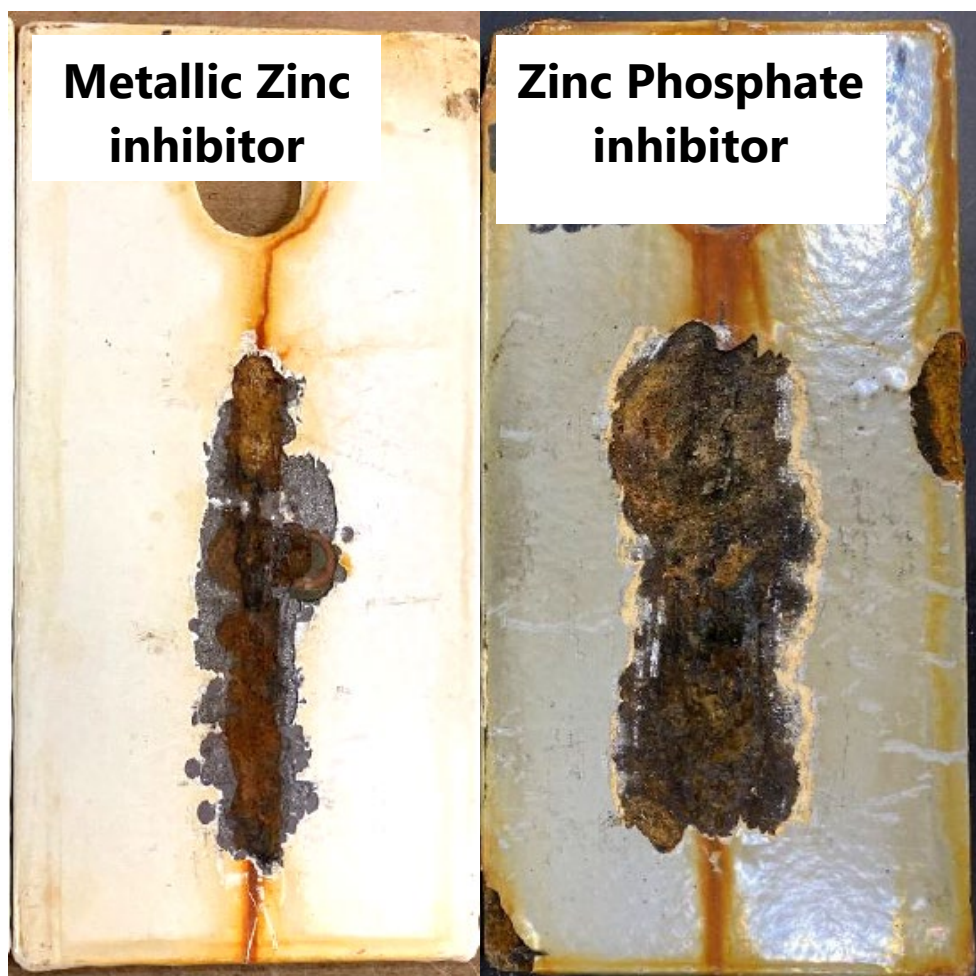# Evaluation of Corrosion Inhibitive Coatings

Science and Technology Program
Research and Development Office
Final Report No. ST-2021-19168-01
Technical Memorandum No. 8540-2021-74

Metallic Zinc inhibitor

Zinc Phosphate inhibitor

U.S. Department of the Interior December 2021

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14. ABSTRACT
Coating systems currently specified for use to protect Reclamation's aging infrastructure are expected to only provide 20-30 years of service before needing replacement. Legacy coating systems like lead-based alkyds, a type of coating called inhibitor coatings, exhibit service lives upwards of 80 years. Unlike barrier coatings that passively act as an obstacle to block the electrolyte from reaching the metal substrate and causing corrosion, inhibitive coatings actively prevent corrosion by stunting or polarizing the reaction. This work comprehensively studied modern inhibitive coating systems through electrochemical impedance spectroscopy (EIS) and rust creep evaluation to understand the resulting barrier properties when subject to accelerated weathering. Adhesion strength, impact resistance, and cathodic disbondment were also evaluated with the overall goal of identifying an inhibitive system that may withstand Reclamation's severe service environments and outperform commonly used barrier coatings. One system containing metallic zinc inhibitors did perform as well as the benchmark, but long-term testing is still needed to better evaluate performance.

15. SUBJECT TERMS
Coatings, corrosion, corrosion inhibitors, service life, infrastructure sustainability

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Evaluation of Corrosion Inhibitive Coatings

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Peer Review

Bureau of Reclamation
Research and Development Office
Science and Technology Program

Final Report ST-2021-19168-01
Technical Memorandum No. 8540-2021-74

Evaluation of Corrosion Inhibitive Coatings

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Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
BOR	Reclamation-developed cyclic testing
CD	Cathodic disbondment
DI	Deionized
EIS	Electrochemical Impedance Spectroscopy
FOG	Fog chamber exposure
HAR	Dilute Harrison's solution
PRO	Prohesion cyclic testing
QUV	UV chamber exposure
Reclamation	Bureau of Reclamation
UV	Ultraviolet

Symbols and Measures

adh	Adhesion failure
CD	Cathodic disbondment
coh	Cohesive failure
°C	degrees Celsius
in	inch
g	Glue failure
g/L	grams per liter
hr	hour
Hz	Hertz
lbs	Pounds
mm	Millimeter
mV	Millivolt
N/A	Not containing inhibitor
O	Organic inhibitor
psi	pounds per square inch
s	Scribed
u	Unscribed
Z	Metallic zinc inhibitor
ZP	Zinc phosphate inhibitor

Contents

Executive Summary

Bureau of Reclamation (Reclamation) coating researchers have traditionally focused their efforts on evaluating barrier-type coating systems—coatings which passively prevent corrosion by physically blocking the electrolyte from contacting the substrate. In laboratory and field studies, barrier coatings have been shown to have service lives of approximately 20-30 years depending on the type of coating and the service conditions. This is in stark comparison to legacy coating systems which were able to protect Reclamation's infrastructure for upwards of 80 years. Some legacy systems, including lead-based alkyds, were another type of coating—inhibitive coatings. Inhibitive coatings actively prevent corrosion via a variety of mechanisms including (but not limited to) reacting with the electrolyte to form metal soaps, forming tightly adherent oxide films, and/or by containing sacrificial pigments which preferentially corrode.

A previous S&T scoping study (Project ID 1703, Review of Corrosion Inhibiting Mechanisms in Coatings) identified metallic zinc, zinc phosphate, and organic pigments as the most common additives in inhibitive coating systems. This work comprehensively studied commercially available and experimental coating systems that contain those corrosion inhibiting pigments to determine if any inhibitive systems exist that meet or exceed the performance of legacy systems. Due to environmental regulations prohibiting testing of lead-based coatings, this work utilized two vinyl systems as the performance benchmark.

The results showed that for cyclic exposures, average rust creep in systems containing zinc phosphate and organic inhibitive pigments is significantly greater than in systems containing metallic zinc. However, on average, zinc phosphate coatings had slightly better barrier properties measured through electrochemical impedance spectroscopy than coatings containing metallic zinc pigments. Metallic zinc pigments were found to greatly improve impact and undercutting resistance compared to their non-inhibitive counterparts and had some of the highest impact resistances of all systems evaluated. However, the high loading of zinc and zinc primer cohesion resulted in decreased adhesion strength. One of the organic inhibitor systems performed well in adhesion and had good barrier protection while the other had excellent impact resistance; however, these systems comparatively missed the mark in all other testing. Electrochemical results showed that some systems' barrier protection improved over the evaluation period, suggesting inhibitor activation or some other self-healing/strengthening of the coating or substrate's passivation layer.

One coating system, a zinc-rich epoxy primer with a polysiloxane topcoat, performed as well as the zinc-rich vinyl benchmark system. Furthermore, the two-coat zinc-rich epoxy system has significant application time and cost advantages over the five-coat zinc-rich vinyl benchmark which requires sanding between each coat. While longer term testing is needed to verify equivalent performance, the results of this study indicate some emerging modern coating systems are meeting the standards of legacy systems.

Introduction

Coating systems currently specified for use to protect the Bureau of Reclamation's (Reclamation) aging infrastructure are only expected to provide 20-30 years of service before they need to be replaced. In addition, regular maintenance and repairs must be performed on most coatings before the service life is even reached. The act of maintaining and relining Reclamation's coated structures costs millions of dollars every year—with full recoating projects costing upwards of $1 million alone—not including revenue lost from taking vital structures out of service while the coating is repaired. Legacy coating systems like lead-based alkyds have exhibited service lives upwards of 80 years. Lead-based alkyds, a type of coating called inhibitor coatings, actively prevent corrosion through multiple mechanisms that all result in the disruption of the electrochemical corrosion reaction. In comparison, barrier coatings, the type of coatings that are widely researched and utilized by Reclamation, passively prevent corrosion by acting as a barrier between the electrolyte and metal substrate.

