

RECLAMATION

Managing Water in the West

Finding a Green Alternative to Vinyl Resin Coatings – Final Report

Research and Development Office
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Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Acronyms and Abbreviations

DOP	di-sec-octyl phthalate
DI	Deionized Water
EIS	Electrochemical Impedance Spectroscopy
ECTFE	Polyethylene chloro trifluoro ethylene copolymer
ETFE	Polyethylene tetrafluoro ethylene copolymer
HAR	Dilute Harrison's Solution
MIBK	methyl isobutyl ketone
PCBTF	Parachlorobenzotrifluoride
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
Reclamation	Bureau of Reclamation
TCP	tricresyl phosphate
USACE	United States Army Corps of Engineers
UV	Ultraviolet
VOC	volatile organic compounds

Executive Summary

Solution vinyl coatings were utilized by the Bureau of Reclamation in the past and are currently used by the United States Army Corps of Engineers as a coating system that can achieve a 30-50 year service life in impacted immersion service conditions. These coatings were commonly used on gates and other equipment, which required a durable coating to withstand frequent ultraviolet (UV) light exposure, immersion service, and impact resistance. Unfortunately, solution vinyl coatings contain high fractions of volatile organic compounds (VOCs) as solvents and diluents. Federal regulation 40 CFR 50 limits the weight fraction of VOCs per volume of applied coating material according to category of use. This relegated solution vinyl coatings to impacted immersion service use only.

Since then, traditional epoxy systems have become a workhorse in the protective coatings industry. Unfortunately, these materials tend to degrade in sunlight, and experience has revealed their service life to be suboptimal compared to legacy coatings systems such as vinyls. Consequently, the Bureau of Reclamation has engaged in an effort to study vinyl coatings and identify potential replacement materials.

This work provides an overview of solution vinyl coating history and formulation as well as results and discussion of initial immersion testing. Corrosion performance and material properties using modern laboratory techniques are used to provide a benchmark for the evaluation of next generation polymer coatings that may someday provide a green alternative to the legacy vinyl systems.

The initial literature review and laboratory testing were presented at the Society for Protective coatings annual conference in 2016 and 2017 respectively and are included as part of this report [1, 2]. Additional products were then subsequently tested at Reclamation's Materials and Corrosion Laboratory. In total, twenty (20) commercially available coating systems and three (3) experimental were also tested side-by-side for comparison including thermoplastic and thermoset materials. Each system was subjected to a series of accelerated weathering laboratory and durability tests. While no single coating system matched the performance in every test, several promising candidates emerged and additional laboratory and field tests are recommended.

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Introduction

Solution vinyl coatings historically provide a 30-50 year service life as evidenced by more than 60 years of field performance data. For example, the radial gate coatings at Cle Elum were found to be in good condition after approximately 30 years of service (Figure 1).



Figure 1. A radial gate at Cle Elum repainted in 1983 with Vinyl Resin VR-6

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Solution vinyl coatings date back to the mid-1930's. The intended use was for the marine and maintenance industries. A conventional spray gun is required to apply this material, although higher build vinyl systems appeared in the 1970s for use with airless spray equipment.

Both the Bureau of Reclamation (Reclamation) and the United States Army Corps of Engineers (USACE) began using these systems on gates and other equipment, beginning in the late 1940's. Their performance characteristics include excellent ultraviolet (UV), impact, and corrosion resistance, most notably for alternating atmospheric and immersion service conditions [3, 4]. Although more costly, solution vinyl coatings were also specified in place of coal tar enamel where service temperatures reach -20 °F because of coal tar enamel's tendency to crack under these conditions [5]. Solution vinyl coatings are also favored in hot and dry exposure conditions. In the 1960's field testing indicated a susceptibility to slurry erosion damage [6, 7]. Laboratory testing showed the erosion resistance to be less than coal tar enamel [8]. The researchers noted that the low erosion resistance is in part due to the low film thickness (7 mils is typical); by comparison, thermoplastic pipes such as PVC are up to 10 times more resistant than coal tar enamel [9].

Solution vinyl resins are copolymers of vinyl chloride and vinyl acetate. The coating properties are dependent on the molecular weight of vinyl chloride as well as the ratio of vinyl chloride to vinyl acetate; the former contributes to coating strength and toughness while the latter improves solubility and flexibility [10, 11]. Therefore, these coating systems require high fractions of solvents and diluents to achieve an appropriate spray-application viscosity, proper substrate wetting, and uniform film formation. The most effective carrier liquids, including toluene, methyl isobutyl ketone (MIBK), and nitropropane, are classified volatile organic compounds (VOCs) and pose health and safety and environmental concerns.

The Environmental Protection Agency's 1999 national rule limits the amount of VOCs that coatings in a given category are allowed to contain [12]. This had the effect of limiting vinyl resins to impacted immersion service [13]. In addition, there are restrictions on coating VOCs that are implemented at the regional, state, and local levels that tend to be more stringent than the national rule. For example, California's South Coast Air Quality Management District VOC limit for *industrial maintenance coatings* is presently 100 g/L [14]. USACE continues to specify solution vinyl coating systems for structures subjected to *impacted immersion service*. This is in compliance with EPA's use category of the same name and with a VOC limit of 780 g/L. Many of these structures experience "run of the river" service environment that are high energy and debris or sediment-laden.

Presently, Reclamation uses epoxies and for applications traditionally served by solution vinyl coatings, but they chalk and degrade in UV light. Epoxy coatings are more brittle and are susceptible to impact damage. They are also more difficult to overcoat and spot repair because they are a crosslinked, thermoset coating [3]. Epoxies absorb a relatively high volume fraction of water and have average corrosion resistance, whereas the solution vinyl coatings provide excellent barrier protection for a number of decades. Reclamation's field performance shows the epoxies to have an anticipated service life of 15-25 years, depending on service conditions and other factors. Aliphatic polyurethane and acrylic coatings have also been examined at

Reclamation and, to date, show a reduced service life. Fluoropolymer coatings are another alternative that is expensive, most require post cure or baking, and is not typically recommended for immersion service [11].

A low-VOC option for applying vinyl coatings is also desirable, should comparable performance be achieved. To lower VOC's, manufacturers researched higher solids vinyl systems which was achieved by lowering the molecular weight. However, this reduced the performance of the coating (chemical resistance and physical properties). USACE evaluated one company's attempt to develop a vinyl system using acetone, an exempt solvent, as the carrier; the results were not satisfactory. In 2009, Dow Chemical discontinued the production of its UCAR solution vinyl resins [10] thus limiting the number of suppliers even further.

A low-VOC replacement for solution vinyl coatings that provides a similar service life could minimize life cycle costs and VOC emissions. Coating maintenance costs at Reclamation are projected to increase in the coming years as the legacy coatings reach the end of their service lives and begin to require replacement.

Research Objective

The objective of this study is to examine the solution vinyl coatings historically used by Reclamation, USACE, and other facility owners with similar service conditions. Formulations, physical properties, and chemical properties are examined within and discussed in the context of corrosion performance and service life.

A second objective is to identify a coating product which would deliver the performance of a vinyl resin without the high VOC levels. Reclamation-specified coatings must meet all Federal standard VOC regulations i.e. 780 g/L for impacted immersion and 450 g/L for industrial maintenance, materials containing less than 250 g/L would allow use in California and 100 g/L or less would meet the most strict air quality requirements (southern California).

Literature Review & Background Information

Role of Coatings in Corrosion Prevention

Corrosion is a naturally occurring degradation of a material as a result of a chemical or electrochemical reaction with its environment. Steel commonly experiences corrosion in several forms including general, crevice, pitting and galvanic. In order for a corrosion cell to form, an anode, cathode, metallic pathway and electrolyte must all be present. In the case of general corrosion, localized areas within the part may serve as either the anode or cathode. In immersion or burial service, the liquid or soil contacting the steel provides acts as an electrolyte for ion transport, in atmospheric exposures, the moisture in the air is the electrolyte.

Coatings disrupt the corrosion process by providing a barrier to block ion migration so the lack of an electrolyte becomes the limiting factor in the corrosion reaction. An effective coating is a poorly functioning electrolyte. All coatings are permeable to some extent and will eventually allow water molecules and ions to pass through. The time it takes for ion migration to occur is one factor in determining the effective service life of the coating. Ion transport kinetics may depend on several factors such as:

1. Density: In general, a dense material has less space for ions to migrate through.
 - a. Crystallinity – Ignoring all other factors, a material that has a greater degree of crystallinity has a greater density.
2. Pathway: Flake pigments are used to create a tortuous path that ions must travel through the coating to reach the metal surface thus increasing the distance.
3. Material degradation:
 - a. Wet dry cycles can accelerate polymer degradation resulting in a greater rate of ion transport.
 - b. UV exposure, embrittlement – UV light exposure can cause chalking and embrittlement and general degradation in susceptible polymers. If microcracks form as a result of substrate flexing, ion transport and corrosion will accelerate.
4. Surface adhesion:
 - a. Once ions reach the surface, lateral transportation can allow the reaction to progress along the substrate-coating interface.
 - b. If the coating is physically damaged or holidays are present, lateral transportation can allow corrosion to propagate away from the defect. Good adhesion to the substrate can potentially reduce ion migration at the surface. Corrosion products have a lower density than steel so the formation of rust products will have the tendency to push any adjacent coating away from the substrate promoting additional propagation.

Ultraviolet Light and Coatings

Ultraviolet light is generally destructive to most polymer networks. Modern coatings such as epoxies begin to degrade, chalk, change color and may become embrittled after prolonged

exposure to ultraviolet light. Architectural coatings such as acrylics, silicone-modified alkyds, aliphatic polyurethanes, and fluoropolymers such as Kynar[®] exhibit increased levels of UV damage resistance. Vinyl resins are known to withstand UV damage as well and may also be placed in immersion.

Aliphatic compounds exhibit superior UV resistance in comparison with aromatic compounds. In contrast, aromatic compounds are stable ring structures and tend to perform better than aliphatic compounds in immersion and chemical exposures. Aliphatic compounds do not contain a benzene ring structure and can have saturated or unsaturated bonds.

Hindered Amine Light Stabilizers (HALS) are used help improve UV resistance by scavenging free radicals that are produced during photo-oxidation. [15]

History of Vinyl Industrial Maintenance Coatings

Vinyl chloride and vinyl acetate copolymers are solvent borne lacquers. Characteristics include a high glass transition temperature, excellent water resistance, flexibility, impact resistance, aging resistance, and wear resistance. [16]

Vinyl coating systems were developed in the mid-1930s for use in the marine and maintenance industries. Higher build vinyl systems were introduced in the 1970s for use with airless spray equipment. [16]

To lower VOC's, manufacturers began experimenting with higher solids vinyl systems which was achieved by lowering the molecular weight. However, this reduced the performance of the coating (chemical resistance and physical properties). [16]

Timeframe, history, evolution of the formulation over time [17]

- 1930s—chlorinated rubber and vinyl resins, except the vinylidene chloride—based latexes and the chlorinated polyolefin
- 1940s—widespread use for protective coatings.
- 1940s-1960s—most vinyls were low-solids/low-build w/ high molecular weights in solvent systems based on ketones
- 1960s – high build vinyl systems are introduced
- 1950s-1970s—alkyd modifications:
 - A polyester modified by addition of fatty acids and other components
- 1970s-1980s—high build vinyls become popular as maintenance paints
 - Solvent systems based on higher boiling ketones and glycol ether acetates
- 1980s—Vinylidene chloride latex systems introduced
- 1989—Chlorinated polyolefins are developed

Composition

Resin

The poly (vinyl chloride-*co*-vinyl acetate) resins used in USACE and Reclamation solution vinyl coating systems are very high molecular weight. They also contain a high ratio of vinyl chloride to vinyl acetate, typically 86:14 by weight [3]. Together, these characteristics impart strength, toughness, and low water absorption to provide a long service life.

The specific resins used are known only by their designated UCAR™ trade name. Table 1 provides the reported properties for each resin discussed in this paper. Resin VYHH is most widely used. Resin VYNS-3 copolymer was used in Reclamation formulations and required a higher concentration of carrier during application [10]. The carboxyl-modified resin VMCH contained 1 wt. % maleic acid to promote adhesion to substrates [11]. Therefore, this was used primarily in primer formulations. Similarly, resin VAGH was hydroxyl-modified with a hydroxyl content of 2.3 wt. % to improve compatibility with wash primers and other coatings [10].

Table 1. UCAR™ solution vinyl resin used in USACE and Reclamation formulations. Reproduced from Ref ¹.

Resin	Vinyl Chloride (Wt. %)	Vinyl Acetate (Wt. %)	Other (Wt. %)	Glass Transition Temperature (°C)	Average Molecular Weight ⁽¹⁾ (Mn)	Typical Solution Solids (Wt. %)
VYHH	86	14	-	72	27,000	20
VYNS-3	90	10	-	79	44,000	15
VMCH	86	13	1 ⁽²⁾	74	27,000	20
VAGH	90	4	6 ⁽³⁾	79	27,000	20

(1) In reference to polystyrene standard.

