

RECLAMATION

Managing Water in the West

Corrosion Protection of Steel Structures by Coal Tar Enamel: 80 Years of Performance

Research and Development Office
Science and Technology Program
Final Report ST-2017-1546-01, 8540-2017-45



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Mission Statements

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Corrosion Protection of Steel Structures by Coal Tar Enamel: 80 Years of Performance

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Acronyms and Abbreviations

Å	Angstroms
AWWA	American Water Works Association
cm ²	centimeter squared
CT	coal tar
DHS	dilute Harrison solution
DFT	dry film thickness
DI	deionized
DSC	differential scanning calorimetry
EIS	electrochemical impedance spectroscopy
FTIR	Fourier transform infrared spectroscopy
Hz	Hertz
mg/hr	milligrams per hour
mV	millivolt
NDSU-CPM	North Dakota State University, Department of Coatings and Polymeric Materials
nm	nanometers
psi	pounds per square inch
Reclamation	Bureau of Reclamation
SEM	scanning electron microscopy
SSPC	Society for Protective Coatings
TEM	transmission electron microscopy
Tg	glass transition temperature
TGA	thermogravimetric analysis
USACE	United States Army Corps of Engineers
wt%	weight percent
XRD	X-ray Diffraction
Zn	zinc

Executive Summary

Reclamation benefited from the application of coal tar enamel linings on several million square feet of penstocks and similar features [1]. Most coating applications occurred after World War II and through the 1960's. Many of these coal tar enamel linings are nearing the end of their service lives, and will need to be replaced. Coal tar enamel field application is not presently feasible, requiring the specification of alternative coating materials.

This research evaluated an SSPC Paint 16 coal tar epoxy, AWWA C222 polyurethane, and a commonly used solvent borne epoxy with glass flake in a side-by-side laboratory comparison to coal tar enamel. It also includes material characterization of solution vinyl coatings and field performance analysis and service data for coal tar enamel. Findings for each of the materials evaluated are summarized as follows:

Coal tar enamel

- Corrosion undercutting protection is excellent in immersion exposures; the greatest undercutting is observed in FOG exposure.
- Impedance data is near 10^{10} Ohms and does not experience a significant reduction during the first 250 days. High frequency data suggested no significant water uptake.
- Adhesion values are very low, 300 to 350 psi, and fail cohesively near the glue; the material at the fractured surface shows signs that it flows during or after the pull-off test.
- Erosion rate is high, greater than 100 mg/hr.
- Material Tg is near 10 °C, has a very broad curve, and may be able to self-heal during service. The amorphous material has electron diffraction spacings similar to graphite and suggests that the cyclic compounds within the material are able to pack into layers.

Coal tar epoxy

- Corrosion undercutting in FOG was more severe than in HAR/FOG, suggesting a preference to immersion service without atmospheric exposure.
- Impedance data is most similar to epoxy data, and greater degradation occurred in immersion exposures. High frequency data suggested significant water uptake.
- Adhesion values are low, 650 to 1000 psi, and most failures occurred at the glue.
- Material Tg is near 48 °C.

Polyurethane:

- Poor corrosion undercutting, particularly in HAR immersion exposure.
- Impedance values are similar to coal tar enamel, but film degradation was greater in cyclic exposures, and the θ neared 0° at low frequencies, suggesting the presence of corrosion reactions. High frequency data suggested some water uptake.
- Adhesion values are high and variable at 1282 to 3273 psi; only FOG exposure resulted in mixtures of adhesive, cohesive, and glue failures, all other exposures were mostly glue failures.
- Erosion rate is low, less than 10 mg/hr.
- Material Tg is near 53 °C.

Epoxy

- Cyclic testing of the material that included immersion, as shown in the HAR/FOG exposure, produced severe undercutting; suggesting accelerated degradation when exposed to immersion service followed by temperature cycling in atmospheric service.
- Impedance data experienced greater degradation in immersion exposures than in cyclic exposures; immersion of epoxy seems to be a greater driver toward degradation than salt fog cyclic exposure. High frequency data suggested significant water uptake.
- Adhesion testing produced many cohesive failures in the range of 1000 to 1300 psi. The low cohesive failure values resulting from DI exposure suggests that this immersion weakens the coating matrix more than HAR exposure.
- Erosion rate is high, greater than 80 mg/hr.
- Material Tg is near 45 °C.

The unique, long service life of coal tar enamel occurs only when the material is kept at consistent temperature and humidity. The material becomes more brittle and begins to crack if its plasticizer leaves the film. For Reclamation's purposes the ideal service environment is immersion in subgrade penstocks, outlet works, trashracks, and other equipment in similar conditions.

Laboratory results showed that the graphite-like structure of coal tar enamel is largely responsible for the high material impermeability, providing superior corrosion resistance in immersion. Other key properties to identify in candidate replacement materials include self-healing through high molecular weight thermoplastic constituents, completely hydrophobic ingredients, and extremely low water uptake.

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Introduction

Coal tar enamel has a long history of use in corrosion mitigation for water conveyance applications. Most of Reclamation's steel conduit, including penstocks and outlet works, were lined with a plasticized, hot applied coal tar enamel, beginning with extensive lining of these features at Hoover Powerplant in 1936 [2]. With superior moisture resistance and a long service life, Reclamation considered this material to be a permanent coating when properly applied [2]. The original enamel remains in service at many facilities today, but experience shows that it requires occasional replacement, estimated to occur after 50 to 100 years of service.

A cold-applied enamel, CA-50, also received use where hot application was not feasible. This report focuses on the hot applied enamel but excludes inaccessible coatings, such as those applied buried pipeline exteriors.

Reclamation and other industries lessened their use of coal tar enamel by the 1970's. The cited reasons include fewer experienced applicators and difficulty controlling the environment sufficiently to protect workers [2, 3]. Alternative materials quickly received substantial market share. Reclamation used epoxy coatings widely by the 1990's. However, these epoxies demonstrated a service life nearer to 20 to 30 years. Several Reclamation penstocks received polyurethane linings during the 2000's as a potential longer service life alternative to the epoxy. Unfortunately, these polyurethanes since produced several delamination failures to date [4].

This research evaluated coal tar enamel, coal tar epoxy, epoxy, and polyurethane products in a side-by-side laboratory comparison. It included data for solution vinyl coatings, which also provide superior corrosion protection. The study also analyzed field data for coal tar enamel. The results demonstrated the uniqueness of the coal tar enamel performance, highlighting the material properties contributing to its long service life. The goal is for the results is to aid in the development of improved alternatives.

Background

Early Coal Tar Products

England provided the first mentions of coal tar coatings in a 1681 patent describing the pitch residues. Commercialization of hot applied coating containing coal tar pitch and mineral filler occurred around 1854 [5, 6]. These materials were primarily used for corrosion protection in the shipping industry. Other coal tar products were also used during the 1800's, including materials for waterproofing and wood preservation [6].

Hot applied coal tar enamel became the preferred coating for protecting steel infrastructure such as ship interiors and dry docks in the early 1900's. The American Bitumastic Enamels Co. published a short booklet advertising the enamel's superior performance, noting decades of extensive use and experience across many industries [7]. This included application throughout the Panama Canal in 1913, covering more than 3.2 million square feet of lock gates, Stoney gate valves, penstocks, and other submerged metalwork [7, 8]. Figure 1 shows miter gates at the canal's Gatun Locks coated with the hot applied enamel.

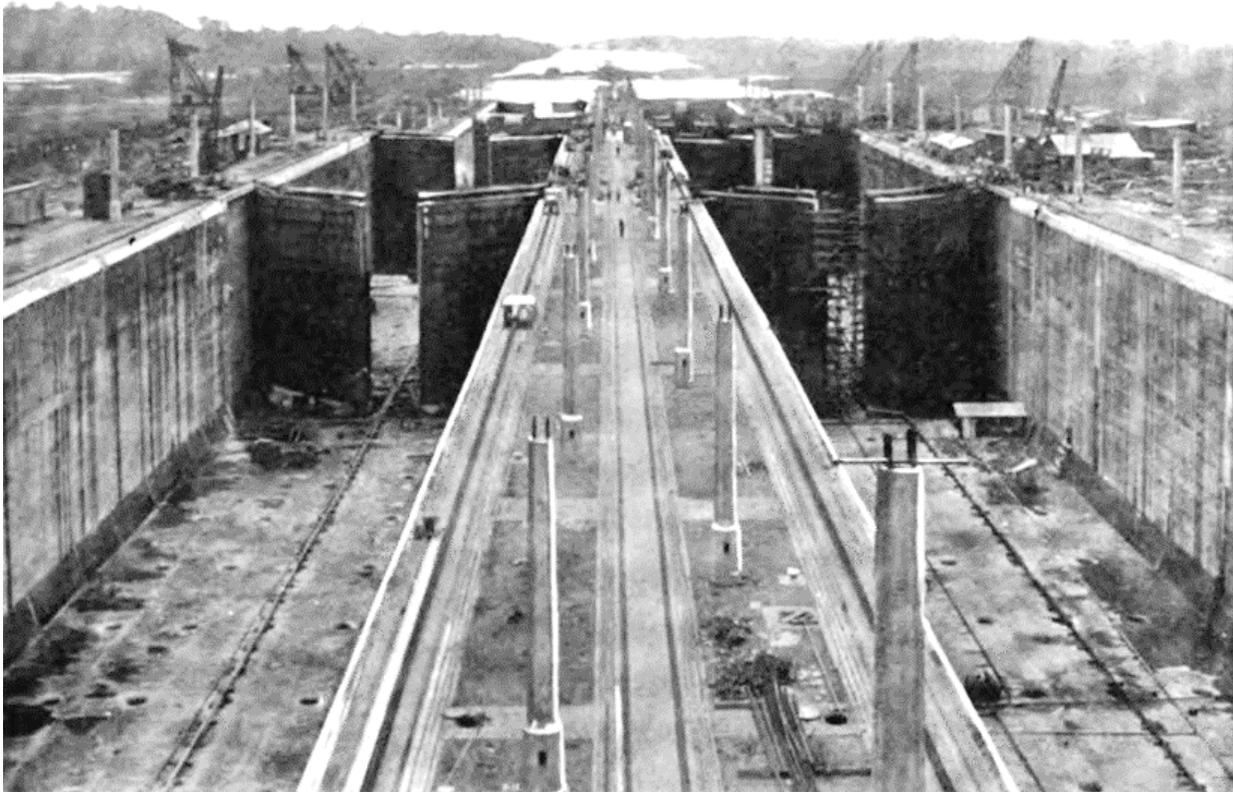


Figure 1. Gatun Locks with coal tar enamel coating applied to the miter gates circa 1913. Reproduced without permission from Reference [7], page 5; copyright (expired), 1915, by American Bitumastic Enamels, Co.

The first mention of a tar-based coating material at Reclamation is in a review published in 1920 [9]. The publication summarized approximately eight years of experience with water gas and coal gas tar systems on metalwork across Reclamation, including the Minidoka No. 1 penstock interior in 1913. These materials are distinct from coal tar enamel and are byproducts of the gas industry. The gas tar provided superior performance to the red lead materials evaluated. The specification required a coat of water gas tar as a primer followed by hot applied coal gas tar.

Early 1900's hot applied enamels received many reports of disbondment and cracking in temperatures below 30 °F [6]. This initial limitation prevented broader utilization in the piping industries, where coated, uninstalled pipes sometimes received exposure to sub-zero temperature. Research in the early 1930's led to the incorporation of high boiling distillate oils from the coal tar to decrease this temperature susceptibility [3, 8]. The resulting plasticized enamel had dramatically improved performance [10]. This plasticized, hot applied coal tar enamel is largely unchanged since.

Traditional Hot Applied Enamel

Coal Tar Enamel Composition

The hot applied coal tar enamel system that gained widespread use during the 1930's combined coal tar pitch, mineral fillers, and plasticizer. Coal tar pitch is a distillate of coal tar, which is produced during the process of coal distillation in coke ovens. The pitch used for protective coatings is a concentrate of the highest molecular weight components of the tar, which are primarily aromatic hydrocarbons [5]. The

molecular spacing of these compounds is approximately 4.5 Angstroms (Å), which is comparable to the 3.6 Å spacing in graphite [5]. This tight spacing contributes to the enamel's superior moisture resistance.

Mineral fillers are the second largest component of coal tar enamel. Their composition is typically 25-30 percent by weight, and they provide toughness and sag resistance [8]. The fillers also improve resistance to deformation in flowing water, and widen the range of service temperatures for use. Plasticizers are included in the formulation as a very small fraction of the composition, but they greatly reduce the brittleness of coal tar enamel.

Expansion of Coal Tar Enamel Use

The plasticized hot applied coal tar enamel's superior properties and long service life quickly led to extensive use on pipelines [3, 11]. The Bouquet Canyon above ground penstock and siphon received an enamel lining in 1933. It was the first large-scale application of a material similar to the present day enamel [5, 12]. The Bouquet Canyon pipe collapsed in 1934 when vacuum relief-valves failed during unwatering; the pipe was slowly refilled under pressure to restore the original shape with only minor coating repairs required [6]. The Santa Ana River siphon is another large pipe that was coated with coal tar enamel in 1937; it showed excellent performance when inspected 28 years later [12].

Reclamation first applied coal tar enamel in 1936 to the Hoover Powerplant penstocks [13]. However, in 1938 personnel discovered significant coating loss along the invert within the main Upper Nevada penstock. Subsequent analysis attributed the cause to slow-heating kettles that resulted in application of insufficiently-heated enamel [14]. The remainder of this original enamel is still in service today and has received minor repairs [2, 15].

As the use of hot applied coal tar enamels expanded, the industry developed standards to improve coating design, handling, application, and inspection practices [16]. The American Water Works Association (AWWA) approved its first edition of the C203 standard in 1940. This standard applies specifically to coal tar enamel coatings and linings for potable water pipes [17]. NACE International also developed a standard for enamel field application to pipe exterior surfaces, which is applicable to oil, gas, and water distribution buried piping [18]. Reclamation adopted AWWA C203 in accordance with the water supply industry requirements [2].

Widespread hot applied enamel use at Reclamation proceeded after World War II. However, many failures occurred during this period, often before the coated pipe was in service. Investigation attributed the failures to improper application and exposure to very low temperatures, i.e. below -10 °F [13]. The low temperature limitation echoed the challenges preceding the plasticized pitch development. Consequent laboratory and field research at Reclamation evaluated the relationship between the enamel's penetration value and low temperature cracking and disbonding. The standard test determines the penetration value by pressing a weighted needle into the film [19]. This value, along with the softening point, determine coal tar enamel's sag and low temperature cracking properties [6]. Coal tar enamel becomes more brittle and begins to crack when its penetration value decreases as a result of plasticizer leaving the film [13]. The Shadow Mountain tests on uninstalled pipe sections in 1950 showed that an applied penetration value of 9 or higher provides excellent performance to -20 °F [20, 21]. Figure 2 illustrates the experimental design used to evaluate a range of enamel penetration values. Reclamation subsequently adjusted its specifications to require applied penetration values of 10 to 20 as measured at 77 °F [2].

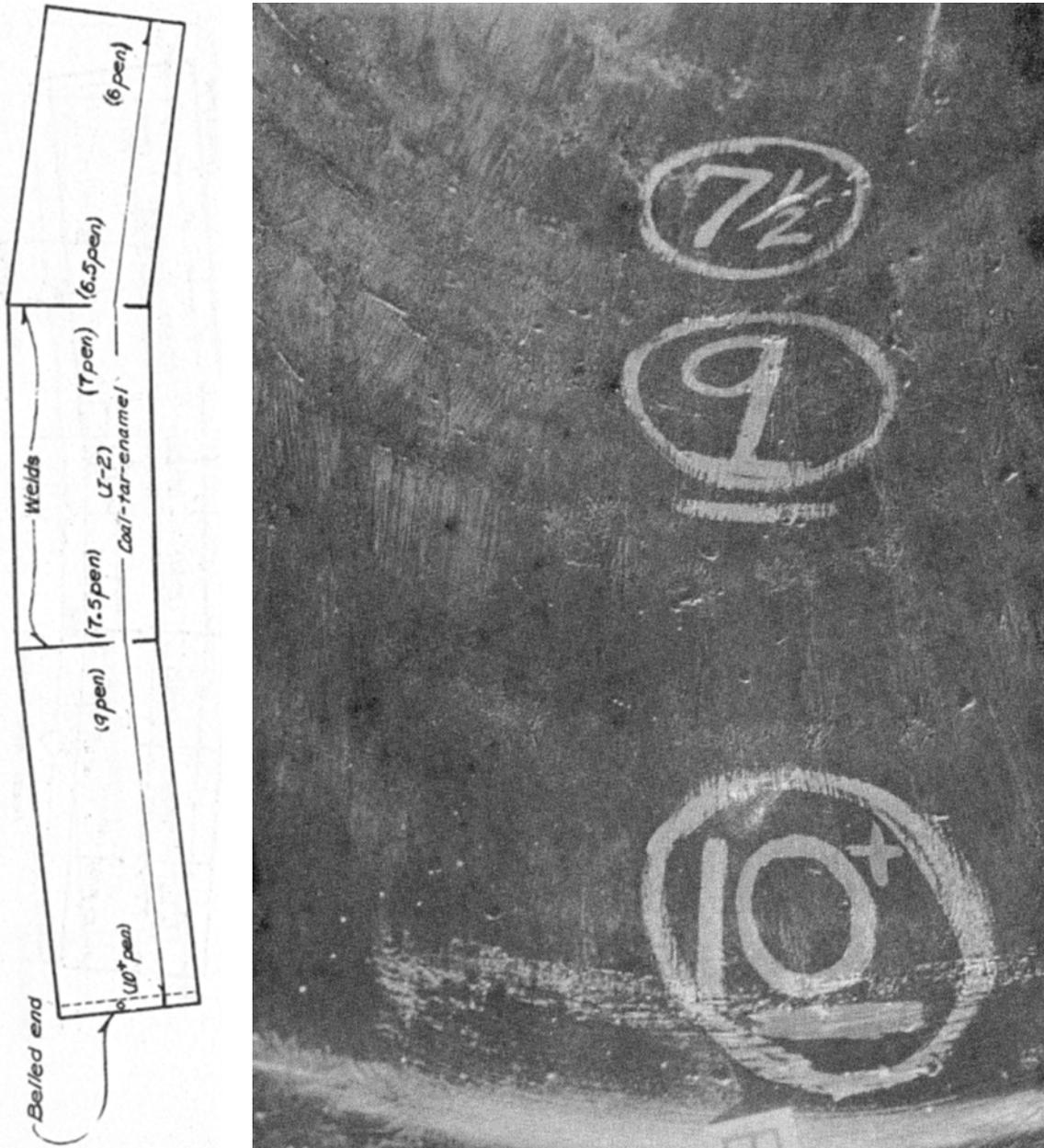


Figure 2. Shadow Mountain test design for pipe with enamel penetration values 6 to 10+ (left) and applied coating before exposure (right). Reproduced from Figures 3 and 9 in Reference [21].

Table 1 provides the specified properties for an AWWA C203 hot applied coal tar enamel system. Reclamation specified the Type II enamel to ensure good resistance to cracking at the lowest service temperatures.

Table 1. Coal tar enamel properties defined in AWWA C203-86, modified from [22]; see standard for full test details.

Test	Enamel Type I		Enamel Type II	
	Minimum	Maximum	Minimum	Maximum
Softening point	220 °F	240 °F	220 °F	240 °F
Filler, % by weight,	25	35	25	35
Fineness of filler, % by weight	90	-	90	-
Specific gravity	1.4	1.6	1.4	1.6
Penetration	5	10	10	20
Penetration at 115 °F	12	30	15	55
Sag at 160 °F	-	1/6-inch	-	1/6-inch
Crack resistance*	-	None	-	None
Direct impact, disbonded area	-	16-inch ²	-	16-inch ²
Indirect impact, disbonded area	-	6-inch ²	-	2-inch ²
Peel test	No peeling		No peeling	

Notes: Test performed at 77 °F unless noted. * Type I tested at -10 °F and Type II tested at -20 °F

Hot applied coal tar enamel required a primer, and the original Type A primer was coal tar based material. This material proved to be very sensitive to application conditions, particularly temperature, giving a limited window for achieving a strong bond and quality product. The industry responded in the early 1960's with the Type B synthetic, fast-drying primer based on chlorinated rubber. Reclamation laboratory studies reported superior bonding of the Type B primer in 1963 and recommended the discontinued use of Type A [23]. The coal tar enamel system was more reliable with the new the Type B primer, and it became widely used [1, 2, 24].

See *Pipeline Protection using Coal Tar Enamels* [5] for a comprehensive review of the AWWA C203 enamel history, use, and properties in accordance with the 1960's protective coating philosophy.

Transition to Modern Coatings

Manufacturers provided epoxy coatings as early as 1949; however, Reclamation laboratory studies demonstrated the materials to be inadequate [25]. The products evaluated in this first study were mid-1950's amine cured and epoxy ester materials. The report also noted ongoing studies of coal tar epoxy, which combines the reactive epoxy binder with coal tar pitch [25].

A subsequent field evaluation of new technologies for steel water pipe interior linings began in 1959. This Southside Canal study incorporated 36 systems onto new sections of 6-foot diameter siphon piping. The 1966 report indicated excellent performance of the established VR-3 vinyl resin, asphalt, and neoprene systems as well as the newer coal tar epoxies, coal tar urethanes, and metallic aluminum with vinyl alkyd aluminum topcoat following four years of service [26]. Coal tar epoxy became the preferred alternative to CA-50 at Reclamation for pipe exteriors [27]. The Shasta Dam long-term study of penstock linings also summarized its 15-year findings in 1966, noting excellent performance for the VR-3 and VR-6 vinyl resin, phenolic paint, and red lead phenolic systems [27]. See Reference [28] for a state of the art discussion on solution vinyl coatings and their historical use on water infrastructure.

Both the Southside Canal and Shasta Dam studies reported the coal tar enamel systems in the remainder of the water pipe to be in excellent condition. The observed enamel degradation included a few hairline cracks in the brush marks along the arch [27]. Reclamation continued to use coal tar enamel for corrosion protection of steel conduits into the 1970's; however, the expansive development of new water projects ceased.

By 1980, nationwide studies estimated that 50 to 80 percent of all steel water pipe had a hot applied enamel lining [3]. Other coating types on these structures were epoxy, coal tar epoxy, and alternative materials recently developed by the coatings industry. Industry use of coal tar enamel declined in the 1980's due to challenges in protecting workers from its carcinogens and finding experienced applicators [2, 3]. Epoxy and coal tar epoxy coatings received greater use in the years that followed by Reclamation and other entities installing steel water pipes.

Reclamation coating and re-coating projects resurged in the 1990's, specifying epoxy coatings where it traditionally specified hot applied coal tar enamel. However, the passing of time again warranted a comprehensive survey of the latest technologies. A study on elastomeric polyurethanes for cavitation service noted good water immersion performance for several systems but acknowledged their historically poor performance [29]. A 1992 laboratory investigation with the United States Army Corps of Engineers (USACE) Construction Engineering Research Laboratory evaluated high solids materials [30]. The study concluded with a recommendation for field evaluation of several non-elastomeric and elastomeric polyurethanes, a modified styrene polyester, and several epoxy amines and polyamides. The testing consisted of 3000 hours of laboratory exposure, specifically fresh water, salt water, and QUV testing. While this report is valuable, the authors concluded that field testing would determine actual performance.

Epoxies, with their attractive ease of application and a relatively quick chemical cure, provide a shorter, 20- to 30-year service life at Reclamation facilities. This prompted renewed investigations of the latest technologies in the 2000's to identify materials with potentially longer service lifetimes. Promising laboratory results lead to the application of polyurethanes at several facilities. The findings suggest its service life may exceed epoxies, but significant adhesion challenges and a delamination failure mechanism remained [4].

Hot applied coal tar enamel application continues for new piping in factory settings where the environmental control makes its use more feasible. The pipes are spin-coated, resulting in a smooth surface of uniform film thickness. At the time of this publication, the only pipe manufacturing facilities

found to be applying hot coal tar enamel in the United States were in Adelanto, CA: Mobile Pipe Lining and Coating, Inc. and Northwest Pipe Company.

Published Literature

An inquiry of the Scopus search engine using keyword “coal tar enamel” returned 45 publications from the years 1960 to 2014. These include scientific, trade, and conference publications, such as *Journal of Protective Coatings and Linings*, *Materials Performance*, *Anti-Corrosion Methods and Materials*, and *Pipes and Pipelines International*. Figure 3 demonstrates the frequency of publications by year to demonstrate the trend through these decades. The data shows an increase from the mid-1970’s to 1990.

