane, polyurea, and hybrid linings [2].

Polyurethane Adhesion

There are two hypotheses that may explain why polyurethane adhesion strength decreases in service. Acid-base theory suggests that stronger adhesion occurs when there is a greater amount of interaction between acids and bases. In a polyurethane-substrate interaction, the polyurethane acts as the base while iron oxide groups of the steel substrate act as the acid [9]. Since most of the excess hydroxyl groups in the polyurethane are expended through reaction with the excess isocyanate, there are few basic groups available to react with the substrate and a weak bond is formed. In addition, polyurethanes cure so quickly that there isn’t enough time to form bonds with all of the remaining groups. Especially in an environment of flowing water and after mechanical damage of the lining, the weak (and sparse) bonds between the polyurethane and the steel substrate can be easily cleaved—ultimately leading to delamination of the lining [10].

Another hypothesis suggests that although initial adhesion is high, immersing polyurethane in water results in the bonds gradually becoming hydrolyzed. The disbonded polyurethane is then susceptible to delamination in the event that corrosion undercutting lifts the edge of the lining. Flowing water can then encroach underneath the lifted edge and easily strip long sections.

Methods to Improve Adhesion

This preliminary research evaluated options for improving polyurethane adhesion to a steel substrate. Two possible approaches for achieving this include modifying the substrate to have more active bonding sites or modifying the formulation of the polyurethane itself.

Plasma pre-treatments are one way to activate a metal surface to promote adhesion. During treatment, active oxygen ions from the plasma bind to active sites on the substrate [11]. The result is a hydrophilic, hydroxylated surface that promotes wetting [12]. The process also results in the ablation of contaminants like surface scales and oils [13]. While effective, use of plasma treatment as a way to “activate” the substrate is not feasible for Reclamation’s structures due to their immense size and current limitations of the technology.

Chemical conversion coatings are another method of modifying the substrate to improve adhesion. Narayanan [14] defines chemical conversion coatings as thin surface films formed in a topochemical reaction between a metal substrate and an acid bath solution. Depending on the type of chemical conversion, the resulting film provides increased corrosion protection and/or a strongly adhesive foundation for subsequent coatings [15].

There are two main types of chemical conversion coatings: chromate coatings and phosphate coatings. Chromate coatings are typically used on zinc, aluminum, magnesium, and cadmium substrates [16]. Hexavalent chromium conversion coatings are regarded as the gold standard of chemical conversion coatings for their self-healing properties and ability to act as an adhesion promoting layer for coatings [17]. However, use of chromate conversion coatings is stringently regulated due to their proven toxicity [18].

Phosphate conversion coatings, or phosphating, are suitable for use on low alloy metals, cast iron, and carbon steel [16]. First patented in 1869, phosphating has continually been improved into the widely established processes utilized today [14]. While there are different types of phosphate conversion coatings, iron phosphate coatings are typically utilized to improve the adhesion of subsequent layers of paint to the substrate [19].

The phosphating process forms a thin film that neutralizes the potential of the anodic sites on the substrate and impedes the corrosion reaction [20]. Concurrently, the substrate is positively charged, increasing the number of active bonding sites.

The phosphating process can involve many steps depending on the desired result. Phosphating procedures may include surface activation prior to immersing in the phosphating solution, a neutralizing rinse after the initial rinse, application of additional coatings or sealers after drying, or other additional steps [14]. The simplest iron phosphating procedure is as follows:

1. Clean and degrease the substrate
2. Immerse substrate in 1-2% phosphoric acid solution (target pH of 2-4) [14, 21]
3. Rinse phosphating solution from substrate
4. Dry substrate

During the phosphating reaction, a thin layer of the iron substrate is etched away and released into the solution—positively charging the surface and resulting in a pH increase at the solution-substrate interface. Solid iron phosphate formed during the reaction falls out of solution and is deposited onto the substrate. Hydrogen gas is also formed as a reaction product. Figure 3 shows the chemical reaction of iron dissolving in a phosphoric acid solution and forming a thin film precipitate.

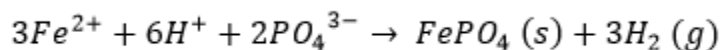


Figure 3: Formation of an iron phosphate precipitate during phosphating.

As the most widely used pretreatment process for preparation of metal substrates, phosphating has been vital to the automotive industry to prevent the development of corrosion and improve adhesion of vehicle body paint [22]. For over 50 years, phosphating has also been a critical practice in metal processing, advancements in dentistry, and the appliance industry, among other industries [23].

In addition to being a component of a phosphating solution, phosphoric acid can also be utilized as an additive to polyurethane coatings to improve adhesion [24]. Adhami, et al. [25] found that adding certain adhesion promoters to the primer or the first layer of a coating system improves the adhesion of the total system. At lower concentrations, adhesion promoters spread uniformly throughout the primer; use of higher concentrations results in the migration of adhesion promoter away from the substrate towards the interface between the primer and a subsequent coating layer.

Phosphoric acids as additives have already been utilized in multiple industries. One 2010 patent describes a method for mixing a phosphoric acid adhesion promoter with a polyurethane coating to reduce incidence of coating delamination from metal food cans and other food containers [26]. In another work, phosphoric acid was added to a fluoride varnish composition to increase the time of adhesion of fluoride to teeth [27].

Procedure

Steel coupons of dimensions 1/8-inch x 3-inch x 6-inch were solvent cleaned and abrasive blasted in accordance with Society for Protective Coatings (SSPC)-SP10 near white metal blast [28]. The control coupons were coated with PPG Amerthane 490, a 100 percent solids, aromatic polyurethane hybrid coating system. The experimental coupons received one of two techniques: 1) phosphating (pretreatment), or 2) addition of phosphoric acid to the non-isocyanate-containing component of the system before the two parts were mixed together (additive).

Four phosphoric acid compounds were evaluated side-by-side with control coupons that did not receive the pretreatment or additive. Table 1 shows the experimental test matrix.

Table 1: Experimental Test Matrix

Acid	Method	Coupon Identifier	Replicates
None (control)	N/A	CONTROL	3
Phosphoric	Pretreatment	PA-P	3
	Additive	PA-A	3
Amino methyl phosphoric	Pretreatment	MPA-P	3
	Additive	MPA-A	3
Amino ethyl phosphoric	Pretreatment	EPA-P	3
	Additive	EPA-A	2
Amino propyl phosphoric	Pretreatment	PPA-P	3
	Additive	PPA-A	3

Pretreatment coupons were immersed in a Ziplock bag containing two weight percent (wt%) aqueous solution of acid for approximately five minutes. The coupons were rinsed with tap water and hung to air dry. Approximately 15 minutes after the coupons were dry, the Amerthane 490 polyurethane coating was spray applied according to the manufacturer's recommendation.

Additive coupons were prepared by dissolving one wt% acid into a methyl isobutyl ketone (MIBK) solvent carrier. The acid-solvent mixture was then added into the non-isocyanate-containing part of the Amerthane 490 polyurethane before combining Part A and Part B. The resulting coating was brush-applied to the coupon to achieve a film thickness of approximately two mils. Additional coats of polyurethane were spray-applied according to the manufacturer's recommendation to reach a total film thickness of approximately 30 mils.