(2) Maleic acid

(3) Vinyl alcohol

Carriers

Solution vinyl coatings require a solvent and diluent. Organic solvents readily dissolve the vinyl acetate polymer segments of the resin [3]. The diluent acts to dilute the solution further for application. The carriers and their concentration are critical to achieving the desired film properties. The solvent is traditionally a strong ketone, such as MIBK. The diluent is an aromatic hydrocarbon with a smaller percentage of aliphatic ones, such as toluene and nitropropane; the ratio is 50:50 by weight [10]. The carriers may contribute to 80 wt. % of the solution.

¹ "UCAR Solution Vinyl Resins," The Dow Chemical Company, Midland, MI (2006) (repeated from above)

Vinyl film formation is a two-stage process. In the first stage the evaporation is controlled by the carrier molecule's release across the film / air interface. The subsequent stage is rate-controlled by carrier diffusion through the film [4]. Carrier evaporation must be carefully controlled to achieve desired film properties. The rate of evaporation is highest immediately following application and decreases over time but not all of the solvent will ever escape from the coating [4]. As a result, the applied coating system is slightly soft initially and gradually hardens over time. The effects of film thickness, solvent and diluent mixture, and other variables on these properties are well characterized [18].

A proper formulation of solvent and diluent produces crystallinity in solution vinyl coatings [19]. These crystalline regions are less permeable than their amorphous counterparts and contribute to increased corrosion resistance. However, XRD analysis performed by NDSU revealed the structure to be primarily amorphous [20].

Pigments

Solution vinyl formulations used a variety of pigments to achieve specific coating properties. These included iron oxide (Fe_2O_3), titanium dioxide (TiO_2), carbon black, and aluminum. Fe_2O_3 is a hard pigment and is used to increase abrasion resistance. TiO_2 and carbon black provide hiding power and UV resistance [3]. Aluminum (Al) improves barrier protection by increasing tortuosity of water pathways; it also improves UV resistance. An undesired attribute of Al is increased solvent entrapment. Special formulations contain red lead or zinc to provide active corrosion protection to defects by corrosion inhibition and cathodic protection, respectively.

Plasticizer

In order to better control the competing solvent evaporation and film formation, a small percentage of plasticizer is included in these formulations. Primarily the plasticizer acts to minimize solvent retention and improve flexibility of the final film [21]. Common plasticizers include Flexol brand products: TCP (tricresyl phosphate), DOP (di-sec-octyl phthalate), and 10-10 (diisodecyl phthalate).

Formulations

SSPC specifications were developed for vinyl paints, aluminum vinyls, and vinyl butyral wash primers [22, 23, 24, 25]. The vinyl wash primer is also specified in Federal Specification DoD-P-15328. The wash primer is 10% solids by volume whereas the top coats are 14% and 17% for aluminum and titanium dioxide respectively. Solution vinyl systems used by USACE and Reclamation and their compositions appear in Table 2, organized by formulation and version. The original specifications are from March 1959 and use MIBK and toluene as solvents. Formulation versions were often prompted by changes to carriers or plasticizers. In addition, the navy also utilized a vinyl paint system with a wash primer similar to Reclamation's and provided MIL specifications for the formulation.

USACE

The development of new and improved solution vinyl formulations at USACE resulted in a progressive naming convention. The solution vinyl formulations V-101, V-102, V-103, V-104, V-106, and V-766 originated in 1959. These formulations predate the current versions and some have been discontinued. Subsequent versions of each system carried a sequential letter such as V-766a; the current version is V-766e. USACE presently uses several coating systems, names shown in boldface, intended for application over a white metal blast-cleaned surface [26]:

- **3** – (four-coat system): two coats V-766e and two coats V-102e
- **3-A-Z** – (four-coat system): one primer coat VZ-108d, two coats V-766e, and two coats V-102e
- **4** – (five-coat system): five coats V-766e
- **5-A-Z** – (four-coat system): one primer coat VZ-108d, one coat V-766e, and two coats V-103c
- **5-C-Z** – (four-coat system): one primer coat VZ-108d and three coats V-106d
- **5-D** – (five-coat system): five coats V-106d
- **5-E-Z** – (four-coat system): one primer coat VZ-108d and three coats V-766e

USACE uses the zinc-rich coating systems in cases where mechanical damage is expected or on structures with complex geometry where adequate coverage is not guaranteed. The original USACE systems were also denoted as V-766 and were therefore formulated with the same resin and pigments but slightly different solvents. Plasticizers are also added to the formulation retain toughness; these have changed over the past 50 years.

Acids such as maleic and phosphoric are added to resins to greatly increase adhesion to steel. The exact mechanism behind the adhesion increase is not well understood; once added, the acids react and are no longer detectable as acid. Silanes are also added to the zinc-rich vinyl primer to promote adhesion to the steel substrate. Diamino has been found to give optimum performance versus monoamino while triamino gave only marginal increases in effectiveness.

Reclamation

The earliest reference to Reclamation's use of solution vinyl coating system is in 1940 when it was tested on the All American Canal [27]. The earliest specifications available for VR-3 and VR-6 systems date back to 1960. They are slightly different than those at USACE. The VR-3 and VR-6 designations were specified for equipment subject to immersion and alternating atmospheric and immersion service [28]. The VR-3 system consisted of three or four coats of the same material for a total thickness of six mils [29]. VR-3 is self-priming and used for the interior of water tanks, surge tanks and steel pipe that, when emptied in winter, are subjected to temperature below -20 °F. Other uses for the VR-3 included discharge tubes, spiral cases, siphons and trash collecting facilities. Despite having only three or four coats, durability was similar to VR-6 in these applications. However, VR-3 was less costly to purchase and apply than VR-6; this also made it better suited for maintenance painting.

The VR-6 system consisted of one coat of primer, three "body" coats of alternating color (iron oxide red and grey), and two aluminum pigmented sealing coats for a total thickness of 10-15 mils [30]. Reclamation specified an abrasive blast-cleaned surface, regardless of the primer used

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[27]. VR-6 applications included needle valves, radial gates, and bulkhead gates. The aluminum topcoats provided the greatest longevity except in abrasive conditions. Here, a different pigmented topcoat was specified.

Occasionally, specifiers selected VR-3 to replace a failed coal tar enamel lining. A 1964 Reclamation laboratory investigation showed that residues are left behind when cold applied coal tar paint (CA-50) is removed by abrasive blast cleaning [31]. Subsequent solvent cleaning failed to remove the residue, which reduced adhesion of the VR-3 coating. The VR-6 primer wash primer was found to provide adequate adhesion to these surfaces. Therefore, replacements for coal tar paint and enamel received a VR-6 wash primer prior to applying the VR-3 system.

With both VR-3 and VR-6, a mastic coating (VR-M) was applied after the first body coat as an edge coat or around rivets. The thick, viscous mastic coat was typically applied with a stiff bristled brush. Reclamation also evaluated a red lead corrosion inhibitor in solution vinyl coatings. The performance of this system was dependent on the water chemistry [28].

Table 2. Tabulation of various historical formulations and their constituents.

Formulation	Date	Org	Resin	Pigment	Carriers	Plasticizer	Other Additives
VR-3	1964	BOR	VYHH, VMCH	(1)	Toluene, MIBK, 2- Nitropropane	Flexol DOP	Asbestine, H ₃ PO ₄
VR-6 Prime	1959	BOR	VMCH	TiO ₂ , Carbon	Toluene, MIBK, 2- Nitropropane	Flexol 10- 10	
VR-6 Body	1959	BOR	VYHH	(2)	Toluene, MIBK, 2- Nitropropane	Flexol 10- 10	
VR-6 Seal	1959	BOR	VYNS	Al (3)	Toluene, MIBK, 2- Nitropropane	Flexol 10- 10	
V-101	1959	USACE	VAGH	Red Lead	Toluene, MIBK	Flexol TCP	Propylene Oxide
V-102	1959	USACE	VYHH	Al	Toluene, MIBK	Flexol TCP	
V-102e (AP)	1981	USACE	VYHH	Al	Nitropropane MEK Toluene	Diisodecyl Phthalate	

Table 2. Tabulation of various historical formulations and their constituents.

Formulation	Date	Org	Resin	Pigment	Carriers	Plasticizer	Other Additives
V-102e	2004	USACE	VYHH	Al	Toluene, MIBK	Diisodecyl Phthalate	
V-103	1959	USACE	VYHH	Carbon	Toluene, MIBK	Flexol DOP	
V-103c	2004	USACE	VYHH	Carbon	Toluene, MIBK	Diisodecyl Phthalate	
V-104	1959	USACE	VYHH	Red Iron Ox	Toluene, MIBK	Flexol TCP	
V-106	1959	USACE	VYHH, VMCH	Iron Ox	Toluene, MIBK	Flexol TCP	Propylene Oxide
V-106d (AP)	1981	USACE	(VYHH) (VMCH)	Iron Ox	Nitropropane MEK Toluene	Diisodecyl Phthalate	Propylene Oxide
V-106d	2004	USACE	VYHH VMCH	Iron Ox	Toluene, MIBK	Diisodecyl Phthalate	Propylene Oxide
V-113 High- Build Additive Package	1981	USACE	VYHH	1/64" Glass Flake	MIBK MEK Ethanol	Diisodecyl Phthalate	Suspending Agent F Silane A
V-766	1959	USACE	VYHH, VMCH	TiO ₂	Toluene, MIBK	Flexol TCP	Propylene Oxide
V-766e (AP)	1981	USACE	VYHH VMCH	TiO ₂ , Carbon	Nitropropane MEK Toluene	Diisodecyl Phthalate	Ortho- Phosphoric Acid
V-766e	2004	USACE	VYHH, VMCH	TiO ₂ , Carbon	Toluene, MIBK	Diisodecyl Phthalate	Ortho- Phosphoric Acid
VZ-108d	2004	USACE	VYHH - Part A- Silane -Part B-	Zinc, Iron Ox	MIBK Methanol		Suspending Agents E & F

(1) White System – Titanium Dioxide, Red System – Synthetic Red Iron Oxide, Black System – Synthetic Black Iron Oxide

(2) Red Body Coat - Synthetic Red Iron Oxide, Grey body coat - Titanium Dioxide, Carbon Black

(3) Per the 1984 Reclamation Specification, multiple finish colors were later added [32]

Vinyl Performance in Field Service

USACE has found that solution vinyl coatings offer excellent impact resistance and commonly deliver a service life of 40 years in immersion. They began using them extensively on a variety of hydraulic equipment circa 1947. These coatings gained immediate favor over their red lead alkyd predecessors, which sustained severe damage within just 6 months of exposure to the abrasive conditions on the lock facilities along the Mississippi River. Since their introduction, solution vinyl coatings have been used to protect steel structures such as turbine runners and gates (tainter, slide, miter, etc.)

Reclamation researchers evaluated numerous coating systems during the 1950's and 1960's to identify the best protection for hydraulic equipment. They applied a suite of 20 coating systems and materials to the Shasta Dam penstocks in 1949 and monitored their performance over a fifteen year period. The solution vinyl coatings were one of seven products that remained in good condition at the study's conclusion [6]. Similarly, researchers applied more than forty coating systems at the Collbran Project in Colorado in 1960 [33]. A four-year report showed that, through these laboratory and field evaluations, many solution vinyl coatings performed well [34]. Solution vinyl coating systems gained widespread use for the protection of gates, penstocks, and other equipment as a result of these early studies.

Adhesion

The adhesion of vinyls varies depending on the adhesives present in the resin and the substrate. Chemically, vinyl resins may have no functionality or may be modified to be either carboxyl or hydroxyl functional. Dow offered all three functionalities in its UCAR™ line of vinyl resin powders with molecular weights that range from 15,000 to 44,000.

In the case of steel, the adhesion values increase from poor to excellent by adding 1% maleic acid. Adhesion is adversely effected by the presence of oils, grease and other contaminants. Both Reclamation and USACE specify that surfaces be blast cleaned and cleaned with solvent if necessary.

Table 3. Table from an unspecified source showing adhesion of vinyl resins to various substrates. Adapted from [17]

Substrates	Unmodified Copolymer VYHH	Hydroxylated Terpolymer VAGH, VAGF	Carboxylated Terpolymer VMCH
Clean metal (non-scarified)	Poor	Poor	Excellent
Phosphated metal	Poor	Fair	Excellent
Sandblasted metal	Poor	Fair	Excellent
Concrete	Good	Good	Excellent
Glass	Poor	Fair	Excellent
Acrylics	Excellent	Excellent	Excellent
Alkyds	Poor	Excellent	Fair

Potential Alternative Coating Systems

Exempt Solvent Solution Vinyl Solution Coatings

VOC's are regulated by the EPA and include solvents which evaporate from the coating system and also take place in a photochemical reaction in the atmosphere to form ozone. Certain solvents such as acetone, methyl acetate, methyl siloxanes and PCBTF (Parachlorobenzotrifluoride) are listed as exempt VOC's. Dow chemical provided product formulation information for a Standard coating system, a HAPS-free version, and a HAPS-free reduced VOC version. The formulation of the latter consists of the VMCH solution vinyl resin and utilizes butyl acetate and acetone as solvents. Solvent content was 5.35 lbs per gallon (640 g/l) but all of this would come from exempt solvents.