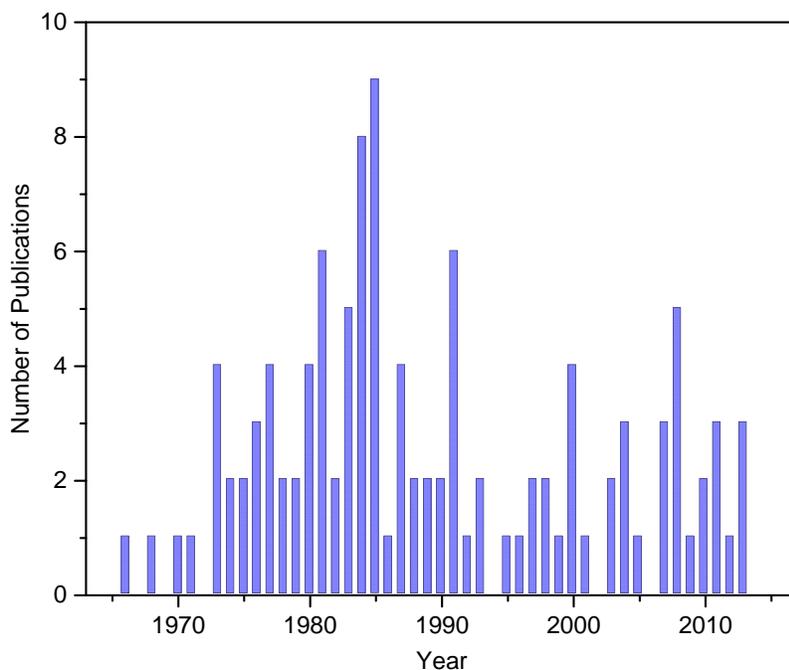


Figure 3. Coal tar enamel publications by year, accessed 8-14-14.

The subject of the publications include enamel properties and performance data, coating selection factors for oil, gas, and water pipelines, and alternative materials. Two publications report on occupational or environmental risks associated with coal tar enamel: a 1978 study analyzing occupational exposures in coating plants as compared to coke oven workers, and a 1993 report on water quality impacts on Alaskan drinking water pipes lined with coal tar enamel. Publications in the 1990’s focus on field recoating processes as well as inspection methods to identify defects on buried pipes. Table 2 highlights noteworthy publications on coal tar enamel with a brief description of the findings; it includes results from Google Scholar and similar internet searches.

Table 2. Example coal tar enamel literature and findings.

Year	Publisher	Summary or Conclusions	Ref
1956	Corrosion Journal	Brief history of coal tar enamel coating uses in the early 1900s. Discusses properties and specifications of different coal tar enamel coatings types and their uses. Part II (1960) shows the effect of surface preparation and primers on service life.	[11]

Table 2. Example coal tar enamel literature and findings.

1957	Corrosion Journal	Discusses specifications and service conditions ideal for different hot applied and cold-applied coal tar enamel coatings. Recommendations are given for coating selection in different conditions.	[31]
1966	Published through Argonne National Laboratory	Outlines chemistry and properties of coal tar enamel coatings, describing different application types. Includes case studies and lab tests showing the water absorptivity and stress analysis of coal tar at different temperatures.	[8]
1976	Anti-Corrosion Methods and Materials	Review of coal tar enamel practices, advantages, and availability. Includes description of performance tests for evaluation coal tar enamel.	[32]
1978	American Industrial Hygiene Association Journal	Analyzes personnel at eight coating plants for exposure to harmful chemicals in coal tar enamel and compares results to studies completed on coke oven personnel.	[33]
1979	National Service Center for Environmental Publications	Provides review of hot applied coal tar enamel coatings on distribution pipelines for potable water systems and characterizes industry trends. Attempts to estimate health risks for coal tar and other available coating systems but is unable to do so due to lack of adequate data or method.	[3]
1984	Anti-Corrosion Methods and Materials	Discusses proper specification by selection of primer, coal tar enamel grade, and glass reinforcements based on service environment, stressing importance of inspection.	[34]
1984	Journal of Applied Toxicology	Evaluates mice exposure to coal tar paints for mutagenic responses. Results were higher than expected based on the polyaromatic hydrocarbon content in coating, suggesting that other components contribute to health hazards.	[35]
1987	Pipe Line Industry	Discusses difficulty in consistently achieving high quality coal tar enamel applications, highlights advanced practices, and stresses good quality control and inspection to prevent damage during installation.	[36]
1990	Journal of Protective Coatings and Linings	Discusses approach used at one natural gas company to assess and reline piping with coal tar enamel coating using a machine. Uses waterjet surface preparation.	[37]
1992	Pipes and Pipelines International	Reviews history of development of corrosion control systems for steel pipes, including coal tar enamel.	[38]
1998	American Society of Civil Engineers Conference	Describes rehabilitation of the Soap Lake Siphons original coal tar enamel, applied in 1948, with a new 3/4-inch cement mortar lining. The pipe is more than 22-foot diameter, more than 8,000 feet in length, and has several sections with 18% grade.	[39]
2010	Materials Performance	Evaluates coal tar enamel and other pipeline coating systems following 500 hours of accelerated weathering exposure.	[40]
2011	Journal of Protective Coatings and Linings	Evaluates removal methods for coal tar enamel versus coal tar epoxy coatings during rehabilitation projects.	[41]
2013	NACE International Corrosion 2013 Conference	Reviews the use of coal tar enamel and other coatings systems over the years. Examines the properties and shortcomings of the coatings. Includes brief introduction to the use and history of coal tar enamel coatings.	[42]

Procedure

Laboratory Testing

The experiment evaluated three coating systems to compare to the coal tar enamel in the laboratory testing. Table 3 provides the test matrix for this experiment. Panels measuring 1/8-inch x 3-inch x 6-inch were prepared by solvent cleaning followed by Society for Protective Coatings (SSPC)-SP10 near white metal blast [43].

Table 3. Test matrix for coal tar materials compared to modern coatings.

Coating Material	Specification	Exposure Label and Replicates			
		HAR ¹	DI ²	HAR/FOG ³	FOG ⁴
Coal tar enamel	AWWA C203, Type II	4	4	4	4
Coal tar epoxy	SSPC-Paint 16; Corp of Engineers C-200 (a)	4	4	4	4
Polyurethane	AWWA C222	3	3	3	3
Epoxy	MIL-DTL-24441, Type IV	3	3	3	3

Notes: ¹ HAR: dilute Harrison's solution (DHS) constant immersion exposure at 25° C; ² DI: deionized water constant immersion exposure at 25° C; ³ HAR/FOG: cycle of 1-week HAR exposure and 1-week salt fog in accordance with ASTM G85 Annex A5; ⁴ FOG: salt fog in accordance with ASTM G85 Annex A5.

The Northwest Pipe Company facility at Adelanto, CA prepared the hot applied coal tar enamel coating in accordance with AWWA C203, Type II [17]. The USACE Paint Technology Center prepared the coal tar epoxy, Sherwin Williams TarGuard, meeting SSPC Paint 16 and USACE Specification C-200(a). The manufacturer prepared and supplied the polyurethane coating, Futura Protec II, which is an aromatic material meeting the AWWA C222 specification. Reclamation applied the epoxy coating, PPG Amerlock 2, and included glass flakes in accordance with manufacturer directions for greater barrier protection.

Coated panels received 5000 hours (approximately 6 months) of laboratory accelerated weathering using the four different exposures outlined in Table 3. The table also designates the number of replicates for each. Two replicates per exposure received an "X" scribe via a Dremel® cutting tool on one side of the panel to expose the steel substrate and evaluate undercutting resistance. Corrosion analysis via ASTM D1654, Procedure A, Method 2, occurred following laboratory weathering [44]. Figure 4 shows the dry film thickness for each of these exposures, as measured by an Elcometer 454. The data represents five measurements per panel and the standard deviation.

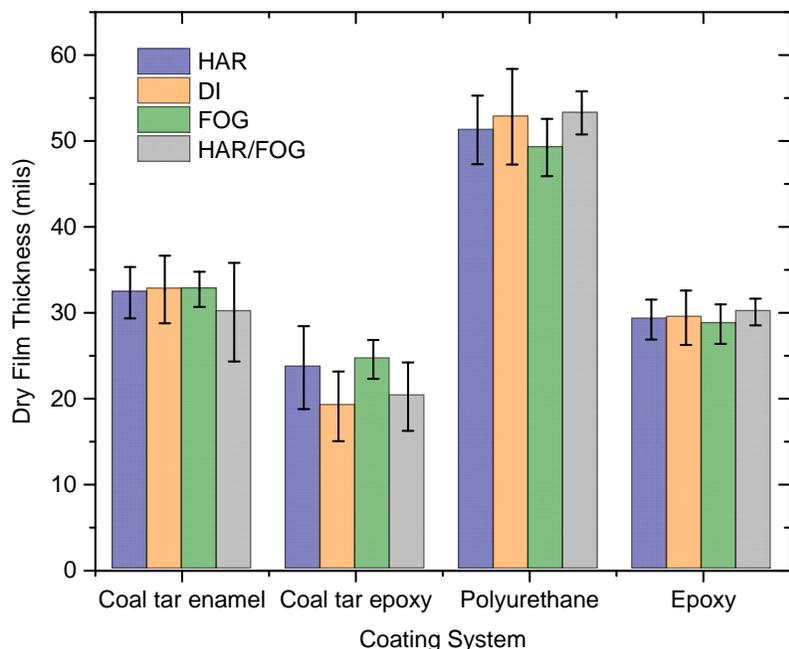


Figure 4. Dry film thickness data for laboratory testing.

The HAR and DI exposures received immersion in a dilute Harrison’s solution (DHS) and deionized (DI) water, respectively, at 25 °C. DHS is 0.35 weight percent (wt%) ammonium sulfate and 0.05 wt% sodium chloride. The DI water is 18 megohm resistivity.

The HAR/FOG and FOG exposures are cyclic tests. The FOG chamber alternates every hour between the DHS salt spray at 25°C and a dry heat at 35°C in accordance with ASTM G85 Annex A5 [45]. The HAR/FOG receives physical rotation of the sample panels between HAR immersion and the FOG chamber each week of the exposure period.

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) evaluation occurred periodically during the exposure period, initially at one week intervals and gradually at greater intervals. The study designated a single epoxy and polyurethane panel and two coal tar enamel and coal tar epoxy panels for EIS measurement. Each unscrubbed panel received a superficial “O” marking to delineate the tested surface.

The test utilized a Gamry FAS2 Femtostat, Warminster, PA, with dedicated software. A glass cylinder was fixed to the panel by *o*-ring and clamp to create a temporary reservoir that isolated a 23 centimeters squared (cm²) surface for evaluation. The test applied 15 millivolt (mV) root mean square perturbations from 10⁵ to 10⁻² Hertz (Hz) at 10 points per decade. Test equipment included a saturated calomel electrode for potential sensing and a platinum coated high surface area mesh for current conduction and sensing. Each panel was ground with a Dremel® tool to expose steel at one corner for connection to the test’s working electrode; this was repeated before each measurement to ensure strong electrical contact.

Evaluation of the resulting EIS data occurred through contract with North Dakota State University’s Department of Coatings and Polymeric Materials (NDSU-CPM). Their report, Appendix A, describes the data compilation and analysis as a complete report, which will not be repeated here.

Adhesion

Tests were performed with a hydraulic adhesion tester in accordance with ASTM D 4541 following accelerated weathering [46]. Each panel received three replicates, using 20 millimeter diameter aluminum dollies glued to the surface with two component epoxy adhesive. Both surfaces were prepared by roughening with 80 grit sandpaper and cleaning with acetone. Each tested area was scored with a hole saw to define the surface area prior to testing.

Slurry Erosion

Two replicates for each material received slurry erosion testing in accordance with the Reclamation test method USBR-5071-2015 to evaluate erosion resistance [47]. The test consists of an 11-inch diameter coated disc fastened to the bottom of a cylindrical tank that is agitated continuously with 1 kilogram of aluminum oxide abrasive and 16 liters of water. The test measures weight loss at 24 hour test increments for a total test period of 96 hours. The data is converted to an erosion rate and standard deviation.

Material Characterization

The contract with NDSU-CPM also facilitated additional material testing and analysis using specialized equipment on extra coated samples for each material. Appendix B provides the complete report, with experimental procedures, and will not be repeated here. The specialized characterizations included are:

- Dynamic mechanical thermal analysis (DMTA)
- Differential scanning calorimetry (DSC)
- Thermogravimetric analysis (TGA)
- X-ray Diffraction (XRD)
- Transmission electron microscopy (TEM)
- Fourier transform infrared spectroscopy (FTIR)
- Scanning electron microscopy (SEM)

Field Performance Testing

Coating evaluations occurred at several Reclamation facilities during scheduled condition assessments to enhance data collection in these inaccessible features. Penstocks and outlet works served as the fundamental structures for coal tar enamel evaluation. These included visual assessments, EIS measurement, description of observed failure modes, and removal of paint chips for material characterization. NDSU-CPM performed the paint chip characterization.

Field EIS testing utilized an Ivium CompactStat.e10800, Fernandina Beach, FL, with dedicated software. A plastic 100 milliliter beaker served as the temporary reservoir by removing the bottom and then gluing the top flange directly to the coating surface with epoxy adhesive. The method utilizes two reservoir test cells for each test that is run. This isolated approximately 25 cm² of the surface for evaluation in each test cell, acquired as electrical circuit elements in series. Test equipment included a saturated calomel or silver-silver chloride electrode for potential sensing and a platinum coated high surface area mesh for sensing. One test cell contains the reference electrode. The second contains the platinum mesh, connected to the counter electrode and working electrode leads.

The established test method applies 15 mV root mean square perturbations from 10⁵ to 0.5 Hz at 5 points per decade. Some tests occurred during the development of test method and apply a higher terminal end frequency and 10 points per decade. See Ref [48] for additional details on this field test method.

Discussion of qualitative inspections and photographs of aging coal tar enamel are also included. The reported information is from recent coating assessments of the large, discharge tubes at the John Keys Pumping Plant and associated facility records, as found.

Facility Records and Surveys

Reclamation construction specifications files show the original material applied to facilities as well as coating maintenance and recoating activities. Data is included that has a high degree of confidence, although it is known that material substitutions occur without documentation or that documentation is absent from these files. Some of the facility information is supported by onsite coating condition assessments by Reclamation coating specialists.

Reclamation researchers completed a coatings performance survey in 1985 [49]. File data from these handwritten and typed documents were transcribed to electronic format via Excel spreadsheet for future use, noting inconsistencies where found. The facilities reported data, including the year of coating application, i.e. service life, whether it is the original coating or a replacement coating, and three qualitative assessments of the coating condition, summarized in Table 4. The survey included graphic aids for each rating of “rusting” and “coating film” to assist the respondent and improve standardization across the results.

Table 4. Qualitative assessments for Reclamation's 1985 coatings performance survey.

Assessment	Rating Notes
Rusting	ASTM D610 [50], percentage of coated surface area that is rusting; “1” = no rusting, “3” = 0.1 percent, “6” = more than 1 percent.
Coating Film	Prevalence of chalking, flaking, blistering, and similar defects; “1” = no defects, “3” = minor, sparse, or widely spaced defects, “6” = widespread defects
General Estimate	Includes usefulness of a coating for the intended purpose; “1” = freshly coated, “3” = may require spot repair in near future, “6” = recoating overdue

The resulting spreadsheet was filtered to review the coatings performance survey data for coal tar enamel in immersion service at Reclamation facilities and provided in this report. Inconsistency between the study’s data sheets resulted in the data not being included in this report.

Results and Discussion

Laboratory Testing

All panels received testing following 5000 hours in laboratory weathering exposures. Figure 5 documents the coatings’ visual appearance following testing for the FOG and HAR/FOG exposure, which generally provided the most severe material degradation.



Figure 5. Full sample sets of FOG, at top, and HAR/FOG, at bottom, after completing six months of exposure: coal tar enamel (top-left), coal tar epoxy (bottom-left), polyurethane (top-right), and epoxy (bottom-right).

Corrosion creep analysis revealed the coating's resistance to corrosion propagation along the scribe interface. The reported measurements are the distance of corrosive undercutting from the scribe after exposure. Figure 6 shows the average corrosion undercutting distance for each of the coating systems and exposures. An error bar provides the standard deviation to indicate the degree of variability between the two samples. All coatings provide excellent protection from undercutting in both immersion exposures. The exception is the polyurethane, which displayed very poor performance, particularly in the presence of the HAR exposure salts. The cause of the polyurethane undercutting could be determined with further investigation.

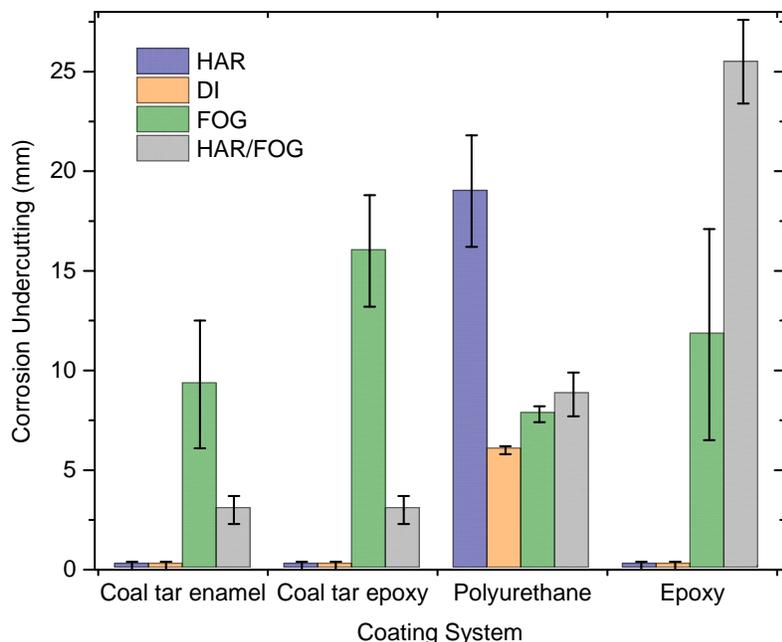


Figure 6. Corrosion undercutting results for all coatings systems and exposures evaluated.

The FOG cyclic testing for the coatings containing coal tar pitch provided more severe undercutting than the HAR/FOG exposure. The FOG exposure provided twice the number of temperature and moisture cycles than the next nearest exposure, HAR/FOG. The results confirm that this cycling cause accelerated degradation of the coal tar pitch containing materials. The coal tar epoxy in FOG exposure provided the third worst corrosion undercutting results observed in this experiment.

The epoxy coating in HAR/FOG exposure produced the most severe undercutting observed in this experiment. The FOG exposure undercutting for epoxy also produced severe undercutting but was less extreme. Accelerated corrosion testing often considers the number of cycles to be an important contributor to degradation. The epoxy results in cyclic testing indicate that placing this system in HAR immersion greatly accelerates the undercutting degradation. The immersion exposure occurs for half of the experiment, and specifically, cycling the epoxy coating between and immersion test and a salt fog cabinet likely accelerated the undercutting failure.

Corrosion in Immersion Exposures

In both the HAR and DI immersion exposures, no undercutting occurred for the coal tar enamel and the coal tar epoxy. The coating could not be removed past the scribe, as shown in Figure 7. This result supports field observations that coatings with coal tar pitch have excellent performance in immersion exposures when temperature and humidity fluctuations are limited.



Figure 7. Corrosion undercutting of coal tar enamel panels after HAR (top-left) and DI (bottom-left) exposures; coal tar epoxy after HAR (top-right) and DI (bottom-right) exposures.

The polyurethane coating easily peeled from the entire surface of the panel in both immersion exposures. Corrosion staining as a result of undercutting occurred only in the area adjacent to the scribe, see Figure 8. The undercutting for the HAR exposure was more severe than for DI. The results indicate a severe loss of adhesion for the polyurethane coating in immersion, despite some protection from corrosion undercutting.

The epoxy had minimal corrosion creep in HAR and DI exposures. In addition, a small band of coating could be removed adjacent to the scribe in both HAR panels and in only one DI panel. The removal of this small section of coating is similar to the polyurethane in that no corrosion undercutting was observed; however, this reduced coating adhesion is much less severe and fails in a more brittle in nature.



Figure 8. Corrosion undercutting of polyurethane panels after HAR (top-left) and DI (bottom-left), and epoxy after HAR (top-right) and DI (bottom-right).

Corrosion in Cyclic Exposures

Figure 9 shows the coal tar enamel and coal tar epoxy panels after exposure. The FOG exposure provided the poorest performance for both coal tar coatings and had a higher variability than seen on other samples. The corrosion undercut area lifted and peeled coating from the substrate. Additional coating is easily removed beyond undercut, but a residue remains adhered to the substrate, which is likely coal tar pitch.

The top layer of the coal tar enamel coating in FOG exposure was easily removed by scraping. This suggests that the outer layers of the material degrade as a result of the cycling.

FOG exposure caused extensive blistering and undercutting on the coal tar epoxy coating as a result of induced cracks and fractures. However, the coating remained strongly adhered beyond the corrosion undercutting area.



Figure 9. Corrosion undercutting of coal tar enamel panels after FOG (top-left) and HAR/FOG (bottom-left), and coal tar epoxy after FOG (top-right) and HAR/FOG (bottom-right).

The coal tar enamel coating exposure to HAR/FOG produced less corrosion undercutting than observed for the other three coating systems. However, both coal tar enamel and coal tar epoxy were very brittle after HAR/FOG exposure and chipped from the substrate easily. Coating was easily removed from the area adjacent to the scribe, but a coating residue remained adhered to the substrate.

These cyclic testing results for coal tar enamel support field observations that it becomes brittle and cracks as a result of cyclic temperature and humidity changes, such as service exposures with frequent fluctuations of warming and cooling as well as humid and dry exposure.

The polyurethane had moderate corrosion undercutting at the scribe for both the FOG and HAR/FOG exposures, see Figure 10. For FOG testing, the coating could be removed minimally from the area adjacent to the scribe. It could be removed more significantly in the HAR/FOG exposure but not nearly as far as observed in polyurethane's immersion exposures.

The epoxy coating FOG exposure produced undercutting that lifted and peeled the coating from the area adjacent to the scribe. The undercutting did not extend beyond the lifted area. Significant blistering also

occurred in the epoxy coating during HAR/FOG exposure that extended to the nearest edges of the panel. Both epoxy exposures had significant undercutting, with very high variability occurring in the FOG test.



Figure 10. Corrosion undercutting of polyurethane panels after FOG (top-left) and HAR/FOG (bottom-left), and epoxy after FOG (top-right) and HAR/FOG (bottom-right).

Electrochemical Impedance Spectroscopy

Figure 11 provides bode plot data for all panels in the DI exposure, shown as impedance magnitude, $|Z|$, versus frequency. The data is not normalized to account for surface area because all measurements are of consistent areal size. Results for the other exposures were similar to these plots with some discernable differences between the degradation in immersion versus cyclic exposures.

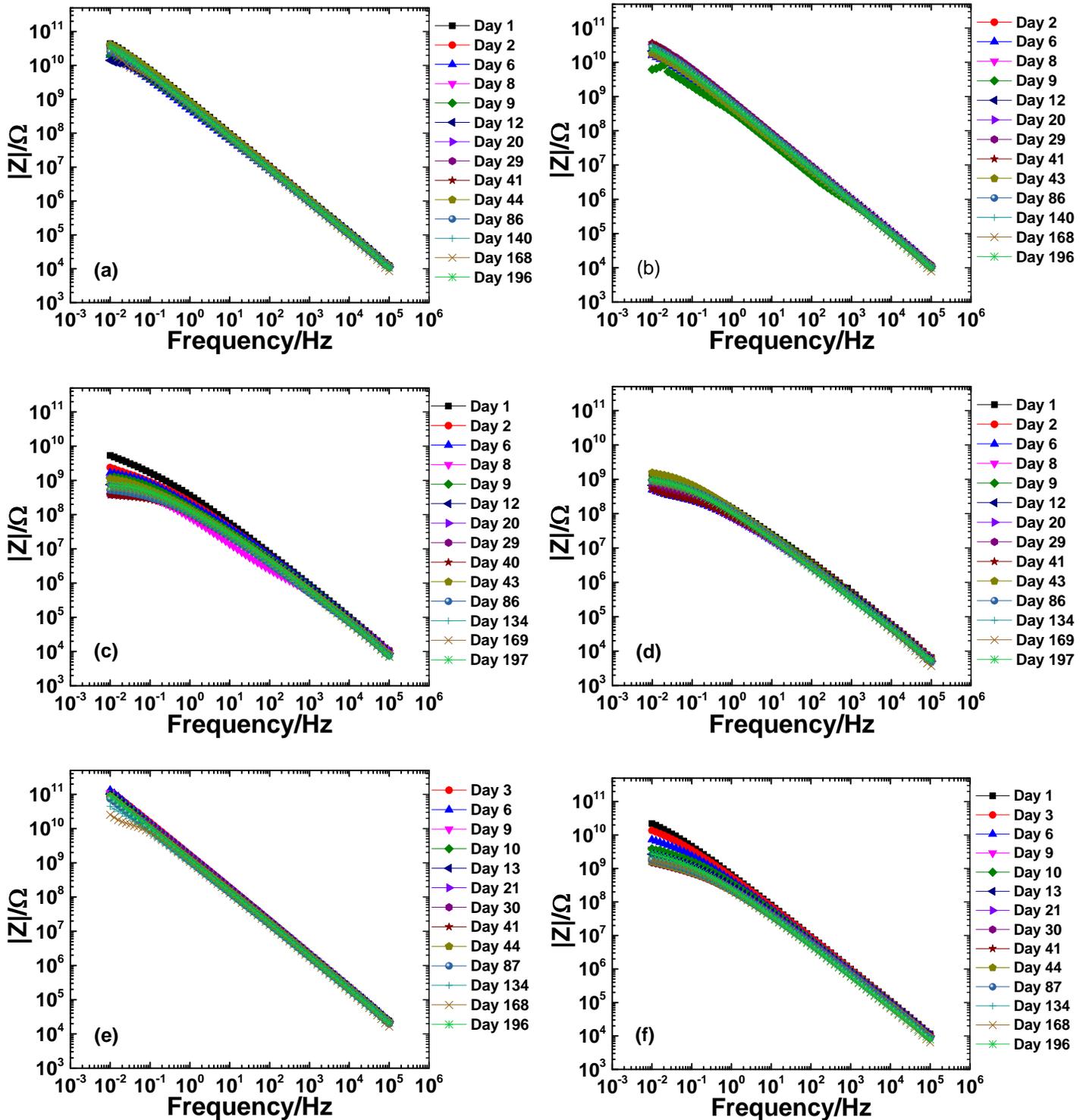


Figure 11. EIS test data for DI exposure plotted as impedance magnitude versus frequency for (a, b) coal tar enamel #1 and #2, (c,d) coal tar epoxy #1 and #2, (e) polyurethane, and (f) epoxy.