The polyurethane coating cured for 7 days to achieve full cure prior to doing pull-off adhesion tests per ASTM D4541 [29] on one coupon from each replicate set. The adhesive cured for 24 hours, and the dollies were scored before being pulled. The remaining coupons were placed in immersion service in dilute Harrison's solution, an aqueous solution of 0.35 wt% ammonium sulfate and 0.05 wt% sodium chloride. After six weeks, the coupons were removed from immersion, and dollies were glued onto the surface. The coupons were placed in a 100 percent humidity chamber for at least 24 hours, and the dollies were scored before pull-off adhesion tests were performed. Three pull-off replicates were performed per coupon before and after immersion exposure.

Results and Discussion

Several observations made during the phosphating process aided in the evaluation of the experimental results. As shown in Figure 4 (left), bubble formation due to hydrogen gas evolution was seen on the surface of the PA-P, MPA-P, and PPA-P coupons, as expected per the iron phosphate equation shown in Figure 3. However, the hydrogen gas bubbles were not observed for EPA-P.



Figure 4: (left) Hydrogen gas formation on a PA-P coupon during immersion in phosphoric acid solution, and (right) phosphated PA-P coupon shows darker hue compared to white metal blast at right.

The surfaces of the PA-P and MPA-P coupons changed color after drying. Figure 4 (right) shows a comparison between the darker phosphated coupon and the white metal blasted coupon at right. This color change is attributed to the formation of an iron phosphate film on the surface. The EPA-P and PPA-P coupons did not produce a noticeable change in color.

Due to the rapid curing time once the two parts of the polyurethane were mixed, preparing the additive components was difficult. The acids did not dissolve into the solvent as anticipated and were possibly not distributed uniformly throughout the coating. In the case of EPA-A, the polyurethane cured so quickly that only two coupons received a brush coat before the paint completely solidified in the mixing container. Therefore, only two replicates of the EPA-A coupon were prepared for testing. Future work should investigate alternative approaches to incorporate the additives. A spray gun could be used instead of trying to brush apply the additive layer. The spray gun would provide a better finish, ensure that all acid additive is utilized, and provide a more uniform coating. The spray gun wasn't used in this work because the amount of polyurethane used was very small (less than 100 grams total).

Adhesion Strength Before Immersion

Three out of the four phosphated coupons resulted in higher adhesion values than the control. However, the control coupon adhesion values were higher than all of the additive coupons. Figure 5 shows all raw adhesion values for each acid derivative and the control coupons, i.e., before and after immersion exposure. The data represents the average of three pull-off replicates per coupon.

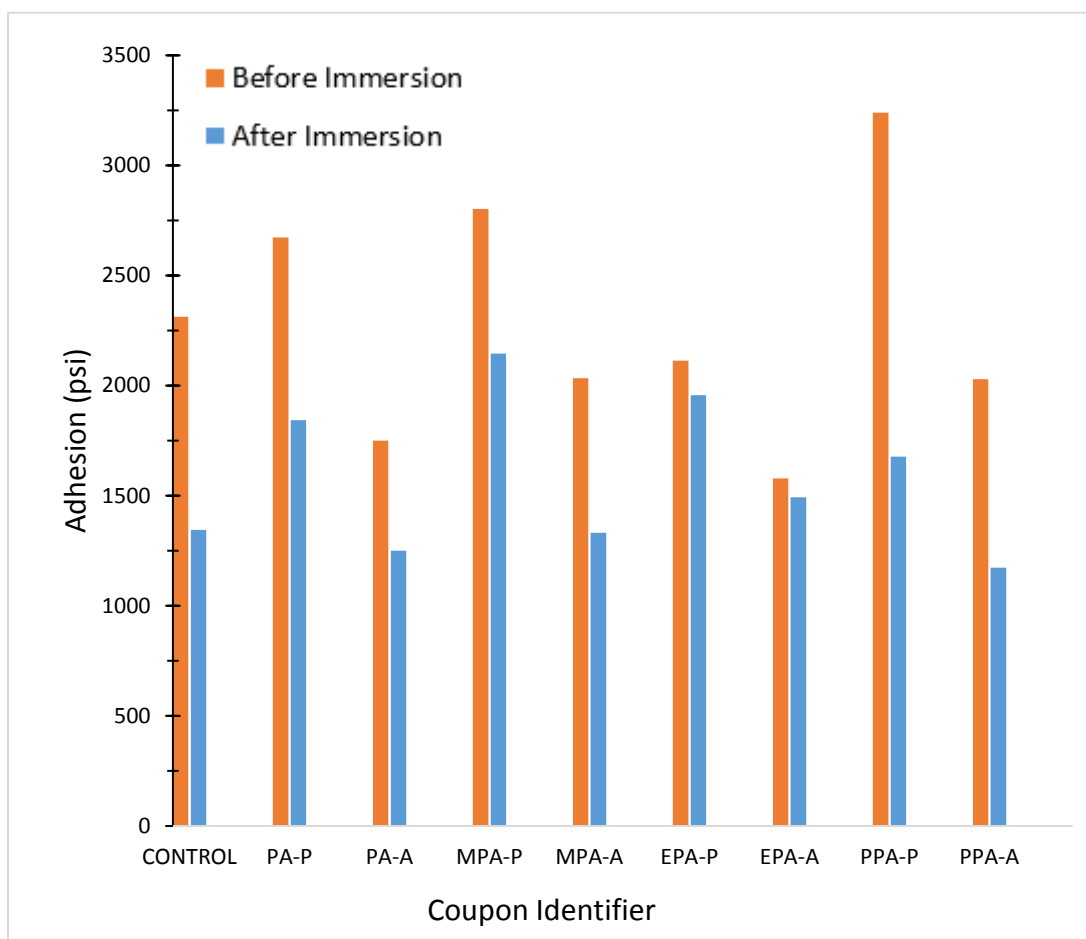


Figure 5: Adhesion results for all coupons before and after immersion.

Pretreated (phosphated) coupons

The adhesion trends seen in Figure 5 indicate that acid derivative may have the effect of increasing adhesion values. Before immersion, PPA-P (longest carbon chain) gave the highest adhesion results followed by MPA-P and PA-P (shortest carbon chain). These trends suggest a possible correlation between chain length and adhesion energy for phosphoric acid adhesion promoters. Other types of adhesion promoters (e.g. silanes) have been found to have increasing or decreasing adhesion energy trends based on chain length [30]. EPA-P gave the lowest initial adhesion values out of all pretreated coupons. Absence of gas bubble formation during the phosphating process and lack of a significant adhesion improvement compared to the control coupon suggests an incomplete or erroneous phosphating process.

Failure modes for most of the pretreated coupons were a mix of adhesion failure, cohesion failure, and glue failure with no obvious trends. EPA-P and PPA-P failed almost entirely due to glue failure. A glue failure during adhesion testing should be interpreted as the minimum

adhesion value; the actual adhesion value is likely higher. The predominant failure mode of the control coupon was adhesion failure.

Additive coupons

The additive coupons performed worse than the control coupon, suggesting the additives had no effect or a negative impact on adhesion. The predominant failure mode was adhesion failure, except for EPA-A which largely failed due to glue failure. Improved methods for preparing the additive coupons should be considered for future work.