Mansour investigated the effect of the use of various solvents in vinyl film formation [35]. EIS is used to benchmark coating performance. Varnishes formulated with MIBK and toluene had better protective films versus resins with xylene or benzene. The optimum toluene concentration was 70%. The ideal solvent is based on the evaporation rate. Toluene has a medium evaporation rate. The study was done with VYHH as the copolymer resin. Evaporation rates seem to be important. The relative evaporation rate of the active solvent versus the diluent should be similar. Furthermore, the evaporation rates of both the active solvent and the diluent should be appropriate for good film formation i.e. not evaporating too fast such that a good film cannot be formed. Also they shouldn't evaporate too slowly lest the bulk of the solvent becomes trapped beneath the surface.

Alternative Thermoplastic Coatings

One of the questions this study sought to answer is whether thermoplastic materials offer any inherent advantage over thermosetting polymers. Vinyl resins and coal tar enamels are both thermoplastic materials that exhibit long service lives under the intended service conditions. A thermoplastic polymer material is not crosslinked together, instead the individual polymer chains entangle to form networks of either crystalline (ordered) structures or amorphous (random) structures. The degree of crystallinity is usually a function of temperature and the threshold for conversion from crystalline to amorphous structure is known as the glass transition temperature (T_g). Crystallinity factors into the mechanical and physical properties that a material exhibits. For instance, in a highly crystalline structure, molecules are packed together more efficiently so the mass density is greater than a similar polymer network with little or no crystallinity. Polyethylene, Polyvinyl chloride (PVC), Polypropylene / Polyolefin, Nylon 11, Polyvinylidene fluoride (PVDF), Polyethylene tetrafluoro ethylene copolymer (ETFE), Polyethylene chloro trifluoro ethylene copolymer (ECTFE) are all examples of powder coated thermoplastic resins to be evaluated and compared to solution vinyl resins for corrosion protection performance.

Alternative Thermoset Coatings

Thermoset materials form cross-linked polymer chains during the curing process. This chemical reaction is driven by thermodynamic driving force and is typically exothermic (generates heat). The reaction is irreversible; thermoset materials do not melt or separate when reheated. Epoxies and polyurethane coatings are two common examples of thermoset coatings. While thermoplastic materials rely on chain entanglement and ordering for strength, crosslinking determines the mechanical properties of thermosets. Crosslink density can be engineered by controlling factors

such as molecular weight and degree of functionality. Setting other factors aside, a highly crosslinked material will have relatively high tensile strength but limited ductility (elongation at break). The ability to work or deform a cross-linked material is limited. Thermoplastics on the other hand can be heated and molded to suit a particular purpose. Convertible (crosslinked) coatings are typically more resistant to chemicals and acids versus a thermoplastic and hence are suitable for a wide range of applications. This is probably another reason why the coatings industry has shifted towards epoxies, polyurethanes and polyureas, but for water immersion service, high chemical resistance is not necessary. Some of the newer AWWA C222 polyurethanes are marketed as 50 year coatings. However, these materials present other challenges. They require a clean surface with an adequate surface profile; they require plural component spray equipment and any deviation from the stoichiometric ratio during spray application will result in defects. They also contain hazardous isocyanates and must typically be applied at relatively high build 50+ mils to achieve the desired service life. Adhesion to the substrate tends to decrease over time in immersion and not all coatings have performed equally in Reclamation's recent laboratory testing program. Problems in the field have also arisen when the fast setting urethanes are applied to a cold substrate such as embedded pipe which can act as a heat sink. This resulted in blistering of the material.

The advantage of using a thermoset coating is that the material can be conveniently applied as an unreacted liquid and then allowed to cure to form a solid material. In contrast, a thermoplastic experiences no chemical reaction and must either be melted or dissolved during the application process. Convenience and elimination of the need for solvents are two reasons that most modern field-applied coating systems are thermoset resins. Several questions must be considered when choosing thermoset coatings versus thermoplastics:

- Do thermosets offer any advantage vs thermoplastics in long term corrosion protection?
- Given the fact that all polymers are permeable to some extent are thermoset materials more or less permeable than thermoplastics of similar density?
- Are thermosets more susceptible to polymer degradation vs thermoplastics? As water molecules and ions are transported through the polymer matrix, the coating becomes compromised and ion pathways can develop. Barrier pigments (especially leafing pigments) help to reduce the pathways for migration. Repeated wetting and drying can accelerate the degradation process. Also, water flow over the coating surface appears to accelerate the degradation process [36], [37], [38].

Alternative thermoset coatings should exhibit good durability (impact resistant, abrasion resistant), resistance to UV degradation, and long term corrosion performance. Potential candidates include novalac epoxies, polysulfide epoxies, aromatic rigid polyurethanes. Epoxy coatings can be formulated with light stabilizers for increased UV protection. Certain pigments such as aluminum flake can be used to reduce damage. Polyurethanes tend to discolor instead of chalking and can be topcoated with an aliphatic PU topcoat if a color change is unacceptable.

Plastisols and Organosols

Plastisols and organosols are polyvinyl chloride (PVC) resins dissolved in plasticizers and then heat treated to 300 to 360 F to solidify the solution [28]. Organosols also contain a small fraction of organic solvents. Dishwasher racks are one example where plastisols and organosols are used. Both types of materials require a primer. These materials would require heat to form a protective coating film. Vinyl dispersions of organosols and plastisols are discussed in [39]. Polyone offers a line of PVC plastisols and organosols [polyone.com]. According to the technical bulletins on Polyone's website, the vinyl plastisols are typically heated to 330 °F during application. This would present a significant challenge for a field coating process.

Alternative Application Methods for Vinyl Resins

Powder Coatings Application

Commercial application of vinyl resin powder coatings dates back to the 1960s. Since then, PVC have been one of the most widely used thermoplastic powders. PVC powders are readily available and sold with pigments and plasticizers already incorporated. Hence, a wide range of physical properties are possible using existing off-the-shelf materials. The melting point of vinyl powder coatings range from 190 °C to 198 °C (375-390 °F). PVC are usable at continuous operating temperatures up to 176 °C or 350 °F. Clark investigated powder coating application of PVC resins using fluidized bed, electrostatic spray, and fluid head application techniques [40]. Of these methods, electrostatic spray and thermal spray is the only method that could be scaled to perform field coating activities. Much like conventional spray application, powder coating requires a clean surface free of oils and rust etc. Once cleaned, the surface may or may not be abrasive blasted depending on the expected service environment.

Electrostatic Spray

Powder coatings are spray applied usually using an electrostatic gun. The gun is electrostatically charged opposite to the work piece so that the sprayed particles are attracted to the surface. Due to the electrostatic charge, this technique has a high transfer efficiency meaning that very little material is wasted in the spray process. In addition, edges and corners are easier to coat. It is possible to build up a relatively thick film in excess of 20 mils due to the fact that vinyl coatings are slightly conductive. In contrast, it may be difficult to achieve sufficient DFT using polyesters and epoxy coatings [40]. Electrostatic spray equipment is inexpensive and is readily purchased. Once the powder is spray applied, the part must be heated above the fusion temperature and cooled to form a solid film. In contrast to thermoset powders, a long heating cycle is not required for proper film formation. Depending on the PVC formula, a primer may be required for adequate adhesion to metal surfaces. However, self-priming powders are available. This process lends itself to smaller items which can fit inside an oven. For example pipe segments are coated in a shop using a powder spray process followed by the application of heat to melt and fuse the material into a continuous protective coating system. However, this would be challenging to scale for field use on large equipment such as penstocks or radial gates.

Thermal Spray

It is possible to use flame spraying to apply polyethylene and polypropylene to field girth joints which must be coated in the field after welding has been performed [41]. In addition, the flame spray process could also potentially be used to apply PVC materials to field structures. However,

flame spray can cause safety concerns in confined spaces and production rates are much lower than conventional spray processes. The resulting surface can be rough and uneven and the film will have some degree of porosity which will compromise corrosion performance. The degree of porosity will depend on the process parameters. Other practical considerations include the level of heat generated in the equipment being coated which may be unacceptable. In addition, the size of the application equipment makes it difficult to coat surfaces with complex geometries.

Fluidized Bed

Fluidized beds use compressed air to lift the powder and allow it to behave as a fluid. The part is preheated to around 500 °F and dipped into the bed. Fluidized bed is used to coat smaller parts, especially parts with irregular geometries. This process does not lend itself to coating large infrastructure.

Hand Daubing

Coal tar enamel is a thermoplastic material that was frequently specified by the Bureau of Reclamation for immersion and burial service. Like vinyl resins, coal tar is now recognized for exhibiting a very long service life under ideal exposure conditions. The material was applied to pipe by heating and melting chips in a large kettle. The molten material would then either be hand daubed or mopped on to the primed surface. This was performed for penstocks of all sizes; however, the noxious fumes presented a hazard to the workers. For shop coating pipe interiors, the molten coal tar enamel was poured inside a pipe segment as the pipe was rotated which resulted in a very smooth finish. The melting point of coal tar enamel ranges from 223-333 °F and the kettles were operated at temperatures less than 400 °F to avoid compromising the physical properties of the coal tar. Thermoplastic materials such as PVC, HDPE and Polypropylene have melting temperatures with ranges similar to coal tar enamel. In addition, these materials are already being used as shop-coatings in oil & gas midstream applications and well as oil and gas. Economics is one question that must be addressed. Coal tar enamel was an inexpensive byproduct material that was a frequently applied in thickness in excess of 100 mils. In contrast, vinyl resins achieved excellent long term corrosion protection from dry film thicknesses as low as 6 mils. While a thicker coating may give an even longer service life, it may not be necessary. Would it be possible to hand apply molten thermoplastic materials such as PVC or HDPE at DFTs in the range of 10-20 mils? Would it be possible to achieve an acceptable finish or would the molten materials exhibit a taffy-like consistency that would make coating application impossible. Alternatively, might the materials viscosity be too low such that runs and sags are a concern. Ideally, the material would be formulated to exhibit thixotropic i.e. “shear-thinning” behavior which means that the liquid’s viscosity decreases at higher shear rates i.e. when the material is being applied. The rheological behavior of any potential materials need to be investigated and additives may be required to optimize application characteristics. Also, vinyl may begin to degrade at high temperatures producing carcinogenic byproducts, especially in the presence of oxygen [42]. This would require investigation and possibly careful control of the temperature if the hand daubing method is to be considered.

Heated Spray Equipment

Plural component spray equipment frequently contains heated delivery lines which serve to reduce the coating's viscosity during the application process. Typically temperature of the lines may range up to 150 °F. It may be possible to modify the equipment or design new equipment that would allow heated lines and spray equipment for temperatures in the 300-400 °F range. Rheological behavior of the material is even more important for spray applications in comparison to hand daubing. It is likely that the production rates of spraying could potentially meet or even exceed the rates of a hand daubing process since the spray gun would be continuously fed with fresh coating. Application equipment would probably be more far more expensive and require increased maintenance over a hand-daubed technique.

The Graco company manufactures equipment for hot application of thermoplastic materials. However, there are practical challenges associated with it: the hose lengths are currently limited to 25 feet due to the electrical requirements for heated lines. Also, since the equipment is intended for application of adhesives, there is not a spray gun available currently that has been designed for specifically for application of molten vinyl resins.

Field Curing of Thermoplastic Coatings

Curing of the coating could be performed after a plastisol is applied as a high solids or 100% solids material in liquid form. Infrared light or another catalyst could be used to begin a chain reaction polymerization process [43]. There may be opportunities for additional research in this area.

Research Methodology

Initial Vinyl Testing

In 2006, a limited number of 1/8-inch thick 3-inch by 6-inch low carbon steel panels coated with solution vinyl coating formulation V-766e were provided to Reclamation by the USACE. The panels were subjected to constant immersion in dilute Harrison solution (HAR) and incorporated into Reclamation's electrochemical impedance spectroscopy (EIS) test program. EIS testing is an established technique used to measure changes in coating barrier properties over time, i.e. coating degradation [3, 44, 45, 46]. A temporary test cell was used for EIS measurement using an o-ring, glass cylinder, and clamp. Dilute Harrison's Solution was added to the cylinder as electrolyte for the experiment. This test cell isolated a 20 cm² surface area of coating film. A three-electrode method containing a working, reference, and current electrode was satisfied using the steel substrate, a saturated calomel electrode, and a platinum electrode, respectively. A Gamry Instruments FAS2 Femtostat performed the measurement with dedicated EIS300 software. Test parameters were 10 mV voltage perturbation versus open circuit and a frequency range of 10⁵ Hz to 10⁻² Hz, collecting ten points per decade.

After 8 years in immersion, the V-766e panels were removed and sent to North Dakota State University's Coatings and Polymeric Materials Department for differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) analysis.

Vinyl Benchmark Testing

In 2015, following the initial testing, a full laboratory test program was initiated to benchmark the performance of two vinyl resin coating systems across a variety of test conditions. The systems tested were as follows:

- USACE System 4: 5+ coats of V-766e vinyl copolymer (12 mils DFT)
- USACE System 5-E-Z: 1+ coats of VZ-108d zinc-rich vinyl resin primer and 3+ coats of V-766e, i.e. (12 mils DFT)

The corrosion testing was performed on coated steel samples and included immersion testing in Deionized (DI) water, immersion in Dilute Harrison's (HAR) Solution, and cyclic testing. Additional testing, included cathodic disbondment, slurry erosion resistance, adhesion testing, knife adhesion testing.