The two coal tar enamel plots, (a, b), are very high impedance, change little over time, and show little distinction between them. Figure 11(b) excludes Day 1 due to noise. The two coal tar epoxy plots, (c, d), are approximately 10^9 Ohms at the low frequency, change more with time, and have some variability

between the two panels. Although there is coal tar pitch in the coal tar epoxy, the material's performance has little comparison to the coal tar enamel. The coal tar epoxy is 33% by weight according to the manufacturer's safety data sheet, which is about half of the composition in the coal tar enamel.

Figure 11 also suggests that polyurethane has high barrier properties, similar to the coal tar enamel, while epoxy and coal tar epoxy are more similar to each other. The latter is likely a result of the bulk of the material being a common epoxy binder. The plot excludes polyurethane's Day 1 data, which was 5×10^{12} Hz at 0.01 Hz. This is at the limit of the instrument, signifying that insufficient saturation occurred for the measurement.

The EIS data for each coating type has a degradation trend that is not dependent on the exposure type. However, the cyclic testing caused more pronounced degradation for the polyurethane. The phase angle, θ , (not shown) indicated a high likelihood of corrosion reactions beneath the film despite a $|Z|$ of 10^{10} Ohms. It is near 0° at low frequencies, which is the θ of a pure resistor and can be interpreted as a predominance of corrosion reactions at those frequencies.

The coal tar epoxy and epoxy demonstrated the opposite effect; degradation was most pronounced in immersion. The θ demonstrates this in Figure 12 for coal tar epoxy; Days 80 and 162 removed from plot (b) due to noise. The DI exposure data, (a), has a θ less than -20° , for all measurements, while the FOG exposure, (b), is nearer to -40° at the low frequency. The HAR/FOG data is intermediate to the trendlines in Figure 12, and the samples are in immersion half of the time.

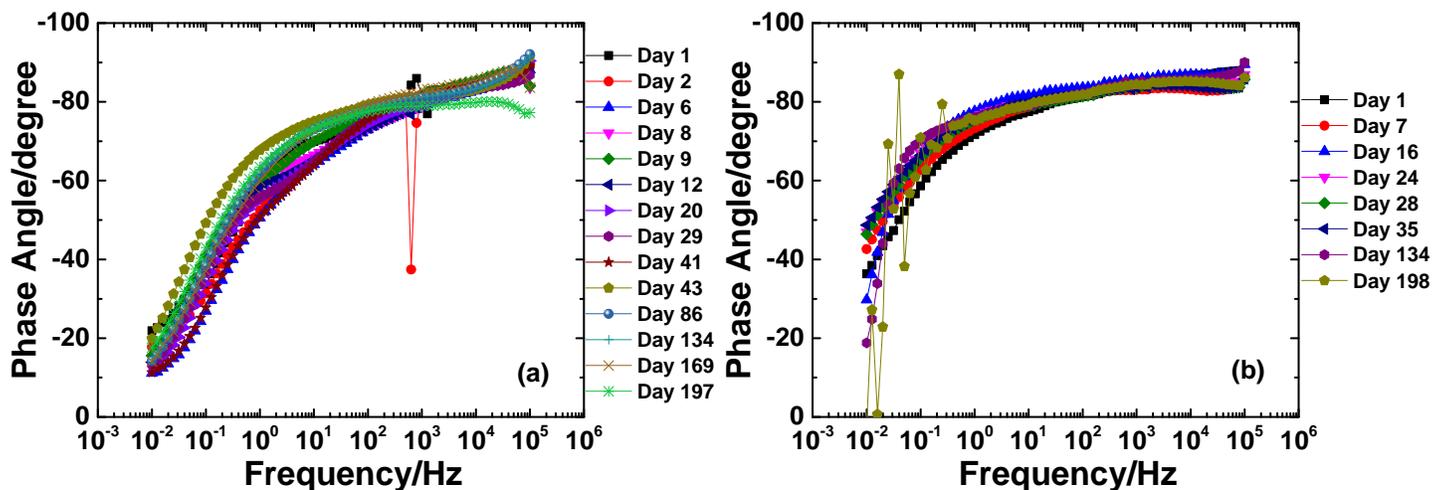


Figure 12. Coal tar epoxy phase angle versus frequency EIS data for (a) DI exposure and (b) FOG exposure.

Figure 13 provides θ versus frequency for epoxy in the DI and FOG exposures for comparison. Days 1 and 134 are removed from plot (b) due to noise. The $\theta_{0.01 \text{ Hz}}$ is approximately 20° lower for the DI exposure than for the FOG exposure. The monotonic reduction at the low frequencies suggests continuous degradation of the polymer film. The glass flakes could be increasing the tortuosity of the film, increasing the path length that the water and ions must travel. Figure 13(a) suggests that this occurs only over the first couple of days, if at all. An epoxy control without glass flake is needed to confirm any observation.

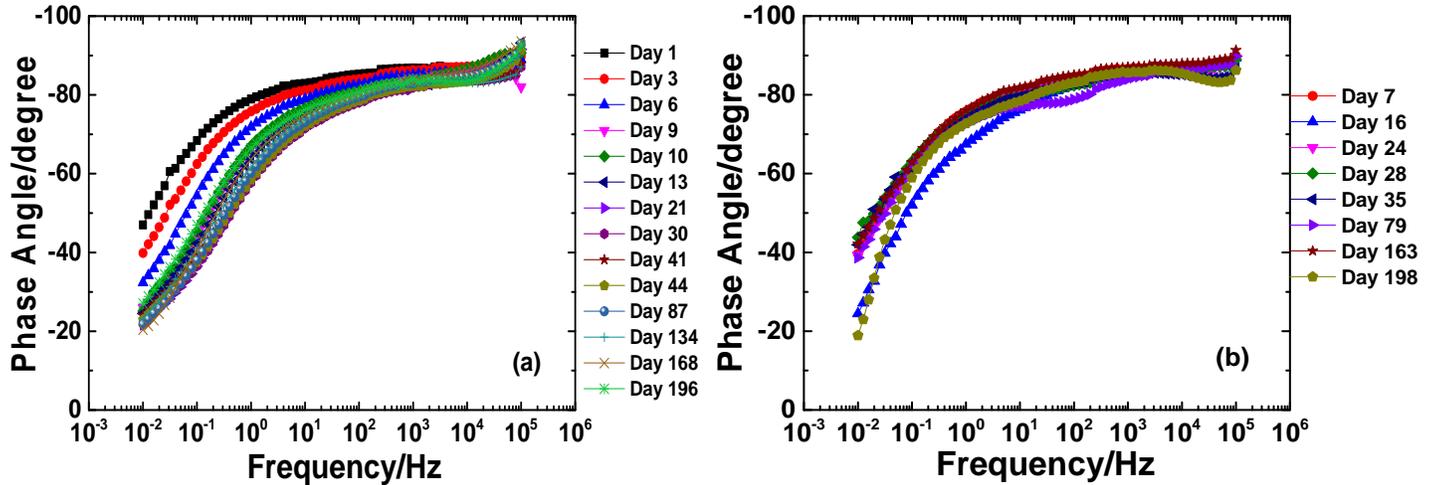


Figure 13. Epoxy phase angle versus frequency EIS data for (a) DI exposure and (b) FOG exposure.

See Appendix A for plots of the $|Z|$ for all coating types and exposures at 0.01 Hz and 10^4 Hz versus the time of exposure. These plots illustrate changes to the coating's total impedance and water uptake, respectively, which are key indicators of both performance and degradation mechanisms.

Figure 14 provides this data for each coating in HAR exposure. The legend between the plots applies to both, and coal tar (CT) is abbreviated. Estimated trend lines appear in each plot to aid the reader in following each data set. Two additional long-term data points were taken at 280 and 440 days but do not vary greatly from the information here.

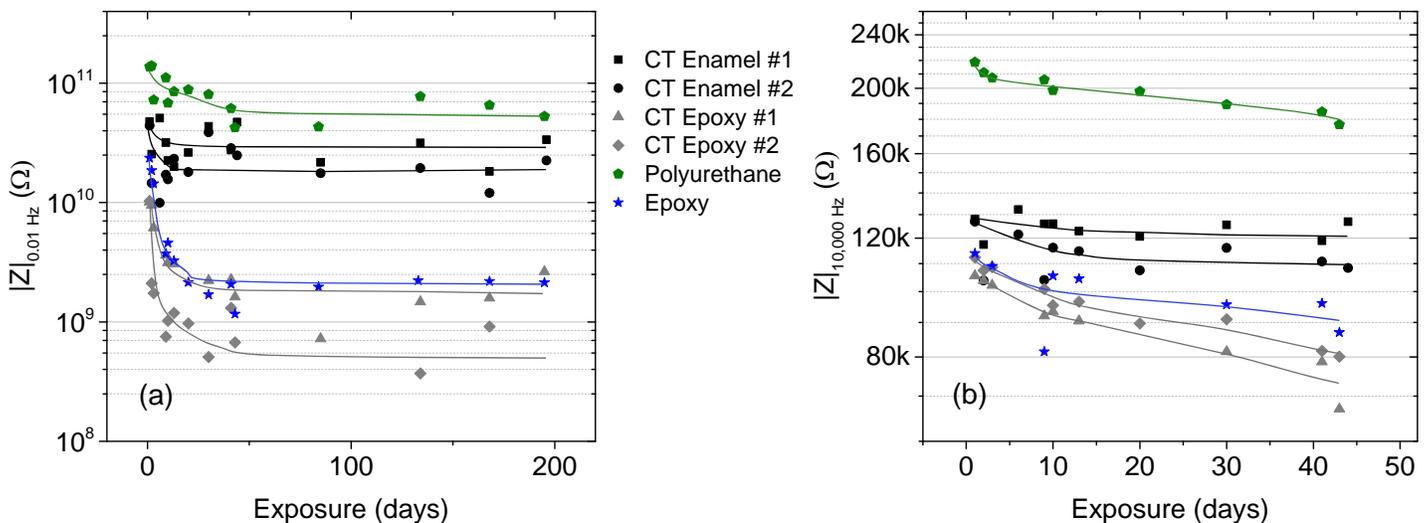


Figure 14. Impedance magnitude versus time of HAR exposure for each coating at (a) 0.01 Hz and (b) 10,000 Hz.

Figure 14(a) shows the 0.01 Hz data. All measurements at Day 51 were suspected of measurement error and removed as well as additional days for coal tar epoxy #1 (Day 20) and #2 (Days 85 and 195) that were less than 10^6 Ohms. The coal tar epoxy and epoxy coatings have a one order of magnitude decrease in $|Z|$ during the first 50 days of exposure from 10^{10} to 10^9 Ohms. After which, the $|Z|$ is more stable but the data has significant variability for coal tar epoxy. The polyurethane is very high $|Z|$ and is quite stable

for the exposure period after a slight decrease in the first 50 days of exposure. The coal tar enamel has the least reduction in $|Z|$ out of the systems evaluated and has a value near 10^{10} Ohms.

Figure 14(b) shows the 10^4 Hz data at the beginning of the exposure to focus on changes to the water content of the film at early times. Data excluded from the graph at these scales are epoxy (Days 2 and 20) and polyurethane (Day 13); each had significantly higher values. The general trend is downward for all coatings except the two coal tar enamel samples. The interpretation given is that coal tar enamel does not adsorb water into the coating matrix, whereas the other coatings have appreciable water uptake. No quantification of water uptake occurred due to variability in the data set and a low number of data points.

Adhesion

Figure 15 summarizes the adhesion testing results. These measurements occurred following the accelerated weathering exposures. The HAR and DI adhesion testing occurred much later than the cyclic tests which may have some impact on the data.

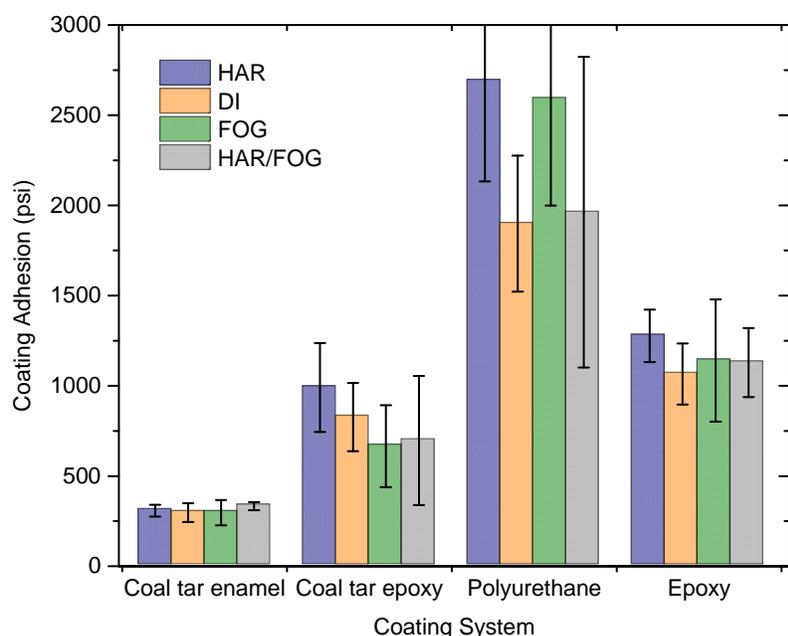


Figure 15. Adhesion testing results following completion of accelerated weathering exposure

The coal tar enamel coating had a significantly lower adhesion than the other coating systems. The average adhesion values for coal tar enamel following all exposures was 300 to 350 pounds per square inch (psi). All of these measurements failed at or just beneath the glue and were considered to be cohesive failures. Coal tar epoxy also has low adhesion values, 650 to 1000 psi, but mostly failed at the glue.

Both coal tar materials left a light brown color on the underside of many of the dollies, likely due to coal tar pitch and other lower molecular weight compounds diffusing into the glue before it cured. The coal tar enamel pull-off locations also contained distinct smooth shapes that are unlike the brittle fracture surfaces observed in pull-off testing of the other three coatings. Figure 16 shows the pull-off surfaces for coal tar enamel following testing. McManus [8] showed that coal tar enamel deforms in the direction of applied force; a blunt rod pressure test showed that 25 psi causes significant deformation for the plasticized coating. The water pressure in penstock service exposures may improve the barrier properties by slight compression of the film.



Figure 16. Coal tar enamel surface following adhesion pull-off testing.

Most epoxy samples were 100 percent cohesion failures, but several were mixtures of adhesion, cohesion, and glue as well as 100 percent adhesion. The DI exposure has a lower adhesion value than HAR exposure and failed by cohesion. The results suggested that DI immersion weakens the coating matrix more than HAR exposure.

The polyurethane coating had the highest adhesion values for all exposures, ranging from 1282 to 3273 psi. The polyurethane FOG results included mixtures of adhesive, cohesive, and glue failures and has high variability in the data. Most of the HAR, DI, and HAR/FOG measurements were glue failures.

Slurry Erosion

Table 5 provides results in milligram per hour (mg/hr). Coal tar enamel testing ended after the first day due to a high erosion rate and the release of significant coal tar material into the water. The epoxy also had a high erosion rate, which may be due to the glass flakes it contained. Polyurethane has a low erosion rate that could be attributed to the film's elasticity and toughness. Coal tar epoxy did not have a sample and was not tested.

Table 5. Erosion rate data for slurry erosion testing.

Result	Coal Tar Enamel	Coal Tar Epoxy	Polyurethane	Epoxy
Erosion Rate (mg/hr)	117.5	Not Tested	8.0	83.9
Standard Deviation (mg/hr)	Not Available	Not Tested	1.2	10.7

Material Characterization

See Appendix B for all test results. Table 6 provides a summary of key findings. Two solution vinyl coating systems and its virgin resin are included. The key comparison between vinyl and coal tar enamel is that both are thermoplastic materials.

Table 6. Test results of materials characterizations for all coating systems and select vinyl-based materials.

Material	DMTA	DSC	TGA Weight Loss			XRD and TEM	FTIR	SEM
	T _g (°C)	T _g (°C)	First (°C)	Total (%)	Notes	Crystallinity Notes	Notes	Notes
Vinyl resin, Vinnol 15-45M & 15-50	70	72	180	95	Initial degradation is likely dehydrochlorination process [1]; second occurs from 400 to 500 °C;	No crystallinity; broad peak spacings of 5.34, 3.71, and 2.25 Å occur; 010 and 210 crystal spacings occur at 5.24 and 3.66 Å, respectively [3]	Consistent with PVC spectrum [4,5]; additional peaks for vinyl acetate copolymer, 1100 cm ⁻¹ , and carbonyl, 1736 cm ⁻¹	Not tested
Zn-rich Vinyl, USACE System 5-E-Z	55	37	100	45	Initial loss is likely plasticizer, which reduced and broadened the T _g ; later material degradation consistent with vinyl resin	Not tested - results anticipated to be consistent with vinyl resin	Spectrum consistent with vinyl resin but less defined due to pigments and extenders	Good continuity between pigments and binder
Vinyl, USACE System 4	30	26	100	55	Initial loss is likely plasticizer, consistent with vinyl resin; total weight loss is greater because there is no Zn pigment	Not tested - results anticipated to be consistent with vinyl resin	Spectrum consistent with vinyl resin and coating	Consistent with Zn-rich vinyl but no Zn
Coal Tar Enamel	Not tested	10	80	40	Material is a mixture of compounds; gradual weight loss over time and no true T _g ; reports of the T _g for coal tar pitch range from -58 to 42 °C [51]; weight loss decays between 400 and 500 °C	No crystallinity; spacings include 4.42, 3.54, 3.05, 2.90, 2.1, 1.92, 1.86, 1.24 Å, from dots and 4.25, 2.48, 1.47 Å from rings; other regions were 3.5 and 4.5 Å, similar to graphite	Not tested	Good continuity between pigments and binder
Coal Tar Epoxy	Not tested	48	50	45	Second degradation occurs at 150 °C and third occurs at 275 °C	Not tested	Not tested	Not tested
Polyurethane	Not tested	53	60	75	First degradation is slight and gradual until 200 °C at which time there is a steady and high rate of weight loss until 450 °C	Not tested	Not tested	Not tested
Epoxy	Not tested	45	60	40	Second degradation occurs at 200 °C and third, and most significant, occurs at 300 °C	Not tested	Not tested	Not tested

The first two data columns in Table 6 provide the glass transition temperature (T_g), which is the temperature at which amorphous materials transition from solid to rubbery or semi-liquid. The T_g of polymer materials, such as coatings, is the movement of long polymer chain segments such that they can slide past one or relieve stress.

Only the vinyl coating system free films received DMTA testing. There is fair agreement between the DMTA and DSC methods. The pigmented vinyl film T_g values reported from the mechanical load-based DMTA curves are higher than the calorimetry-based DSC curves, particularly for the coating containing zinc (Zn) pigments.

Vinyl and coal tar enamel are thermoplastic materials and have lower T_g values than the thermoset systems evaluated. The Zn-rich vinyl coating showed the highest T_g among the thermoplastic materials, which is again likely a contribution of the Zn pigment. The USACE System 4 vinyl coating T_g is around

30 °C. This T_g is within the range of warm-weather service conditions, suggesting that the vinyl polymers may be able to achieve occasional minor restructuring or stress relief during service. It is possible that this is a self-healing activity that contributes to the long service life observed for these systems.

Table 6 reports a T_g of 10 °C for coal tar enamel, but its curve does not have distinct features as is typically seen by homogeneous materials. Figure 17 reproduces the DSC plots provided in the NDSU-CPM report for coal tar enamel and the three thermoset coatings evaluated. Coal tar enamel is a heterogeneous material, and the broad T_g curve is a result of the lowest molecular weight materials becoming mobile at small additions of heat or stress. The plasticizer in coal tar enamel contributes to the broad T_g curve and is critical to ensuring that the material is not brittle in service. The measured T_g for coal tar pitch was reported as ranging from -58 to 42 °C [51]. Identifying the T_g for coal tar enamel is challenging and has little value. The coal tar enamel polymeric components may also be able to restructure or self-heal during service, as is proposed for the solution vinyl coatings.

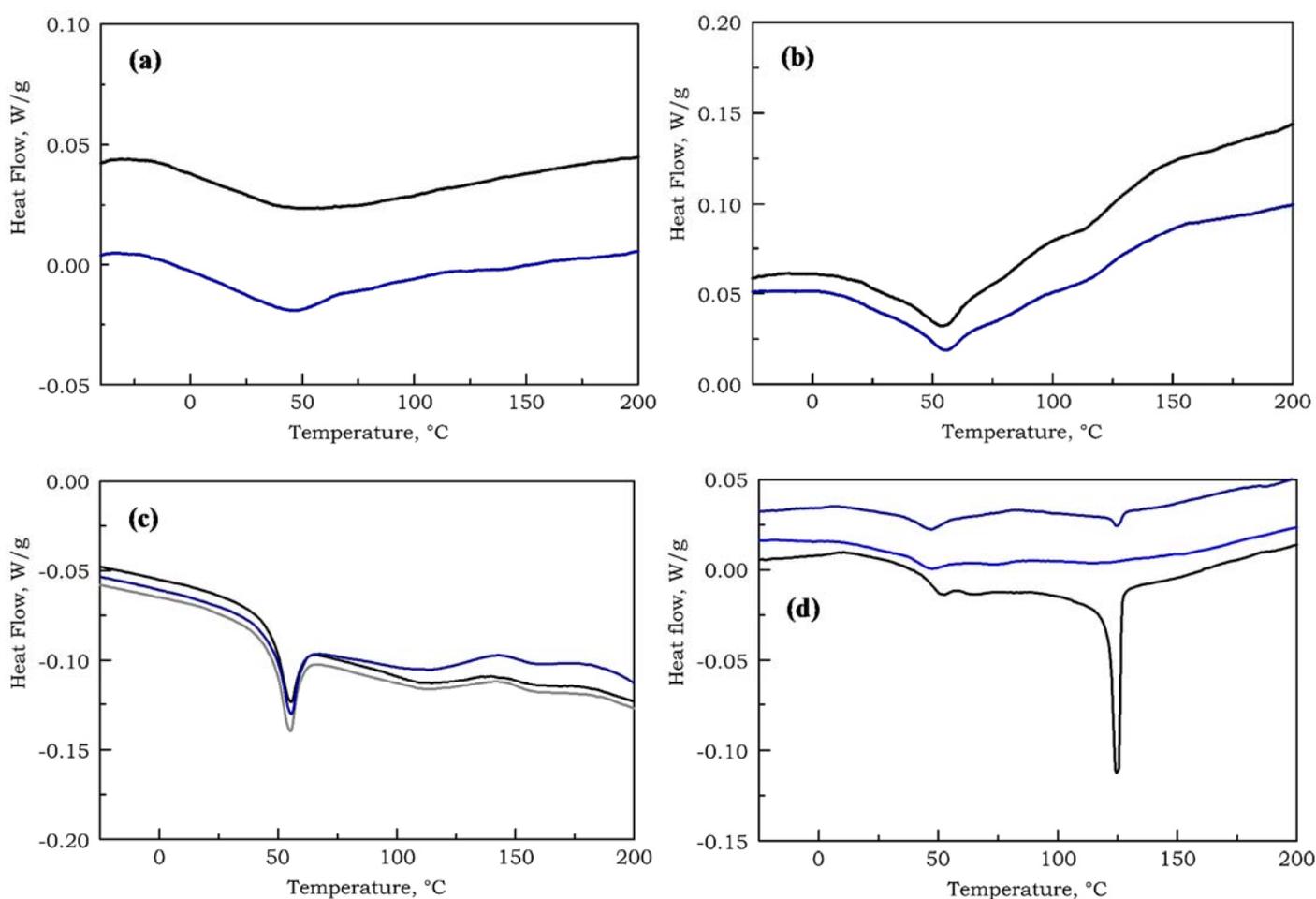


Figure 17. DSC curves used to derive T_g reproduced from NDSU-CPM report for (a) coal tar enamel, (b) coal tar epoxy, (c) polyurethane, and (d) epoxy.