While most of Reclamation's research focuses primarily on barrier coating systems for use in immersion service, little work has been done to comprehensively study inhibitor coatings for use on structures that face severe atmospheric conditions. Features like penstock exteriors and the downstream side of gates regularly face conditions like severe heat or cold and constant UV exposure. The present work builds upon a literature review in which a variety of corrosion inhibiting pigments were identified. Those inhibitors were metallic zinc, zinc phosphate, and organic inhibitors. While other types of inhibitive pigments exist, i.e., chromates and the forementioned lead, they are hazardous in nature and no longer approved or appropriate for use on Reclamation's structures.

The present work systematically evaluated commercially available and experimental inhibitive coating systems containing metallic zinc, zinc phosphate, and organic pigment inhibitors. Coated coupons underwent a suite of accelerated weathering, electrochemical evaluation, and mechanical testing. The results were compared to those of a benchmark system, the U.S. Army Corps of Engineers 5EZ zinc-rich vinyl, which has traditionally provided excellent protection in severe service environments but can now only be used in limited applications due to environmental regulations.

Previous Work

This current study builds off the findings of S&T Project ID 1703, Review of Corrosion Inhibiting Mechanisms in Coatings, which is in Appendix A. S&T Project 1703 identifies the various types of corrosion inhibiting pigments commonly found in legacy and modern coating systems and evaluates the mechanisms by which they actively prevent corrosion.

Methods

Coating Systems

Table 1 lists the coating systems evaluated in this study. All inhibitive pigments were in the primer component of the coating systems. Systems Z-4 and Z-4(N/A) are the benchmarks. To directly compare inhibitor performance, the same topcoats were used for systems ZP-1 and Z-1 (polysiloxane A), and systems ZP-2 and Z-2 (polysiloxane B). Systems Z-3 and the zinc-rich vinyl benchmark (Z-4) were evaluated alongside non-inhibitor-containing versions of the same system, Z-3(N/A) and Z-4(N/A), respectively. Surface preparation and application of coating systems were conducted according to manufacturer recommendations.

Table 1 Evaluated coating systems and corrosion inhibitor types

System ID	Primer/ /Topcoat	Inhibitor Type
ZP-1	Epoxy A/polysiloxane A	Zinc phosphate
ZP-2	Epoxy B/polysiloxane B	Zinc phosphate
Z-1	Zinc-rich epoxy A/polysiloxane A	Metallic zinc
Z-2	Zinc-rich epoxy B/polysiloxane B	Metallic zinc
Z-3(N/A)	Polysulfide epoxy	N/A
Z-3	Zinc-rich polysulfide epoxy	Metallic zinc
Z-4(N/A) *benchmark*	Vinyl (5 coats)	N/A
Z-4 *benchmark*	Zinc-rich vinyl/4 coats vinyl (4 coats)	Metallic zinc
O-1	Urethane/epoxy	Organic
O-2	Epoxy	Organic

Test Protocols

Table 2 shows the corrosion test protocol for each coating system. The testing was performed on coated 3 in x 6 in x 0.125 in steel coupons, either scribed (s) or unscribed (u) as noted. The "one-sided" rust creep for each panel was determined by measuring with a caliper after coating removal. The full width of the rust area was measured on each panel at six equidistant locations along the scribe, averaged, adjusted for the initial scribe width, and divided by two.

Table 2 Corrosion test protocol summary showing number of scribed (s) and unscribed (u) coupons tested

Immersion Exposure		Cyclic Exposure			
Dilute Harrison (HAR)[1]	Deionized Water (DI)[2]	Salt Fog (FOG)[3]	UV + Condensation (QUV)[4]	Prohesion (PRO)[5]	Immersion + Salt Fog + QUV (BOR)[6]

2s/1u	2s/1u	1s/1u	1s/1u	2s/1u	2s/1u

[1]*ASTM D870: Harrison's Solution is 0.5 g/L NaCl, 3.5 g/L $(NH_4)_2SO_4$, testing performed at room temperature.*
[2]*ASTM D870: DI water, testing performed at room temperature.*
[3]*ASTM G85 Annex A5: 1 hr fog at ambient temperature using Harrison's Solution, 1 hr dry-off at 35 °C.*
[4]*ASTM D4587: Test condition "B," 4 hrs UV at 60 °C followed by 4 hrs condensation at 50 °C.*
[5]*ASTM D5894: 1-week alternating exposure in QUV and FOG.*
[6]*1-week alternating exposure schedule in the following repeating order: QUV, FOG, HAR, FOG.*

Electrochemical impedance spectroscopy (EIS) was performed on the unscribed immersion coupons periodically throughout the 30-week evaluation period. Test parameters for all EIS measurements were 10 mV sinusoidal perturbations at the open circuit potential, a frequency range of 10^5 to 10^{-2} Hz, and ten data points per decade.

Cathodic disbondment (CD) testing was performed on a 3-in diameter pipe. Adhesion testing was performed both prior to immersion and after prolonged immersion of at least 7 months (wet). For the wet adhesion test, the panel was removed from the Harrison's solution, dried, and dollies were attached with glue. The panel was then placed in 100 percent humidity for 24 hours while the glue cured prior to pull off testing. Adhesion pull-off tests that had more than 20 percent glue failure were excluded from results. Table 3 shows the cathodic disbondment and mechanical test protocol for each coating system.

Table 3 Mechanical test protocol and substrates utilized for testing

Cathodic Disbondment ASTM G8	Impact Resistance ASTM D2794	Pull-off Adhesion ASTM D4541	Pull-off Adhesion (wet) ASTM D4541	Knife adhesion test (wet) ASTM D6677[1]
3 in diameter pipe	3 in x 6 in x 1/8 in coupon(s)	3 in x 6 in x 1/8 in coupon	3 in x 6 in x 1/8 in coupon	DI and HAR coupon(s)

[1]*Test performed on HAR and DI panels, post immersion.*

Results and Discussion

A full set of tabulated results and coatings' rating criteria can be found in Appendix B and Appendix C, respectively. Due to material availability, some coating systems did not undergo every test; those instances are designated as "not tested" in the tables. For example, the organic inhibitor systems' results are largely found in the appendices which provide and discuss all testing results. Most findings of this work were disseminated through a conference paper that was supposed to be presented at the 2021 Coatings+ conference held in Phoenix, AZ from December 13-16, 2021. At the time of the conference, Reclamation staff were unable to travel due to COVID-19 restrictions and the paper was pulled; thus, the paper is pending submission to a different (yet to be determined) conference. Once the new conference has occurred, this interim report will be updated with the final conference paper and finalized. The conference paper, titled "Evaluation of Inhibitor Coating

Systems for Use in Hydropower Applications," is reproduced in Appendix D, and includes results and discussion for corrosion undercutting, impact resistance, pull off adhesion, and EIS. Readers should refer to Appendix D for a thorough discussion of those results; the results in the subsequent sections of this report summarize the findings from the cathodic disbondment testing, wet pull-off adhesion, and knife adhesion testing which are not discussed in the conference paper.

Cathodic Disbondment

The results of the cathodic disbondment testing are shown in Figure 1. Of the five coating systems evaluated, all three of the test systems performed better than the vinyl benchmark systems. System ZP-1 had the only excellent rating, with ZP-2 and Z-2, each with a disbondment radius of 0.25 in having a "good" rating. Interestingly, the zinc addition to the vinyl system lowered the disbondment radius from 3.125 in to 1 in; however, neither system would be applied in conjunction with a cathodic protection system.
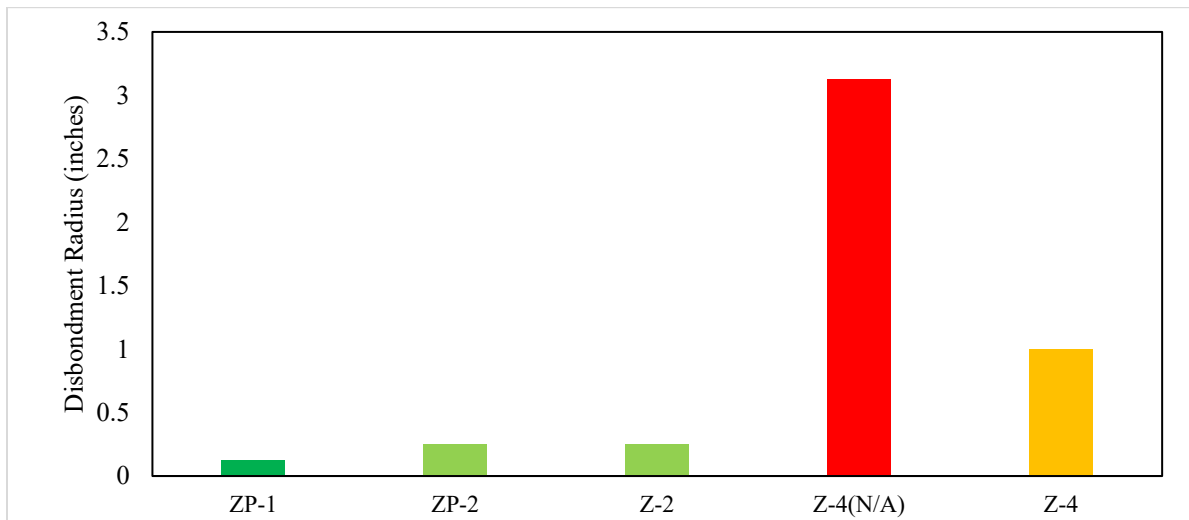

Figure 1. Cathodic disbondment results for coating systems tested. Systems ZP-1, ZP-2, and Z-2 have significantly lower disbondment radii from the vinyl benchmark systems (Z-4) and Z-4(N/A).