Adhesion Strength After Immersion

Adhesion values for all coupons decreased after immersion. Figure 6 shows the percent decrease in adhesion for each coupon. Percent decrease was calculated by subtracting the final adhesion from the initial adhesion and dividing by the initial adhesion. A low value for decrease in adhesion is preferred because it suggests that immersion in water has minimal effect on the coating's adhesion strength. All phosphated coupons performed better than the control coupon, i.e., a low value for decrease in adhesion. The coupons with the additives performed similarly to the control.

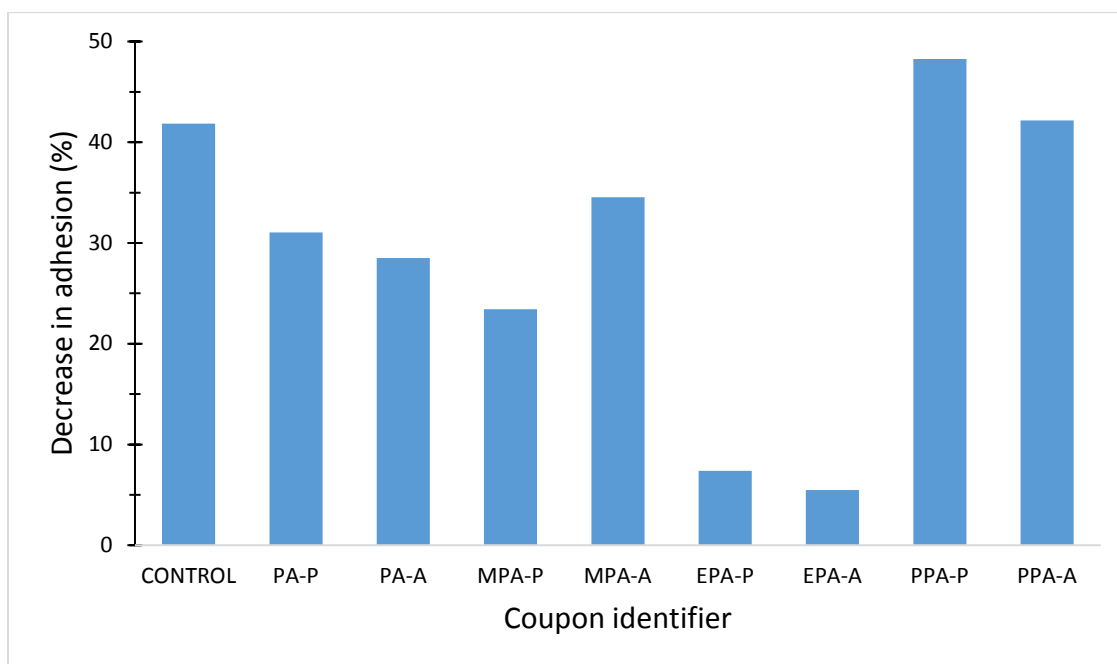


Figure 6: Percent decrease in adhesion for each coupon after immersion.

The results for both approaches using the amino ethyl phosphoric acid derivatives, EPA-P and EPA-A, showed less than a 10 percent decrease in adhesion following immersion. Figure 7 shows EPA-P and EPA-A along with the control coupon after immersion and adhesion testing. The glue failures observed in the EPA-P coupon suggest that the reduction in adhesion is even less than the 7 percent shown in Figure 6. The results for EPA-P and EPA-A are promising evidence that these approaches support an increase in the durability of the adhesion strength.



Figure 7: EPA-P (left), EPA-A (center), and control (right) coupons after immersion; adhesion values are written below respective pull-off location.

Pretreated (phosphated) coupons

After immersion exposure, MPA-P had the highest raw adhesion values, followed by EPA-P. PA-P and PPA-P had similar adhesion results. On average, adhesion decreased by approximately 28 percent. However, PPA-P decreased by nearly 50 percent while EPA-P only decreased by approximately seven percent. EPA-P was minimally affected by immersion in solution and had the second highest adhesion strength after immersion, suggesting the formation of strong, permanent bonds. EPA-P may be a good choice for field implementation.

Failure modes were a mix of adhesion failure and glue failure. PA-P failed entirely due to glue failure.

Additive coupons

The additive results appeared to follow an opposite trend from the phosphated coupons, with the PPA-A and MPA-A coupons having the highest adhesion values followed by PA-A and EPA-A, as seen in Figure 6. Although the additive results seem to suggest that increasing chain length correlates to an improvement in adhesion, the datasets are too small to make any definitive conclusions and further research is warranted. In addition, results are too similar to the control, and it just may be that the additives had no effect on the adhesion.

On average, adhesion again decreased by approximately 28 percent. PPA-A decreased the most (42 percent) while EPA-A decreased by only 5.5 percent. EPA-A was minimally affected by immersion in solution, suggesting formation of permanent bonds.

Failure modes were almost exclusively adhesion failure. The control coupon failed entirely by adhesion failure.

Future Work

The findings warrant a larger-scale, longer-term study of the extent to which phosphating promotes adhesion of polyurethane. The study should include a large enough dataset for the results to be statistically significant. The following additional testing should also be performed to determine the effect of phosphating on other coating properties:

- Undercutting resistance to evaluate how well phosphating impedes corrosion.
- Knife adhesion to evaluate ease of delamination.
- EIS to evaluate long-term degradation and corrosion resistance.
- Impact resistance testing.

Future work should also focus on determining the role of carbon chain length in adhesion promotion. In addition, a small-scale field study should be conducted to investigate the practicality of phosphating Reclamation's structures and validate its usefulness outside of a lab setting.

One replicate of each coupon (except EPA-A) remains in immersion for long-term adhesion testing that will be performed at a future date.

Conclusions

A reduction in in-service adhesion and catastrophic delamination has deterred Reclamation from specifying polyurethane coating systems for application in outlet works and penstocks. Pretreating or phosphating the interior of these features prior to coating application could eliminate those challenges and allow Reclamation to benefit from the abrasion resistance, flexibility, and long service lives that polyurethane coatings could provide. Phosphating has been used for decades in metal processing to prevent corrosion and improve coating adhesion.

The results of this project indicate that phosphating improved polyurethane adhesion to steel coupons before and after immersion. The adhesion after immersion tended to decrease as chain length increases. The percent change in adhesion, which may be the best indicator of improved adhesion, indicated that the pretreatment and additives may be temporary for most cases. However, the ethyl phosphoric acid pretreatment and additive resulted in a less than 10 percent average decrease in adhesion after immersion, compared to 40 percent for the control. This suggests that ethyl phosphoric acid aided in the formation of strong, permanent bonds. A larger sample size is needed to determine if the trends are significant.

In general, the use of phosphoric acid derivatives as additives did not result in an increase in adhesion values. Challenges experienced during preparation of these samples render the results inconclusive. The additive experiment should be repeated with a larger sample size and improved preparation methods.

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Appendix A – Trials and Tribulations in Finding the Optimum Coating

TRIALS AND TRIBULATIONS WITH FINDING THE OPTIMAL LINING MATERIAL

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ABSTRACT

Historically, the Bureau of Reclamation observed coating service lives of 50 to 80 years when lining its water conveyance structures with coal tar enamel (CTE). Changes to regulations have largely eliminated CTE as a field coating option, and existing CTE is beginning to show signs of degradation or has already been repaired or recoated. Reclamation has been working to find an appropriate alternative to CTE.