As an example Table 1 and Table 2 summarize the testing methods used for V-766e. The corrosion testing was performed on coated 3"x6"x1/8" steel coupons either scribed or un-scribed as noted. A 0.075-inch wide dremel tool was used to scribe an "X" on one side of each scribed panel. The cathodic disbondment testing was performed on a 3-inch 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 glued down. The panel was then placed in 100% humidity for 24 hrs

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while the glue cured prior to pull off testing. Any glue failures were not included in the test scoring.

EIS testing was performed periodically throughout the test period. Qixon and Wang determined that coating degradation occurs more quickly in pure water vs 3.5% NaCl solution [47]. This is presumed to be due to the fact that pure water holds a greater concentration of dissolved oxygen which diffuses through the coating (9.1 mg/L vs. 7.2 mg/L). EIS measurements were performed on DI and HAR immersion samples as well as BOR, PRO, and FOG test panels.

Table 4. Corrosion test protocol summary for V-766e, number of 3”x6”x1/8” panels (scribed/unscribed) used for each test.

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/2u	2s/2u	0s/1u	1s/1u	2s/1u	2s/1u

¹ ASTM D870: Dilute Harrison’s Solution (HAR) is water with 0.5 g/L NaCl, 3.5 g/L NH₄2SO₄, 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 using HAR solution, 1 hr dry-off at 35 C.

⁴ ASTM D 4587: Test condition “B” 4 h UV/60 C followed by 4 h Condensation/50C

⁵ ASTM D5894: 1 week alternating exposure schedule in the following repeating order: QUV, FOG

⁶ 1 week alternating exposure schedule in the following repeating order: QUV, FOG, HAR, FOG

Table 5. Mechanical test protocol and substrates utilized for V-766e testing.

Disbondment ASTM G8	Erosion Resistance USBR-5071-2015	Abrasion Resistance ASTM D 4060 ¹	Impact Resistance ASTM D2794	Pull-off Adhesion ASTM D4541	Pull-off Adhesion (wet) ASTM D4541	Knife adhesion test (wet) ASTM D6677 ²
3-inch diam. pipe	2 – 11”diam. discs	2 – 4” diam. discs	3”x6”x1/8” coupon	3”x6”x1/8” coupon	3”x6”x1/8” coupon	DI and HAR

¹ASTM D4060 weight loss measured after 1000 cycles, CS-17 wheels resurfaced after 500 cycles, 1 Kg load

²Test performed on HAR and DI panels, post immersion.

The complete results are detailed in individual laboratory test reports 8540-2017-031 (system 4) and 8540-2017-032 (system 5) produced by Reclamation’s Materials and Corrosion Laboratory [48] [49].

Properties of free films were also tested by North Dakota State university [20]. These tests included Dynamic Mechanical Thermal Analysis (DMTA), Dynamic Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Infrared Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Electron Diffraction.

Testing of Candidate Replacement Materials

A similar test program was used to evaluate a variety of thermoplastics and thermoset materials. A laboratory test report was generated which summarizes the test program and results for each product. Below is a list and general description of the products which were selected for evaluation:

Thermoplastics

Four thermoplastic materials were selected for testing: PVDF, ECTFE, Nylon (NY), and Polyolefin (PO) (see Table 6). Each material was powder coated by a specialty products applicator. Details for each of these products are provided in laboratory test reports for each system [50, 51, 52, 53].

Table 6. Thermoplastic materials selected for laboratory evaluation

Product ID	Average DFT (mils)	Generic Chemistry	Notable product features for vinyl replacement (as per mfr)	Lab Report #
NY	8.6 +/- 2.4	Nylon	Potential alternative thermoplastic material	8540-2017-015 [50]
PVDF	7.1 +/- 0.8	Polyvinylidene fluoride	Potential alternative thermoplastic material	8540-2017-016 [51]
ECTFE	11.6 +/- 1.1	Polyethylene chloro trifluoro ethylene copolymer	Potential alternative thermoplastic material	8540-2017-017 [52]
PO	13.9 +/- 1.9	Polyolefin	Potential alternative thermoplastic material	8540-2017-018 [53]

Thermosets

Several types of thermoset materials were selected for evaluation including epoxy, polyurethane, polyurea and hybrid materials (see Table 7).

Table 7. Thermoset materials selected for laboratory evaluation

Product ID	Average DFT (mils)	Generic Chemistry	Notable product features for vinyl replacement (as per mfr)	Lab Report #
PU1	40.9 +/- 2.9	100% solids aromatic polyurethane	AWWA C-222-08. Impact resistance is reported as > 85 in-lbs	8540-2017-013 [54]
PU+ALPU	48.4 +/- 4.4	100% solids aromatic polyurethane AWWA C-222-08 with an aliphatic polyurethane topcoat	Topcoat is a solvent-borne aliphatic polyurethane for UV resistance	8540-2017-014 [55]
EP1	36	100% solids novolac epoxy	Abrasion resistant, product is designed to be applied as a single coat at 20-30 mils	8540-2017-019 [56]
EP2	42 +/- 11	100% solids epoxy	Color stable, abrasion and impact resistant. can be applied up to 40 mils thick in a single coat	8540-2017-020 [57]

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Table 7. Thermoset materials selected for laboratory evaluation

Product ID	Average DFT (mils)	Generic Chemistry	Notable product features for vinyl replacement (as per mfr)	Lab Report #
PU2	36.5 +/- 3.8	100% solids polyurethane	Formulated to have a longer gel time (80-100 sec) to allow for compatibility with robotic coating application systems. Elongation of 30%.	8540-2017-021 [58]
EP3	45.1 +/- 4	100% solids multi-functional epoxy, with a uniquely modified aliphatic/cycloaliphatic amine hardener.	UV stable, abrasion resistant. Impact resistance is reported as 158 in-lbs. Can be applied up to 60 mils in a single coat.	8540-2017-022 [59]
EP4	42.3 +/- 6.2	100% solids “poly-sulfide based phenyl novolac and hydrogenated epoxy blend.”	Experimental product for evaluation by the USBR. Excellent impact resistance and UV stability. Can be applied at thicknesses up to 40 mils per coat. 50°F minimum application temperature.	8540-2017-023 [60]
EP+ALPU	13.7 +/- 1.5	PCS-#1111 is a 100% solids modified epoxy system PCS-#4300 is a fluoropolyurethane topcoat	Basecoat with good flexibility & elongation (> 40%). Topcoat provides excellent UV resistance	8540-2017-024 [61]
EP5	13.7 +/- 1.5	100% solids modified epoxy system	aluminum flake pigmented version of PCS-#1111	8540-2017-025 [62]
EP+PS 1	25 +/- 7	Primer: solvent-borne epoxy w/ glass flake pigment Topcoat: polysiloxane	The epoxy is intended to provide corrosion protection whereas the topcoat is included for weathering resistance	8540-2017-033 [63]
EP+PS 2	21 +/- 5	Primer: solvent-borne epoxy Topcoat: polysiloxane	The epoxy is intended to provide corrosion protection whereas the topcoat is included for weathering resistance.	8540-2017-034 [64]
EP6	28.6 +/- 2.4	100% solids epoxy	Zero V.O.C.	8540-2017-036 [65]
EP7	30.3 +/- 6.7	Hi-solids epoxy	N/A	8540-2017-037 [66]
EP8	37 +/- 8.1	100% solids epoxy	High build, zero V.O.C.	8540-2017-038 [67]
EP/PU	40 +/- 13.6	100% solids, novolac epoxy/polyurethane hybrid	Bio-based, zero V.O.C.	8540-2017-039 [68]
EP/PUA	27 +/- 5.2	100% solids, “novolac epoxy/polyurea” hybrid	Bio-based, zero V.O.C.	8540-2017-040 [69]
PU3	30 +/- 15	100% solids polyurethane	Zero V.O.C.	8540-2017-041 [70]
EP9	32 +/- 5.9	100% solids epoxy	Zero V.O.C.	8540-2017-042 [71]
EP10	39 +/- 10.6	100% solids polycyclamine epoxy	Zero V.O.C.	8540-2017-043 [72]

Results

Initial Testing

EIS

EIS results indicate predominantly capacitive behavior for the solution vinyl coating formulation V-766e in HAR immersion. Figure 2 shows the data as impedance magnitude and phase angle versus frequency; no adjustment is made for the measurement surface area. The phase angle is near -90° for all measurements. Several trend lines show a decrease in this value at lower frequencies, i.e. less than 10^0 Hz. This suggests the presence of corrosion reactions at the steel interface. However, the data at 5.9 years is again capacitive at all frequencies, signifying a recovery of corrosion protection. The impedance magnitude has a featureless trend line for all exposure times. The uniformity of these trend lines also suggests a very low concentration of water uptake. Figure 3 shows the data as a complex plane plot (imaginary versus real impedance). The trend lines are depressed semicircles with a significant contribution of imaginary impedance. Figure 4 shows the evolution of the low frequency impedance magnitude for all data taken during the exposure period. The values are very high and stable, ranging from 2.1×10^9 to $7.3 \times 10^9 \Omega$. Impedance magnitude values greater than $10^9 \Omega$ indicate that the coating is a strong barrier to water and ions, providing excellent corrosion protection [73, 74].

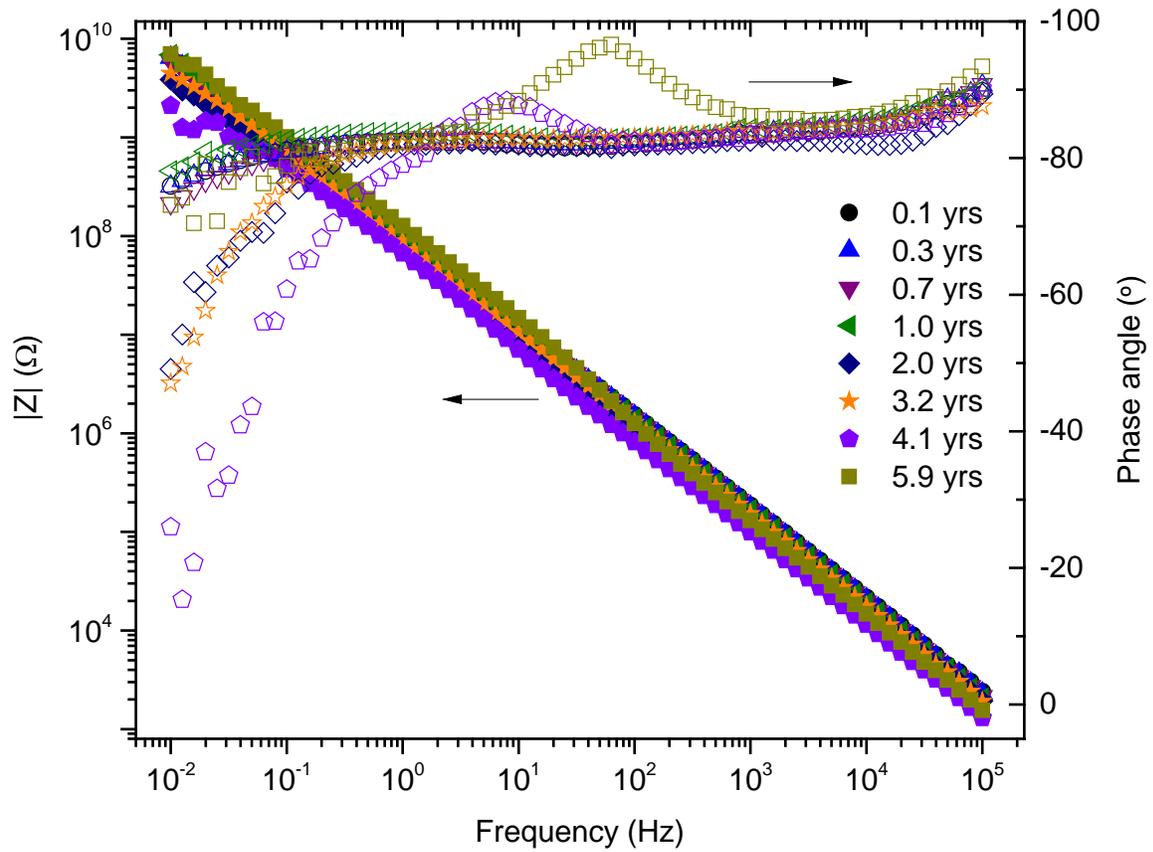


Figure 2. Solution vinyl coating formulation V-766e EIS data plotted as impedance magnitude (left y-axis) and phase angle (right y-axis) versus frequency at various exposure times.