Wet Adhesion

Figure 2 gives the results of the wet adhesion testing for systems having less than 20 percent glue failure. Both vinyl benchmark systems had glue failures exceeding 20 percent. None of the systems evaluated met the criteria for an "excellent" rating (greater than 2,000 psi). Both zinc phosphate systems had higher wet adhesion strengths than any of the other systems evaluated and were greater than 1,000 psi, thus garnering a rating of "good." System Z-2 had the worst wet adhesion strength at an average of 551 psi, nearly ranking in the "poor" category. The other metallic zinc containing system evaluated, Z-3, had an average wet adhesion strength of exactly 1000 psi indicating "good" adhesion. System Z-3(N/A), which doesn't contain the metallic zinc inhibitors, had a slightly lower average wet adhesion strength, indicating the metallic zinc pigments do not necessarily affect wet adhesion strength.
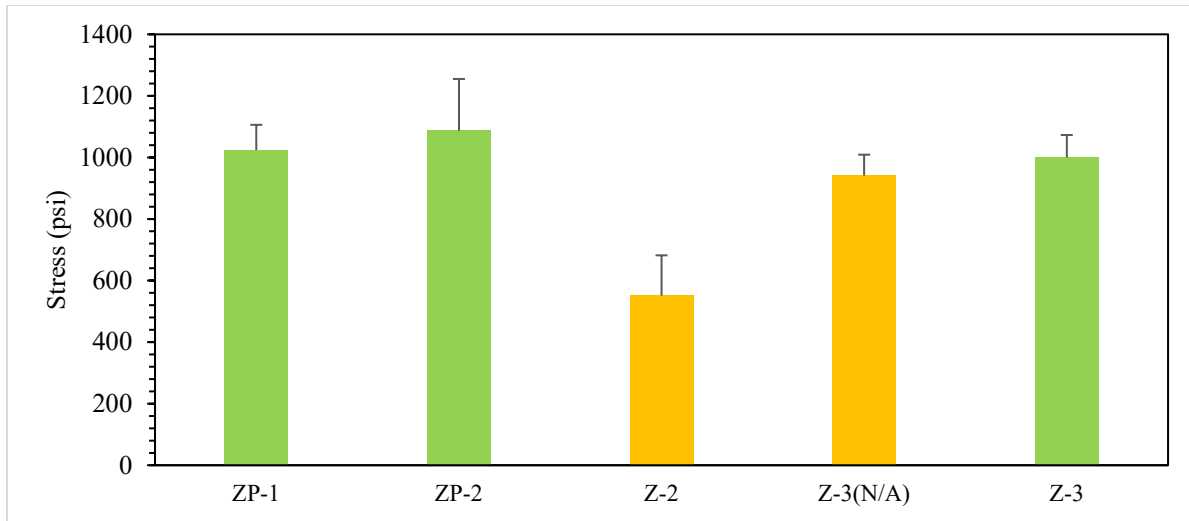
Figure 2. Wet adhesion strength results for systems having less than 20 percent glue failure. Most evaluated coating systems had good wet adhesion strength, but none met the criteria for an "excellent" rating.

Knife Adhesion

Figure 3 shows the results of the knife adhesion testing. The two evaluated zinc phosphate systems had the maximum ASTM rating of 10, indicating it was very difficult to chip away the coatings. System Z-2 had a "poor" rating, with the topcoat able to be peeled away from the primer using fingers. The addition of the metallic zinc in system Z-3 increased the ASTM rating from 6 to 8, but both are still considered to be "good." Both versions of the benchmark vinyl system had the same "fair" ASTM rating.
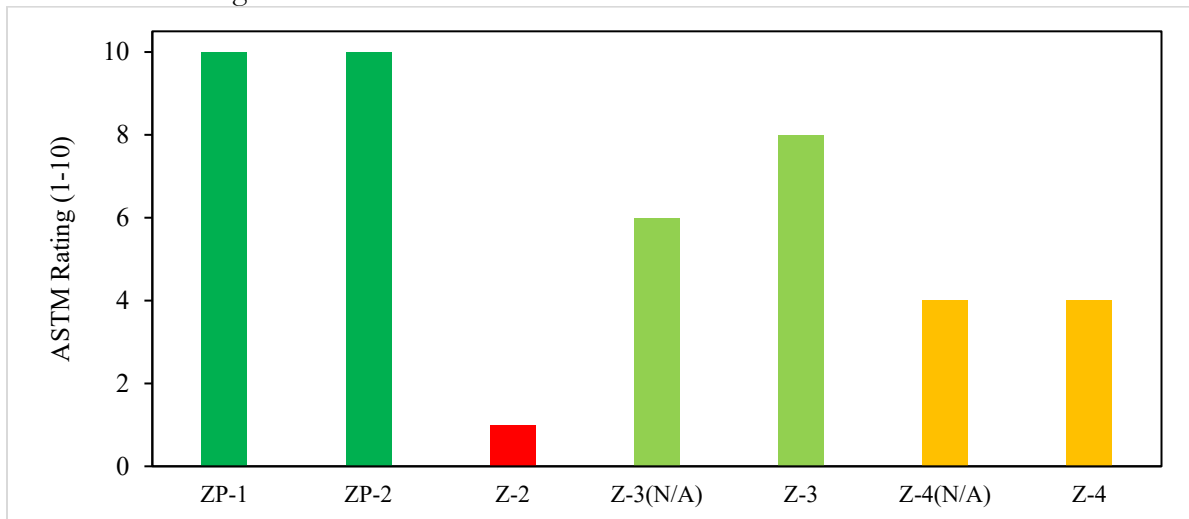

Figure 3. Knife adhesion results for coating systems evaluated. The zinc phosphate systems both have the maximum ASTM rating of 10, indicating the coating was very difficult to chip away from the panels. The vinyl benchmarks both rated as "fair."

Conclusions

This work has exemplified that multiple corrosion and physical evaluations are necessary for fully understanding a coating system's performance in a variety of service conditions. In hydropower applications where impact from debris is an issue, metallic zinc-containing systems may be most appropriate. Zinc phosphate-containing systems may provide better overall corrosion protection and may be more suitable for use in general service environments without special considerations. While longer term testing is needed to verify equivalent performance, the results of this study indicate some emerging modern coating systems are meeting the standards of legacy systems. Once performance is validated, Reclamation should consider inhibitor-containing coating systems for use on its infrastructure. Successful implementation of the results of this work may result in longer service lives and, ultimately, benefit Reclamation through time and cost savings.

Specific conclusions of this work are below. Conclusions include findings from all testing associated with this project. A full set of quantitative results is in Appendix B.

- In cyclic exposures, metallic zinc systems had significantly less rust creep than zinc phosphate and organic inhibitor systems.
- Metallic zinc pigments improved impact and undercutting resistance compared to the same system without the inhibitors; adhesion strength decreased when pigments were added.
- Zinc phosphate coating systems had better barrier properties measured through EIS than metallic zinc coating systems.
- Organic inhibitors showed mixed results for adhesion, barrier protection, and impact resistance; in general, results were inconclusive.
- For some systems, inhibitor activation was noted through electrochemical testing with barrier property improvement over the evaluation period.
- System Z-1 was found to perform similarly to the benchmark (over short evaluation periods). Z-1 has the added benefits of being a two-coat system with significant application time and cost advantages over the five-coat benchmark which may necessitate sanding between each coat. Longer term testing of System Z-1 is required to verify performance.