Elastomeric polyurethanes have superior flexibility and abrasion resistance, with expected service lives between 20 to 40 years. However, adhesion and delamination problems observed both in the laboratory and in the field currently render them unsuitable for most of Reclamation's needs.

Rigid polyurethanes also have good flexibility and abrasion resistance, but develop blisters during application to the cold steel of buried pipes. Blisters develop as a result of the reduced reaction rate (curing) at the steel interface while the bulk material cures at ambient air temperatures.

100 percent solids epoxies are abrasion resistant, have good adhesion, and do not have brittle failures. Reclamation has had some field experience with 100 percent solids epoxies as penstock or outlet works linings, but have used them primarily for maintenance and repairs of CTE and elastomeric polyurethanes. The life expectancy of 100% solids epoxy is 15 to 30 years.

Reclamation's coatings research is ongoing, but questions remain whether commercially available products exist that can match the service life that CTE provided inside penstocks while suiting modern application technologies, methods, and logistical challenges.

INTRODUCTION

The US Bureau of Reclamation (Reclamation) maintains 492 dams across the 17 western states of Arizona, California, Colorado, Idaho, Kansas, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington, and Wyoming [1].

These dams provide 10 trillion gallons of water for municipal, residential, and industrial use to 31 million people per year; and 60 percent of all vegetables grown in the United States (US) are produced using Reclamation water. In addition, Reclamation's 53 hydroelectric power plants generate 40 billion kilowatt hours of energy per year—15 percent of the total hydropower in the US. Figure 1 gives the locations of Reclamation's dams, hydropower plants, and pumping plants.

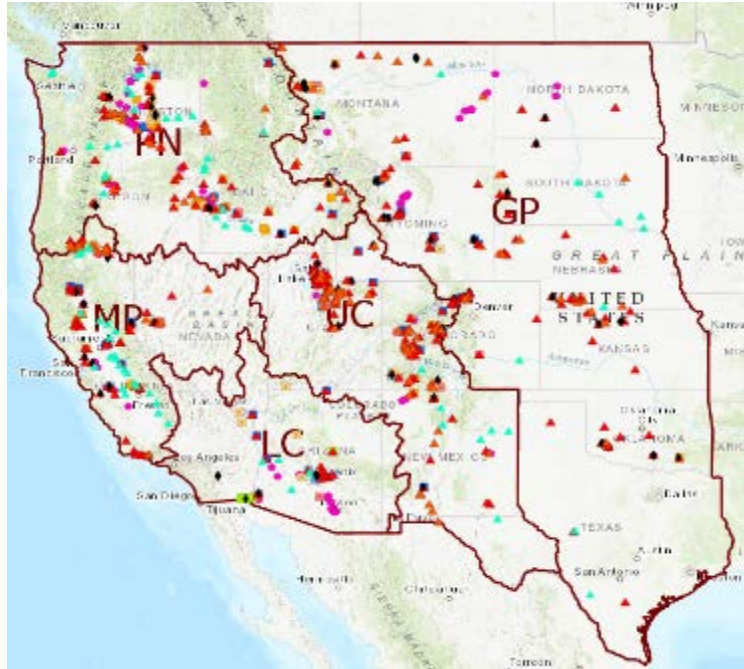


Figure 1: Dams, hydropower plants, and pumping plants in the 17 Western states serviced by Reclamation.

Managing and maintaining so much critical infrastructure has been an ongoing effort. With its first dams constructed around the turn of the 20th century, and the period of large dam construction ending in the late 1960s, Reclamation's portfolio is severely aged [2, 3]. Compounding the issue of age, service conditions for dams, pumping plants, and associated structures are diverse and can be punishing. Structures located outdoors face extreme temperature fluctuations and ultraviolet (UV) light exposure from the sun. Structures can also be subjected to varying levels of salt spray, cyclic or continuous immersion in water, and mechanical damage from debris.

Reclamation's gates, trashracks, and thousands of miles of water conveyance structures endure some of the most challenging service conditions, and are a few among the many steel features that are in a constant battle against corrosion. Reclamation's Materials and Corrosion Laboratory (MCL), works to slow or prevent corrosion by use of cathodic protection and protective coatings.

MCL focuses its efforts on conducting applied research to assess new materials and corrosion mitigation methods. In-house protective coatings specialists have been systematically testing coatings and coatings systems for over a decade. In-house accelerated testing includes, but is not limited to:

- long-term immersion in dilute Harrison's solution (DHS) in accordance with ASTM D870 (modified) [4],
- long-term immersion in deionized (DI) water in accordance with ASTM D870,
- exposure in a salt fog chamber in accordance with ASTM G85 Annex A5 [5],
- fluorescent UV light exposure in a UV cabinet in accordance with ASTM D4587 [6],

- a cycle of fluorescent UV light exposure and salt fog chamber exposure in accordance with ASTM D4587 and ASTM G85 Annex A5,
- slurry erosion in accordance with Reclamation test method USBR-5071-2015 [7],
- cathodic disbondment testing in accordance with ASTM G8 [8].

In addition, the following is a non-exhaustive list of tests conducted during and/or after accelerated weathering:

- Electrochemical Impedance Spectroscopy (EIS),
- Adhesion testing in accordance with ASTM D4541 [9],
- Impact testing in accordance with ASTM D2794 [10],
- Corrosion undercutting and creep adapted from ASTM D7087 [11].

MCL also performs field performance testing and field inspections of coatings where applicable.

Finding an optimal lining material for Reclamation's aging structures has been a challenging undertaking. With the comfortable days of using hazardous-yet-effective legacy coatings long gone, modern coating systems struggle to provide even close to the same superior protection. This paper summarizes Reclamation's past, present, and future efforts of using protective coatings in the fight against corrosion.

LEGACY COATINGS

Early Reclamation engineers curtailed corrosion of critical structures by using protective coatings like coal tar enamel, lead-based paints, and chromates [12].

Coal Tar Enamel

Coal tar enamel proved to be particularly effective in protecting features subject to raw water immersion. Penstocks, for example, face constant immersion and a range of water pressures and flow rates. In certain circumstances, mechanical damage from ice, personnel carrying equipment, or other debris can wreak havoc on penstock interiors.

Commercial coal tar technologies have been used to protect against corrosion since the mid-1800s [13]. Reclamation's first documented application of coal tar enamel was in 1936 when it was applied to the interior of the penstocks at the newly-constructed Hoover Powerplant. Over 80 years later, portions of the original coating continue to offer excellent corrosion protection.

Regarded to be a permanent coating in its early days of use, the application of coal tar enamel at Hoover Powerplant marked the beginning of what would become Reclamation's go-to strategy for protecting steel conduit from corrosion [14]. While it is unknown exactly how many of Reclamation's pipelines were coated with coal tar enamel, 50 to 80 percent of the US's steel water conveyance structures were protected with some type of hot applied enamel by the 1980s [15].

In a comprehensive study of coal tar enamel and its composition, Merten [16] concluded that the enamel's superior corrosion resistance is due in-part to the graphite-like microstructure of the coal tar pitch—rendering it impervious to water over long time periods. The thermoplastic nature allows the material to flow and self-heal as well as to compress its pore spaces during

pressurized immersion service. In addition, mineral fillers impart toughness and resistance to deformation, while plasticizers reduce brittleness.