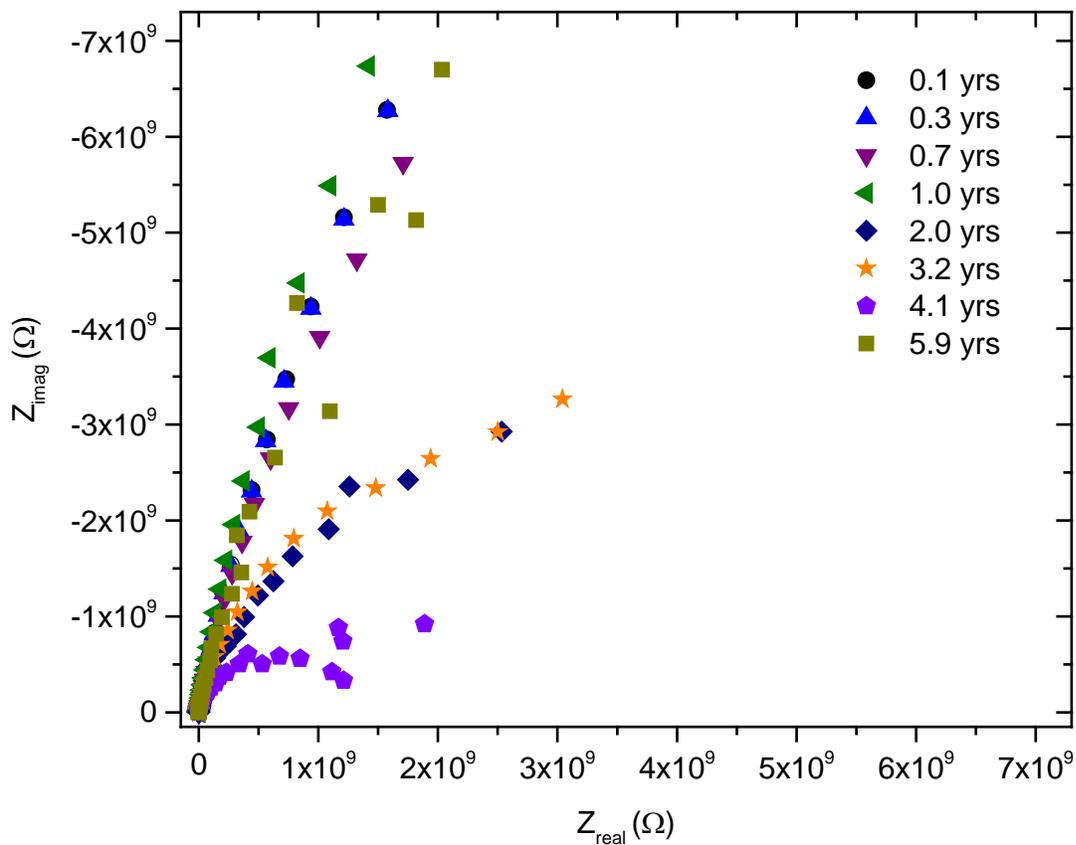


Figure 3. Solution vinyl coating formulation V-766e EIS data plotted imaginary versus real impedance at various exposure times.

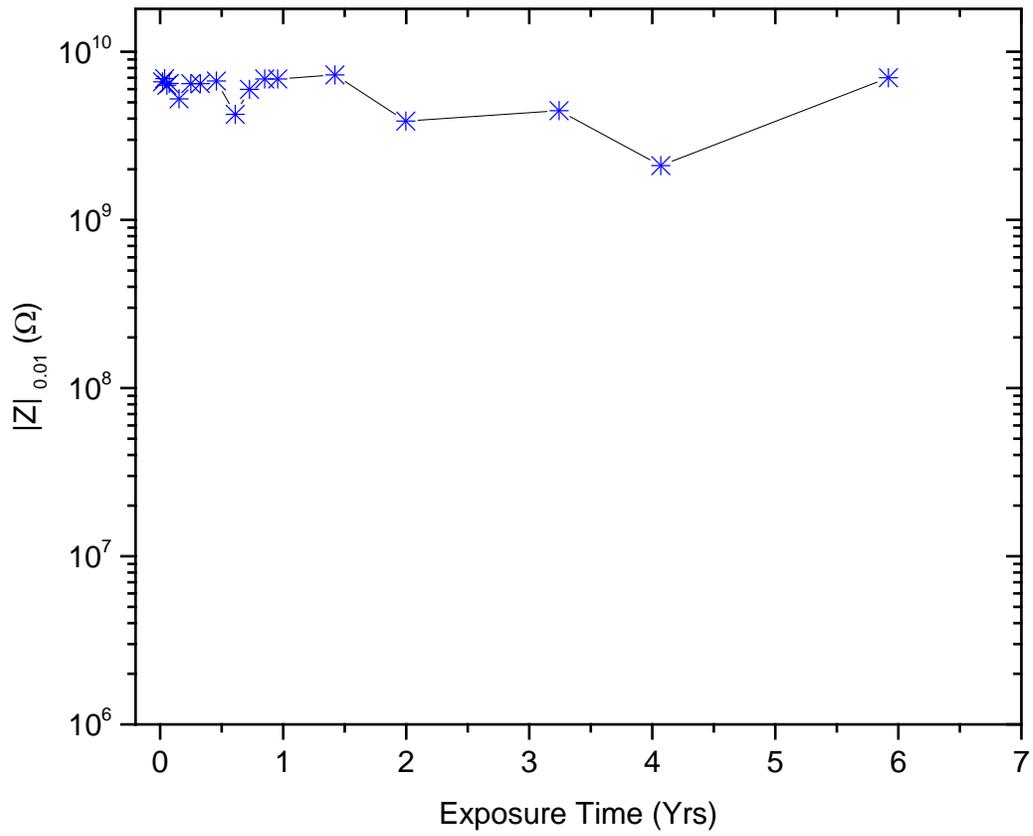


Figure 4. Solution vinyl coating formulation V-766e EIS data for impedance magnitude at 0.01 Hz versus total exposure time.

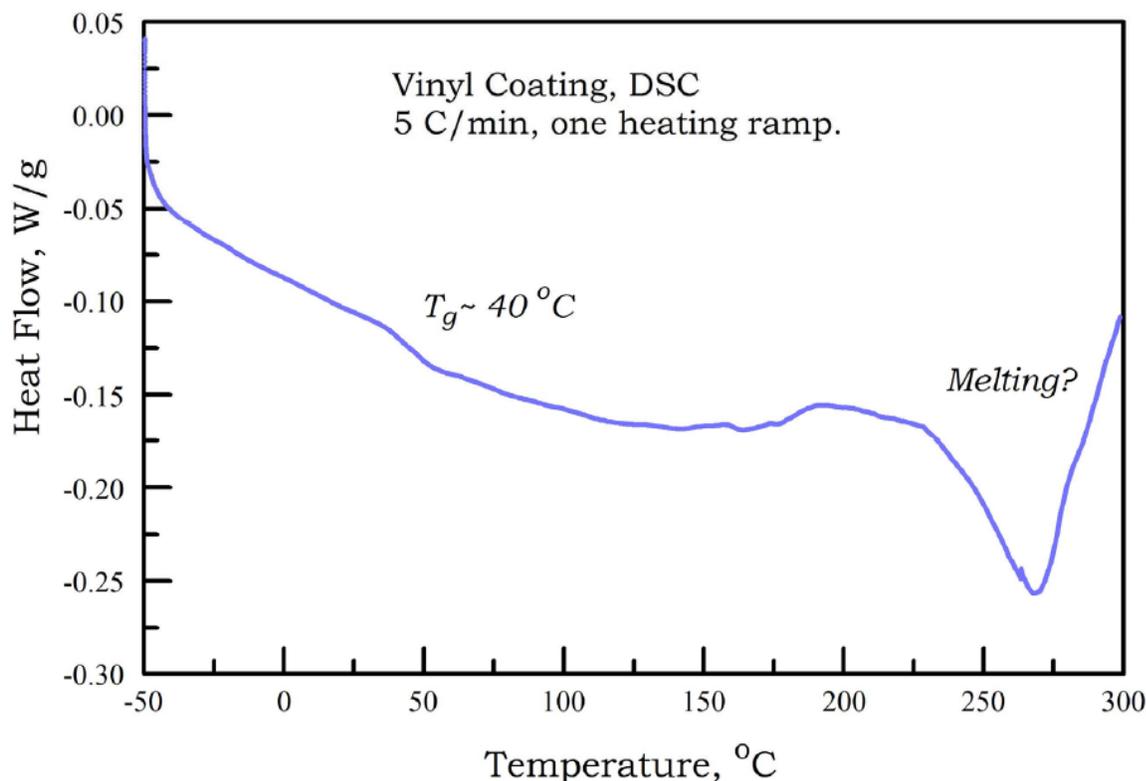


Figure 5. DSC Scan for Vinyl Resin Coating Sample V-766e after approximately 8 years immersion service exposure. Image Credit: North Dakota State University.

Figure 5 shows data from a DSC test performed on the solution vinyl coating sample after 8 years in HAR immersion. The DSC scan rate was $5^\circ\text{C}/\text{min}$. The sample has a glass transition temperature (T_g) of approximately 40°C . It is likely that many solution vinyl coating installations experience temperatures higher than the T_g ; however, the effect is not detrimental. On the contrary, these thermoplastic coatings may experience a small degree of self-healing as a result.

Figure 6 shows an SEM image of a cross section of a solution vinyl. Note the pigment particles and agglomerates that are visibly interspaced throughout the vinyl copolymer network. These network pores are several hundred nanometers in diameter, which should fill with water and ions during immersion. However, the image also shows the vinyl network to be tortuous, suggesting that the pores are isolated from one another. The EIS data supports this isolation, showing a lack of ionic connectivity through the film. While the surface of the film appears quite porous, EIS shows that the electrolyte does not easily move through the film to interact with the underlying steel surface [44].

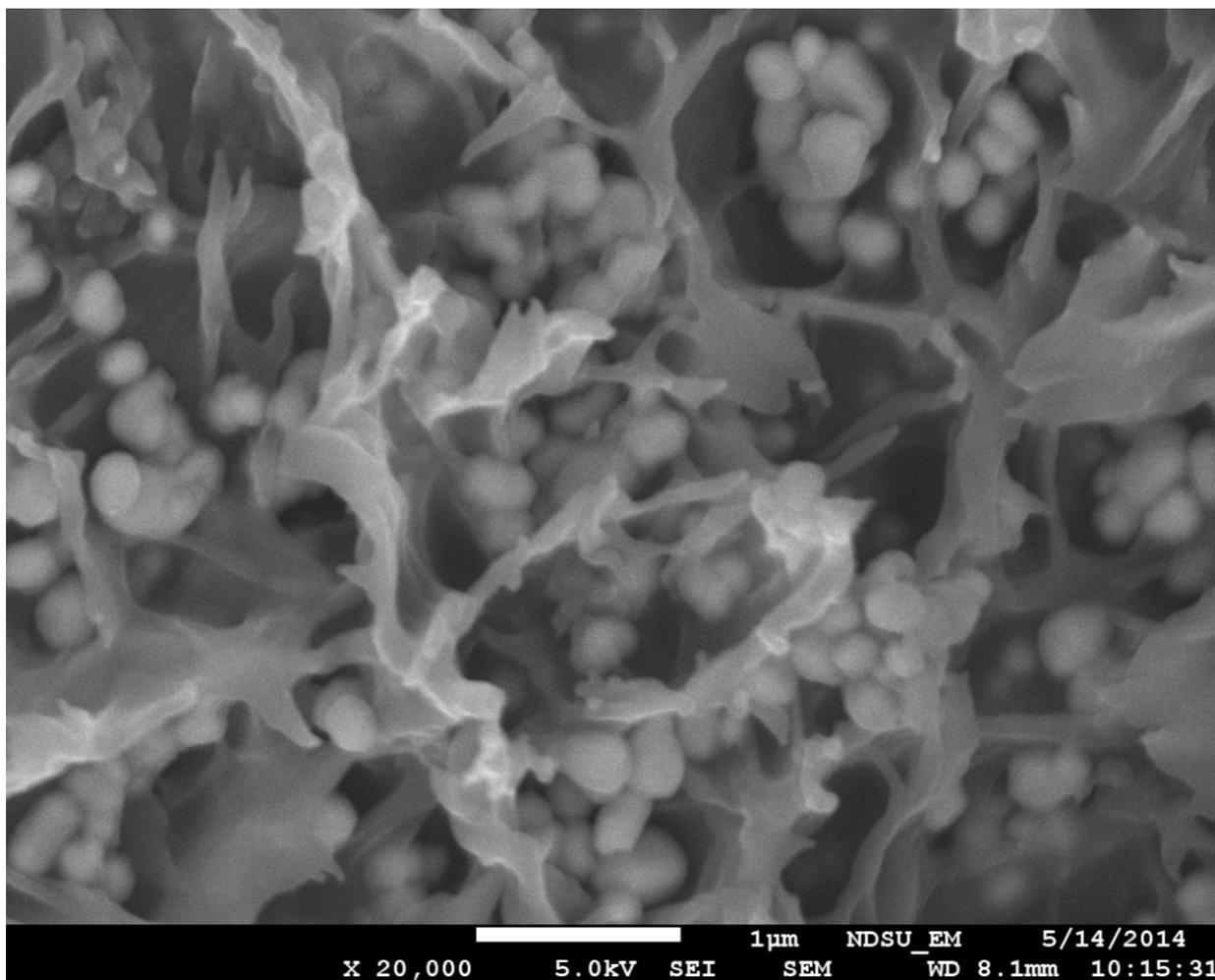


Figure 6. Scanning Electron Microscopy image for vinyl resin coating after 8 years laboratory immersion. Image Credit: North Dakota State University.

Benchmark testing vs Replacement Materials

Immersion Testing

After a period of prolonged immersion, the “one-sided” rust creep for each panel was determined by measuring using a caliper after coating removal. For most panels, this analysis was performed after approximately 7 months (5040 hrs). However, several products were tested for slightly more than one year and the results were prorated to 7 months. For immersion testing, the full width of the rust area was measured on each panel at six predetermined locations along the scribe, averaged, adjusted for the scribe width, and divided by two. The minimum and maximum values were also measured and recorded. A rating was assigned in accordance with the following guidelines based on the maximum creep observed:

- Excellent: No visual defects
- Good: No blistering, minor rust creep $\leq 1/8''$
- Fair: No blistering, moderate rust creep $\leq 1/4''$
- Poor: Blistering, delamination or rust creep $> 1/4''$

The results for the materials evaluated are shown below in Figure 6.