Appendix A – Review of Corrosion Inhibiting Mechanisms in Coatings

RECLAMATION
Managing Water in the West

Review of Corrosion Inhibiting Mechanisms in Coatings

**Research and Development Office
Science and Technology Program
(Final Report) ST-2017-1703**

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September 2017

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14. ABSTRACT
Modern coatings used by the Bureau of Reclamation have service lives of 20–25 years, whereas legacy coatings that contained red lead and chromate pigments had service lives of over 50 years. The mechanisms of corrosion protection of lead- and chromate-based coatings were researched, and literature was analyzed to identify nontoxic substitutes for these pigments. All inorganic pigments analyzed exhibited corrosion prevention mechanisms similar to that of red lead, in which metal soaps were formed with certain binders, and, in a secondary mechanism, the surface of the substrate was passivated. Conducting polymers, specifically pigments of polyaniline, were also found to be potential substitutes. The greatest challenge moving forward is to be able to quickly and objectively test commercially available coatings containing nontoxic pigments to determine if they perform as well as coatings that contained red lead or chromate.

15. SUBJECT TERMS
anticorrosion coatings, corrosion inhibitors, lead paint, inhibiting pigments

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Review of Corrosion Inhibiting Mechanisms in Coatings

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ACRONYMS AND ABBREVIATIONS

A_e	anticorrosion efficiency
c/PANI	polyaniline-coated graphite
PANI	polyaniline
PmAS	poly(m-anisidine)
PoAP	poly(o-aminophenol)
PoAT	poly(m-anisidine)
Reclamation	Bureau of Reclamation
UV	ultraviolet

Symbols

>	greater than
<	less than

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EXECUTIVE SUMMARY

Legacy coatings used by the Bureau of Reclamation (Reclamation) to protect the metalwork associated with water infrastructure often had service lives of 50 years or more. These coatings, however, contain toxic pigments such as red lead and chromate and are no longer specified for use. The currently specified coating systems, such as epoxies, have service lives of only 20–25 years, which results in extra costs incurred by Reclamation to recoat structures more frequently.

The long service lives of legacy coatings can be attributed to certain pigments within coatings that are considered corrosion inhibitors. Usually, a coating works to prevent corrosion by three general mechanisms: a physical barrier to prevent corrosive species from reaching the steel substrate, a sacrificial coating to corrode instead of the steel substrate, and a corrosion inhibitor that undergoes chemical reactions with the corrosive species to stop or impede corrosion. Since lead- and chromate-based coatings are no longer used by Reclamation, barrier and sacrificial coatings are the only types that are currently specified.

Red lead and chromate-based paints work well because they are inhibiting pigments. In the case of red lead-based coatings, the lead tetroxide pigments react with a component of the coating's binder to form a metal soap. These soaps degrade into a water-soluble lead salt, which can migrate to defects and inhibit corrosion by reacting with specific ions to form a stable, insoluble compound. As a secondary mechanism, lead tetroxide also passivates the metal, rendering the surface of the substrate unreactive by forming a thin, inert layer of oxides.

This literature review aimed to identify nontoxic inhibitive pigments that prevent corrosion using the same or similar mechanisms as lead and chromate pigments. Three broad categories of pigments were researched: inorganic, organic, and metallic. Inorganic pigments showed the most promise for becoming a replacement for lead. Of the four broad types of inorganic pigments researched (phosphates, molybdates, silicates, and ferrites), findings indicated that all can form metallic soaps in certain types of binder systems, specifically oleoresinous systems. The presence of zinc also seemed to be an important factor for soap formation. Strontium and calcium were also common additions.

Much of the research surrounding organic inhibiting pigments focuses on conducting polymers. Polymers that conduct electricity and act as a strong oxidant to steel result in shifting the potential to the noble direction and induce passivation. Polyaniline is the most commonly studied conducting polymer, and it has shown good promise as a corrosion inhibiting pigment [1]. In one study, polyaniline coated with graphite significantly outperformed other tested pigments, including a commercially available pigment specifically branded as "anticorrosive" [2].

Polyaniline was also tested against other organic polymers, including poly(m-anisidine) (PmAS) [3]. In that study, it was found that the chelating efficiency of the polymer greatly impacted its corrosion resistance. PmAS had a greater chelating efficiency than the other polymers and more reactive functional groups, giving it the best corrosion-resistant properties.

Metallic pigments, especially zinc pigments, inhibit corrosion by acting as sacrificial pigments and corroding preferentially to steel. Aluminum pigments have also been found to be inhibitors, particularly when coated with silica, a semiconductor. In another study, aluminum flakes were shown to form tightly interlocking structures on steel substrates and impede the movement of corrosion species to the steel.

A significant amount of work is being done to identify inhibitive pigments that can replace lead and chromate. However, it is exceedingly difficult to compare each individual research study, thus each pigment's performance, to one another. Further complicating matters, some pigments require a lag time when exposed to an aqueous environment before their corrosion prevention mechanisms are fully enabled. This issue would make it difficult to equally compare the coatings' performances in accelerated laboratory tests.

The first step to continue this research is to analyze current, commercially available coating systems that contain inhibitive pigments identified in this review and determine their expected failure mechanism. Knowing how the coating will fail will aid in predicting when it will fail—potentially saving valuable testing time. Next, accelerated laboratory testing aimed at emulating atmospheric service should be performed on the coatings to quickly determine their performance against one another. To account for the lag time that some pigments exhibit, it is suggested that those coatings undergo preconditioning in a humid environment (depending on typical lag times) prior to accelerated testing.

INTRODUCTION

Protective coatings prevent corrosion by one or a combination of three mechanisms: barrier protection, sacrificial (galvanic) protection, and corrosion inhibitive pigments. The first two mechanisms are not complex. Barrier coatings contain binders and pigments designed to impede the migration of an electrolyte to a substrate. Sacrificial pigments corrode preferentially to steel to prevent corrosion. Corrosion inhibitors generally function by disrupting the corrosion reaction typically through a competing reaction, but the exact mechanism or reaction depends on the specific pigment type.

Lead-based paints are a good example of a coating that utilizes inhibitive pigments to prevent corrosion. "Red lead" (lead tetroxide, Pb_3O_4) was used extensively within the Bureau of Reclamation (Reclamation) and industry in atmospheric service environments to provide corrosion protection to steel lasting upwards of 50 years. However, the exact mechanism for the success of lead paint is still not fully understood. Lead paints have been largely phased out due to environmental, health, and safety hazards. However, existing lead coatings continue to provide excellent corrosion protection on many Reclamation structures. Replacing old legacy coating systems such as lead-based paint with safe and modern equivalents is an important but challenging proposition for Reclamation. Many of the coatings specified today rely solely on barrier protection and provide a fraction of the service life, at 20–25 years, versus legacy coatings (50+ years).

This literature review aims to determine what other corrosion inhibitive pigments are available for use on steel infrastructure – specifically, how Reclamation can achieve similar anticorrosion performance (as lead-based paints) using environmentally compliant inhibitors or materials in coatings.

COATINGS BASICS

Most polymeric coatings contain multiple components: resin (binder), solvent, additives, and pigments. Corrosion inhibitors are part of the binder, additives, or pigments.

The binder is the backbone of the coating, and it provides most of the coating's features and functions. The type of binder used (acrylic, epoxy, polyurethane, etc.) usually lends its name to the generic coating name. Binder resins protect the substrate by wetting out the surface and adhering to it as a cured or dried film. Therefore, the resins transform from a liquid to a solid during film formation. Binders provide barrier protection for the underlying metal substrate, protecting the substrate from cathodic reactants such as oxygen, water, and corrosive anions [4]. However, binders are inherently permeable, and corrosive agents will reach the substrate at varying rates.

Solvents are added to a binder or resin to transform them into a liquid state or to reduce viscosity during application. The two most important properties of a solvent in a coating system are the solvency power, or the ability of the solvent to dissolve the resin or binder, and the volatility, or how quickly the solvent will evaporate from the coating after it has been applied. Once the coating is applied and cured, the solvent has no remaining role in the coating system. Some coating systems are formulated without any solvent at all.

Additives are important in providing coating systems with their unique properties and are added to perform a specific function. Additive functions can ensure coating stability, aide application and increase pot life, provide added ultraviolet (UV) resistance, increase shelf life, and influence curing times.

Pigments are discrete particulate solids that do not dissolve in the coating. Pigments are used for corrosion protection, to impart color, to increase water resistance, and to modify the coating's mechanical or electrical properties.

CORROSION BASICS

Corrosion is an electrochemical reaction that deteriorates a metal or an alloy [5]. Reclamation's structures are particularly susceptible to this deterioration based on their proximity to bodies of water and atmospheric exposure. Structures like gates, valves, penstocks, piping, and other exposed features are among some of the most prone to corrosion from condensation, spray, rain, and other environmental conditions.

Corrosion of steel requires four elements to complete the electrochemical cell: an anode (the metal that readily gives up electrons), a cathode (the metal that readily accepts electrons), an electrolyte (the liquid that helps the electrons move), and a metallic pathway for electron movement. The interaction of these elements is also known as a corrosion cell. Corrosion inhibitors interrupt the corrosion cell by removing one of these elements.