Widespread use of coal tar enamel on Reclamation's structures tapered in the 1970s due to difficulty in finding experienced applicators, safety concerns, and the emergence of modern coating systems. While some Reclamation structures have original coal tar enamel that is in good condition, other existing coal tar enamel is beginning to show signs of degradation or has already been repaired or fully recoated. Reclamation has yet to find an appropriate or comparable alternative.

Lead-based Paints

Lead-based paints are another type of legacy coating that provide superior corrosion protection and long service lives. Rather than acting as a simple barrier, inhibitive pigments within red lead coatings undergo chemical reactions with corrosive species to stop or impede corrosion [17]. In a secondary mechanism, the lead pigments were found to passivate the metal substrate, rendering it unreactive.

Reclamation applied lead-based paints to its structures as early as the late 1930s, with the longest-known service life being 77 years before recoating. Use of lead paints ceased in the mid-1980s due to their high toxicity [18]. The last documented application of lead-based paints on a Reclamation structure was in 1985, and the original coating is still in service as of this writing.

Chromates

Reclamation briefly replaced red lead-based paints with chromate paints, another inhibitive coating. Health and environmental concerns quickly stymied their use and they were only specified until 1995. All original chromate coatings on Reclamation structures are still in service today.

CTE REPLACEMENT CASE HISTORIES

For over a decade, Reclamation's MCL has been focusing its research on modern barrier coatings like polyurethanes and epoxies to find a comparable alternative to coal tar enamel and other legacy coatings. A summary of the challenges with each type of coating is documented herein.

Polyurethanes

Polyurethane coatings exhibit excellent barrier and impact resistance properties, which could make them suitable for use in the high flow, high pressure, and constant immersion environments like Reclamation's penstocks and outlet works. In addition, polyurethane can cure at temperatures that are below freezing, enabling work during winter months and allowing for faster return to service. Table 1 lists properties for some polyurethanes that Reclamation has used to line penstocks and outlet works.

Table 1: Polyurethanes used by Reclamation to line penstocks and outlet works.

Coating Material	Use	Observed Service Life	Slurry Erosion (mg/hr)*	Pull-off Adhesion (psi)	Undercutting (in)	Impact (in-lbs)
Polyurethane A (rigid)	Repairs	< 1 year	8.0 ± 1.2	2695 ± 690	0.738	150**
Polyurethane B (elastomeric)	Full lining	< 4 years	Not Tested	1555	0.3125	160
Polyurethane C (aromatic)	Full lining	< 1 year	Not Tested	1821	0.286	160

*Reclamation test method USBR-5071-2015. Test consists of an 11-inch diameter coated disk fastened to the bottom of a cylindrical tank that is continuously agitated with 1 kilogram of aluminum oxide abrasive and 16 liters of water. Test measures weight loss at 24-hour test increments for a total test period of 96 hours.

**Manufacturer specified.

With hope that polyurethanes might be an ideal replacement for legacy coatings such as coal tar enamel and lead-based paints, MCL specified polyurethanes for use at three facilities: Flatiron Penstocks, the outlet works at Ender's Dam, and the outlet works at Platoro Dam.

In 2015, MCL coatings specialists inspecting the Unit 2 penstock at Flatiron Penstocks in Loveland, Colorado discovered a catastrophic lining delamination in a buried portion of the pipe. Approximately 933 square feet (sq. ft.) of a total of 111,000 sq. ft. of lining was missing—including two sections that were 40-ft. long [19]. The joints in the affected area were older-construction sleeve-type couplings that are designed to move with thermal expansion and contraction and the area had been subjected to the highest amount of head. Figure 2 shows one area of delaminated lining that required emergency repairs.

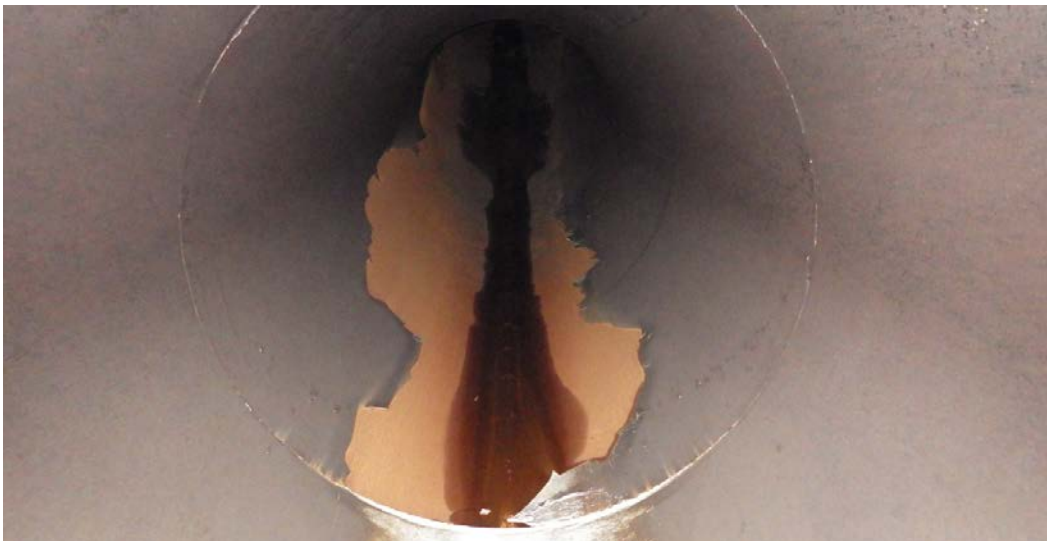


Figure 2: Delaminated elastomeric polyurethane lining in the Unit 2 penstock at Flatiron Penstocks.

The coating in question, an elastomeric polyurethane (Polyurethane B) which had been applied just four years earlier, failed well before the end of its expected 20 to 30-year service life. During prior inspections of the penstock, cracks had been observed in the area but they were not rectified. The delaminated lining was repaired with a 100 percent solids epoxy and low temperature cured vinyl esters.

Additional emergency repairs of delaminated areas were made using a fast set, rigid polyurethane (Polyurethane A). Photographs taken shortly after application of the lining show the formation of blisters throughout the repaired area. An application guide from one polyurethane manufacturer states that spray application of some fast set urethanes onto cold metallic substrates may cause blisters to develop [20]. This heat-sink phenomenon occurs when the first coat does not cure properly due to the exothermic reaction being stunted by the cold substrate. Additional coats cure properly, but blisters develop between the substrate and the partially-cured first coat or within the first coat. Figure 3 shows one area of extensive blistering of the newly applied polyurethane.