The T_g for coal tar epoxy, polyurethane, and epoxy are in the range of 45 to 53 °C. These T_g values are slightly higher than the thermoplastic materials. The crosslinks within these thermoset materials limit the amount or possibility of restructuring and self-healing within these coating systems. The higher T_g also ensures that any large-scale polymer segment movement is not possible during regular service conditions.

One disadvantage of this is that poorly crosslinked or porous regions of the polymer matrix may not be able to self-heal. These regions are prone to increasing and storing water and ions in the film.

The TGA results show the material's initial degradation temperature, the total weight loss as a percentage, and key notes for the experiment. The thermoplastic materials degrade at higher temperatures, in the range of 80 to 100 °C. The coal tar epoxy, polyurethane, and epoxy have their initial degradations at 50 to 60 °C, which is just above its T_g. Polyurethane's first degradation is very slight; most of the degradation occurs above 200 °C and results in a total weight loss that is nearly double that of coal tar enamel, coal tar epoxy, and epoxy. All of these degradation temperatures exceed the typical service conditions, assuring that thermal degradation does not occur during service.

XRD and TEM testing for the thermoplastic materials failed to show distinct crystallinity in the films. Figure 18 shows TEM images for coal tar enamel at top; the scale bars in the lower left-hand corner are 20 nanometers (nm) and 50 nm for (a) and (b), respectively. The ordered lines in Figure 18(b) reveal organized regions of the material that could provide superior barrier properties. The very close spacing in solution vinyl coatings and coal tar enamel likely contribute to strong physical barrier to the permeation of water and ions. Ring spacings observed within the coal tar enamel samples were in the range of 3.5 to 4.5 Å. The smaller spacing is near that of graphite [5]. The heterocyclic ringed compounds and polynuclear aromatic hydrocarbons in coal tar enamel possibly organize in planar layers at the 4.5 Å spacing [16].

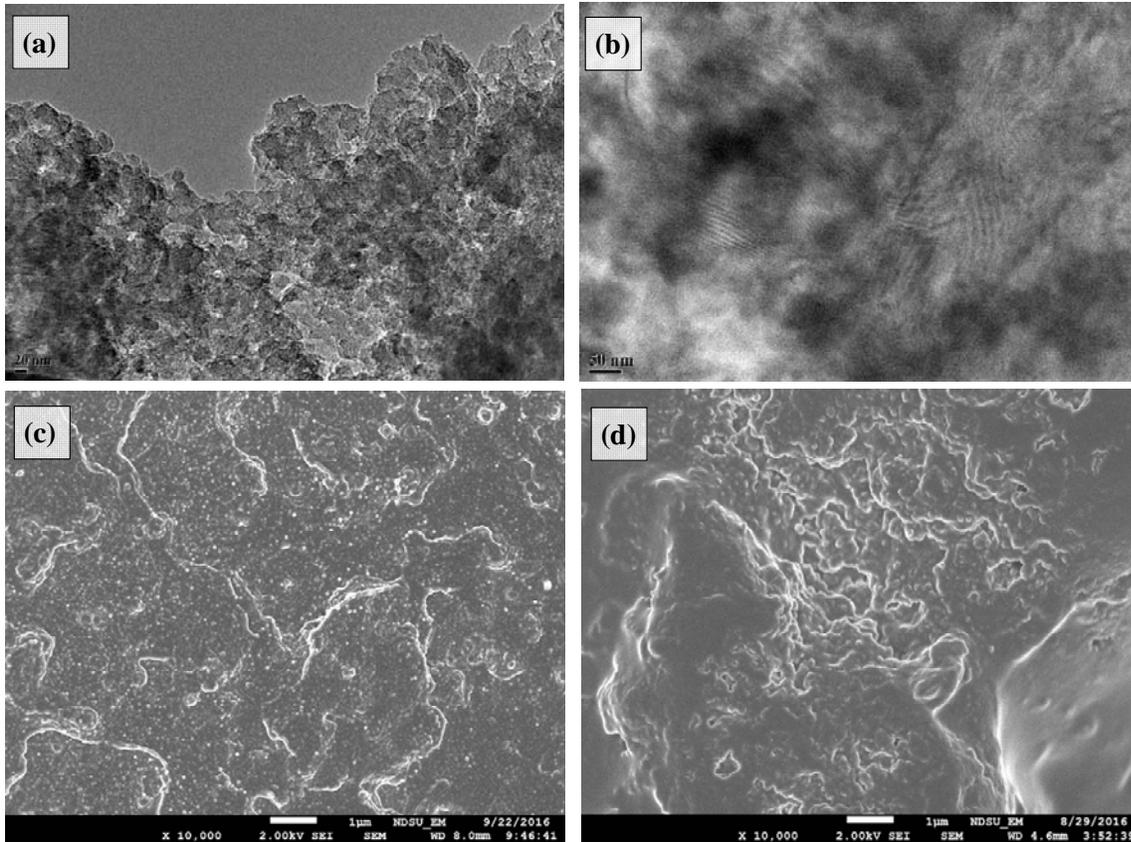


Figure 18. Micrograph images reproduced from NDSU-CPM report showing TEM of coal tar enamel at (a) high magnification and (b) with electron diffraction pattern as well as an SEM cross section of (c) vinyl and (d) coal tar enamel.

The two bottom images in Figure 18 are SEM cross sections of solution vinyl coating and coal tar enamel. Both materials have very good continuity between the binder and pigments, which is essential to good corrosion protection. The scale bars for both images are 1 micron.

Field Performance Testing

EIS field testing occurred at several facilities on coal tar enamel penstock linings, see Figure 19. The first four legend items represent tests performed during test method development. The field coating was unwatered for a significant period of time and likely did not achieve saturation prior to testing. This results in artificially high test results, which cannot be confirmed. The testing performed at Green Mountain was on completely saturated coating systems; see curves for the last four legend items.

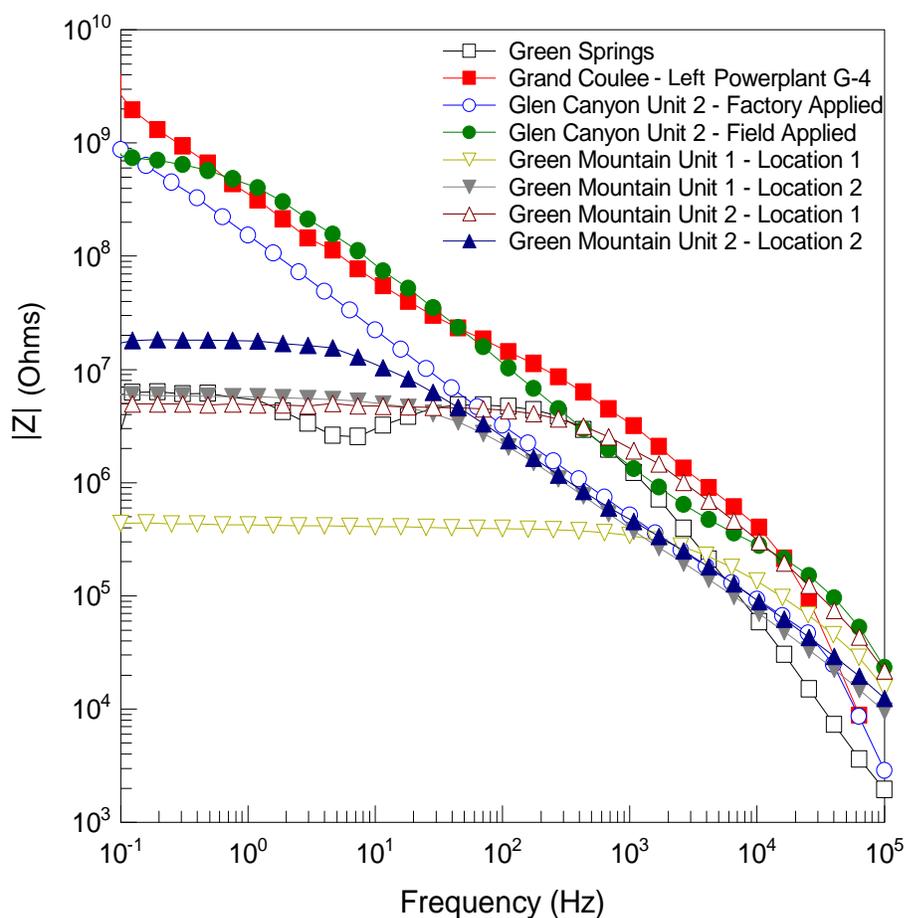


Figure 19. EIS test data for coal tar enamel penstock linings at various facilities.

The EIS testing at Green Mountain demonstrated the coating impedance to be approximately 10^7 Ohms at most test locations following approximately 74 years of service. One test location in Unit 1 provided an impedance value of 4×10^5 Ohms. This is a very low level of protection and could be the result of a pinhole or hairline crack to the substrate, although no defect was visible. Unit 1 was unwatered for one service year, which appeared to degrade the lining to a greater extent than Unit 2. The visual inspection supported this hypothesis.

Field evaluation indicates that coal tar enamel degrades by distinct cracking as it loses its elasticity. Figure 20 shows a test cell location on coal tar enamel with minor surface cracking. The EIS data was approximately 10^{10} ohms at 0.01 Hz. This indicates superior dielectric properties despite the surface cracking. The test data was not included above due to short saturation times that likely increased the impedance artificially. However, even at these short saturations the EIS data should have shown a short-circuiting effect, i.e. impedance values closer to 10^6 ohms at 0.01 Hz, if a crack or pinhole exists that reaches the bare steel.



Figure 20. Coal tar enamel coating condition at EIS test cell at Grand Coulee Powerplant G-21 with minor surface cracking.

Traditional field performance evaluations are qualitative, resulting in inspection reports with photographs and additional context describing coating condition. Coal tar enamel has three general characteristic appearances that result from the coating application method. See Reclamation’s Paint Manual [2] for more information; the types are summarized here:

- Shop applied – smooth surface throughout pipes except at weld hold-back areas
- Field applied by hand dauber – brick pattern as a result of 18-long swaths using a 6-inch wide application tool
- Field applied by mop – thick and rough surface texture often with drip, sags, or other defects

The shop applied coating often provides the longest service life because the shop conditions are more easily controlled. However, most of the earliest coal tar enamel linings were applied by hand-dauber, also called “shingling [6].” Figure 21 gives examples of the mop and hand-dauber applications as may be encountered during field inspection. These and the following photos in this report are from various the John Keys Pumping Plant’s pump-generating units.



Figure 21. Coal tar enamel (top) applied by hand-dauber in good condition, (bottom-left) applied by mop in good condition, and (bottom-right) applied by hand dauber beginning to crack, chip, and degrade.

Figure 22 provides photographs of the coal tar enamel and various stages of degradation. Each stage is significant, the steel surface beneath the coating is corroding to a corresponding degree. The photograph at top-left is a section of above-ground piping. This demonstrates the premature failure of coal tar enamel in this service. The diurnal heating and cooling by the sun caused complete failure of the top half of this pipe. The photographs shown at the bottom are much more representative of a failing coal tar enamel coating, and they should be considered for future replacement once they reach these conditions.



Figure 22. Coal tar enamel hand-dauber degrees of degradation in service: (top-left) severe with close-up at (top-right), (bottom-left) moderate, and (bottom-right) minor-to-moderate.

Conventional coating systems fail by a different mode than shown above for coal tar enamel. Figure 23 (top) provides an example of an epoxy coating with moderate degradation that should be considered for recoating. The photographs at the bottom are examples of coal tar epoxy at good and replacement conditions, respectively. The decision to replace a coating system must be weighed against the facility's maintenance program priorities and an assessment of how much of the system is in need of replacement. If only a few areas are in need of repair, spot or zone repair options may be preferable. See Reclamation's coal tar enamel repair manual provides more information on determining the appropriate maintenance approach [52].



Figure 23. (top) Assumed to be epoxy coating with moderate degradation and coal tar epoxy (bottom-left) in good condition and (bottom-right) with moderate degradation.

Table 7 summarizes information on the twelve pump generating unit discharge tubes. It includes visual inspection details and incorporates facility records, as available. The type of coating system is estimated and could be confirmed by analytical testing. The information in Table 7 shows the upper and lower sections of the tubes separately. The upper section is above ground and experienced severe degradation

on the upper have of the pipe, see Figure 22 (top-left). The lower section is buried at a steep slope. Much of the coal tar enamel in this section has at least 60 years of service and is in fair condition.

Table 7. John Keys Pumping Plant discharge tube coating assessments for upper and lower tube sections.

Unit	Upper Tube*	Relined	Years Aged	Upper Tube Notes	Lower Tube^	Relined	Years Aged	Lower Tube Notes
1	Coal tar epoxy	1984	33	Spot repair as needed	Coal tar enamel	N/A	66	Good condition, spot repair 710 square feet
2	Coal tar epoxy	1984	33	Spot repair as needed	Coal tar enamel	No	66	Good condition, spot repair 150 square feet
3	Coal tar enamel	No	66	Coal tar enamel is severely degraded, Reline	Coal tar enamel	No	66	Good condition, spot repair 75 square feet
4	Coal tar enamel	No	66	Coal tar enamel is severely degraded, Reline	Coal tar enamel	No	66	Good condition, spot repair 25 square feet
5	VR6 primer/VR3	1975	42	Coating is in average condition, Spot repair as needed	Coal tar epoxy	1975	42	Most of coal tar epoxy is gone, relining is needed
6	Coal tar enamel	No	66	Coal tar enamel is severely degraded, Reline	Coal tar enamel	No	66	Good condition, spot repair 25 square feet
7	Coal tar enamel	No	66	Coal tar enamel is severely degraded, Reline	Coal tar enamel	No	66	Good condition, spot repair 170 square feet
8	Coal tar enamel	No	66	Coal tar enamel is severely degraded, Reline	Coal tar enamel	No	66	Good condition, spot repair 105 square feet
9	Coal tar epoxy	1982	35	Reline due to wide spread corrosion	Coal tar enamel	No	66	Good condition, spot repair 360 square feet
10	Coal tar epoxy	1982	35	Reline due to wide spread corrosion	Coal tar enamel	No	66	Good condition, spot repair 285 square feet
11	Coal tar epoxy	1982	35	Reline due to wide spread corrosion	Coal tar enamel	N/A	66	Good condition, spot repair 295 square feet
12	Vinyl or Epoxy	1982	35	Gray coating, not coal tar epoxy. Reline due to wide spread corrosion.	Coal tar enamel	N/A	66	Good condition, spot repair 475 square feet

Facility Records and Surveys

Figure 24 provides information on the age of coal tar enamel linings at several Reclamation facilities. Most of these linings are still in service and may have received spot repairs. For example, Reclamation file information suggests that Hoover and Joe's Valley received spot repairs in 2005 and 1998, respectively. Glen Canyon also received repairs or possibly recoated entire units in 2001. Flatiron

penstocks were relined entirely in 2010; the low achieved service life is attributed to the pipes being above ground and subjected to wide temperature fluctuations.

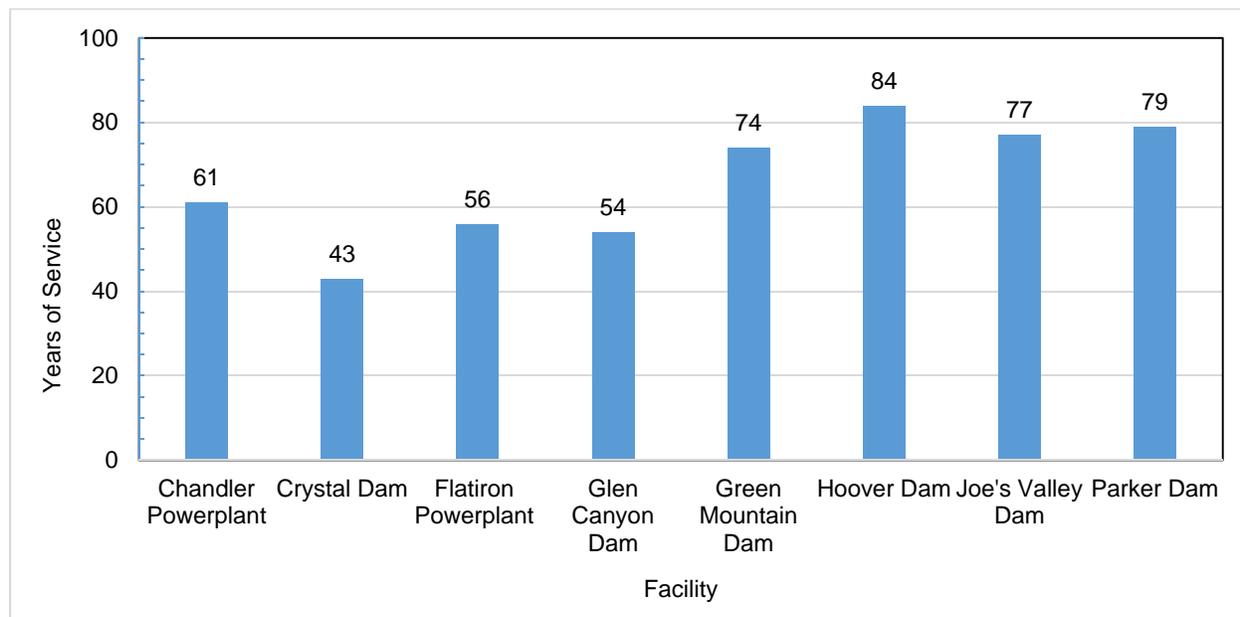


Figure 24. Age of coal tar enamel lined penstocks at several Reclamation facilities.

The figure also represents the oldest and newest coal tar enamel applications. Hoover Dam has the first lined penstocks at Reclamation. Crystal Dam was one the last facilities lined with the material, occurring in 1974.

Based on coating condition assessments, it is known that most of the penstocks at Grand Coulee Powerplant presently have coal tar enamel linings. It is not known if relining has occurred on any of the units. Additional facilities, including Green Springs Powerplant, are known to have coal tar enamel lining, which is likely the original from plant commissioning in 1960.

The 1985 coating survey included responses from several facilities with coal tar enamel. Figure 25 reproduces the information in that survey report for equipment coated with coal tar enamel. The rusting, coating film, and general estimate assessments are giving as a bar graph and the years of service as a scatter plot, linked on the right y-axis. The “needle valves” are in poor condition following a very short service period. The respondent indicated poor surface preparation for the “needle valves” and the “penstock” at 53 years of service.

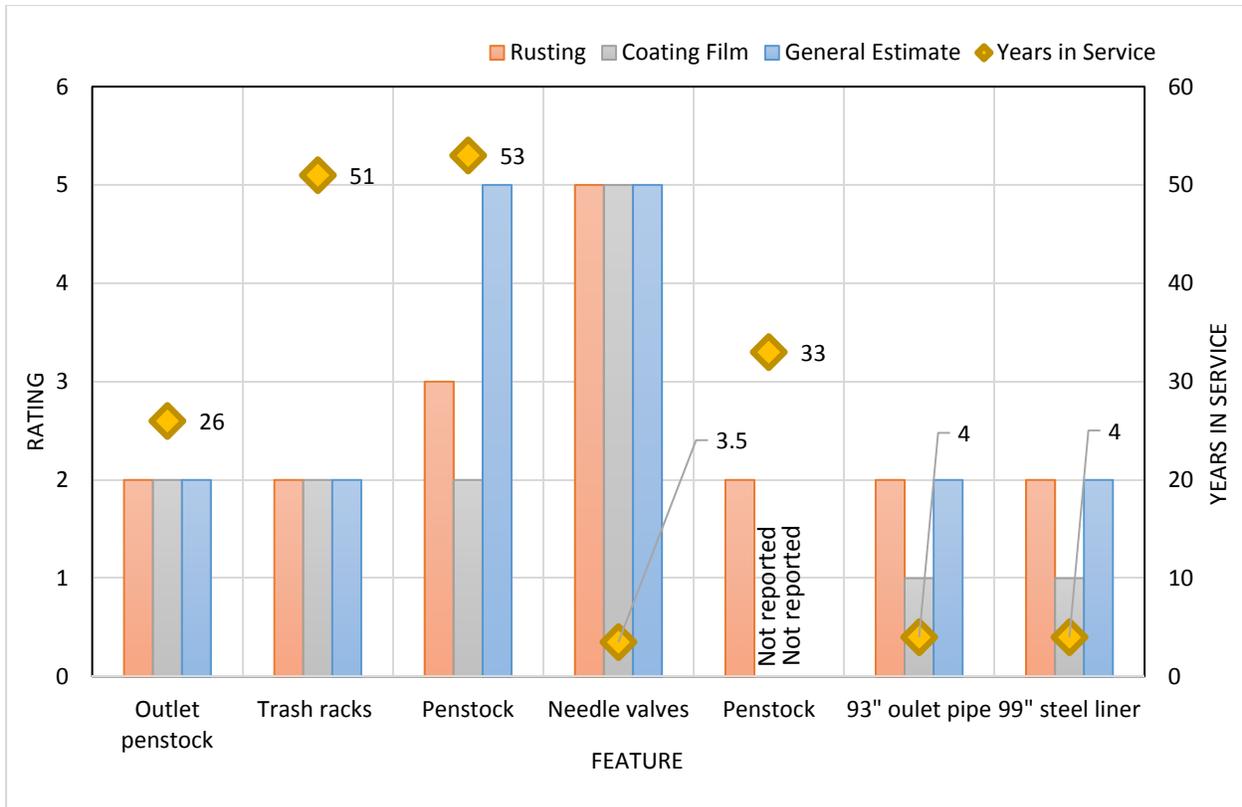


Figure 25. 1985 survey data for coal tar enamel in immersion service, including film condition assessments and years in service.

Conclusions

Coal tar enamel lining provides a longer service life than any coating material available today or used previously. The long service life occurs only when the material is kept at consistent temperature and humidity. For Reclamation's purposes this ideal service environment is the subgrade penstocks, outlet works, trashracks, and other equipment in similar conditions.

This research evaluated coal tar enamel's material properties in a side-by-side comparison to an SSPC Paint 16 coal tar epoxy, AWWA C222 polyurethane, and a commonly used solvent borne epoxy with glass flake. Results showed that amongst other unique characteristics, the graphite-like structure is largely responsible for the superior degree of impermeability for coal tar enamel. Laboratory data for these materials supported field experience showing the superior performance of coal tar enamel, particularly in EIS and corrosion undercutting. Key findings for each of the materials evaluated are summarized below.

Coal tar enamel

- Corrosion undercutting protection is excellent in immersion exposures; the greatest undercutting is observed in FOG exposure.
- Impedance data is near 10^{10} Ohms and does not experience a significant reduction during the first 250 days. High frequency data suggested no significant water uptake.
- Adhesion values are very low, 300 to 350 psi, and fail cohesively near the glue; the material at the fractured surface shows signs that it flows during or after the pull-off test.

- Erosion rate is high, greater than 100 mg/hr.
- Material Tg is near 10 °C, has a very broad curve, and may be able to self-heal during service. The amorphous material has electron diffraction spacings similar to graphite and suggests that the cyclic compounds within the material are able to pack into layers.

Coal tar epoxy

- Corrosion undercutting in FOG was more severe than in HAR/FOG, suggesting a preference to immersion service without atmospheric exposure.
- Impedance data is most similar to epoxy data, and greater degradation occurred in immersion exposures. High frequency data suggested significant water uptake.
- Adhesion values are low, 650 to 1000 psi, and most failures occurred at the glue.
- Material Tg is near 48 °C.

Polyurethane:

- Poor corrosion undercutting, particularly in HAR immersion exposure.
- Impedance values are similar to coal tar enamel, but film degradation was greater in cyclic exposures, and the θ neared 0° at low frequencies, suggesting the presence of corrosion reactions. High frequency data suggested some water uptake.
- Adhesion values are high and variable at 1282 to 3273 psi; only FOG exposure resulted in mixtures of adhesive, cohesive, and glue failures, all other exposures were mostly glue failures.
- Erosion rate is low, less than 10 mg/hr.
- Material Tg is near 53 °C.