In general corrosion of steel, the steel acts as the anode, with adjacent areas acting as cathodes. In order to complete the corrosion cell, the steel is also a metallic pathway, and water or soil can be the electrolyte [6, 7].

Elemental iron is naturally unstable and releases electrons at the anode in the presence of oxygen to become a more stable ferrous iron, Fe^{2+} [8]. Those electrons move to the nearby cathodic sites on the surface, forming hydroxyl ions (OH^-) as they combine with oxygen and water. The Fe^{2+} from the anode reacts with the OH^- at the cathode to produce ferrous hydroxide and ultimately red rust.

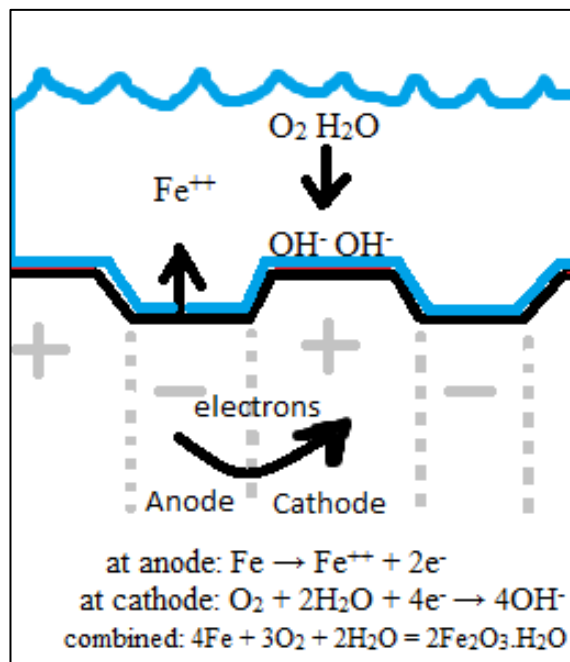Figure 1, below, depicts the corrosion mechanism for steel.

Figure 1: Corrosion mechanism for steel.

In general, the rate of corrosion is determined by the electrolyte and the difference in nobility between the metals or the area of steel, with the galvanic series determining which material is most noble. Typically, the more noble material, the cathode, is more resistant to corrosion than the less noble material, or the anode. Over long periods of time, the loss of metal from anodic sites is fairly uniform over the surface. This type of corrosion is known as general corrosion and usually does not result in catastrophic failure, although preventative measures should still be taken to prevent it. Pitting corrosion and crevice corrosion are considered localized corrosion and are more commonly associated with catastrophic failures of the structures. In both cases, there can be severe or complete loss of material from the anodic area if not detected.

Cost of Corrosion

NACE International estimated that the global cost of corrosion is $2.5 trillion, approximately 3.4 percent of the global gross domestic product [9]. In the United States alone, corrosion is estimated to cost over $276 billion, with $22.6 billion in costs directly associated with the corrosion of infrastructure [10]. If optimum corrosion management practices were employed, NACE estimates that 25–30 percent of this cost could be saved.

INHIBITIVE COATINGS CORROSION PROTECTION MECHANISM

Inhibitive coatings are typically included in the primer, or the first coat, of a coating system where they are in contact with the substrate to be effective. In general, inhibitive coatings reduce the rate of an electrochemical reaction that causes corrosion through the use of pigments.

Inhibiting pigments' various physical and chemical factors limit the rate of an electrochemical reaction by stunting or polarizing it [11]. Polarization can be anodic or cathodic and is the shift of electrode potential resulting from a net current. In cathodic polarization, electrons are sent to the substrate. Slow reaction rates cause a buildup of electrons, and the surface potential becomes negative. In anodic polarization, electrons are emitted from the metal. This deficiency causes a positive potential on the surface.

Coatings utilizing inhibitive pigments release soluble species from the pigment into the electrolyte once is has saturated the coating [12]. These species inhibit corrosion in a process called passivation by facilitating the growth of protective surface layers.

When metals lose chemical reactivity, it is called passivation. The metals are rendered inert and act more noble due to the formation of thin, tightly adherent oxide layers. There are two mechanisms of passivation: imposed passivation, which occurs by anodic polarization of the metal, and spontaneous passivation, which occurs in the presence of an oxidant [13]. Near-insoluble compounds are formed when a metal becomes anodic in a solution that only contains anions [11].

Sinko describes all active corrosion inhibitor pigments as inorganic salts with the general formula $A_m^{n+}B_n^{m-}$ [14]. Since corrosion is an aqueous process, corrosion inhibitor activity of pigments can be specifically characterized by their solubility in water. In general, the solubility of these pigments ranges from sparingly to slightly soluble. Thin, inert oxide layers form on the substrate when the solubility of pigments at saturation and normal temperature (expressed in molar concentration) is greater than the critical concentration of the anion, B^{m-}. Therefore, the anion inherently influences the rate of corrosion. The salt's cation has little effect on the pigment's inhibitive properties (with one exception being Zn^{2+}).

Inhibitive pigments can also protect macroscopic defects by leaching out from adjacent areas into the defect [15]. This self-healing mechanism, also known as active corrosion protection, is most commonly associated with coatings containing chromate pigments and is discussed in more detail under the "Chromate Pigments" section.

Red Lead Pigments

The two oxides of lead are litharge (PbO) and red lead (Pb_3O_4) [16]. Litharge, a yellow substance, is formed when elemental lead reacts with oxygen as it is melted. Upon further heating, the unstable litharge becomes red lead when it is oxidized. One of the first recorded pigment inhibitors, red lead has been used widely in primers for structural steel [17].

Sparingly soluble (solubility of < 0.001 percent) lead pigments are not actually direct inhibitors, but they can react with certain resin systems, linseed oils, or other oils to form metal soaps that are active inhibitors and appear to be the mechanism by which lead pigments inhibit corrosion on both new and rusted steel [18, 19, 20]. These soaps degrade into water-soluble lead salts, which can migrate to defects and inhibit corrosion by reacting with certain ions to form a stable, insoluble compound. Soluble lead compounds and organic acids are then released in the presence of water and oxygen as fatty acids degrade [21]. Examples of lead salts are azelaic acid ($C_9H_{16}O_4Pb$), suberic acid ($C_8H_{14}O_4Pb$), and pelargonic acid ($C_9H_{18}O_2Pb$), which have been proven to be corrosion inhibitors [22, 23].

These salts lower the pH of a solution by contributing hydrogen ions as it hydrolyzes water and produces iron(III) oxide-hydroxides. The liberated hydrogen promotes passivation by strengthening the metal's oxide film until it becomes impermeable, impeding corrosion [24]. According to Mayne and Ramshaw, the inhibitive efficiency of lead salts increases with the length of the carbon chain to a maximum of 9 carbon atoms [25]. This effect can be attributed to a compound's enhanced surface activity. In addition, the polar functional groups containing oxygen atoms are adsorbed onto the steel substrate and act as barriers blocking corrosion sites [26].

Chromate Pigments

Although chromates have not been used as extensively as lead throughout Reclamation's history as corrosion inhibitive pigments, they are among the most efficient passivators. Generally, hexavalent (Cr^{6+}) chromium (a strong oxidizer) and trivalent (Cr^{3+}) chromium ions provide high corrosion resistance to chromate coatings [27]. When under corrosive attack, the hexavalent chromium undergoes active corrosion protection and reduces to form trivalent chromium. The insoluble trivalent chromium can then end the attack.

Coating manufacturers have been able to tailor chromate's ability to dissolve and release ions due to the wide range of solubilities of different chromate pigments [22]. If the solubility is too high, and the pigment is under long-term moisture conditions, blisters may form. Chromate pigments are therefore not suitable for use in immersion conditions or other conditions with long periods of exposure to moisture.

In general, use of chromates as inhibitive pigments in coatings is declining due to health and environmental concerns, and regulations prevent Reclamation from using them.

HISTORY OF INHIBITIVE PIGMENT USE ON RECLAMATION'S STRUCTURES

Red Lead Primer

Alkyd primers and drying oils containing "red lead" had been used extensively by Reclamation to protect its structures, specifically formulations TT-P-86 type I linseed oil, II Linseed oil/alkyd, III alkyd, and IV phenolic resin tung oil. Types I, II, and III were specifically used for atmospheric exposure only; type IV could be used in immersion service. Application on the exterior of penstocks and on bulkhead gates was most common. Figure 2, below, shows the lead-coated penstock exteriors at Flatiron Powerplant in 2007.

Figure 2: Lead-coated penstock exteriors at Flatiron Powerplant in 2007. The exteriors were recoated with a zinc-rich primer and polyurethane topcoat in 2010.

A Reclamation analysis of some of these structures revealed that the average service life of red lead primer was 64 years. This value was calculated by only considering the service lives of the red lead primer on the structures that have since been repainted.