Figure 7 shows photographs of the best and worst performing materials and a comparison to the two vinyl systems benchmarked for DI immersion.

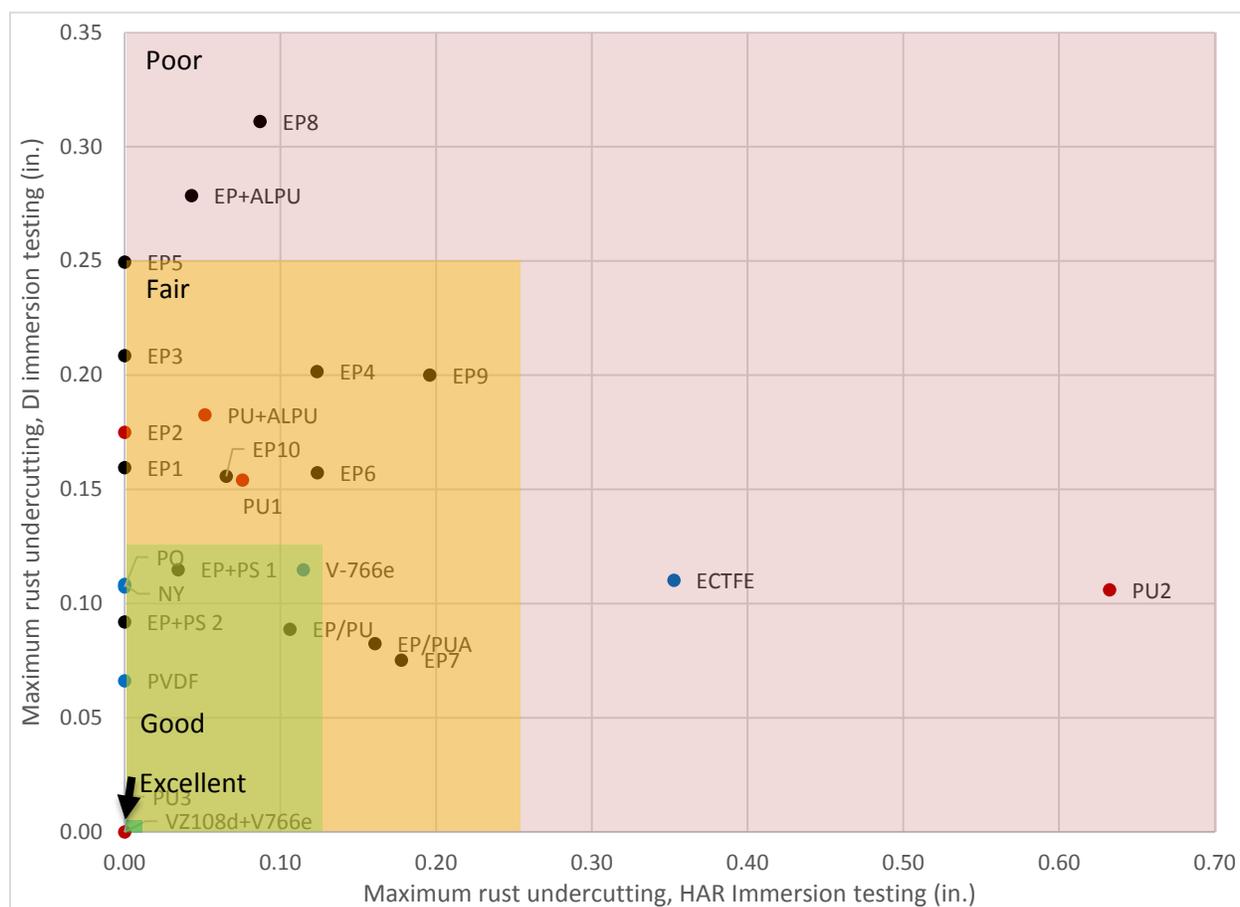


Figure 7. Rust Creep performance for materials subjected to steady state immersion.

Note that in most cases, the DI immersion resulted in higher undercutting than the HAR exposure. This is counterintuitive because Dilute Harrison’s Solution contains chlorides and sulfates and is therefore considered to be a more aggressive and corrosive environment. However, the test doesn’t measure actual metal loss, instead it is an indication of how readily an electrolyte is able to migrate from a coating defect along the coating-substrate interface. Since actual service conditions and water chemistry will vary widely, testing in both immersion conditions is appropriate. The best performing materials in steady state immersion were zinc-rich vinyl, PU3, PVDF, EP+PS1, EP+PS2 and EP/PU. V-766e also performed well. Note that the

HAR immersion test panels for PU3 contained some rust which appears to have originated from the scribe during scraping but this is uncertain and no score was assigned for HAR immersion.



Figure 8. DI Immersion Cyclic test panels post-test after coating removal. Rust creep measured following 5040 hrs of cyclic exposure testing.

Electro-chemical Impedance Spectroscopy

EIS data was collected for samples exposed to immersion and cyclic weathering testing. The EIS score is determined from performance of immersion test panels over a 7 month (5040 hr) exposure period. Additional data continues to be collected and may be used for future analysis. A general ratings criteria guideline was established as follows for samples after at least 5000 hours of immersion:

Excellent: Minimal degradation < 1 order of magnitude @ 0.01 Hz and $\geq 10^9$ ohms

Good: Minor degradation ≤ 2 order of magnitude @ 0.01 Hz and $\geq 10^8$ ohms

Fair: Moderate degradation ≤ 3 orders of magnitude @ 0.01 Hz and $\geq 10^7$ ohms

Poor: Signification degradation after 5000 hrs > 3 orders of magnitude @ 0.01 Hz

Table 8 summarizes the results for all materials tested. The worst performers in the EIS test were epoxies most of which tended to show a notable decrease in impedance over the test duration. However, there were exceptions such as EP8 which maintained high impedance and scored excellent. Several other epoxies received scores of good. One possible explanation for the variation is that materials such as EP8 appear to benefit from the use of hydrophobic pigments in the formulation. All thermoplastic materials including vinyl gave excellent performance. Polyurethanes also performed well in general as did the epoxy systems with a polysiloxane topcoat (EP+PS1 and EP+PS2).

Table 8. EIS scoring summary.

Excellent	Good	Fair	Poor
PU1	EP1	EP2	
PU+ALPU	EP5	EP3	
NY	EP+PS 2	EP4	
PVDF	EP9	EP6	
ECTFE	EP10	EP7	
PO			
PU2			
EP+ALPU			
V-766e			
VZ108d+V766e			
EP+PS 1			
EP8			
EP/PU			
EP/PUA			
PU3			

Cyclic Testing

The “one-sided” rust creep for each panel was determined by measuring using a caliper after coating removal. For immersion testing, the full width of the rust area was measured on each panel at six predetermined locations along the scribe, averaged, adjusted for the scribe width, and divided by two. The minimum and maximum values were also measured and recorded. A rating was assigned in accordance with the following guidelines:

Excellent: No blistering, minor rust creep $\leq 1/8$ ”

Good: No blistering, minor-moderate rust creep $\leq 1/4$ ”

Fair: No blistering, moderate rust creep $\leq 1/2$ ”

Poor: Blistering, delamination or rust creep $> 1/2$ ”

The cyclic test results for the materials evaluated are shown below in Figure 9.

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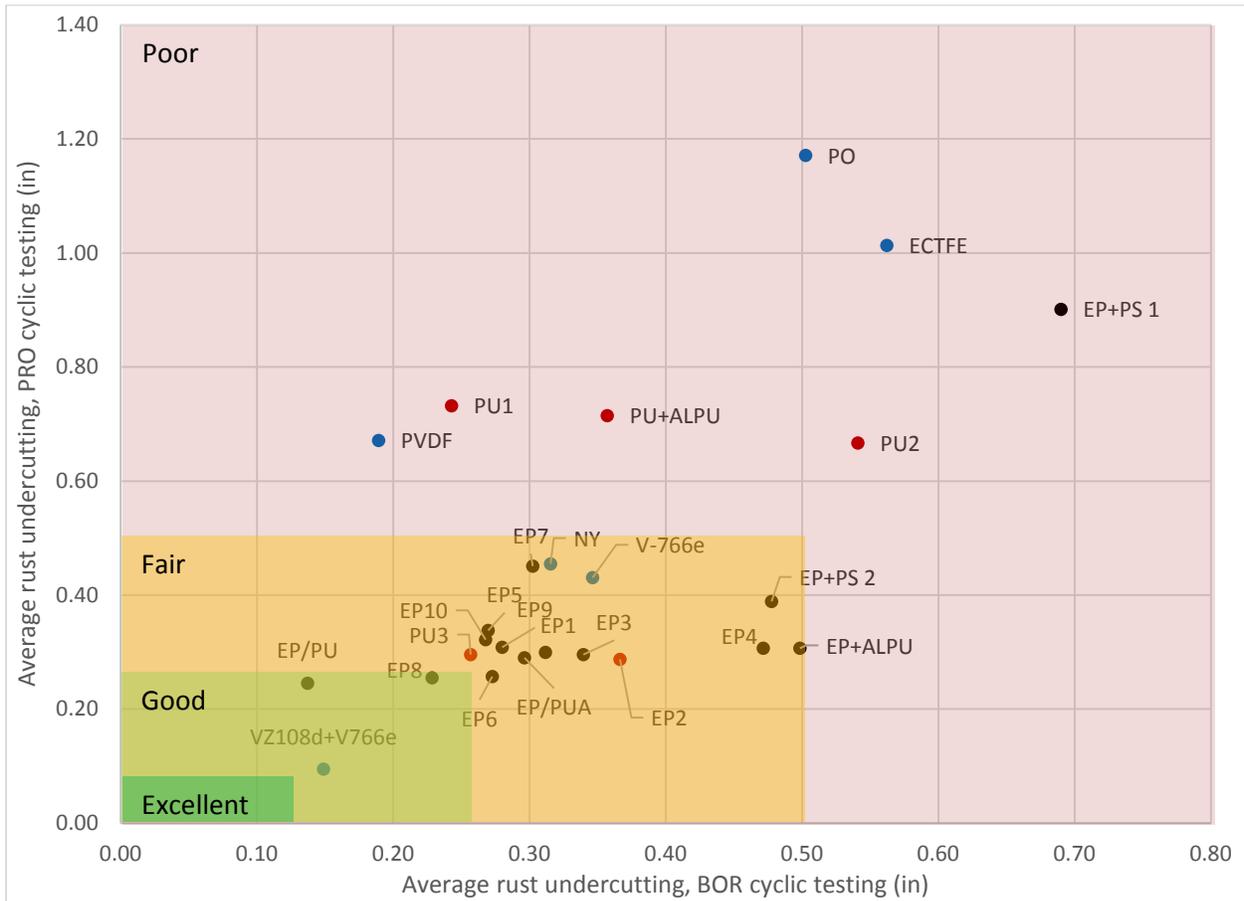


Figure 9. Rust creep measured following 5040 hrs of cyclic exposure testing.

Figure 10 shows photographs of the best and worst performing materials and a comparison the two vinyl systems benchmarked.

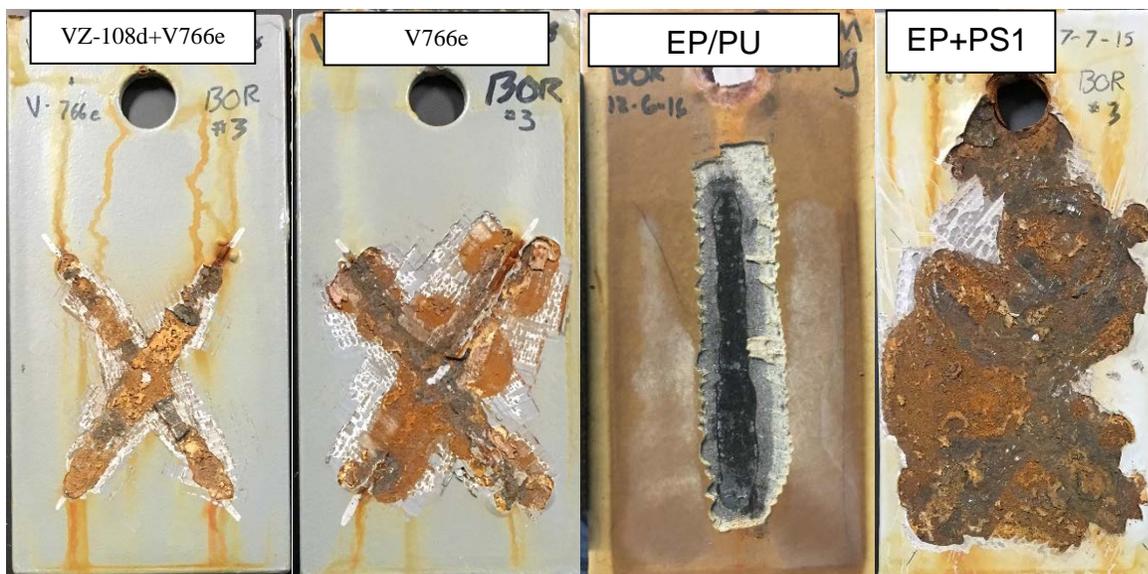


Figure 10. BOR Cyclic test panels post-test after coating removal. Rust creep measured following 5040 hrs of cyclic exposure testing. The best and worst performing materials and compared with vinyl resins V-766e and VZ-108d+V-766e

QUV Testing

Table 9 gives a summary of the results for QUV accelerated weathering testing of the products. Each material was assigned a qualitative rating based on the following guidelines:

Excellent: No visual defects

Good: No blistering, no rust creep, minor color change

Fair: No blistering, moderate color/gloss change, chalking, or undercut up to 1/8"

Poor: Any of the following: blistering, delamination, undercut/rust creep > 1/8"

The best performing material was the polyolefin (PO) and as expected, the vinyl materials performed well with very minor color changes occurring. Other strong performers included the epoxy/polysiloxane systems (EP+PS 1 and EP+PS 2), the epoxy polyurea hybrid system (EP/PUA) and two thermoplastics: nylon (NY) and Polyvinylidene fluoride (PVDF). The remaining products either chalked, sustained undercutting, or experienced a noticeable color change and were scored accordingly.