Epoxy

- Cyclic testing of the material that included immersion, as shown in the HAR/FOG exposure, produced severe undercutting; suggesting accelerated degradation when exposed to immersion service followed by temperature cycling in atmospheric service.
- Impedance data experienced greater degradation in immersion exposures than in cyclic exposures; immersion of epoxy seems to be a greater driver toward degradation than salt fog cyclic exposure. High frequency data suggested significant water uptake.
- Adhesion testing produced many cohesive failures in the range of 1000 to 1300 psi. The low cohesive failure values resulting from DI exposure suggests that this immersion weakens the coating matrix more than HAR exposure.
- Erosion rate is high, greater than 80 mg/hr.
- Material Tg is near 45 °C.

Future studies could evaluate replacement materials for coal tar enamel linings. New materials could target properties identified above and within this report. Key properties may include a graphite-like structure or component of the material, self-healing through high molecular weight thermoplastic constituents, entirely hydrophobic ingredients, and extremely low water uptake.

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Appendix A – EIS Analysis Report

To: Dr. D. Tordonato, Bureau of Reclamation
Cc: Dr. B. J. E. Merten, Dr. A. D. Skaja, Bureau of Reclamation.
From: S. G. Croll, North Dakota State University
Date: 20th December, 2016

Report: EIS Data

This report summarizes the work done at North Dakota State University in analyzing Electrochemical Impedance Spectroscopy, EIS, data gathered by at the Bureau of Reclamation (BoR). Dr. Vinod Upadhyay transcribed the original data files into Excel spreadsheets and then into Bode plots using Origin scientific graphing software.

Work on the EIS data is reported separately from the analytical work done on this project simply due to the amount of the material.

Exposure regimes used at the Bureau:

Measurements at intervals in the following exposures (EIS cylinder of 23 cm² area with DHS solution):

DI: immersion at laboratory temperatures in deionized water.

HAR: EIS, immersion in Harrison's solution.

FOG: continual exposure in a Q-Fog cabinet that uses dilute Harrison's solution, DHS, (not sodium chloride) and cycles between 35 °C dry and 25 °C with the fog.

HAR-FOG: a two-week rotation cycle: 1 week Q-Fog and 1 week in Harrison's immersion.

BOR: a four week rotation cycle of 1 week QUV cabinet, 1 week Q-Fog, 1 week DHS immersion then another week in Q-Fog,. Q-Fog occurs for half of the BOR exposure period. Spending a sensible fraction of the exposure in immersion is thought to help the accelerated weathering to be more consistent with actual exposure conditions.

Vinyl coatings have "BOR" results, but the coal tar experiment was modified to "HAR-FOG" because they are never to be used in exterior (UV) exposure.

There was one data set labeled VZ108d PRO but the coating under test was the same VZ108d +V766e combination investigated here, so the label is now VZ108d + V766e PRO. However, for consistency with the original files as submitted, the Excel file retains the original label.

Coatings investigated:

Vinyl topcoat formulation: V766e, without and without primer vinyl zinc rich primer formulation:
VZ108d
High solids epoxy: PPG Amerlock 2
Coal Tar Enamel
Coal Tar Epoxy
Aromatic Polyurethane: ITW Futura

Results.

The original .dta files have been converted into Excel[®] spreadsheets that group the data according to the coating material under test. The data is organized in the spreadsheets so that data from longer exposures is to the right hand side. At the end of each series, the impedance modulus and phase angle are consolidated so that they can be more easily manipulated or copied into other software.

Bode plots at each exposure interval, of the modulus of the impedance and the phase angle, are given in a separate file. It is difficult to embrace such a large amount of data so separate graphs were extracted of how the impedance at 0.01 Hz and at 10^4 Hz changed as the exposure continued. These are presented in the body of the report here.

The low frequency impedance is often used as an approximation of the equivalent coating resistance and is used to assess the overall coating integrity. Any reduction seen in this impedance reflects a loss in the corrosion barrier properties. The impedance at 10^4 Hz can be used to calculate the coating capacitance and thus to calculate whether any water has penetrated the coating. Water penetration increases the capacitance and thus diminishes the impedance at this frequency. A systematic decrease in either of these values of impedance indicate that the coating in question is less able to protect the substrate. However, the Brasher-Kingsbury equation that is commonly used to quantify how much moisture has entered a coating from changes in its capacitance shows that a 5% uptake of water yields only a 24% increase in capacitance which would not be obvious on the logarithmic graphs here (and difficult to quantify reliably within the variations in results seen here).

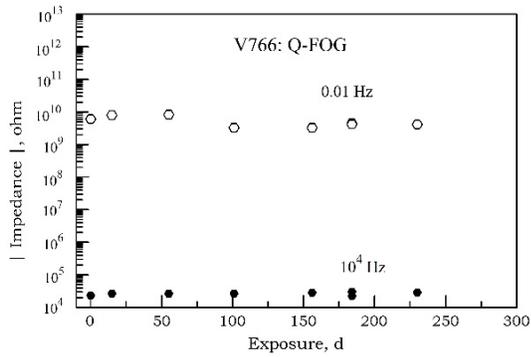
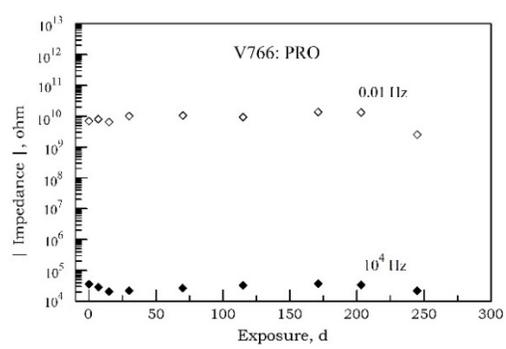
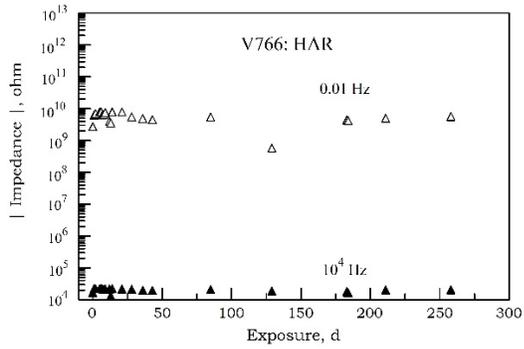
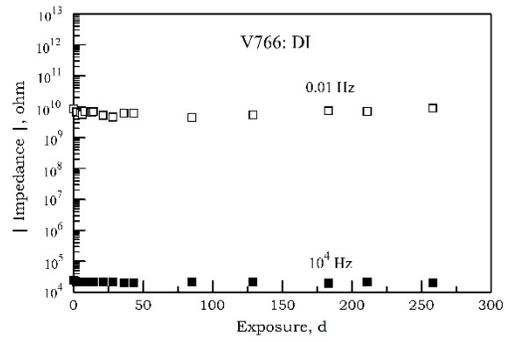
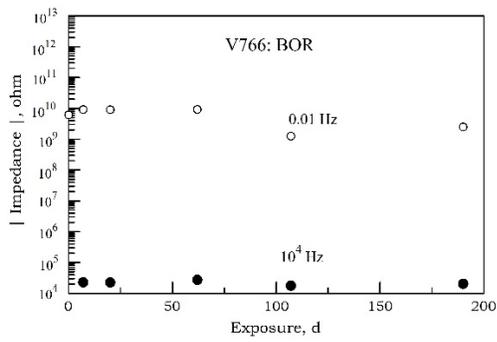
A system that permits current (ions, electron) to pass is conductive (resistive). The current is exactly in phase with the voltage change, i.e. zero phase angle. A purely capacitive system is a dielectric that can keep charges (ions etc.) separate. In a capacitor, a current passes only after the voltage changes and lags the voltage by 90° (a quarter cycle, $\pi/2$). If a coating can be thought of as a combination of resistive and capacitance, the resistive behavior can be seen at low frequencies, where the phase angle might be close to zero, and the capacitive behavior can be seen at higher frequencies where the phase lag would be close to 90° . As coatings fail, in service, they tend to change from being good capacitors to exhibit more resistive behavior.

Both the impedance at low frequency and at high frequency are linearly proportional to the intact thickness of the coating film, so thick films have higher values and should have better barrier properties regardless of other properties, and vice versa.

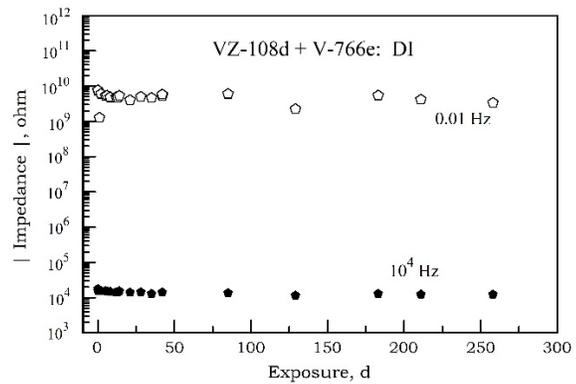
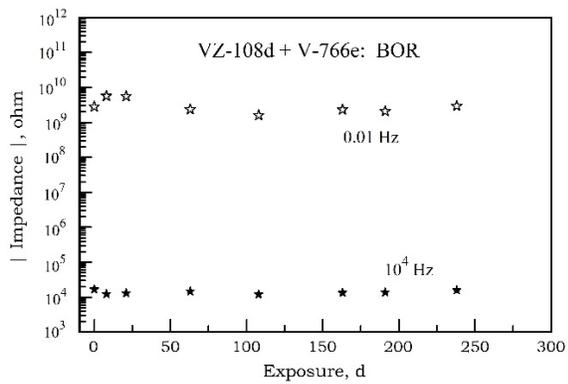
Each of these plots is labeled with the coating material and the exposure type, see above.

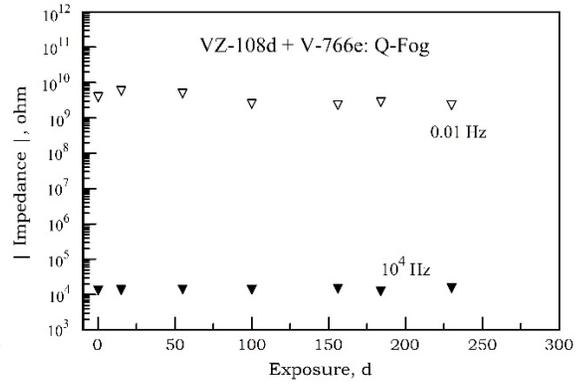
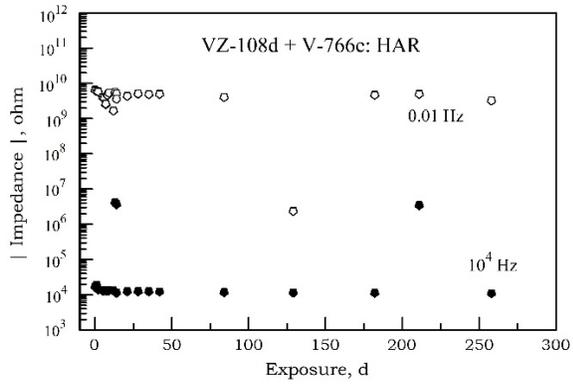
Analogous graphs derived from the changes in phase angle with exposure have not been attempted due to the variations in the data. Phase angle is constructed from the ratio of the in-phase and out-of-phase components of the impedance rather than the modulus of the impedance so it should be sensitive to changes occurring but it is also more sensitive to experimental issues. Nevertheless, some comments on the phase angle changes are given in the discussion.

Vinyl Formulation V766e

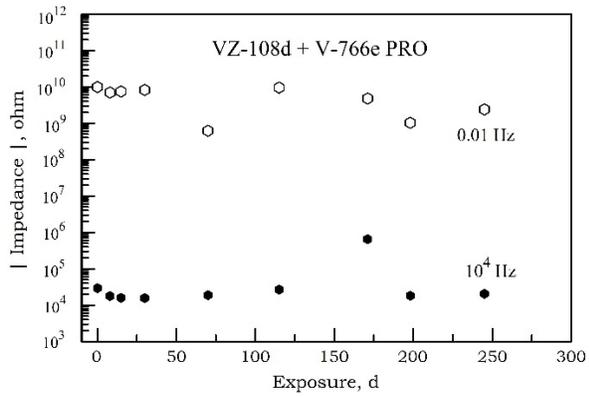


Topcoat Formulation V-766e over Primer VZ-108d

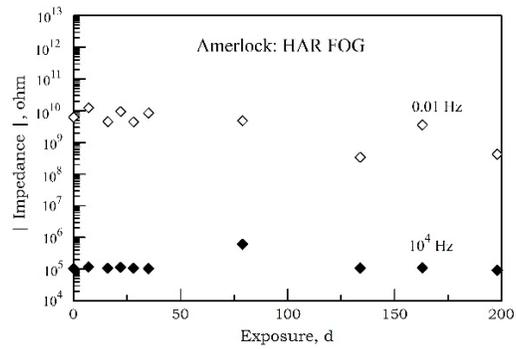
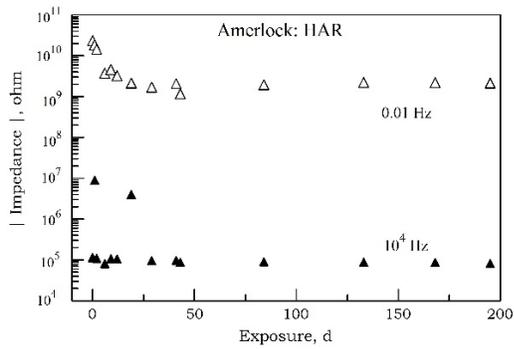
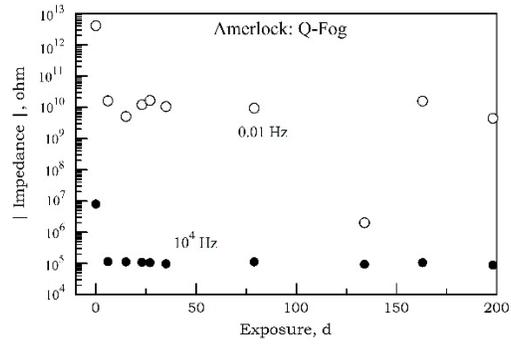
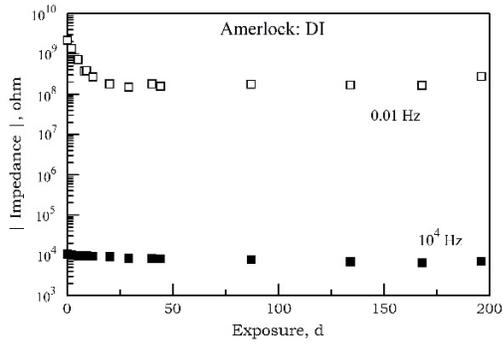




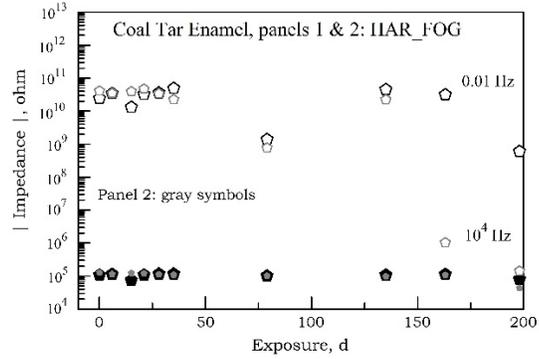
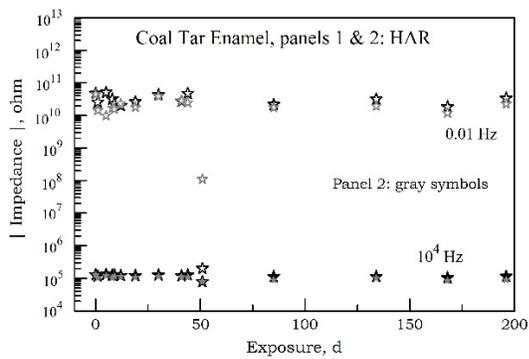
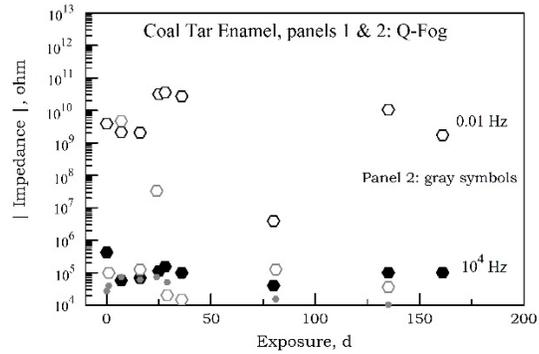
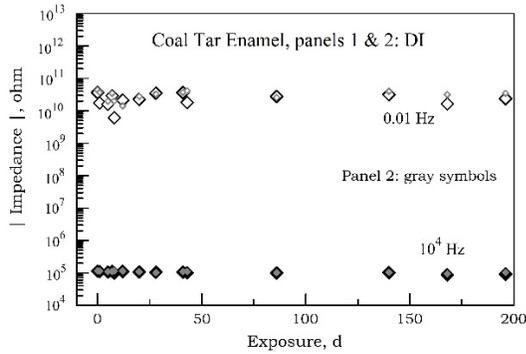
(Originally labelled VZ108d PRO)



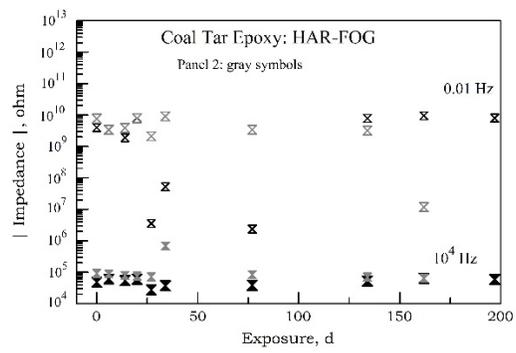
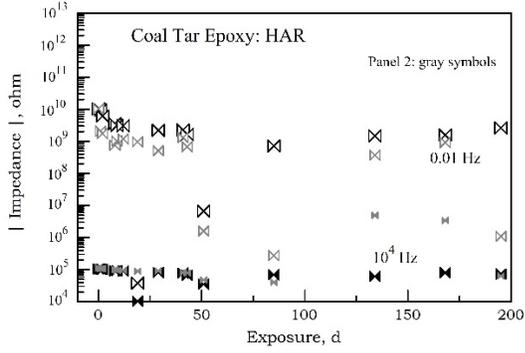
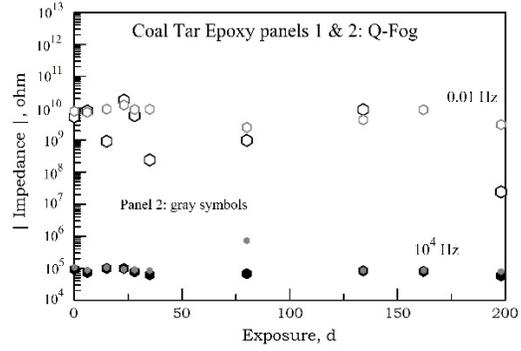
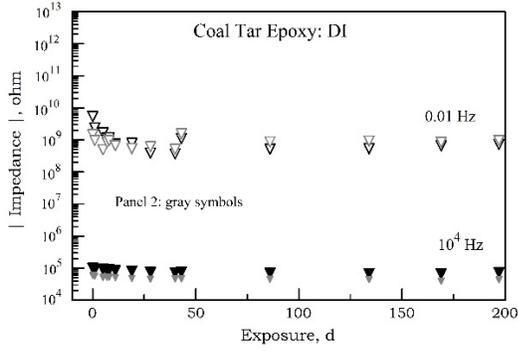
Amerlock



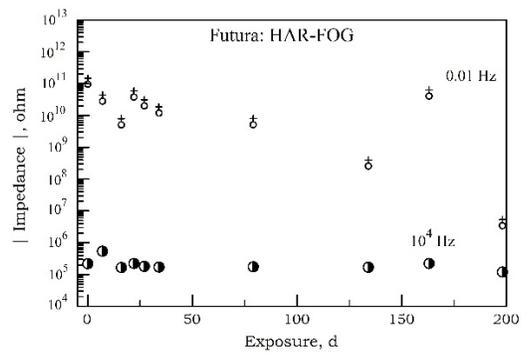
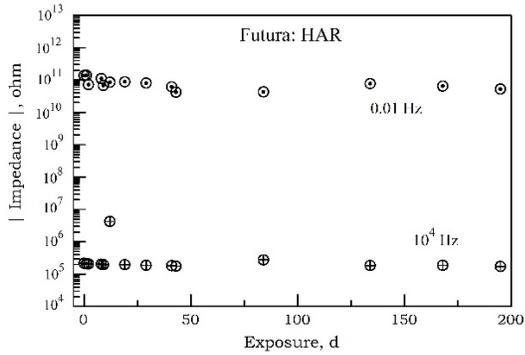
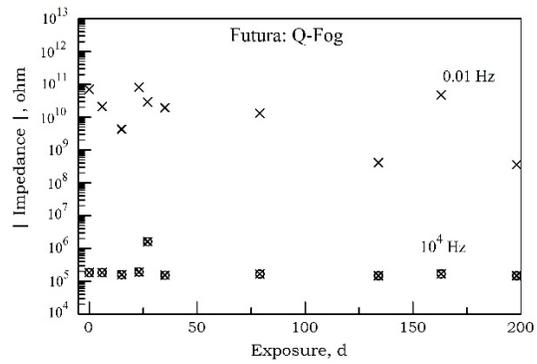
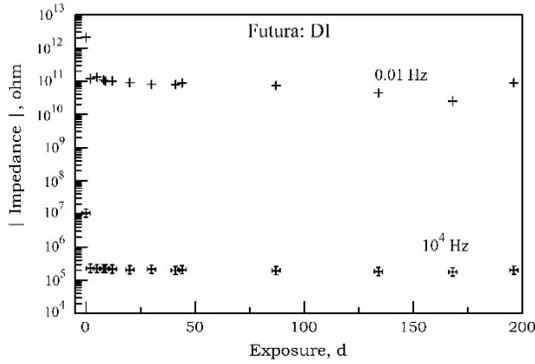
Coal Tar Enamel



Coal Tar Epoxy



Futura



Discussion

There are some systems where the results are inconsistent, which is most probably due to unseen experimental vagaries rather than a problem with the coating itself. Careful reconsideration of some of the individual EIS spectra may reveal trends that are not apparent at present.

Vinyl Coatings: V766e, VZ108d

It is difficult to perceive a systematic reduction in impedance at 0.01 Hz or 10^4 Hz in any of the exposure protocols used here where the topcoat is used. There may be some small reduction in impedance with exposure but there are fluctuations in the results that disguise any small trend that might be present. The BOR exposure seems to have a small effect on the low frequency impedance for the V766 by itself and in conjunction with the primer, but not on the high frequency results. If there is any loss in coating resistance caused by the ultraviolet radiation, it is not causing a perceptible increase in water uptake as measured by the capacitance. If one examines the changes in phase angle (graphs available in a separate file) one might say that QFOG and DI exposure have a more progressive effect than the other types of exposure for the topcoat alone, but in combination with the primer, the BOR and QFOG exposures show a greater effect. "Progressive" in this sense implies a gradual change with exposure rather than a sudden change (which might be an artefact).

Epoxy: Amerlock

The epoxy coating shows a consistent reduction in low frequency impedance over the first few days as the exposure continues, except perhaps in the alternating Q-Fog (DHS version) - DHS immersion cycle where there is only a slight reduction in the low frequency impedance. This consistent with changes seen in phase angle. The high frequency impedance shows some downward trend with exposure, showing that there is water uptake, but there is enough variation in the data to make quantification unreliable.

Coal Tar Enamel.

The results from exposure in Q-Fog, in particular, and the HAR-FOG exposure show considerable inconsistencies. The phase angle results may show some greater susceptibility in the HAR-FOG than the other exposures. These may be experimental artefacts from sample preparation or sample handling. Otherwise, it seems probable that Coal Tar enamel is very stable in exposure and shows no sign of moisture absorption. Coal Tar Enamel is somewhat resistive in nature due to its composition so one can see a resistive component on the Bode plots in the initial results as well as later in a series.

Coal Tar Epoxy

This combination of coal tar and epoxy seems to behave like the more conventional epoxy (Amerlock) in that the low frequency impedance decreases significantly early in the exposure. In this case, the two exposures using the immersion in DHS yield the less consistent results.