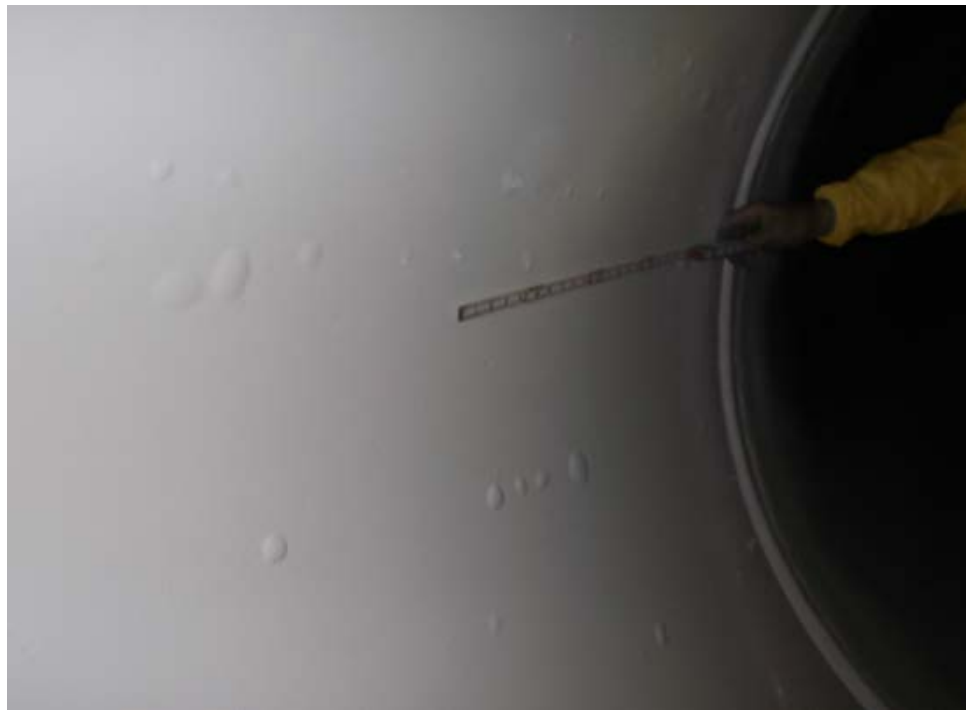


Figure 3: Extensive blistering shortly after the application of a fast set polyurethane lining caused by a heat-sink phenomenon. Flatiron Penstocks, 2017.

The polyurethane lining failure in the Flatiron penstock was not an isolated incident. Inspection reports from Enders Dam in Enders, Nebraska show that disbonded lining was discovered in the outlet works in 2011 [21]. The lining, an elastomeric polyurethane (Polyurethane C), had only been in service for one year. The damage, located around two manholes, was repaired with a 100 percent solids epoxy. Figure 4 shows damaged lining around the interior of a manhole.



Figure 4: Damaged lining around a manhole at Enders Dam after one year of service.

In 2016, another inspection of the polyurethane lining at Enders Dam revealed additional regions of disbonded lining at expansion joints and near valves. Cracked and damaged coating with underlying corrosion was also found at other transition points within the pipe. Figures 5 and 6 show regions of disbondment near a jet valve [21].



Figure 5: One area of disbonded elastomeric polyurethane in the outlet works at Enders Dam [7]. Disbonded polyurethane was found after one and six years of service.



Figure 6: Polyurethane termination point near a jet valve. Cracking and subsequent corrosion undercutting caused the lining to disbond and lift off the pipe surface.

At both Flatiron Penstocks and Enders Dam, inspection reports noted that regions of delamination and disbondment occurred near termination points of the coating—the point where the spray coat ends. They found that polyurethane failure occurs when cracks develop near the termination points. Corrosion then develops in the cracks and advances underneath the lining. This undercutting results in a slightly lifted edge of lining that can be delaminated by flowing water. Findings of one laboratory study showed that polyurethanes have much poorer corrosion undercutting than coal tar enamel and epoxies, particularly when in immersion service [16].

Reclamation also used Polyurethane B to line the outlet works at Platoro Dam in southwestern Colorado. A subsequent inspection report showed that the lining was performing well with no observable issues after five years of service [22]. Figure 7 shows the condition of the polyurethane around an expansion joint. No signs of blistering or delamination were observed.



Figure 7: Typical coating condition at an expansion joint in the outlet works at Platoro Dam. The polyurethane lining had been in service for five years.

While the failure of some elastomeric polyurethanes is detailed in inspection reports, the reason why this behavior occurs is not easily reproduced. Although penstocks and outlet works are notoriously difficult environments for any modern coating, Reclamation has lined these structures with coatings other than polyurethanes without encountering large section disbondment and delamination.

Rigid polyurethanes have also shown mixed results. A factory-applied rigid polyurethane on the interior of a 108-inch raw water bypass line at a municipal water treatment plant has been in service for nearly 20 years with no major problems [23]. A 2018 inspection report documents a

visual inspection as well as the results of Field Electrochemical Impedance Spectroscopy (F-EIS).

The visual inspection of the bypass found the lining to be in generally good condition with regions of lining delamination near pipe joints as well as clusters of blisters that the inspection report attributed to application defects [24]. F-EIS results from three locations within the bypass showed that the lining has remarkably high barrier properties in some locations, while other locations suggest lining deterioration despite visually appearing to be in good condition. F-EIS results are shown in Figure 8.

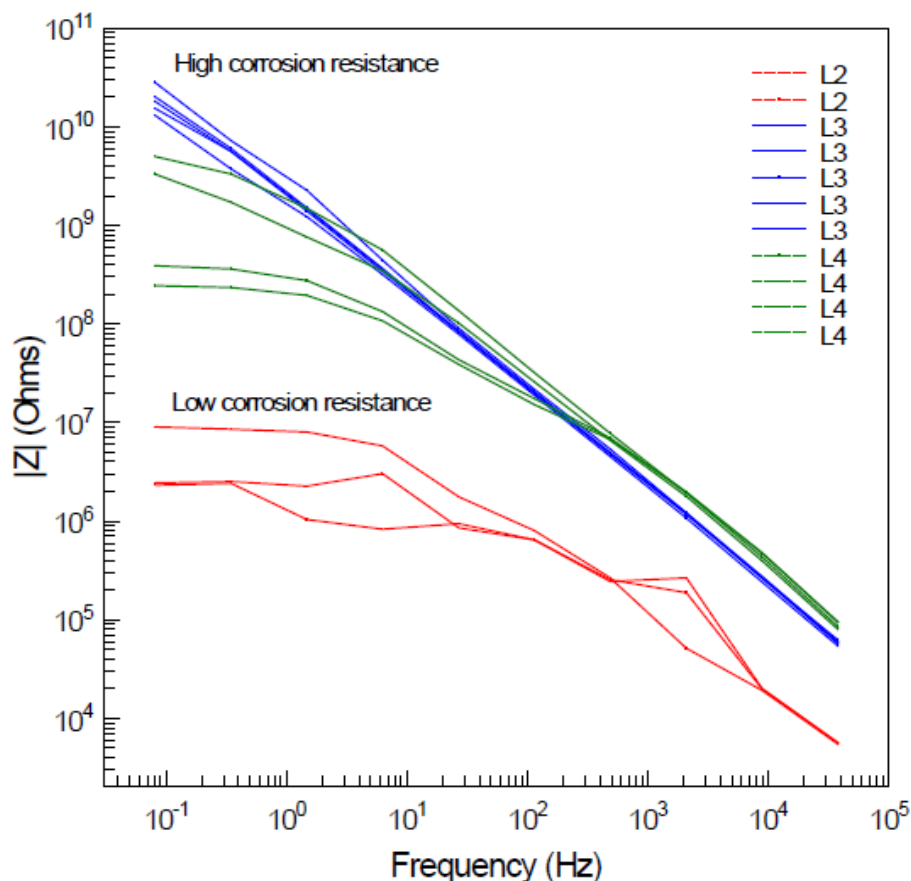


Figure 8: F-EIS bode plot of a rigid polyurethane lining in a water bypass. After nearly 20 years in service, two locations had excellent barrier protection and one location suggests lining degradation [24].