Table 9: QUV test results.

Excellent	Good	Fair		Poor
PO	V-766e	PU1	EP6	ECTFE
	VZ108d+V766e	PU+ALPU	EP7	EP+ALPU
	EP+PS 1	EP1	EP8	EP5
	EP+PS 2	EP2	EP/PU	
	NY	PU2	PU3	
	PVDF	EP3	EP9	
	EP/PUA	EP4	EP10	

Mechanical Properties and Cathodic Disbondment

Cathodic disbondment, slurry erosion, tabor abrasion, impact, pull-off adhesion (initial), pull-off adhesion (post immersion), knife adhesion (post immersion) testing were performed for most of the candidate replacement materials. The following ratings criteria were established during the test program and used during the evaluations:

Cathodic Disbondment (ASTM G8)

Excellent: Disbondment radius $\leq 0.25''$

Good: Disbondment radius $\leq 0.5''$

Fair: Disbondment radius $\leq 1''$

Poor: Disbondment radius $> 1''$

Erosion (USBR-5071-2015):

Excellent: < 30 mg/hr average loss

Good: < 50 mg/hr average loss

Fair: < 100 mg/hr average loss

Poor: > 100 mg/hr average loss

Tabor Abrasion (ASTM D4060):

Excellent: < 30 mg loss

Good: < 40 mg loss

Fair: < 100 mg loss

Poor: > 100 mg

Impact:

Excellent: ≥ 160 in-lbs

Good: ≥ 100 in-lbs

Fair: ≥ 50 in-lbs

Poor: < 50 in-lbs

Adhesion (initial, dry):

Excellent: $\geq 2,500$ psi

Good: $\geq 1,500$ psi

Fair: $\geq 1,000$ psi

Poor: $< 1,000$ psi

Wet Adhesion:

Excellent: $\geq 2,000$ psi

Good: $\geq 1,000$ psi

Fair: ≥ 500 psi

Poor: < 500 psi

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.

Table 10 gives a summary of the cathodic disbondment and mechanical testing for the two vinyl benchmarks and all candidate replacement materials evaluated. The results were compiled from individual laboratory test reports [48, 72]. Each cell contains the result and is color coded in accordance with the qualitative score assigned.

Cathodic Disbondment: The vinyl products did not perform well in this test and there are a number of viable alternatives including epoxies and polyurethanes.

Slurry Erosion: The vinyl materials performed well in this test with a score of “good.” There were at least 15 materials in the study that performed as well or better than vinyl including other thermoplastics, epoxies, polysiloxanes, and polyurethanes.

Tabor Abrasion: The tabor wheel abrasion test was performed on a limited number of products and vinyls were not included in this test. The best performing materials of those tested were thermoplastics (PVDF, NY, PO) and an aromatic polyurethane (PU1).

Impact Testing: The zinc-rich vinyl (VZ-108d+V-766e) outperformed the standard vinyl material significantly (100 inch-lbs vs 20 inch-lbs of energy absorbed). Several materials outperformed the zinc-rich vinyl including epoxies and polyurethanes: PU1, PU+ALPU, EP4, EP6, EP8.

Adhesion Testing: To determine the adhesion of the coating to substrate pull-off adhesion was performed both initially following the coating application and cure, and post-immersion (after at least 7 months). However, no score could be assigned for materials when a glue failure occurred. Several materials including vinyls and other thermoplastics were problematic in this regard. In general, the epoxies scored highest in the test following immersion but the extent in which this may be used to predict field performance is not known.

Knife adhesion: Vinyl materials performed just fairly in the knife adhesion test. This is most likely due to the material’s ductility which results in a tendency to peel rather than chip. Other thermoplastic materials performed worse than vinyls. Materials which score well were all epoxies: EP+PS1, EP+PS2, EP1, EP10.

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Table 10. Summary of cathodic disbondment and mechanical testing

	Cathodic Disbondment	Slurry Erosion	Tabor Abrasion	Impact	Pull-off Adhesion	Pull-off Adhesion	Knife Adhesion (wet)
	Radius (inches)	Stabilized weight loss rate (g/hr)	Total weight loss, mg	Threshold with no cracking or holidays (inch-lbs)	Stress (psi)	Stress (psi)	ASTM Rating (0-10)
V-766e	3.125	0.039 +/- 0.003	N/A	20	1412 +/- 125 g/coh	769 +/- 56 g	4
VZ108d+V766e	1	0.041 +/- 0.004	N/A	100	1012 +/- 226 g or g/coh	N/A	4
EP+PS 1	0.375	0.033 +/- 0.004	N/A	80	1299 +/- 123 50/50 coh/adh	N/A	8
EP+PS 2	0	N/A	N/A	50	1250 +/- 164 coh		6
PVDF	1.5	0.003 +/- 0.003	13.4 +/- 0.1	30	825.5 +/- 32.5 g	947.3 +/- 233 g/coh	2
NY	1	0.004 +/- 0.004	3.8 +/- 0.0	30	N/A	1040 +/- 45 g	2
PO	9	0.006 +/- 0.006	10.3 +/- 0.6	20	505 +/- 6 g	601 +/- 61 g	0
ECTFE	0, topcoat disbonded	0.004 +/- 0.005	31.3 +/- 2.1	80	272 +/- 13.7 g	267 +/- 27 g	2
PU1	0.5625	0.005	11.9	160	965 +/- 141 g	922 +/- 354 g	2
PU+ALPU	0.5625	0.066	115.5	160	1203 +/- 95 g/ic	883 +/- 136 g/ic	2
EP1	0	0.016 +/- 0.003	0.065	50	1724 +/- 98 25/75 adh/coh	1261 +/- 24 1/62/37 g/adh/coh	8
EP2	0	0.022 +/- 0.002	0.045 +/- 0.006	100	1869 +/- 571 45/55 adh/coh	1315 +/- 107 100% adh	4
PU2	0.68	0.009 +/- 0.002	0.086 +/- 0.023	140	2620 +/- 246 adh/coh	1220 Adh	2
EP3	0	0.017 +/- 0.002	0.041 +/- 0.009	70	2917 adh	1233 +/- 229 adh	4
EP4	0.625	0.016 +/- 0.005	0.091 +/- 0.018	120	1389 g	652 +/- 109 adh	2.5
EP+ALPU	0.31	0.026 +/- 0.005	0.113 +/- 0.003	10	1258 g	558 +/- 30 Coh	4
EP5	4.5	0.068 +/- 0.005	0.102 +/- 0.004	10	1677 +/- 96 coh	643 +/- 61 coh	5.5
EP6	0	0.067 +/- 0.019	N/A	160 (30 backside)	1605 40/30/30 g/adh/coh	1122 87/13 adh/coh	4.25
EP7	0.4	Test in progress	N/A	30	1384 coh	1366 7/93 adh/coh	5
EP8	0	0.011 +/- 0.003	N/A	110 (40 backside)	2034 +/- 261 40/13/47 g/adh/coh	1029 87/13 adh/coh	10
EP/PU	1	0.022 +/- 0.002	N/A	20 (holiday, no cracking)	1446 +/- 255 coh	1023 +/- 87 57/43 adh/coh	4
EP/PUA	3.1	0.03 +/- 0.061	N/A	40	1135 +/- 234 35/12/53 g/adh/coh	515 +/- 71 adh	1
PU3	N/A	0.013 +/- 0.004	N/A	30	1712 +/- 163 62/37/2 g/adh/coh	1591 +/- 147 44/53/3 g/adh/coh	4
EP9	0	0.034 +/- 0.006	0.072 +/- 0.004	50	1331 +/- 209 48/20/32 g/adh/coh	1596 +/- 280 3/68/28 g/adh/coh	5.25
EP10	1.5	0.054 +/- 0.008	0.050 +/- 0.001	60	1829 +/- 129 70/30 g/coh	1293 +/- 265 33/30/37 g/adh/coh	4.75

Discussion

Corrosion Protection

One objective of this study was to identify which characteristics of vinyl resins may be responsible for its good performance and longevity?

Nine years of EIS test data shows that solution vinyl resin coatings retain a capacitive behavior over long term immersion exposure. Previous laboratory testing by Reclamation's Materials and Corrosion Lab has shown that many epoxies and polyurethane coatings tend to decrease markedly over similar timeframes. These initial observations gave rise to questions regarding the properties of thermoplastic materials which this study attempted to address:

- Are thermoset coatings inherently more prone to permanent damage versus a thermoplastic?
- Can a thermoplastic polymer network continually re-arrange itself during ion infiltration where a thermoset polymer would gradually experience cumulative and irreversible micro-damage?

The results from the current study show that EIS performance is not unique to vinyls; there were some thermoset and thermoplastic materials which also achieved excellent ratings in the EIS testing. All of the thermoplastic materials also maintained high impedance values over the test period and achieved excellent ratings. This performance is notable considering the relatively thin dry film thickness of the thermoplastic coatings which typically ranged from 6-10 mils in comparison to the thermosetting materials most of which were in the 30-50 mil range. The thermosetting materials that performed well included aromatic polyurethanes (PU1, PU2, PU3, PU+ALPU), an epoxy/polyurethane hybrid, an epoxy/polyurea hybrid, epoxies with topcoats (EP+ALPU, EP+PS 1) and one epoxy material (EP8).

Cyclic testing such as PRO and BOR testing is an aggressive accelerated test that subjects a coating system to repeated stresses throughout the test duration. The V-766e vinyl coat system performed fairly while the zinc-rich vinyl system (VZ-108d) was the strongest performer in the study. Of the materials that performed well in EIS testing, only three systems also performed well enough to achieve a rating of "good" in both cyclic test protocols: VZ-108d+V-766e, EP/PU and EP8. Again, good performance in the cyclic test programs was not unique to vinyl. Vinyl without zinc performed fairly and on par with many other materials in the study. Several other thermoplastics performed poorly in prohesion testing possibly due to inadequate surface profile.

Performance in cyclic exposure for EP/PU and EP8 was better than V-766e and similar to VZ-108d+V-766e. However, both EP/PU and EP8 were inferior to vinyl for the QUV test which includes cyclic exposure to UV light. Both products would require a protective topcoat to perform well in atmospheric exposure, especially in applications where aesthetics are important.

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For immersion exposure, EP/PU received a score of good, performing slightly better than V-766e but worse than VZ-108d+V-766e. EP8 performed well in HAR immersion but one panel undercut up to a maximum of 0.31 inches in DI immersion and received a score of “poor.” (see Figure 8). A more thorough immersion test with additional replicates may be warranted prior to specifying this product for use on Reclamation infrastructure.

In the remaining tests (shown in Table 10), EP8 performed on par or better than both vinyl materials and was the clear winner. EP/PU performed fairly on cathodic disbondment and erosion resistance was excellent which was better than both vinyl materials in both tests. EP8 was excellent in cathodic disbondment but slurry erosion had not been completed at the time this report was generated.

While it was not possible to directly compare pull-off adhesion data, both EP/PU and EP8 achieved scores of “good” after prolonged immersion. EP8 provided the best performance in the knife adhesion (ASTM score 10) vs vinyl (both ASTM score 4) and EP/PU (ASTM score 4).

One major difference was impact resistance; EP8 outscored both vinyl materials with a score of good (110 in-lbs). EP/PU produced holidays when 20 in-lbs was exceeded and received a score of poor, a performance on par with V-766e.

Of the all products tested, EP8 appears to be the most likely to achieve longevity in immersion environments where impact resistance is required. However, a UV topcoat is needed for atmospheric service. There was also undercutting observed on one of the DI immersion panels and additional investigation may be warranted. EP/PU appears to provide properties and performance which are similar to vinyl but provided low resistance to impact damage.

Another significant finding is that the performance of vinyl was significantly enhanced with the addition of zinc pigment to the primer coat. VZ-108d+V766e outperformed V-766e in cyclic exposure, steady state immersion, cathodic disbondment, and impact testing. It is possible that a zinc-rich primer may be beneficial to the products that retained good or excellent barrier properties and had good QUV resistance but performed poorly or fairly in cyclic/immersion testing. Candidate materials include EP+PS1, EP+PS2, EP/PUA. Also EP+ALPU PU+ALPU (scored fair in QUV due to undercutting).