Polyurethane (Futura)

If one looks over the data, one can see a small downward trend in the low frequency impedance data, but it is not nearly as evident as the trend seen in results from the epoxy and coal tar epoxy samples. This coating seems to be comparatively unaffected by DI water but its impedance diminishes (and its phase angle becomes more resistive in nature) when there are salts dissolved in the water used in the exposure.

Exposure Protocols.

There is a great deal of data here within which it is difficult to say that one type of exposure is more useful or aggressive than the others. Each of the coating types has its own pattern of response and susceptibility which is probably a more realistic conclusion than extrapolating coating performance using data from only one type of exposure.

Summary

The original data files have been transformed into spreadsheet files so that the results can be much more easily studied. Bode plots have been made and are given in a separate file.

The investigations, so far, of these data show that the vinyl and coal tar enamel coatings exhibit much less systematic reduction in performance, as measured by EIS, than the epoxy coating, the coal tar epoxy coating and the polyurethane coating. However, within that lesser group, the polyurethane coating changes much less than the epoxy or coal tar epoxy and thus is the best candidate for a barrier coating from within this group.

There is no single exposure procedure in those explored here that discriminates clearly between each of the coatings. These coatings are very different in composition, so it is unlikely that they would all follow the same pattern of behavior in a series of environments. Corrosion is probably determined by acidic ions e.g. chloride, rather than just water and oxygen, so laboratory exposure testing should include ionic species. Apart from that, unfortunately, an accurate, predictive, accelerated testing protocol has yet to be devised by anyone.

Appendix: formulation

Formula V-766e (AP), Vinyl-Type White (or Gray) (from Beitelman)

INGREDIENTS	Percent by Weight
Vinyl Resin, Type 3	5.4
Vinyl Resin, Type 4	11.1
Titanium Dioxide and (for Gray) Carbon Black	12.5
Diisodecyl Phthalate	2.9
Toluene	11.2
Nitropropane Solvent	48.0
Methyl Ethyl Ketone	8.7
Ortho-Phosphoric Acid	0.2
<i>Total</i>	100.0

Appendix B – Material Characterization Report

To: Dr. D. Tordonato, Bureau of Reclamation
Cc: Dr. B. J. E. Merten, Dr. A. D. Skaja, Bureau of Reclamation.
From: S. G. Croll, North Dakota State University
Date: 20th December, 2016

Report: Material Characterization

This report summarizes the work done at North Dakota State University in characterizing materials from the Bureau of Reclamation.

Work on the EIS data is reported separately from the analytical work done on this project simply due to the amount of the material, but the conclusions are repeated in the summary here. A list of the references used is at the end.

Materials investigated:

Free film of vinyl topcoat formulation V766e with vinyl zinc rich primer formulation VZ108d.
Free film of vinyl V766e only.
Panel coated with high solids epoxy: PPG Amerlock 2
Panel coated with Coal Tar Enamel
Panel coated with Coal Tar Epoxy
Panel coated with aromatic polyurethane: ITW Futura Protec II
Wacker Vinnol 15-45M resin powder
Wacker Vinnol 15-50 resin powder.

Experimental Methods

All thermal analysis and infrared spectroscopy was performed by Dr. Chunju Gu, Laboratory Manager for the department of Coatings and Polymeric Materials, NDSU.

Samples were cut or otherwise derived from the coated panels, free films and resins supplied by the Bureau of Reclamation.

These brief descriptions are of the techniques listed in the statement of work. Other data is presented and a description of the method is given with the data.

Dynamic Mechanical Thermal Analysis, DMTA

In order to make free films for mechanical measurements, Wacker Vinnol resins were first dissolved in cyclohexanone to make free films, but ultimately they were compression molded because the solvent cast films retained solvent tenaciously. The equipment used was a TA Instruments, Q800 Dynamic Mechanical Analyzer.

Dynamic Scanning Calorimetry, DSC:

TA Instruments, Q1000 Modulated Differential Scanning Calorimeter. There is some difficulty if making a suitable chip from a cured coating; a sample should be flat enough to maintain good thermal contact with the DSC pedestal via the bottom of the aluminum pans used to contain the sample. It was found easier to scrape material from the surface of the harder coatings, e.g. the Amerlock, in order to make a suitable powder. Differential Scanning Calorimetry, DSC, was done at 5 degree/minute in hermetically sealed pans starting from -50 °C to 300 °C. Starting at a low temperature means that any transitions occurring around normal ambient temperatures are clear, and the data continues usually until high temperatures where the material degrades. However, graphs presented here display only the temperature range that was significant.

The glass transition temperature was identified from the point of inflection in the heat flow which can be done for all the samples and it avoids the effect of any physical aging overshoot, as seen in the Vinnol resins, for example. The estimates could be made with an uncertainty of ± 2 °C, unless otherwise stated.

Thermogravimetric Analysis, TGA:

The heating rate used was 10 degrees/minute and the experiments were conducted under a nitrogen atmosphere in a TA Instruments Q500 Thermogravimetric analyzer. The temperature derivative of the weight loss is also shown with the graphs of weight loss.

Infrared Spectroscopy

Infrared spectra were taken in reflection using a diamond anvil ATR accessory (SMART iTR™) with a Nicolet 8700 FTIR spectrometer. Spectra from all the samples could be obtained with this accessory and compared readily.

X-ray Diffraction, XRD

XRD was performed by Dr. Angel Ugrinov, senior scientist in the Department of Chemistry and Biochemistry at NDSU, on a Bruker D8 Discover with GADDS Multipurpose X-Ray Diffractometer (XRD) using the copper K α line at 0.15418 nm. The scans were done using an angle increment of 0.02 degree and a time per step of 1 sec. This is a standard, relatively slow scan speed.

Scanning Electron Microscopy, SEM

Scott Payne of the Electron Microscopy Laboratory at NDSU performed all the examinations using the electron microscopes. The equipment:
JEOL JSM-6490LV high-performance variable pressure SEM,
JEOL JSM-7600F field-emission SEM,
JEOL JEM-2100 multipurpose analytical high-resolution transmission electron microscope (TEM).

Electron Diffraction

Sometimes, it is difficult to produce a sample that can be examined in X-ray diffraction to determine its crystallography. For example, a sample where there might only be small regions of order that are difficult to detect in a normal experiment XRD typically studies more macroscopic samples, e.g. powder samples or samples that have a substantial number of crystals. In a

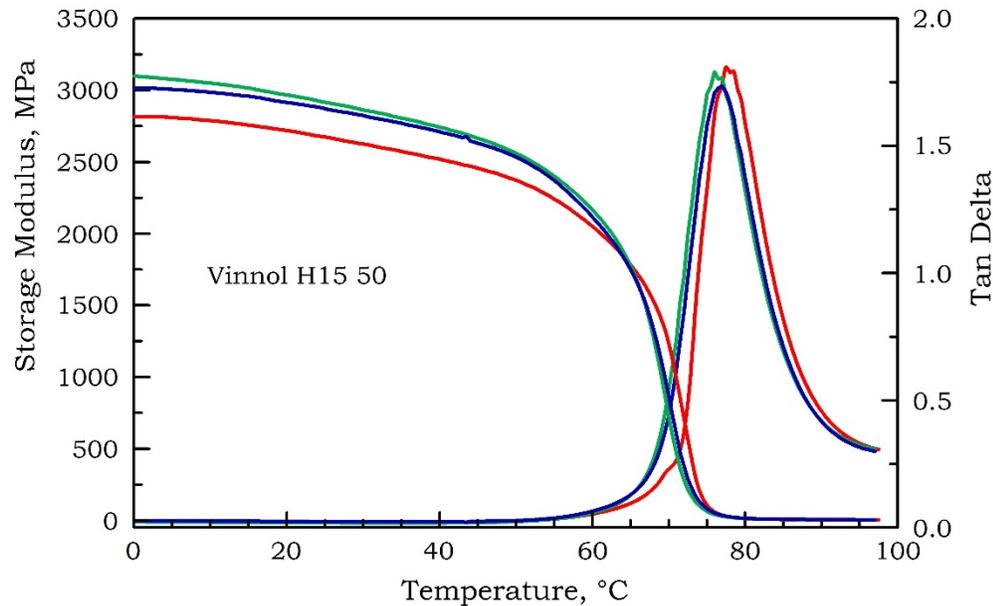
transmission electron microscope, TEM, electrons are accelerated to high and well defined energies, ~200 kV, that are diffracted by structures of the same spacings that are examined by x-rays (although the electrons have much shorter effective wavelength). However, the useful advantage here is that in a TEM a very small region may be focused on and examined.

Results

For simplicity, the results are grouped by sample and material, not technique. The vinyl systems are first, with the coal tar group next, and the modern coatings at the end.

1. Wacker Vinnol H15-50.

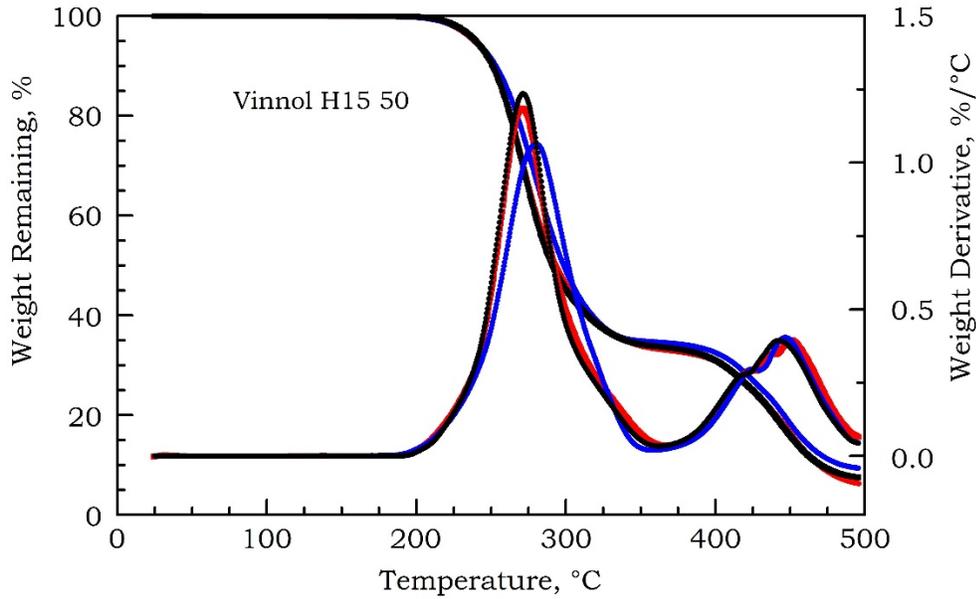
Dynamic Mechanical Thermal Analysis, DMTA



This material is a copolymer of vinyl chloride and vinyl acetate. The glass transition temperature given by the manufacturer is 70 °C. The DSC results are consistent with this, but the dynamic mechanical thermal analysis on solvent cast films gave rather low results due to solvent retained in the resin from the film preparation. Additional samples were made by compression molding thin plaques from the resins, and those samples gave results that are much more consistent with the DSC results and expectations from the manufacturer's literature. It was difficult to cut 3 replicate test strips for testing since the compression molded material was much thicker than a solvent cast film and very tough.

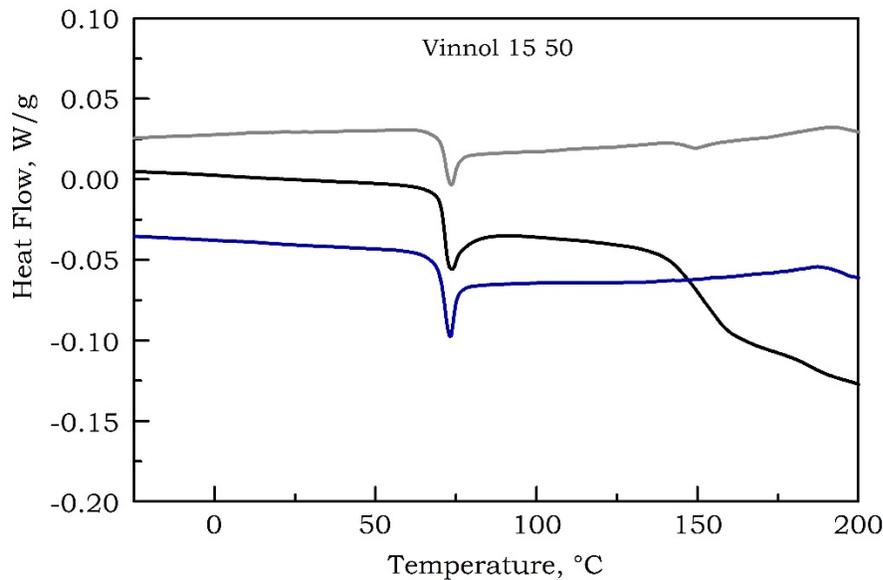
The storage modulus above the glass transition is very small and there is no sign of an increase with temperature which would indicate a significant level of crosslinking.

Thermogravimetric Analysis, TGA



TGA results were obtained on the powdered resin that was supplied by the Bureau of reclamation and were very consistent. In a nitrogen atmosphere, the vinyl polymer is stable until the temperature exceeds 180 °C, at this temperature rate (10 degrees/minute). There are two large steps in the weight loss. The one at 200-300 °C is probably the dehydrochlorination process [1] which also happens to PVC during weathering [2].

Differential Scanning Calorimetry, DSC

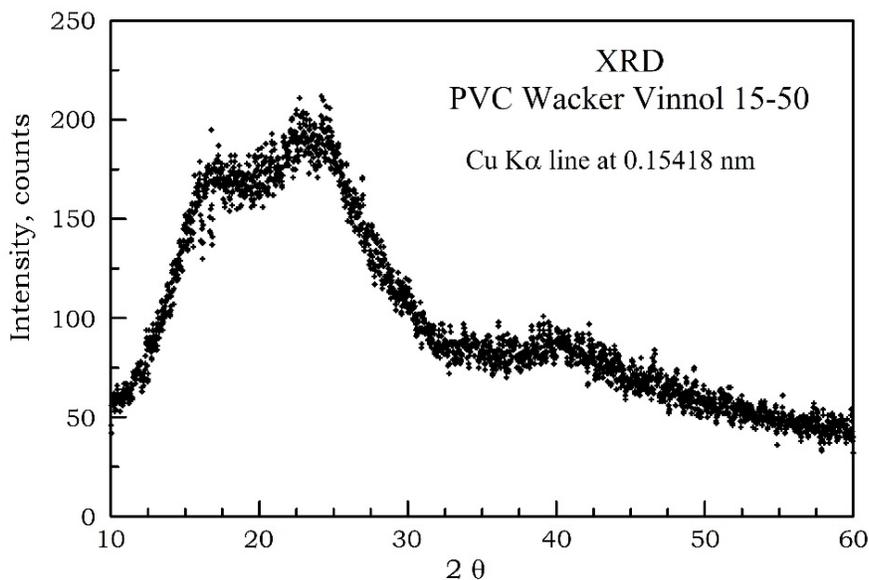


The results from three resin powder samples are shown in the diagram. The difference in absolute value is probably due to minor differences in thermal contact with the DSC heating

pedestal. The glass transition temperature is approximately 70 °C, depending on how one identifies it; here the point of inflection on the downward slope is at 72 °C. If the temperature is continued to 300 °C, there is an endotherm that is sometimes smooth (depending on the integrity of the hermetic pan containing the sample) and reminiscent of a melting peak but it is almost certainly due to loss of material, i.e. the decomposition noted in the TGA results, however, it is shown in the results for the Vinnol 15 45M resin.

X-ray Diffraction, XRD

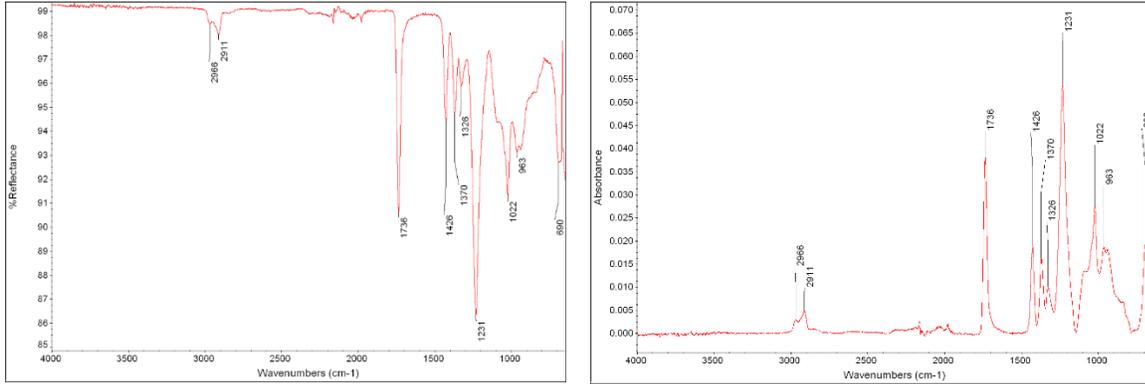
Results for the Vinnol 15-50 resin are shown in the following graph.



The diffraction does not show sharp peaks that would demonstrate the presence of crystals. The broad, poorly defined peaks are characteristic of the diffraction patterns seen in amorphous solids. However, one can calculate the spacing corresponding to the peaks at 16.6, 24, and 40 degrees seen in the graph. These correspond to spacings of 0.534 nm, 0.371 nm and 0.225 nm respectively. One should remember that Vinnol 15-50 is a copolymer containing 14% of vinyl acetate, so it is less likely to form crystals than pure PVC. The spacing of 0.534 nm is slightly larger than the 010 crystal spacing (0.524 nm) [3] and 0.371 is slightly larger than the 210 spacing (0.366 nm) found for PVC crystals which suggest that these are the average spacings between polymer chains in an amorphous PVC resin. It is difficult to identify the crystal equivalent to the smallest spacing found here since there are several possibilities.

The possibility of very small crystals being present that are undetectable by XRD was investigated using electron diffraction in a transmission electron microscope, but this technique also failed to find any evidence of crystallinity.

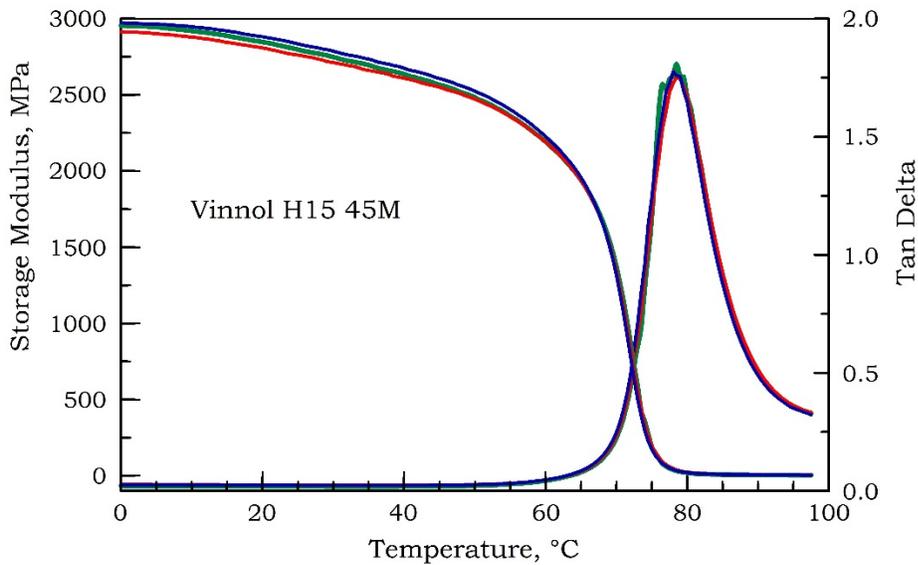
Fourier Transform Infrared Spectroscopy FTIR



The spectrum on the left is the original ATR (reflectance spectrum) which was converted to its corresponding absorbance spectrum, which is given on the right. The spectrum closely matches the expected spectrum of PVC [4, 5] with the added carbonyl peak at 1736 cm^{-1} and the shoulder around 1100 cm^{-1} , due to the acetate copolymer. The spectra for the two Vinnol resins and the two coatings systems are very close and very similar to that of PVC [4, 5] although the carbonyl peak from the vinyl acetate is readily apparent in the spectra. More investigation might reveal differences, but according to the manufacturer's literature, the two resins differ only by approximately 1% of a dicarboxylic acid which would be difficult to detect by infrared spectroscopy.

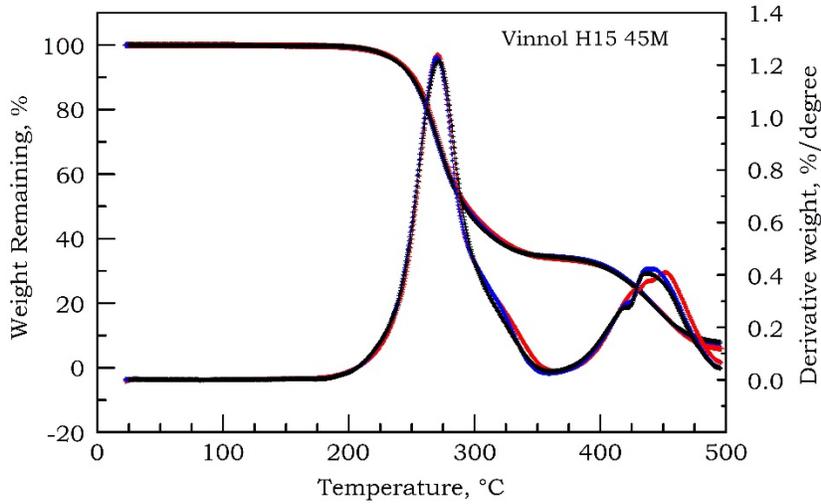
2. Wacker Vinnol H15-45M.

Dynamic Mechanical Thermal Analysis



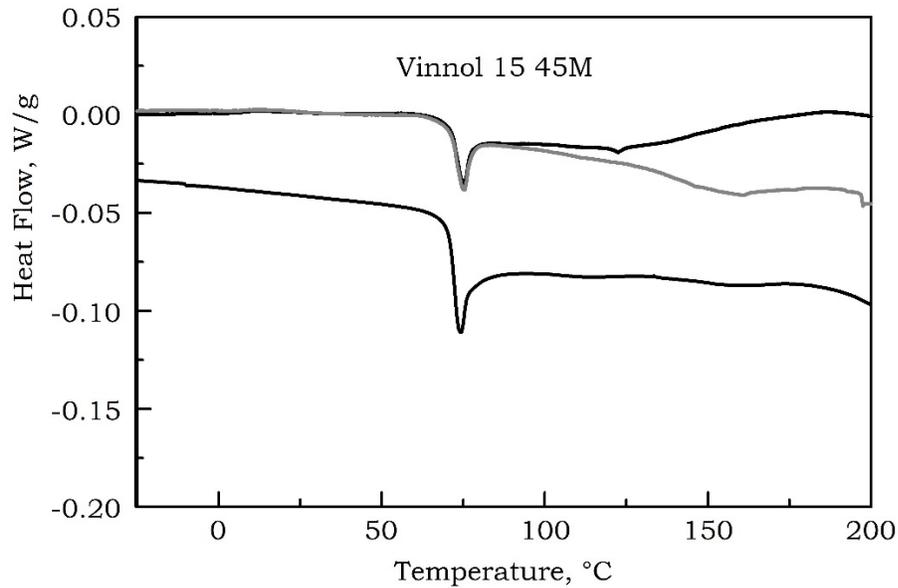
This data was taken using compression molded material. Again, as with the Vinnol 15-50 resin, solvent loss substantially reduced the moduli and the glass transition of the polymer. The Vinnol resins are very similar in their dynamic mechanical results.

Thermogravimetric Analysis TGA



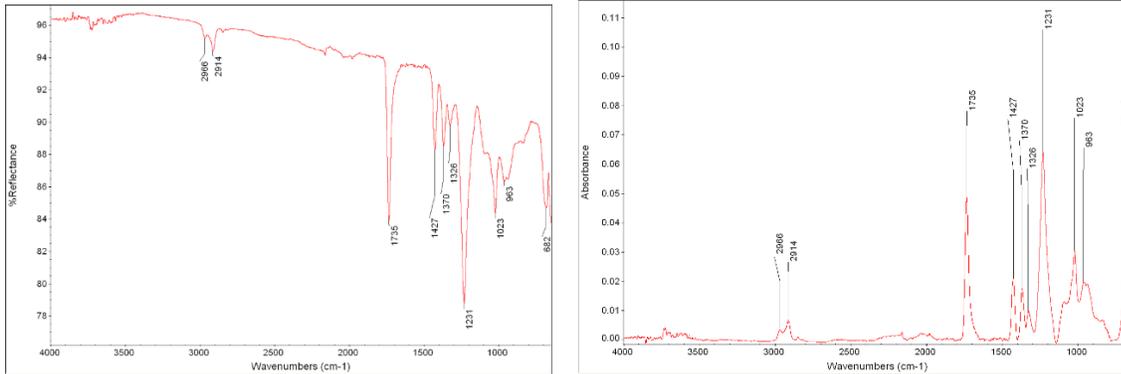
TGA does not reveal any perceptible difference between the two vinyl resins examined here.