Table 1, below, depicts the original red lead coating date of structures at various Reclamation facilities.

Table 1: Original red lead coating date of structures at various Reclamation facilities

Facility	Structure	Original coat date
Colorado River Basin Salinity Control Project*	Delivery piping and valve seat	1985
Crystal Dam*	Exterior penstock	1977
Flatiron Dam	Exterior penstock	1954
Grand Coulee Dam*	Exterior discharge tube, interior spiral case	1950
Havasu Pumping Plant*	Structural steel, tanks, bulkhead gate	1978
Parker Dam	Bulkhead gate	1938
Pole Hill Powerplant	Bulkhead gate	1951
Southern Nevada Water Project*	Unspecified	1970

* Denotes a structure with original red lead coating.

Figure 3 shows the service life of red lead primer on various structures at Reclamation facilities. The data represent all "as reported" information obtained from historical coatings submittals and other documents.

Notably, there are some facilities with structures that still have the original red lead coating (designated by *). These original coatings are all currently over 30 years old. All of the repainted structures had red lead primer service lives of at least > 50 years, with the red lead primer on the bulkhead gates at Parker Dam in California having the longest service life of 77 years.

While it was not possible to obtain accurate coatings data from all structures at Reclamation's facilities, this survey shows the efficacy and longevity of red lead primer as an inhibitive pigment coating.
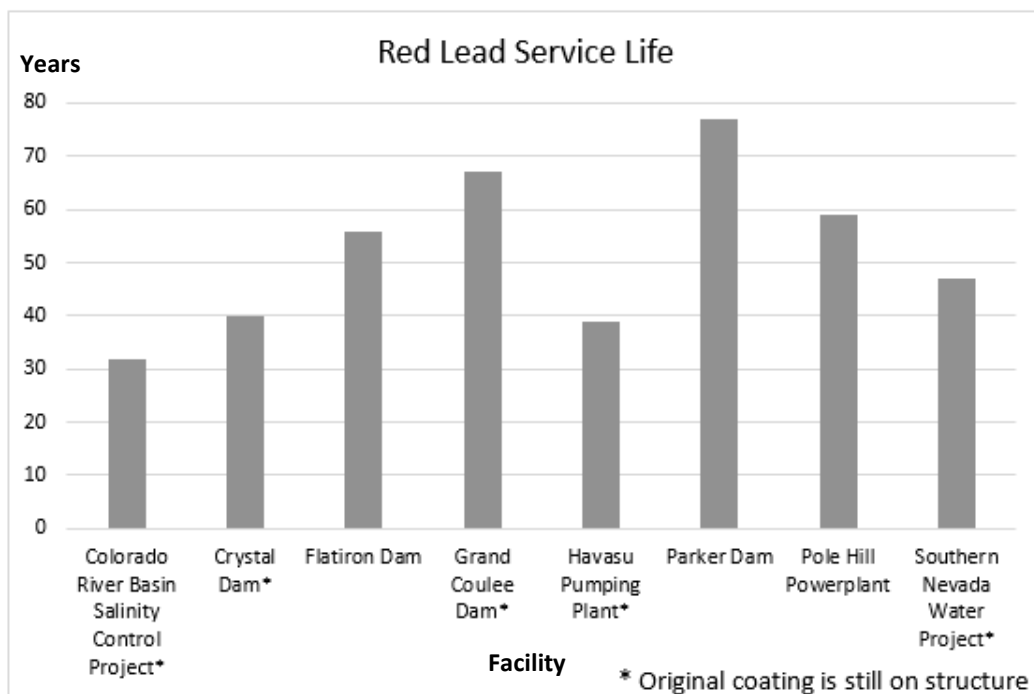
Figure 3: Red lead service life on various structures at Reclamation facilities.

Chromates

Chromate pigments, typically in the form of zinc chromates under Federal specification TT-P-636, were also found to have been used at some of Reclamation's facilities. Structures coated with zinc chromate primer included the exterior of penstocks at Coolidge Dam in Arizona, exterior housings at the Gallegos Pumping Plant in New Mexico, and access bridges at Jordanelle Dam in Utah, among others.

Reclamation did not use zinc chromate primers until the mid-1980s, when they were required to remove lead-based paints from their specifications. The analysis showed use of zinc chromate primers as late as 1995. None of the structures coated with the zinc chromate primer have been repaired or recoated as of 2017. Existing chromate primers on Reclamation's structures have already met or exceeded the 20–25 year service lives expected for modern coating systems currently specified [28].

Modern Inhibitive Pigments

Lead and chromate pigments have been found to be highly toxic. Among unfavorable health effects, extensive exposure to lead-based paints has been shown to cause motor neuron disease [29], and chromates are

carcinogenic [30]. The continued use of these elements has become undesirable, and coatings containing them are almost completely nonexistent.

Historically, Reclamation has used coating systems containing lead and chromate pigments. Reclamation discontinued use of paints and coatings containing lead and chromate in the 1980s and 90s but without an equal substitute replacement.

There is a need for Reclamation to use coatings that provide much longer service lives than the current offerings. Understanding the corrosion protection mechanisms of red lead and chromate pigments may provide information in finding modern inhibitive pigments that may provide better corrosion protection.

Modern Pigments

For the purpose of this review, modern pigments will be regarded as those that are nontoxic (lead and chromate free). The three general classes of modern inhibitive pigments are inorganic pigments, organic pigments, and metallic pigments.

Inorganic Pigments

Inorganic pigments are made from compounds that are not based on carbon and are usually metallic salts precipitated from solutions. This review will discuss the corrosion prevention mechanisms of four general groups of inorganic pigments: phosphates, molybdates, silicates, and ferrites.

Phosphates

Phosphates refer to a wide variety of pigments that contain a phosphorous and an oxygen functional group as seen on figure 4, below [22].
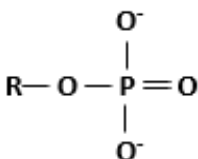

Figure 4: Phosphates contain a phosphorous and an oxygen functional group, designated as "R".

One of the most common and effective phosphate-based corrosion inhibitors are zinc phosphates. Zinc phosphates are extremely versatile due to their low solubility and can be used with many different types of binders and resins in a variety of coating systems [31].

There are multiple mechanisms through which zinc phosphates provide corrosion protection. Slight hydrolysis of zinc phosphate occurs as water enters the coating. This hydrolysis results in the formation of secondary phosphate ions that prevent anodic corrosion by forming a protective passive layer on the substrate [32]. Another mechanism requires the presence of soluble zinc phosphate pigments. A protective film of y-Fe_2O_3 that prevents the diffusion of iron can be created on the anode when dissolved oxygen is adsorbed onto the metal [33]. Phosphate ions complete or maintain the film by filling gaps with anion precipitates of Fe(III) ions. In another mechanism, when the zinc phosphate becomes hydrated and dissociated, it can create complexes with components of some specific binders. Much like the mechanism that gives red lead good anticorrosion properties, metal soaps (and subsequently, salts) are formed through the reaction [34]. Finally, the substrate can become polarized due to the adherence of insoluble salts that prevent dissolved oxygen from nearing the surface. These salts also polarize the substrate's cathodic areas [35].

Due to their very low solubility, zinc phosphates commonly perform poorly in accelerated testing despite performing well in the field [36]. This can be explained by the theory that the protective phosphate complex forms slowly on a substrate, creating an initial lag time that cannot be sped up in accelerated testing. Corrosion initiation in the field typically takes longer than the formation of the protective complex on the substrate; however, in accelerated testing, time to corrosion occurs much more quickly, causing unfavorable results.

Zinc phosphates are not the only phosphate-based compound that can prevent corrosion. Hydrated dihydrogen aluminum triphosphate is an acid that, when dissolved, can dissociate into triphosphate ions [37]. The triphosphate ions can then passivate the substrate by chelating with iron ions. An insoluble layer of ferric triphosphate is formed when the anion $(P_3O_{10})^{5-}$ reacts with anodic iron. Unlike other phosphate compounds, the corrosion protection can be entirely attributed to the phosphate.

Molybdates

Molybdates refer to pigments that involve a molybdenum- and oxygen-containing anion with molybdenum in its highest oxidation state [38]. Molybdates passivate the substrate, forming an insoluble, protective layer of ferric molybdates on the surface of steel, inhibiting the anodic corrosion reaction. In addition, when they contain zinc, molybdate pigments can also form inhibitive zinc soaps in certain binders. Figure 5, below, shows the formula for zinc molybdate.
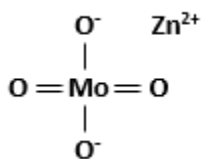
$$O = Mo = O$$

with O^- and Zn^{2+} above, and O^- below.

Figure 5: Zinc molybdate structure.