Epoxies

Reclamation has had some field experience with 100 percent solids and high solids epoxies as outlet works linings, but have used them primarily for maintenance and repairs of coal tar enamel and polyurethanes. They are abrasion resistant, have good adhesion, and do not have brittle failures. Table 2 gives properties of some 100 percent solids epoxies and one high solids epoxy that Reclamation has specified as spot repair or full recoat materials.

Table 2: Properties of some epoxies that Reclamation has specified.

Coating Material	Use	Observed Service Life	Slurry Erosion (mg/hr)	Pull-off Adhesion (psi)	Undercutting (in)	Impact (in-lbs)
Epoxy A	Full lining	>8 years	Not Tested	2190 \pm 390	0.297	100
Epoxy B	Lab testing	N/A	11.0	2034 \pm 261	0.05	110
Epoxy C	Repair	>7 years	Not Tested	1833	0.5	87
Epoxy D	Lab testing	N/A	Not Tested	1390	0.281	100
Epoxy E (high solids)	Lab testing	N/A	83.9 \pm 10.7	1278 \pm 280	.002	32

Epoxy C was used as a repair material at Flatiron Penstocks and at Enders Dam. Epoxy A was used as the coating for the interior of the outlet works at Shadehill Dam. For some epoxies, corrosion undercutting is much lower than that of the polyurethane materials.

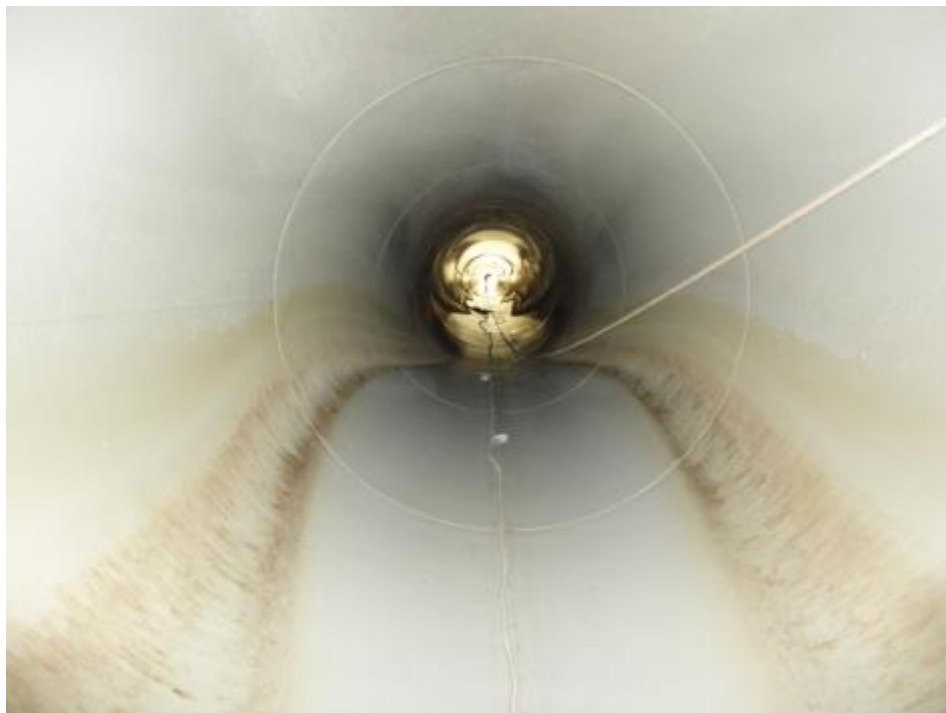


Figure 9: General condition of an epoxy lining after one year of service in the outlet works at Shadehill Dam.

The epoxy lining the outlet works at Shadehill Dam near Lemmon, South Dakota, has been in service for eight years—longer than any other epoxy specified by Reclamation as a full coal tar enamel replacement. The service conditions and how frequently the outlet works is used is unknown. An inspection report after one year of service showed that the lining was in good condition with one small area of delamination and minor rust deposits at the expansion joints [25]. The report attributed the expansion and contraction of the joints as cause for the damage and did not suspect the coatings to be faulty. A brief follow-up inspection in 2017 found no major issues. Figures 9 and 10 show the general condition of the lining and detail of the rust deposits at the expansion joints, respectively.



Figure 10: Rust deposits along the expansion joint in the outlet works at Shadehill Dam after one year of service. The inspection report attributed the rust to the expansion and contraction of the joints and did not find the epoxy to be at fault.

Although epoxies are a promising candidate to replace coal tar enamel, their ability to provide long-term corrosion protection is unsubstantiated. With observed service lives of between 15 and 30 years, modern epoxies need further development to fully match the performance of coal tar enamel [26]. On the other hand, Epoxy A and Epoxy C are still in good condition despite nearing the midpoint of their expected service lives.

Laboratory EIS results provide a method of comparing the barrier properties and rate of degradation of polyurethane and epoxy coatings over time. Figure 11 compares the barrier properties of Polyurethane B and Epoxy A over a period of six years in immersion. Polyurethane B shows higher initial impedance with a smaller change over time compared to Epoxy A. Figure 12 shows the bode plots for Epoxy C and Polyurethane C during a period of two years. The rate of degradation of Epoxy C is greater than that of Polyurethane C due to the epoxy's water uptake over time. Newly developed epoxies like Epoxy B (bode plot shown in Figure 13) have similar

barrier properties through one year in immersion compared to Polyurethane C. Further monitoring is needed to determine the extent of Epoxy B's water uptake over time.

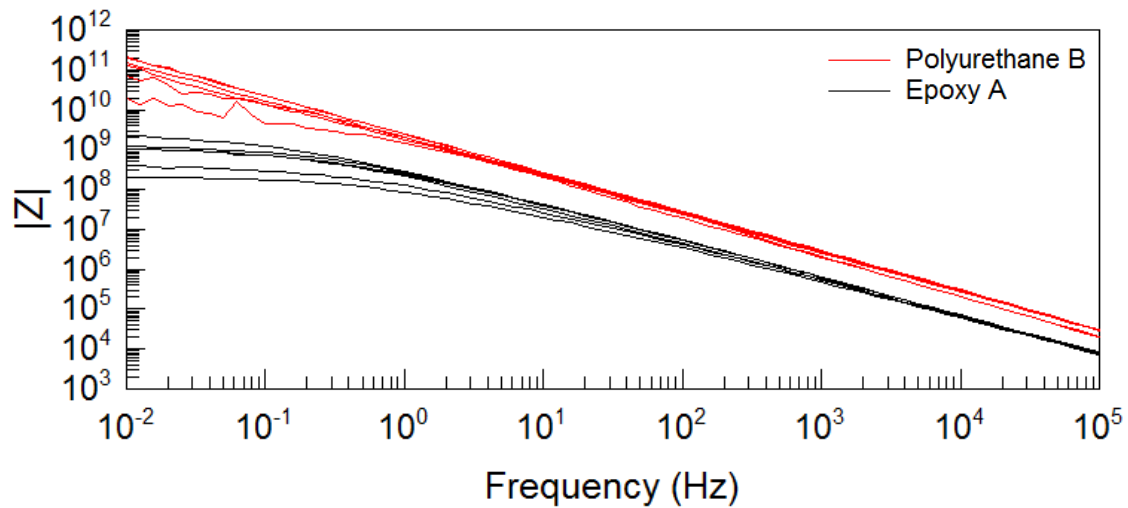


Figure 11: Bode plot comparing Polyurethane B and Epoxy A over 6 years in immersion. Polyurethane B had a higher initial impedance than Epoxy A.