Differential Scanning Calorimetry



There is no difference apparent in the DSC results between the two Vinnol resins.

Fourier Transform Infrared Spectroscopy FTIR

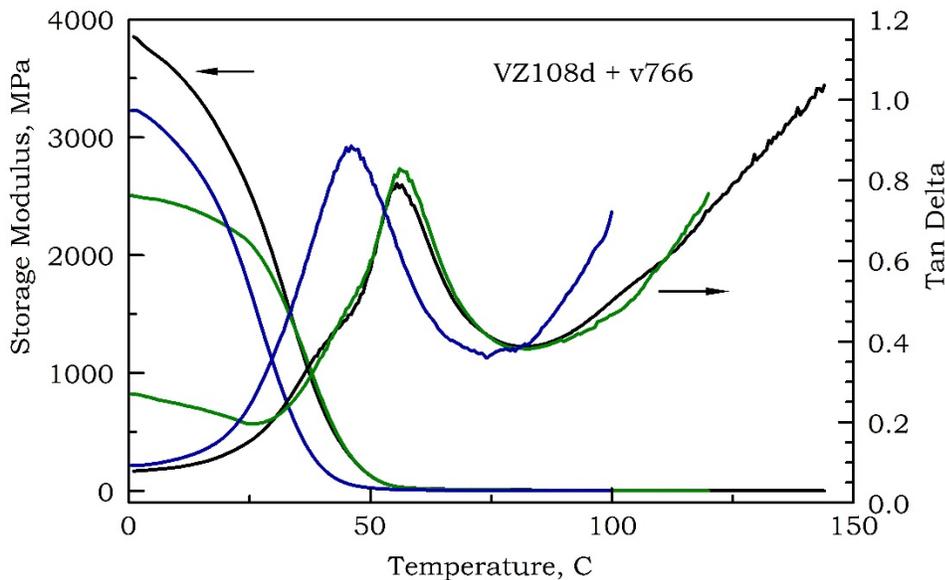


Again the calculated absorbance spectrum is on the right. There is no difference in the IR spectra between the two resins. The quantity of dicarboxylic acid in the 15-45M is only 1%; usually a moiety should be present at a level of more than 3% to be reliably distinguished. The acid would be observed in a broad -OH band around 2800 cm⁻¹ and a more complicated carbonyl region around 1700 cm⁻¹ with other details in the fingerprint region.

3. Army Corps of Engineers vinyl resin coating systems

(i) 1 coat of VZ-108d/ with 4 coats of V-766e.

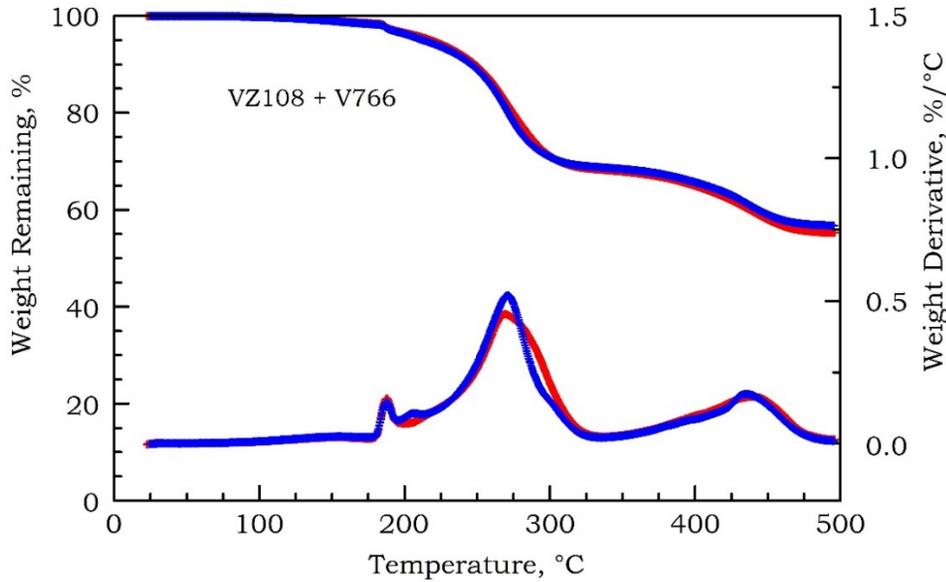
Dynamic Mechanical Thermal Analysis



These samples are quite glossy, hard and textured so proved to be difficult to grip for tensile testing in the DMTA, so the three samples showed some variation. Higher values of modulus are

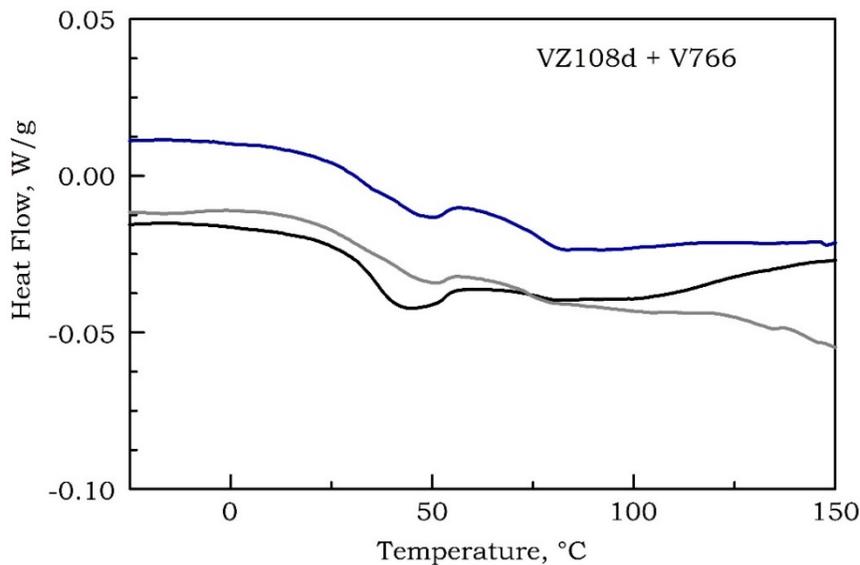
more likely to be the correct data. The tan delta peak is at 55 °C approximately and thus shows how the plasticizer has diminished the T_g from that of the Vinnol resin, 80 °C, see above.

Thermogravimetric Analysis



This type of sample has two materials in layers although the V766 should dominate since there is much more of it (see the electron microscope images). The pattern of weight loss is very similar to that of the resins themselves, although there is a slow, small weight that starts below 100 °C which is probably the plasticizer in the formulation. The pigment and extender remain at very high temperatures whereas the resin by itself (above) diminished to almost nothing at high temperatures.

Differential Scanning Calorimetry



The plasticizer has reduced and broadened the glass transition temperature compared to that seen in the resins. Using the same method of choosing T_g , at the inflection point results in a value of 37 °C. The results above 50 °C are different to the sample that was only V766, see below, probably due in some way to the small VZ108 component, although it is difficult to separate in these results.

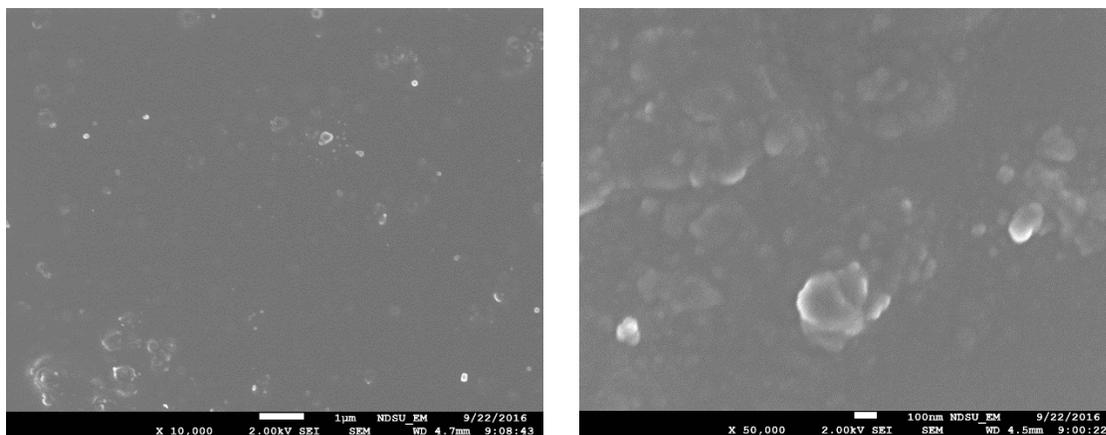
X-ray Diffraction, XRD

This was not done since XRD results on the Vinnol 15-50 resin (see elsewhere) showed that there was probably nothing to be gained. The only crystallinity to be observed would be that of the pigments and fillers in the coatings. Other results were sought using electron diffraction using a transmission electron microscope on the Vinnol resin, but did not find any evidence of crystallinity in the PVC resins.

Scanning Electron Microscopy, SEM

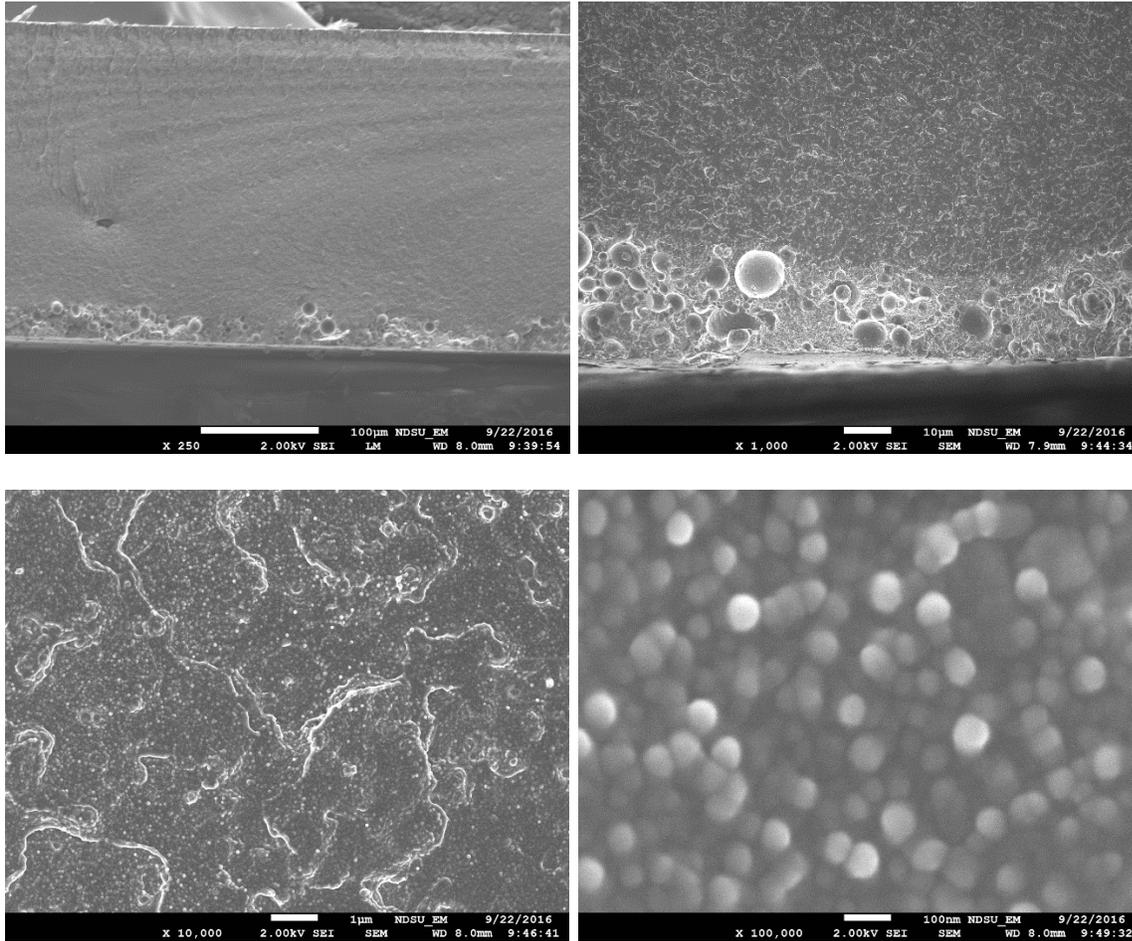
Scanning electron micrographs of the top surface and cross-section (liquid N₂ fracture) of this material were taken at a variety of magnifications in a JEOL JSM-7600F field-emission scanning electron microscope. This microscope is capable of very high magnification, as seen below (length scale bars are at the bottom of each image).

(i) Top, outer surface



The top surface was smooth and rather featureless, although at very high magnification both the carbon black (small round) and titanium dioxide (larger ~ 2-300 nm) pigment particles can be seen. There is good continuity between binder and particles.

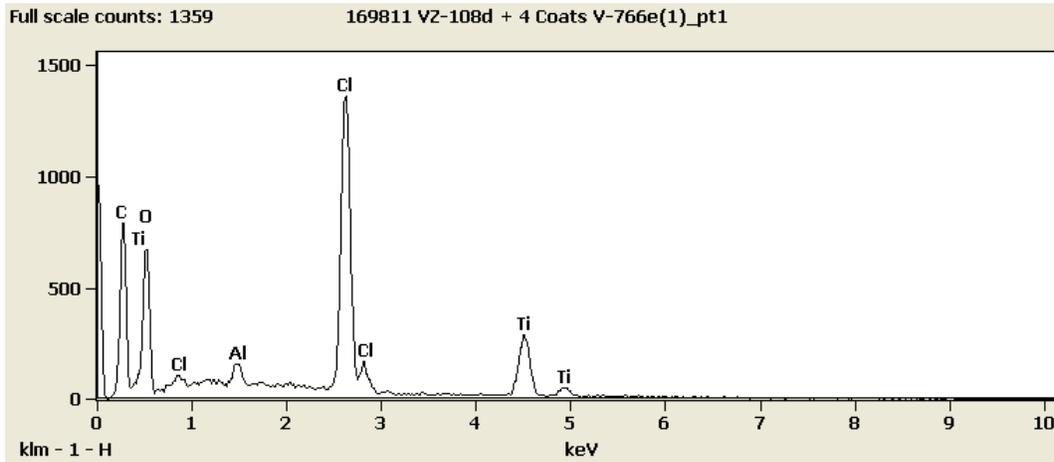
(ii) Cross section.



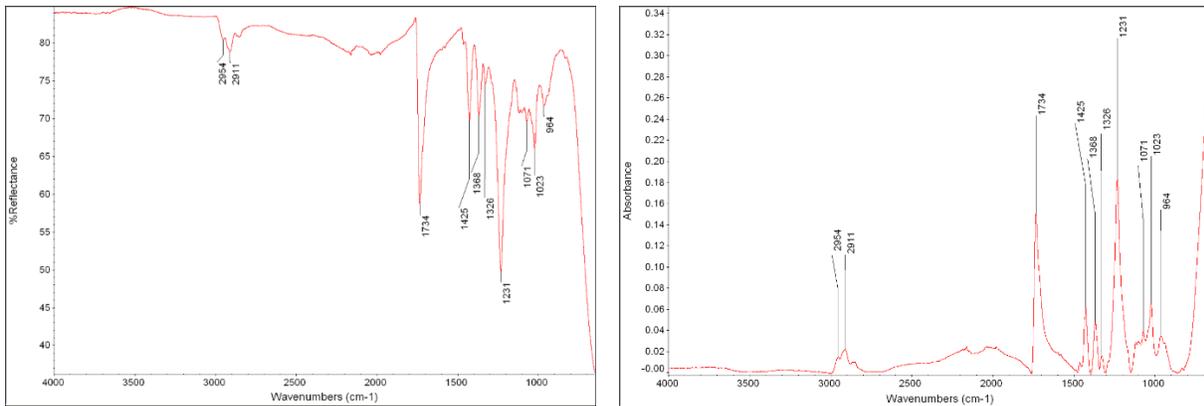
The low magnification view on the left top shows that the several applications of the coating and the primer layer at the bottom can be distinguished. An expanded view of the primer layer and its interface with the outer coating is shown in the upper right hand side. There appears to be good continuity at the interface with the primer. At high magnifications each of the vinyl layers looked very similar, see image in the lower two images. The round particles are carbonaceous and are almost certainly particles of carbon black pigment since they are the expected size. There seems to be very good cohesion between the carbon black particles and the binder here (contrast that with other images later). Carbon black particles are very much more numerous than the titanium dioxide pigment particles which are much larger (~ 300 nm).

(iii) Elemental Analysis

The X-Ray dispersive analysis of an area of the top surface is shown below. The titanium and aluminum signals are from the white pigment in the gray color. The chlorine signal is typical of rutile titanium dioxide made by the chloride process and the aluminum signal may have several sources but could also be from the hydrated alumina surface treatment on the titanium dioxide pigment.



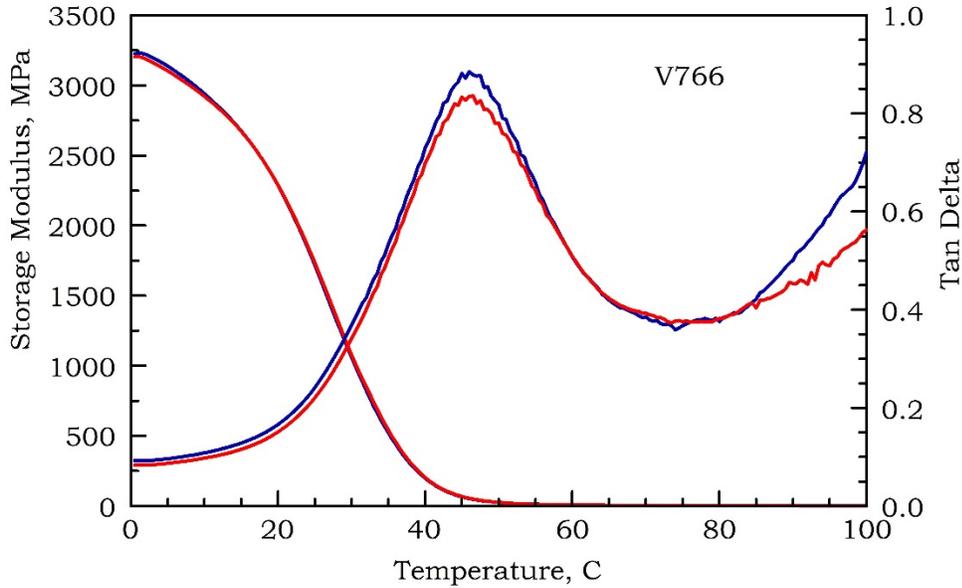
Fourier Transform Infrared Spectroscopy



The cured, pigmented coatings were examined with the ATR system on the V766 side. The reflectance spectrum is on the left and the calculated absorbance spectrum is on the right, as for the other materials. The spectra are not as well defined as those from the resins due to the diluting and scattering by the pigments and extenders, but there are no features that could be used to identify the other components.

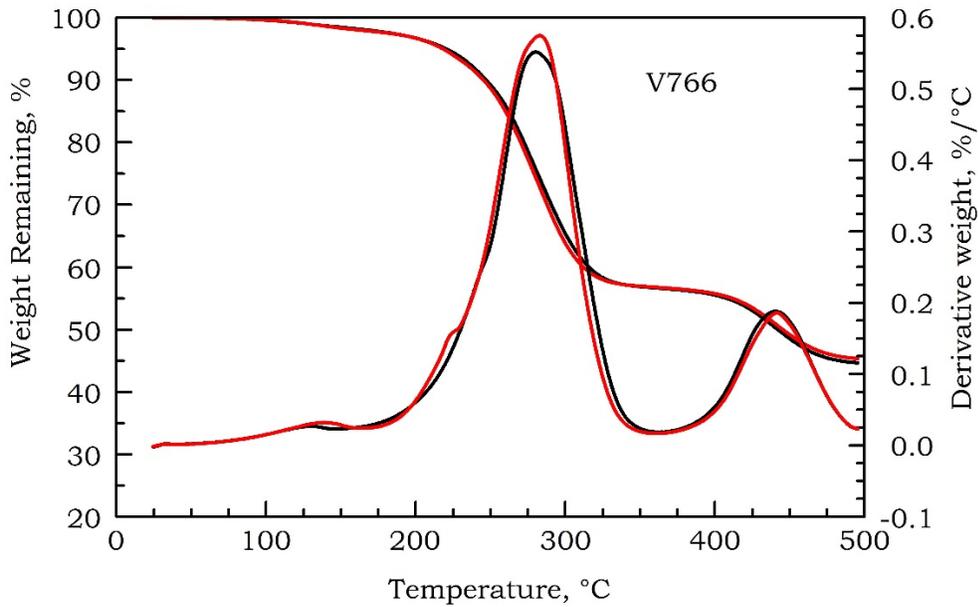
(ii) 5 layers of formulation V-766e

Dynamic Mechanical Thermal Analysis



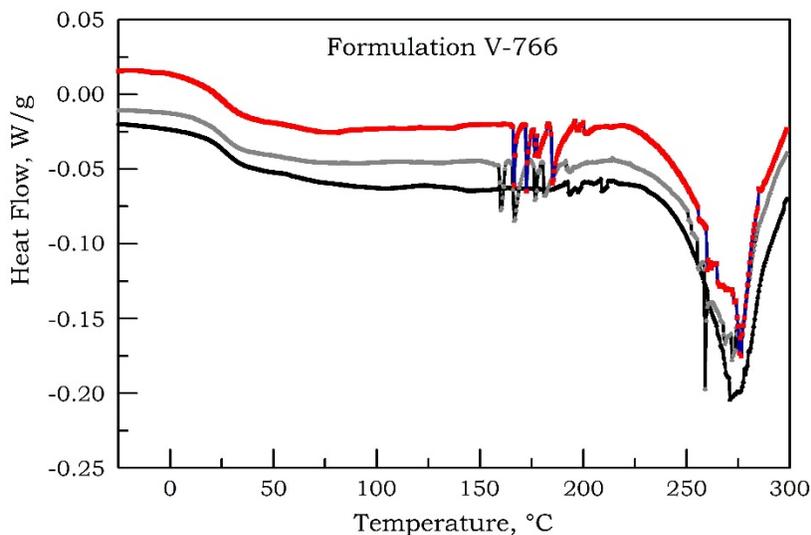
If one uses the temperature at the peak of the tan delta curve, the plasticized coating system has a T_g that is approximately 30 °C lower than the resin. In calorimetric results, the difference is larger. However, it is common that T_g results differ when examining different properties.

Thermogravimetric Analysis



As with the other cured film sample, there is a slow, small weight that starts below 100 °C which is probably plasticizer loss from the formulation. The weight remaining at high temperatures of pigment and extender content is less here because there is no zinc metal in a primer layer.

Differential Scanning Calorimetry



DSC results here are extended to 300 °C, to show the large apparent endotherm that is probably the dehydrochlorination, i.e. mass loss, of the resin although it does resemble a (broad) melting peak. The other noisy part of the results is probably due to the samples shifting in the DSC as volatile degradation products escape from the sample pan and possibly corresponds to the small weight loss process seen in the TGA over approximately the same temperature range. The glass transition temperature of the coating films, measured from the point of inflection is 26 °C.

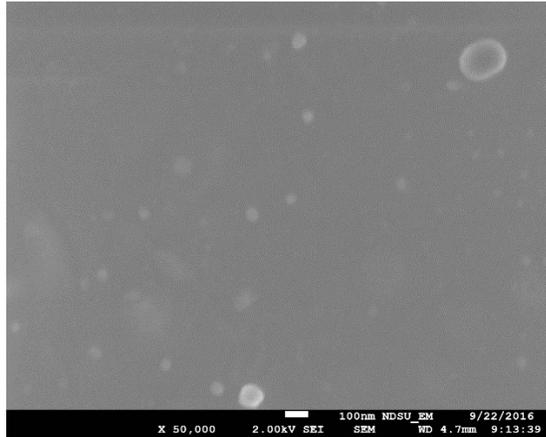
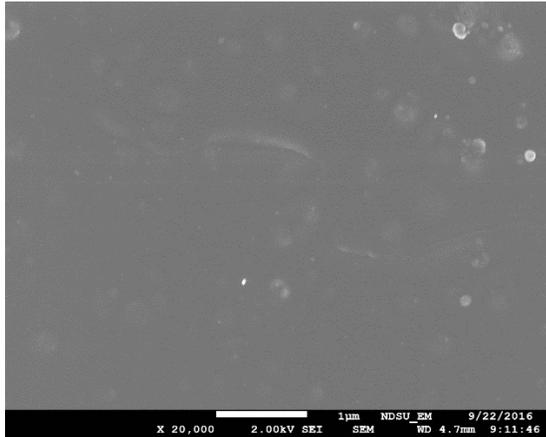
X-ray Diffraction, XRD

This was not done since XRD results on the Vinnol 15-50 resin showed that there was probably nothing to be gained. The only crystallinity to be observed would be that of the pigments and fillers in the coatings. Other results were sought using electron diffraction using a transmission electron microscope on the Vinnol resin.