In general, tests of these pigments as corrosion inhibitors in paint formulations have had varied results [22]. One main disadvantage is that molybdates experience premature binder aging, which can cause coating embrittlement [39]. Another drawback of molybdate pigments is that they are relatively expensive compared to other types of pigments. To lower costs and improve adhesion, zinc phosphate versions of the molybdate pigments have been considered [40]. Molybdates are thought to be nontoxic; however, according to the American Conference of Governmental Industrial Hygenists, they can release toxic fumes when subjected to cutting or welding [41]. In addition, molybdates have been found to be toxic to some freshwater and marine organisms [42].

Silicates

Silicates refer to pigments containing silicon and oxygen [22]. The most common, nontoxic metals used in silicate pigments are calcium, strontium, and zinc. Figure 6, below, shows the formula for zinc silicate.

$$O^- - Si - O^-$$

with O^- and Zn^{2+} above, and Zn^{2+} and O^- below.
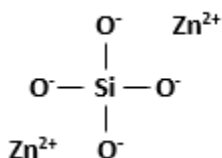
Figure 6: Zinc silicate structure.

Much like the mechanism of red lead, silicates can react with oleoresinous binders to form metal soaps of barium, calcium, strontium, and zinc. Mayne observed that these metal soaps, specifically the metal soaps formed from calcium phosphosilicate and borosilicate, degrade and form products containing soluble, inhibitive anions [43]. As a secondary inhibition mechanism, it was also observed that the alkalinity near the substrate had increased.

Ferrites

Ferrites refer to pigments composed of Fe_2O_3 and another metal, typically magnesium, calcium, strontium, barium, zinc, or manganese.

Similarly to red lead, ferrite pigments also protect steel by reacting with fatty acids in the binder to form metal soaps [44]. Further corrosion protection is achieved by the formation of an alkaline environment at the interface between the coating and the substrate. This alkaline environment promotes the passivation of the metal.

Ferrite pigments were also tested in an epoxy binder, which does not usually produce soap with metal ions [45]. When analyzed using electrochemical impedance spectroscopy, all ferrite pigmented epoxy coatings performed better after immersion in a 3-percent sodium chloride (NaCl) aqueous solution than the red lead pigments in the same binder. However, there was a noted lag time between the initial immersion and passivation due to the time it took for the water to permeate the coating and reach the interface between the coating and the substrate.

Organic Pigments

Organic pigments are based on carbon chains and carbon rings. They can also contain inorganic elements to help stabilize the properties of the organic component. Most organic corrosion inhibiting pigments can form tightly packed complexes with the substrate, thus blocking active sites as an additional mechanism of protection [4].

Conducting polymers (organic polymers that conduct electricity) have been an intriguing area of research since their discovery in the 1970s [1]. Conducting polymers have more positive corrosion potentials than those of metals, enabling them to preferentially undergo reactions with corrosive species [46]. In addition, they are theorized to release dopant ions in the presence of electrolytes and are then re-oxidized by oxygen [47]. These polymers are nontoxic and are highly permeable to liquids and gases due to their porous structure [2]. Their impact on the field of science was recognized in 2000 by the awarding of the Nobel Prize for Chemistry to the researchers who discovered them [48].

The most studied conducting polymer is polyaniline. Polyaniline has been shown to provide multiple mechanisms of corrosion protection, including barrier effect and internal sacrificial electrode formation, in which the polymer reduces cathodic reactions by transferring them from a metal-electrolyte interface to an electrolyte-polymer interface [49]. Wessling et al. have further suggest that passivating oxide layers are formed when polyaniline is galvanically coupled with steel [50]. This work suggests that polyaniline functions similarly to chromate with its self-healing properties: the steel substrate is automatically passivated if a scratch or breach in the coating develops.

Kalendova, in 2008, experimented with coating graphite pigments with polyaniline [2]. Graphite has good conductivity, thus enhancing the properties of

the polyaniline by ensuring the efficient transport of electrons involved in the reduction-oxidation processes. Graphite's flat, lamellar structure also promoted barrier formation while ensuring favorable contact with the substrate [2]. Graphite's structure also gives the pigment excellent mechanical properties such as good adhesion, impact resistance, and ductility.

Table 2, below, shows the polyaniline-coated graphite (C/PANI) pigment's anticorrosion efficiency, A_e, after 500 hours in a condenser chamber. The graphite/polyaniline pigment outperformed all other tested pigments, including a patented "anticorrosion pigment" composed of silicate zinc-strontium-calcium hydrated phosphate. In table 2, "PANI" is polyaniline.

Table 2: Anticorrosion efficiency of polyaniline-coated graphite (C/PANI), reproduced from reference [2]

Pigment	Surface blistering	Corrosion in a cut (millimeters)	Surface corrosion (percent)	Anticorrosion efficiency (A_e)
C	–	0.5 – 1	3	83
PANI	8MD	0 – 0.5	3	65
C/PANI	–	0 – 0.5	0.03	97
a-Fe$_2$O$_3$	4M	1 – 2	50	38
a-Fe$_2$O$_3$/PANI	6M	1 – 2	16	53
"Anticorrosion pigment"	8D	1 – 2	3	51
Binder without pigment	2MD	2 – 3	33	33

The data in table 2 were obtained using the following standards: ASTM D714-87: "Evaluating Degree of Blistering of Paints" [51], ASTM D1654-92: "Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments" [52], and ASTM D610-85: "Evaluating Degree of Rusting on Painted Steel Surfaces" [53].

Other types of organic polymer pigments have also been studied to determine their corrosion inhibitive properties. In a 1998 study by Abd El-Ghaffar et al., a series of poly(aromatic amines) were prepared and incorporated into various paint formulations to replace the typical, toxic inhibitive pigments [3]. Poly(o-aminophenol), or PoAP; poly(o-aminothiophenol), or PoAT; poly(m-anisidine), or PmASl; and polyaniline were prepared by chemical oxidation of their monomers using ammonium persulfate. Figure 7 depicts the monomers of PoAP, PoAT, PmAS, and polyaniline. The study found that all of the polymer pigments inhibited corrosion more than the control, which did not contain a coating with an inhibitive polymer pigment. Table 3 shows the corrosion rate data for each polymer at 1.0 percent concentration.
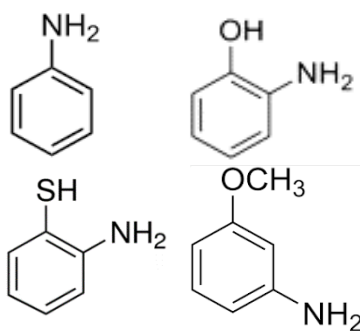
Figure 7: Monomers of polyaniline (top left), PoAT (bottom left), PoAP (top right), and PoAS (bottom right).

Table 3: Corrosion rate data for a series of poly(aromatic amines) [3]

Polymer	Average weight loss (grams)	Corrosion rate x 10^2 (mg/cm^2 per day)
Blank	0.0160	57.15
Polyaniline	0.0083	29.64
PoAP	0.0082	28.30
PoAT	0.0077	27.50
PoAS	0.0076	26.14

The authors concluded that the mechanism of corrosion inhibition was related to the chelating efficiency of each material (i.e., the ligand's ability to bond to a central metal atom at two or more points). This chelation effect, thus the corrosion inhibition, is a result of the delocalized electrons on the nitrogen atoms forming a thin layer of metal-polymer complex between the steel substrate and the nitrogen. The other groups on the ring (e.g., OH, SH, and OCH$_3$) contribute their own free electrons, and the corrosion rate is attributed to the order of chelation efficiency of those groups. The methoxy (OCH$_3$) group of PmAS has the highest chelation efficiency; thus, the PmAS pigment provided the best corrosion protection.

When incorporated into various paint formulations, all films containing polymer pigments were found to have good adhesion properties, good impact resistance, and high ductility and hardness compared to the control. Painted panels were immersed in sea water, and after 28 days, the PmAS panel showed little to no rusting compared to the other polymers tested. All of the polymers, however, exhibited some degree of blistering.

Bio-based aromatic acids have been studied for use as "green" corrosion inhibitors [54]. Salts of vanillic, cinnamic, ferulic, and mandelic acids were prepared by reacting each acid with an alkaline material. In immersion testing, the salts of vanillic, cinnamic, and ferulic acids provided excellent corrosion protection to a steel substrate due to their ability to adsorb onto the substrate and form a protective film that increased the electrical resistance [55]. While the results indicate that these pigments show potential for corrosion inhibition, and their environmentally friendly nature may be attractive to Reclamation, these pigments are currently more of a novelty. Much more research and testing must be completed before they can be considered a substitute for lead or chromate.

Metallic Pigments

Metallic zinc pigments are some of the most widely used protective pigments in coatings but generally offer corrosion protection to steel by acting as a sacrificial pigment and not as an inhibitive pigment [56].