Economics of Proposed Alternatives to Vinyls

The costs of a coatings job include material costs, labor for surface preparation, and labor for application. Overall lifecycle costs are controlled by mobilization costs, labor and production rates and costs, material costs, and longevity of the coating.

Longevity has been an advantage of vinyl materials in the past. However, if equivalent longevity can be realized with thermosetting materials, these products can have similar lifecycle costs as vinyls. Solvent free thermosetting materials can be applied in one or two coats vs vinyls which require up to six coats to achieve an adequate film build due to the solvent content. Fewer coats

shortens application times and cuts down on labor. Surface preparation is similar for both material types. Material costs are a smaller factor than labor costs in most jobs but should be similar for both products. However, there are now fewer suppliers of vinyl resin materials so these products may increase in cost at a higher rate than epoxies, polyurethanes, or polysiloxane material.

Conclusions

Solution vinyl coating systems have a history of longevity and extreme durability in freshwater service as experienced throughout Reclamation and USACE. Their ability to provide long-term corrosion protection in field service while withstanding impact and abrasion damage in service has been unmatched by modern coating systems at Reclamation. History shows that although each agency developed unique formulations and specifications, performance was strong and consistent for both.

Long-term laboratory EIS data correlates well with this field experience, which indicates this may be a good benchmark for evaluating replacement candidates. The solution vinyl coating formulation V-766e showed no degradation during a nine year exposure period.

Additional benchmark and comparison testing identified multiple thermoset and thermoplastic materials which retained excellent barrier testing over a shorter 8 month period. This test duration was sufficient to see significant degradation in many of the epoxy materials. A suite of other tests highlighted the strengths and weaknesses of solution vinyl resins and provided a comparison with modern materials. Two products (EP8 and EP/PU) seem to provide performance that is on par with vinyls in most situations however, a UV protective topcoat is required for atmospheric exposure. Additional products may also benefit from the addition of a zinc-rich primer to help curb rust creep when a defect in the coating is created.

Future Work

1. Retest EP8 in DI immersion with additional replicates.
2. Test EP8 and EP/PU with a UV resistant top coat for fluctuating immersion
3. Test one or more of the following with a zinc-rich primer: EP+PS1, EP+PS2, EP/PUA, EP+ALPU PU+ALPU.
4. Field scale-up of successful products.

Works Cited

- [1] D. Tordonato, B. Merten, A. Skaja and A. Beitleman, "Secrets to Success - Examining the History and Chemistry behind the Performance of Vinyl Resin Coatings," in *SSPC's Greencoat*, San Antonio, TX, 2016.
- [2] D. Tordonato, A. Skaja and B. Merten, "Past versus present – Comparing laboratory performance of Vinyl Resin Coatings with Modern Epoxy-Polysiloxane Coating Systems," in *SSPC's Greencoat Conference*, Tampa, FL, 2017.
- [3] D. A. Jones, *Principles and Prevention of Corrosion*, 2nd Edition ed., Upper Saddle River, NJ: Prentice-Hall, Inc., 1996, pp. 477-511.
- [4] J. Zeno W. Wicks, F. N. Jones and S. P. Pappas, *Organic Coatings Science and Technology*, 2nd Edition ed., New York, NY: John Wiley & Sons, Inc., 1999, p. 286.
- [5] G. Burnett and P. Lewis, "New Developments in Tests of Coatings and Wrappings," Bureau of Reclamation, Denver, CO, 1955.
- [6] J. Kiewit and H. Uyeda, *Fifteenth-Year Evaluation of Experimental Test Linings in Shasta Dam Penstock Final Summary Report*, Denver, CO: Bureau of Reclamation, 1966.
- [7] J. Kiewit, "Field Tests of Water Pipe Linings," Bureau of Reclamation, Denver, CO, 1972.
- [8] Bureau of Reclamation, "Erosion Studies of Pipe Lining Materials - A Progress Report," Bureau of Reclamation, Denver, CO, 1958.
- [9] H. Johns, "Erosion Studies of Pipe Lining Materials - Fifth Progress Report," Bureau of Reclamation, Denver, CO, 1984.
- [10] UCAR Solution Vinyl Resins, December, The Dow Chemical Company, Midland, MI, 2006.
- [11] J. Zeno W. Wicks and S. P. P. Frank N. Jones, *Organic Coatings Science and Technology*, New York, NY: John Wiley & Sons, Inc., 1999, pp. 319-321.
- [12] Environmental Protection Agency, "National Volatile Organic Compound Emission Standards for Architectural Coatings," Government Printing Office, Washington, D.C., 2012.
- [13] S. D. A.D. Beitelman, "Demonstration and validation of an environmentally compliant vinyl coating system for cold locations, ERDC/CERL TR-14-10," US Army Corps of Engineers, Champaign, IL, 2014.
- [14] "South Coast Air Quality Management District," [Online]. Available: www.aqmd.gov/docs/default-source/rule-book/reg-xi/r1113.pdf. [Accessed 6 September 2013].
- [15] [Online]. Available: https://en.wikipedia.org/wiki/Polymer_degradation#Photoinduced_degradation.
- [16] R. J. Burns, "Vinyl Resins for Coatings," in *Paint and Coating Testing Manual*, Philadelphia, PA, ASTM, 1995, pp. 99-.
- [17] C. H. Hare, "Vinyls and Chlorinated Rubbers," in *Generic Coating Types*, Pittsburgh, Technology Publishing Company, 1996, pp. 69-84.
- [18] D. Newmann and C. Nunn, "Solvent Retention in Organic Coatings," vol. 3, pp. 221-243, 1975.

- [19] G. Das and A. Banerjee, "Solvent-Induced Crystallization of Compatible Poly(styrene-co-acrylonitrile) and Poly(vinyl chloride-co-vinyl acetate) Blends," vol. 8, pp. 973-977, 1996.
- [20] S. Croll, "Report: Material Characterization," North Dakota State University, Fargo, 2016.
- [21] C. G. Munger, *Corrosion Prevention by Protective Coatings*, Houston, TX: National Association of Corrosion Engineers, 1984, pp. 85-87.
- [22] "Paint Specification 8 - Aluminum Vinyl Paint," SSPC: The Society for Protective Coatings, Pittsburgh, PA, 1992.
- [23] "Paint Specification 9 - White (or colored) Vinyl Paint," SSPC: The Society for Protective Coatings, Pittsburgh, PA, 1982.
- [24] "Paint Specification 27 - Basic Zinc Chromate-Vinyl Butyral Wash Primer," SSPC: The Society for Protective Coatings, Pittsburgh, PA, 1982.
- [25] "Paint Specification No. 106," SSPC: The Society for Protective Coatings, Pittsburgh, PA, 1982.
- [26] United States Army Corps of Engineers, *Unified Facilities Guide Specifications*, 2004.
- [27] Bureau of Reclamation, *Paint Manual*, 1st ed., Denver, CO: United States Government Printing Office, December 1951.
- [28] Bureau of Reclamation, *Paint Manual*, Third Edition, Denver, CO: United States Government Printing Office, 1976, pp. 17, 74.
- [29] Bureau of Reclamation, *Specifications for Vinyl Resin Paints VR-3 System*, Denver: Bureau of Reclamation, 1984.
- [30] Bureau of Reclamation, *Specifications for Vinyl Resin Paints VR-6 System*, Denver, CO: Bureau of Reclamation, 1984.
- [31] Bureau of Reclamation, "Bond Tests of VR-3, VR-6," Denver, CO, 1964.
- [32] B. o. Reclamation, *Specifications for Vinyl Resin Paints VR-6 System*, Denver, CO: USBR, 1984.
- [33] W. Garstka, "Application of experimental protective linings - Southside Canal - Collbran Project, Colorado," Bureau of Reclamation, Denver, CO, 1960.
- [34] J. Kiewit and H. Uyeda, "Fourth-Year Laboratory and Field Inspection of Experimental Protective Linings," Bureau of Reclamation, Denver, CO, 1966.
- [35] E. Mansour, A.-G. A.M., B. A.-E. Nabey, A. Tadros, H. Aglan and A. Ludwick, "Solvent Effect on the Protection Efficiency of Vinyl Resin Varnish for Preventing the Corrosion of Steel Using Electrochemical Impedance Spectroscopy," *Corrosion*, vol. 58, no. 2, pp. 113-118, February 2002.
- [36] Y. Wang and G. Bierwagen, "A new acceleration factor for the testing of corrosion protective coatings: flow-induced coating degradation," *Journal of Coatings Technology Research*, 2009.
- [37] Y. Wei and L. Z. W. Ke, "Comparison of the degradation behaviour of fusion-bonded epoxy powder coating systems under flowing and static immersion," *Corrosion Science*, vol. 48(6), pp. 1449-1461, 2006.

- [38] Y. W. Q. Zhou, "Flow-accelerated coating degradation: influence of the composition of working fluids.," in *NACE 2012*, Salt Lake City, UT, 2012.
- [39] M. Glaser and P. Rosenburg, "Vinyl Dispersion Coatings in the Organic Finishes Industry," in *Vinyls in Coatings and Laminates*, Cherry Hill, NJ, 1966.
- [40] Robert Clark, "Principles of Coating with Vinyl Heat Fusible Powders," *Powder Coating 94' Proceedings*, pp. 371-388, 1994.
- [41] A.W. Hughes, "Pipeline Field Joints," *Journal of Protective Coatings and Linings*, pp. 43-51, 2014.
- [42] D. Braun, "Thermal Degradation of Polyvinyl Chloride," *Pure and Applied Chemistry*, vol. 26, pp. 173-192, 1971.
- [43] J. Brasher, "Enhanced plastisol," *Materials Performance*, pp. 16-19, November 2014.
- [44] B. Hinderliter, S. C. D. Tallman, Q. Su and G. Bierwagen, "Interpretations of EIS Data from Accelerated Exposure of Coated Metals Based on Modeling of Coating Physical Properties," *Electrochimica Acta*, vol. 51, pp. 4505-4515, 2006.
- [45] F. Mansfeld and C. Tsai, "Determination of Coating Deterioration with EIS. Part I. Basic Relationships," *Corrosion*, vol. 47, pp. 726-737, 1991.
- [46] D. Loveday, P. Peterson and B. Rodgers, "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy. Part 2: Application of EIS to Coatings," *JCT Coatings Tech*, pp. 88-92, 2004.
- [47] Z. Qixon and Y. Wang, "Comparisons of Clear Coatings Degradation in NaCl Solution and Pure Water," *Progress in Organic Coatings*, vol. 76, pp. 1674-1682, 2013.
- [48] Bureau of Reclamation, "Coatings Test Report 8540-2017-031," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [49] Bureau of Reclamation, "Coatings Test Report 8540-2017-032," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [50] Bureau of Reclamation, "Coatings Test Report 8540-2017-015," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [51] Bureau of Reclamation, "Coatings Test Report 8540-2017-016," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [52] Bureau of Reclamation, "Coatings Test Report 8540-2017-017," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [53] Bureau of Reclamation, "Coatings Test Report 8540-2017-018," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [54] Bureau of Reclamation, "Coatings Test Report 8540-2017-013," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [55] Bureau of Reclamation, "Coatings Test Report 8540-2017-014," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [56] Bureau of Reclamation, "Coatings Test Report 8540-2017-019," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [57] Bureau of Reclamation, "Coatings Test Report 8540-2017-020," Materials and Corrosion Laboratory, Denver, CO, 2017.

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Resin Coatings – Final Report
ST-2017-8835-1, 8540-2017-49**

- [58] Bureau of Reclamation, "Coatings Test Report 8540-2017-021," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [59] Bureau of Reclamation, "Coatings Test Report 8540-2017-022," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [60] Bureau of Reclamation, "Coatings Test Report 8540-2017-023," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [61] Bureau of Reclamation, "Coatings Test Report 8540-2017-024," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [62] Bureau of Reclamation, "Coatings Test Report 8540-2017-025," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [63] Bureau of Reclamation, "Coatings Test Report 8540-2017-033," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [64] Bureau of Reclamation, "Coatings Test Report 8540-2017-034," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [65] Bureau of Reclamation, "Coatings Test Report 8540-2017-036," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [66] Bureau of Reclamation, "Coatings Test Report 8540-2017-037," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [67] Bureau of Reclamation, "Coatings Test Report 8540-2017-038," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [68] Bureau of Reclamation, "Coatings Test Report 8540-2017-039," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [69] Bureau of Reclamation, "Coatings Test Report 8540-2017-040," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [70] Bureau of Reclamation, "Coatings Test Report 8540-2017-041," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [71] Bureau of Reclamation, "Coatings Test Report 8540-2017-042," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [72] Bureau of Reclamation, "Coatings Test Report 8540-2017-043," Materials and Corrosion Laboratory, Denver, CO, 2017.
- [73] R. Bacon, J. Smith and F. Rugg, "Electrolytic Resistance in Evaluating Protective Merit of Coatings on Metals," *Industrial & Engineering Chemistry*, vol. 40, no. 1, pp. 161-167, 1948.
- [74] H. Leidheiser, "Towards a Better Understanding of Corrosion Beneath Organic Coatings," *Corrosion*, vol. 39, pp. 189-201, 1983.