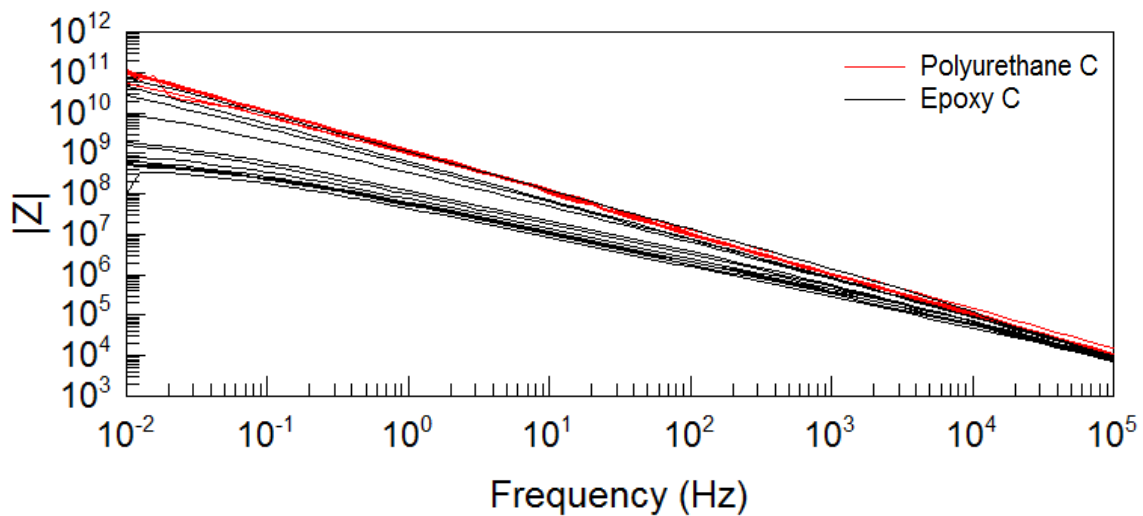


Figure 12: Bode plot comparing Polyurethane C and Epoxy C over 2 years in immersion. Epoxy C has a higher rate of degradation due to water uptake.

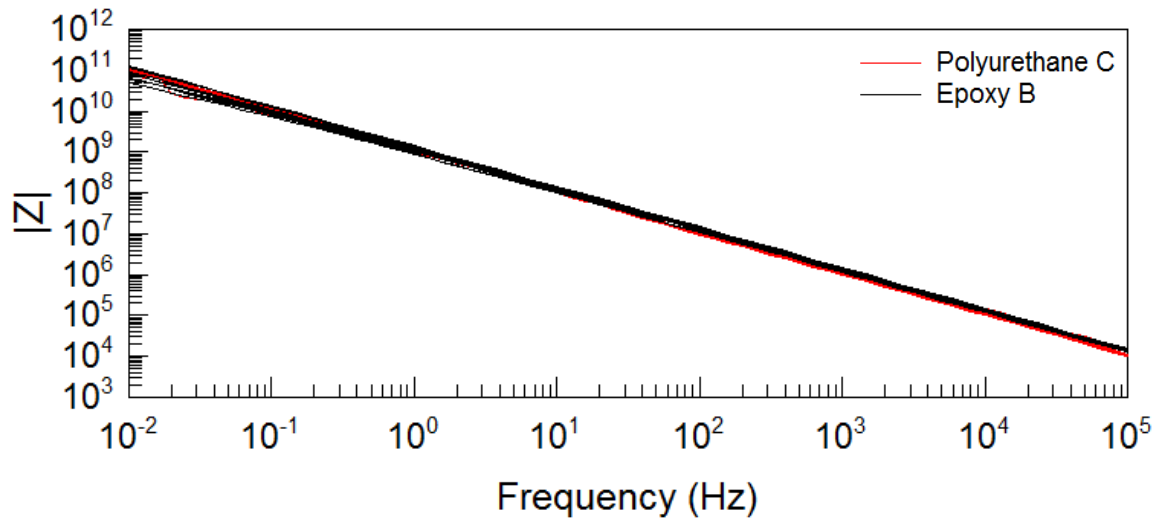


Figure 13: Bode plot comparing Polyurethane C and Epoxy B over one year in immersion. Newly developed Epoxy B has similar, if not slightly better, barrier properties to Polyurethane C.

THE FUTURE

The future of coatings technology is yet to be seen, although we can be certain that robotics will play a big role. Whether robotics will be used to apply brand new coating systems or the hazardous coatings of the past, their widespread use will mark a new era in the protective coatings industry.

The biggest benefit that will come about due to the use of robotics in surface preparation and coating application is cost savings. One report estimates that 30 to 40 percent of the total cost of a coatings application job goes toward activities related to readying the workspace for human access and reducing safety risks [27]. In addition to the human element, cost savings will come about directly and indirectly through a shortened outage period, increased production capabilities and product quality (resulting in an increased coating life), and higher efficiency resulting in a reduction of blasting and coating materials needed.

Robots are already being used to clean and recoat steel pipes that were previously lined with coal tar enamel and other coatings. One major painting contractor removed existing coating from, abrasive blasted, and relined a 104,000-sq. ft. penstock in just 90 days using specially designed robots [28]. The penstock, which was the site of the most recent of five robotics-assisted relinings over 100,000 sq. ft., is sloped at 45 degrees.

One major hurdle is getting the coating material to the robot. In some situations, access points within the pipeline are few and far between or even non-existent. For robotics technology to become mainstream, engineers and paint manufacturers must find solutions for pumping the coating long distances, and formulate coatings that can withstand the journey.

CONCLUSION

Ever since coal tar enamel has been phased out, Reclamation has been working to find alternative coating systems that will perform well in the service conditions of its penstocks and outlet works. Catastrophic issues with adhesion and delamination of some polyurethane coatings has essentially put a hold on Reclamation specifying them for use as lining materials until the exact cause of the failures is learned. Other polyurethane linings, however, are still performing well after nearly 20 years in service.

Epoxies have been used by Reclamation as the primary repair material for coal tar enamel and polyurethanes, but long-term data is insufficient to determine the extent to which they will degrade after decades in immersion. In addition, EIS data suggests that their barrier properties are inferior to those of some polyurethanes due to water uptake. Recent examination of a newer-generation epoxy, however, has shown that barrier properties are improved at least over shorter time scales.

The big question remains: where do we go from here? Will advances in coating formulations resolve the issues of undercutting and poor barrier properties? Or will the advance in robot technologies for coating application elicit a resurgence of the use of legacy coatings or solvent-based coatings normally too risky to apply in confined spaces?

This is a call to action for facility owners, coatings manufacturers, and coatings researchers to come together to take a serious look at the current state of protective coatings technologies. To share experiences. To become aware of the persistent issues and to formulate new coatings that can solve them. To overcome the trials and tribulations involved with finding an optimum lining material we all have to work together.

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