Modern research has indicated that other metallic pigments may be successful corrosion inhibitors. Aluminum pigments, specifically aluminum flake pigments, have been studied on their own as corrosion inhibitors [57]. A patent filed in 2002 claims that a coating material comprised of high content (upwards of 25 percent by weight) of aluminum flakes can provide mechanical and UV protection to a metal substrate. The aluminum flakes have been found to lie flat on the surface, forming an interlocking scale-like structure that resists abrasion and is impermeable to corrosive agents. The matrix configuration protects the underlying surface and it is also protected from UV light.

In another application, aluminum pigments were coated with a layer of silica to enhance chemical stability and dispersibility [58]. Compared to bare aluminum pigments, the coated sol-gel pigments had better anticorrosive properties (determined by alkaline stability testing, which measured the time until 5 milliliters of hydrogen gas was formed, and boiling water testing, which measured the time it took for 410 milliliters of gas formation). For comparison, the uncoated aluminum failed both tests after less than 1 hour, while the coated aluminum lasted approximately 7 hours in the boiling water test and over 100 hours in the alkaline stability test. This improvement can be attributed to silica's ability to react its negatively charged species with the substrate's metallic cations to form a protective film, or passivation layer.

CONCLUSION

There has been a significant amount of research dedicated to finding a replacement for lead and chromate pigments in corrosion inhibiting coatings. While an attempt was made to survey a broad swath of the current research, there

is still an incredible amount that has not yet been reviewed. This work should be ongoing, especially as new pigments and technologies are continuously developed.

Further research is warranted for some of the pigments described in this review—especially the inorganic pigments that, like red lead, form metal soaps when reacted with certain binders. These pigments may also be the easiest to further analyze, as they can be found readily in bulk and would not need to be synthesized or formulated like some of the organic pigments. With that said, it is also worth doing further research on conducting polymers, specifically polyaniline. The use of polyaniline as a corrosion inhibiting pigment was discussed multiple times for a variety of different applications during review of the literature.

In addition, it is worthwhile to analyze commercially available coating systems that Reclamation currently does not use for the presence of some of the pigments discussed in this review. Analyzing currently available coating systems would be the quickest way to begin testing alternative inhibitive pigments. This type of work would not require Reclamation to have to formulate new coatings on its own. Reclamation could also engage with coatings manufacturers via cooperative agreements to aid in developing new formulations.

One of the biggest challenges in finding a suitable replacement for red lead and chromate pigments is shortening the testing cycle by finding ways to predict when or how a coating will fail [59]. This would save significant costs by allowing testing of more of the inhibitive pigments in a shorter timescale. In order for this to be achieved, a better understanding of the mechanisms of paint failure and how the individual components of a coating system interact to achieve the overall service lifetime is needed. Therefore, further research needs to be done to determine exactly how the coatings will fail and in what timeframe so that these signs can be identified early in the testing.

Replacing old legacy coatings systems such as lead-based paint with safe and modern equivalents is an important but challenging proposition for Reclamation. With further investigation into inhibitive pigments, including testing current offerings, formulating new components, and learning more about their failure mechanisms, service lives can be increased from the current 20–25 years to the desired 50+ years exhibited by legacy coatings.

RECOMMENDATIONS FOR FUTURE WORK

- Further investigation is warranted to identify additional pigments that offer similar corrosion protection as red lead and chromate pigments without the harmful health and environmental effects.

- Commercially available coating systems not currently used by Reclamation should be evaluated for the presence of certain pigments that have been identified to be corrosion inhibiting. Accelerated and field testing of these coatings should be performed to determine if they are more suitable for use than the current coatings used.

- Further research is needed to determine an expected service life and mechanism of failure for the modern pigments identified in this review as likely to be a nontoxic substitute for red lead and chromate.

- There is a need to account for the corrosion inhibition lag times exhibited by some pigments. Field testing, or exposing these specimens to a humid environment for a period of time before accelerated testing, may be necessary to ensure that pigments selected for further examination are analyzed appropriately and equally.

- Electrochemical impedance spectroscopy should also be employed to monitor the performance of coatings during field testing. The obtained data can then be extrapolated to project the service life.

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ATTACHMENT A

Supporting Information

Datasets that Support the Final Report

The dataset used in the section "History of Inhibitive Pigment Use on Reclamation's Structures" to illustrate use of red lead and chromate coatings in the Bureau of Reclamation's (Reclamation) history can be found at the following share drive location:

T:\ENGRLAB\MERL\COATINGS_Project Data

The creators of this file were Allen Skaja (askaja@usbr.gov, 303-445-2396) and Stephanie Prochaska (sprochaska@usbr.gov, 303-445-2323).

This file contains information about historical coating data, including project name, structure(s) that was/were coated, the coating system used, whether or not it was an original coating, spot repair or recoat, and the date(s) that the coating was applied. The data were collected predominantly from reviewing old paper files, including, but not limited to, specifications, submittals, submittal responses, and memorandums.

This dataset is in no way inclusive of all historical coating projects completed by Reclamation.

Approximate file size: 120 kilobytes (KB)

Appendix B – Coatings Test Data

Table B-1 Corrosion undercutting and EIS test results.

Specimen ID	HAR Immersion (rust creep, inches)	DI Immersion (rust creep, inches)	FOG Cyclic (rust creep, inches)	QUV Cyclic (rust creep, inches)	PRO Cyclic (rust creep, inches)	BOR Cyclic (rust creep, inches)	EIS (|Z| at 0.01 Hz, ohms)
ZP-1	0.00	0.00	0.28	0.00	0.22	0.25	4.3×10^9
ZP-2	0.00	0.00	0.20	0.00	0.52	0.46	9.9×10^9
Z-1	0.00	0.00	0.10	0.06	0.11	0.14	9.0×10^9
Z-2	0.00	0.00	0.04	0.00	0.20	0.16	2.5×10^9
Z-3(N/A)	0.00	0.08	0.23	0.02	0.26	0.62	2.0×10^9
Z-3	0.00	0.00	0.08	0.00	0.18	0.18	1.1×10^8
Z-4(N/A)	0.11	0.11	Not tested	0.00	0.43	0.35	4.8×10^9 *after 7 months
Z-4	0.00	0.00	Not tested	0.00	0.09	0.15	3.0×10^9 *after 7 months
O-1	0.00	Not tested	0.39	0.06	0.60	0.81	1.4×10^9
O-2	0.02	Not tested	0.08	0.00	0.14	0.19	1.2×10^5

Table B-2 Mechanical test results.

Specimen ID	Cathodic Disbondment (disbondment radius, inches)	Impact (in-lbs)	Pull-off Adhesion (stress, psi/failure mode)	Pull-off Adhesion (wet) (stress, psi/failure mode)	Knife Adhesion (wet) (ASTM rating 0-10)
ZP-1	0.125	70	>20% glue failure	1024 ± 82 g/adh/coh 00/00/100	10
ZP-2	0.25	10	>20% glue failure	1087 ± 168 g/adh/coh 00/00/100	10
Z-1	Not tested	80	793 ± 91 g/adh/coh 02/00/98	N/A	N/A
Z-2	0.25	220	1014 ± 140 g/adh/coh 10/00/90	551 ± 131 g/adh/coh 00/100/00 primer	1

Z-3(N/A)	Not tested	10	>20% glue failure	941 ± 68 g/adh/coh 00/00/100	6
Z-3	Not tested	80	>20% glue failure	1000 ± 73 g/adh/coh 00/00/100	8
Z-4(N/A)	3.125	20	>20% glue failure	>20% glue failure	4
Z-4	1.00	100	>20% glue failure	>20% glue failure	4
O-1	Not tested	20	1465 ± 450 g/adh/coh 16/01/83	Not tested	Not tested
O-2	Not tested	240	>20% glue failure	Not tested	Not tested

Appendix C – Coatings Rating Criteria

Immersion Testing (Dilute Harrison, Deionized) Maximum Creep:

Excellent: No visual defects
Good: No blistering, minor rust creep ≤ ⅛ in
Fair: No blistering, moderate rust creep ≤ ¼ in
Poor: Blistering, delamination or rust creep over ¼ in

Cyclic Weathering Testing (BOR, Prohesion, FOG) Average Creep:

Excellent: No blistering, minor rust creep ≤ ⅛ in
Good: No blistering, minor-moderate rust creep ≤ ¼ in
Fair: No blistering, moderate rust creep ≤ ½ in
Poor: Blistering, delamination or rust creep > ½ in

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 in
Poor: Any of the following: blistering, delamination, rust creep > ⅛ in

EIS (immersion):

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

Impact:

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

Cathodic Disbondment (ASTM G8)

Excellent: Disbondment radius ≤ ¼ in
Good: Disbondment radius ≤ ½ in
Fair: Disbondment radius ≤ 1 in
Poor: Disbondment radius > 1 in

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

Appendix D – Evaluation of Inhibitor Coating Systems for Use in Hydropower Applications (to be updated upon conference publication)