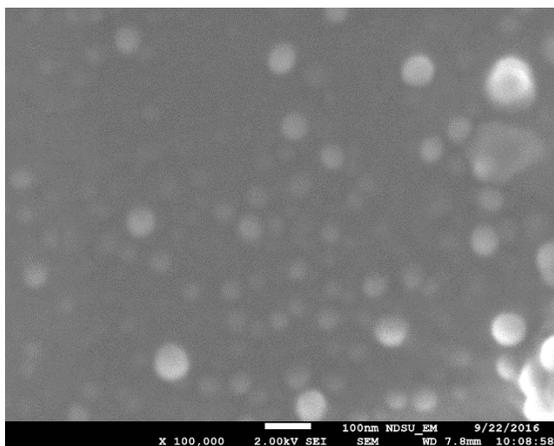
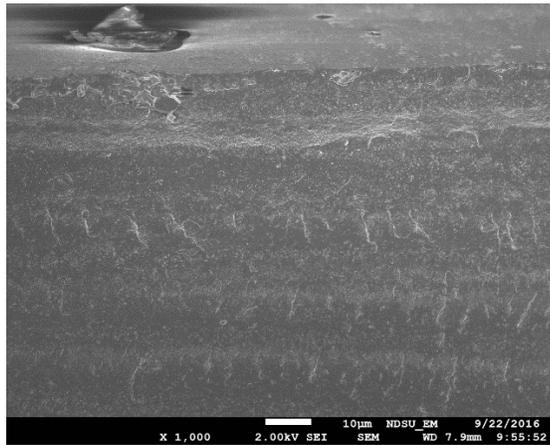
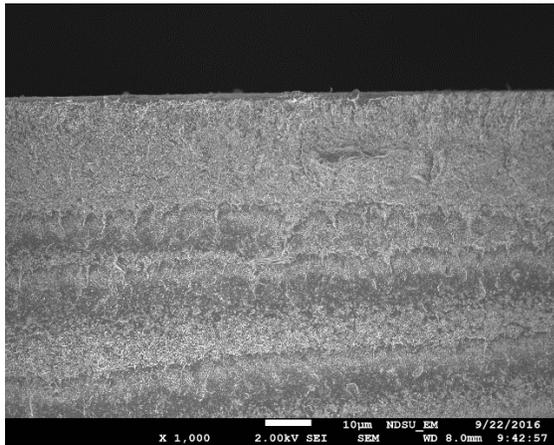
Scanning Electron Microscopy SEM

SEM images of this version of the vinyl coatings looked very similar to the one above, except that there was no primer layer.

(i) Top surface



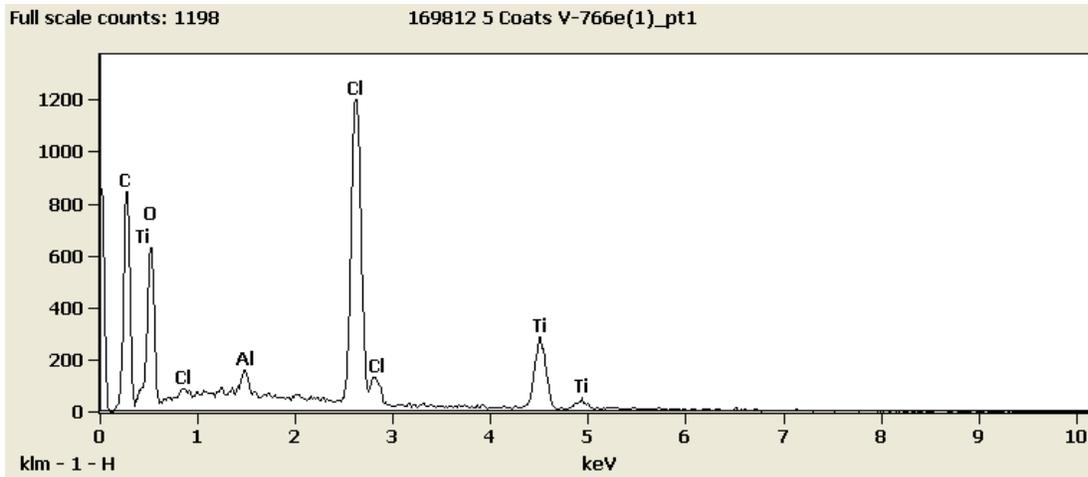
(ii) Cross section.



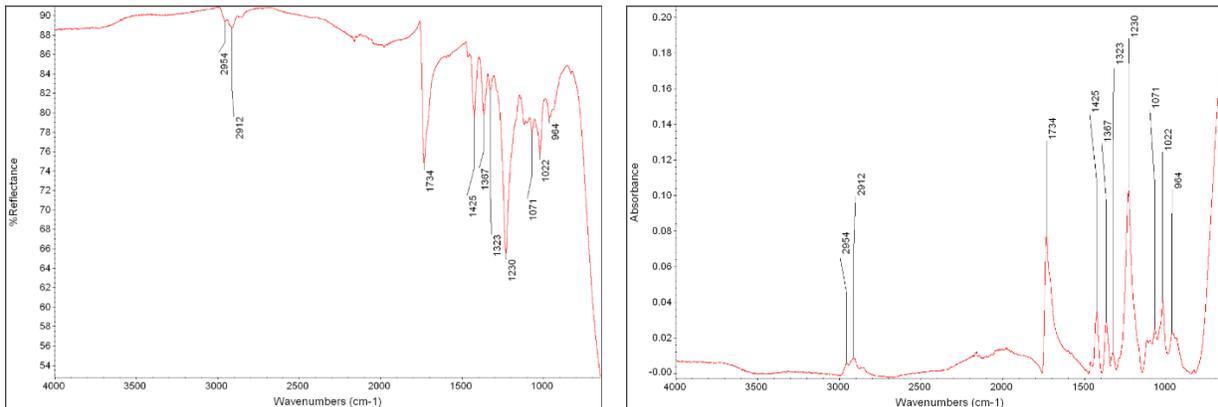
Again, the several applications of the coating can be distinguished and there appears to be good cohesion between the particles of pigment etc. and the binder.

(iii) Elemental Analysis

The X-Ray dispersive analysis of an area of the top surface is shown below. It is very similar to the elemental analysis done on the VZ108-V766 combination, above.



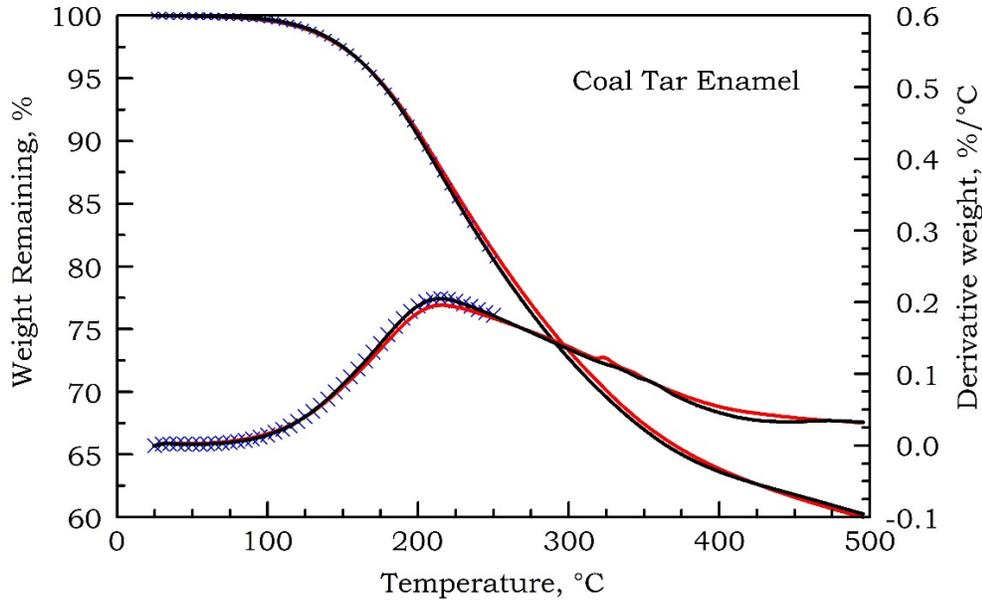
Fourier Transform Infrared Spectroscopy FTIR



The absorbance spectrum on the right is that calculated from the original reflectance spectrum on the left. These are indistinguishable from the prior results.

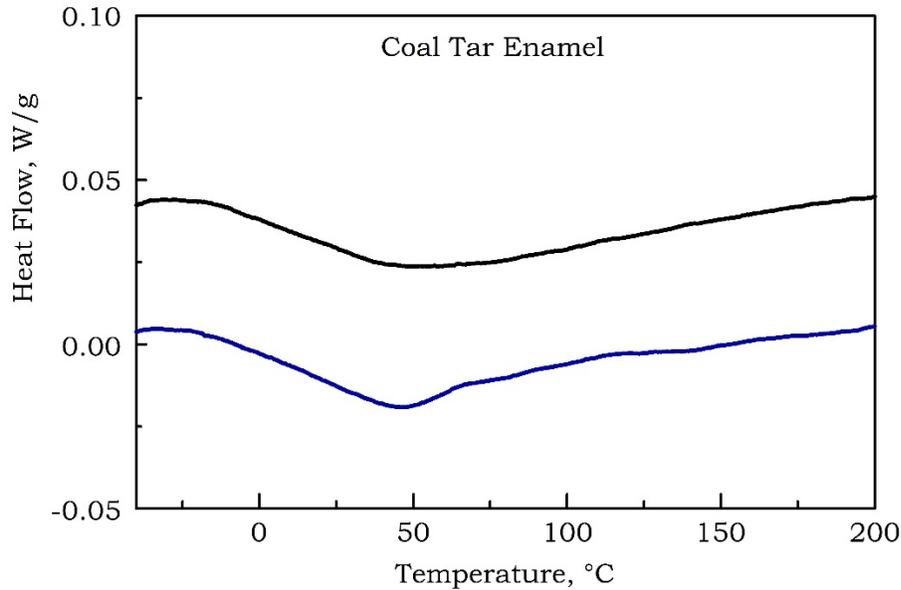
4. Coal Tar Enamel. AWWA Type II

Thermogravimetric Analysis



All the samples show the same gradual loss of weight as the temperature increases.

Differential Scanning Calorimetry



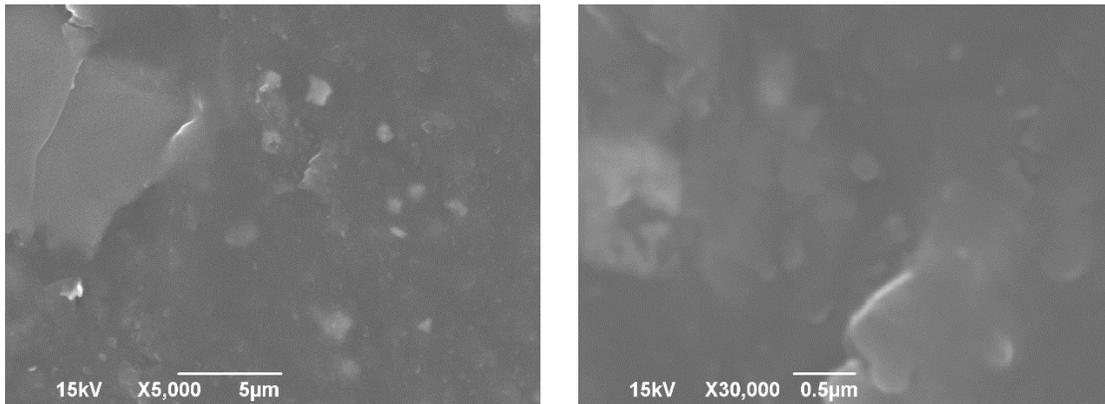
It is probably not justified to assign a glass transition temperature to coal tar enamel since it is a mixture of a wide variety of compounds where no single compound is in the majority, but if the same approach is used as for the other materials in this study, then the T_g would be $10 (\pm 10) ^\circ\text{C}$.

The glass transition temperature, T_g , of a coal tar pitch varies depending on the source and treatment of the pitch, and has been measured from -58 to 42 °C [6] with broad transitions.

Scanning Electron Microscopy

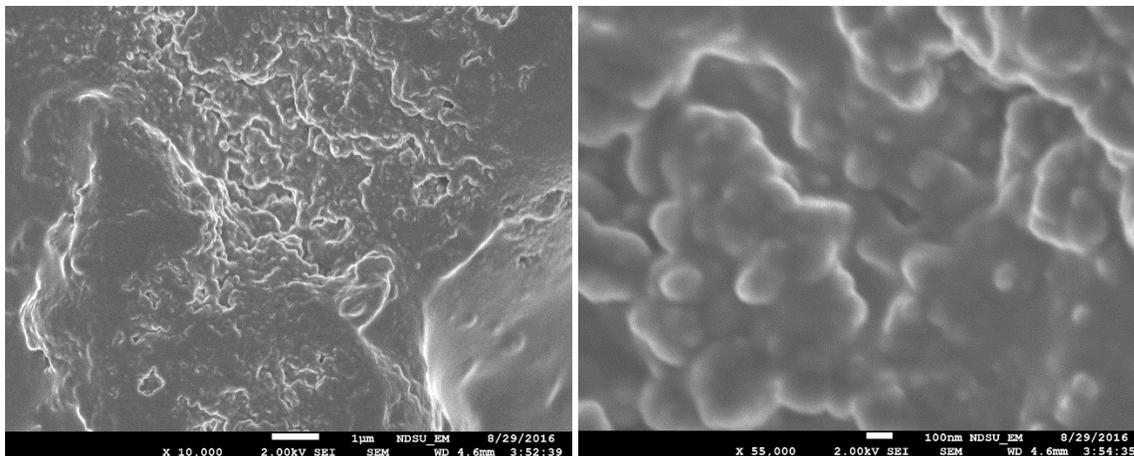
Although this was not part of the original scope of work, SEM images of the coal tar enamel are shown here. Small samples were taken from the fat edge on one of the panels.

(i) Exterior surface



These images above were taken with the JEOL JSM-6490LV high-performance variable pressure SEM where the sample was conductive enough that it did not need to be coated.

(ii) Cross Section

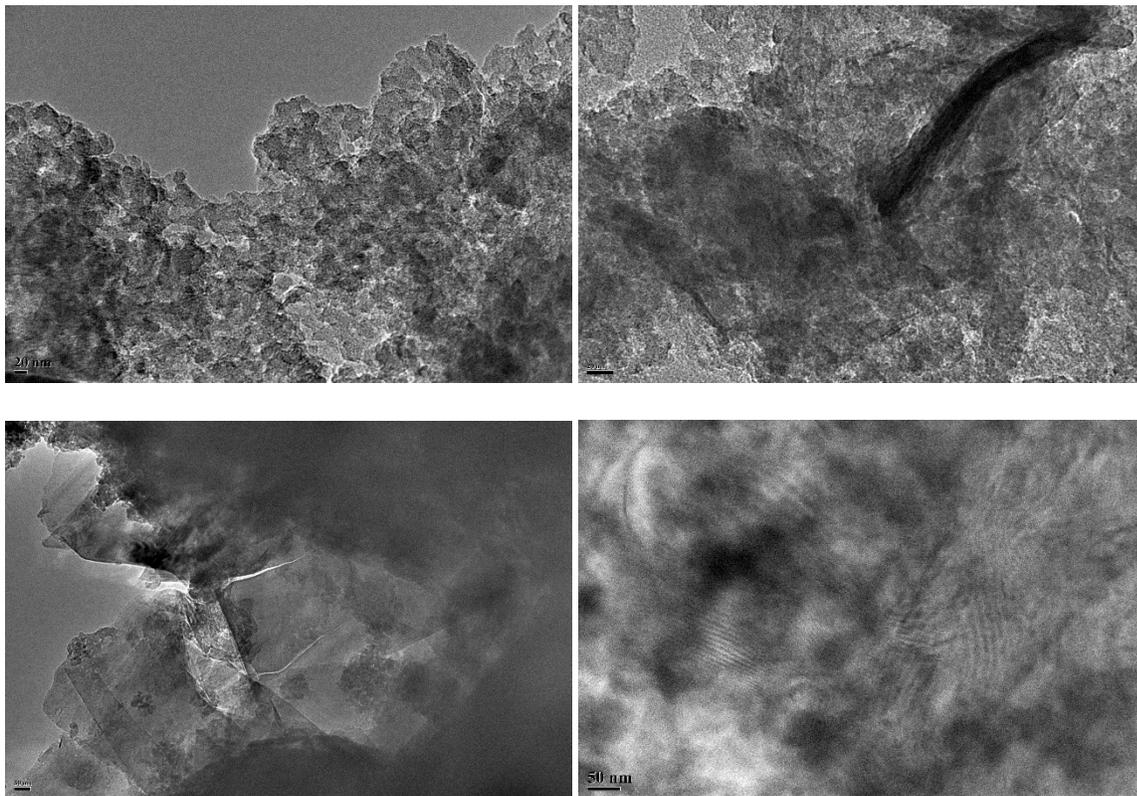


These images were taken in the JEOL JSM-7600F field-emission scanning electron microscope, as were those for the vinyl coatings. The samples had to be glued to a sample holder with conductive glue, but were otherwise uncoated. These show, again, that the binder has very good continuity with the particulate material.

An additional sample of coal tar enamel was available, from the Grand Coulee Dam Scroll case. This showed a different particulate shape, but otherwise was very similar.

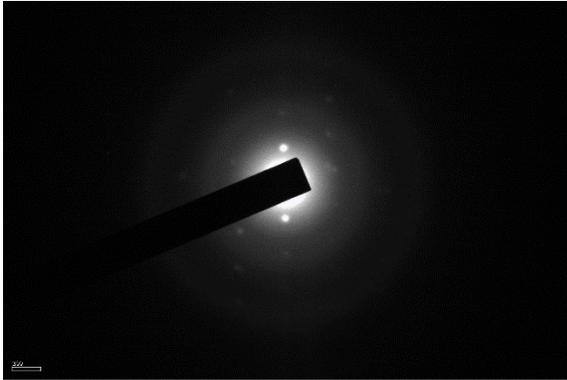
Transmission Electron Microscopy

Tiny particles suitable for TEM could be gathered from the debris made when the chip of material was cut for the SEM examination. TEM gives the opportunity to examine structures at very high magnification and to explore whether any part of the sample might give structural information based on electron diffraction. The images show amorphous material, thin flakes of probably mineral crystals from slate or talc minerals and a few regions that display some organization in the binder (lower right), but which are probably not crystalline.



Electron diffraction was measured in many of the areas. From the dimensions of the microscope, the energy of the electrons and the diffraction pattern, the spacing between crystal planes in a corresponding crystal can be determined.

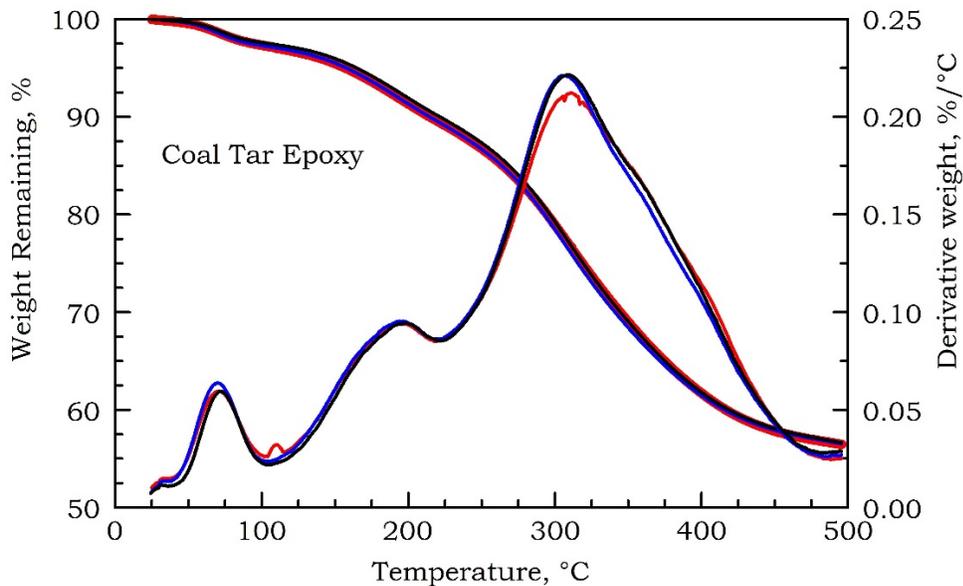
Some of the areas which were probably focused on an inorganic filler particle showed very distinct spots. Others, see image below, were much less distinct and had diffuse halos as well as spots.



Halos usually correspond to the average distance between molecules in an amorphous phase. The example diffraction pattern yielded the spacings (\AA) from the dots - 4.42, 3.54, 3.05, 2.90, 2.1, 1.92, 1.86, 1.24, and from the rings - 4.25, 2.48, 1.47. Several other regions of the sample had diffraction patterns that corresponded to spacings of 3.5 and 4.5 which seem to be associated with graphitic structure (see discussion). A more complete and rigorous investigation is outside this project, but might be rewarding in light of some of these images, especially those showing a banded structure.

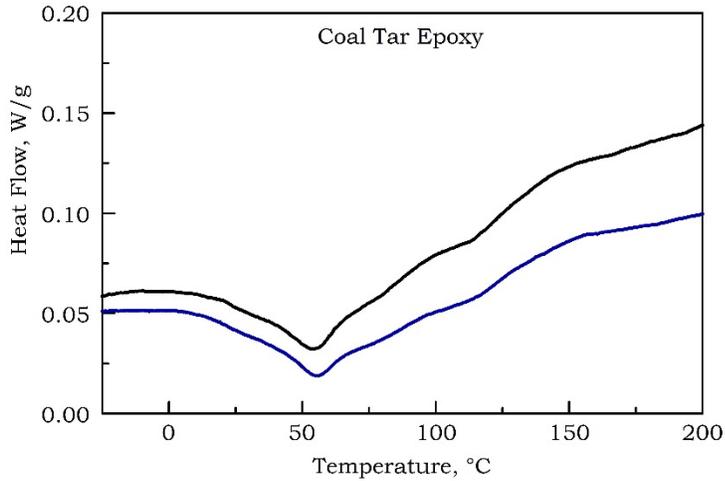
5. Coal Tar Epoxy

Thermogravimetric Analysis TGA



The coal tar epoxy shows approximately the same final weight loss as does the coal tar enamel. However, there are three distinct weight loss regimes.

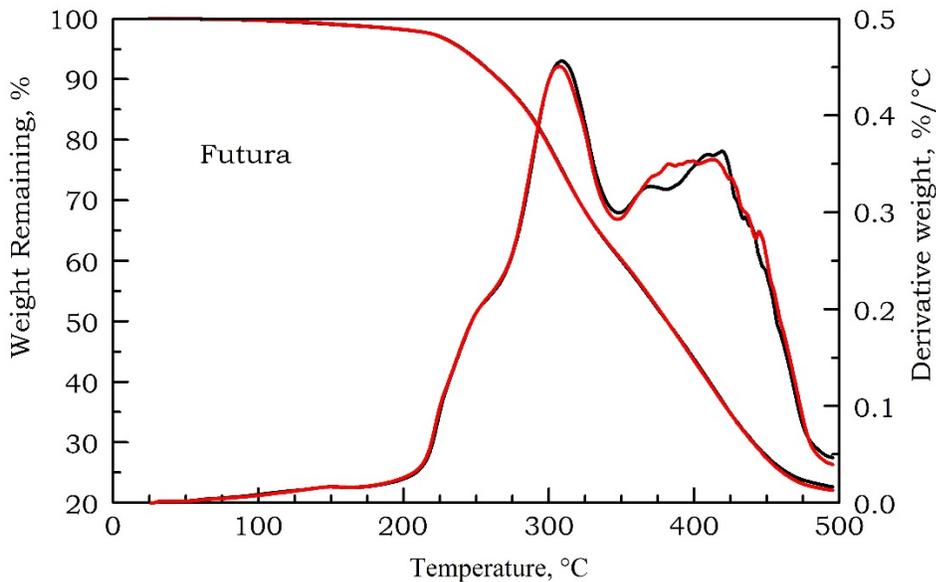
Differential Scanning Calorimetry DSC



Again, with coal tar pitch used in this coating, it is not completely justifiable to select a T_g , but in this case the point of inflection is at 48 °C, but the transition seems to spread over much of the range that occurred in the coal tar enamel.

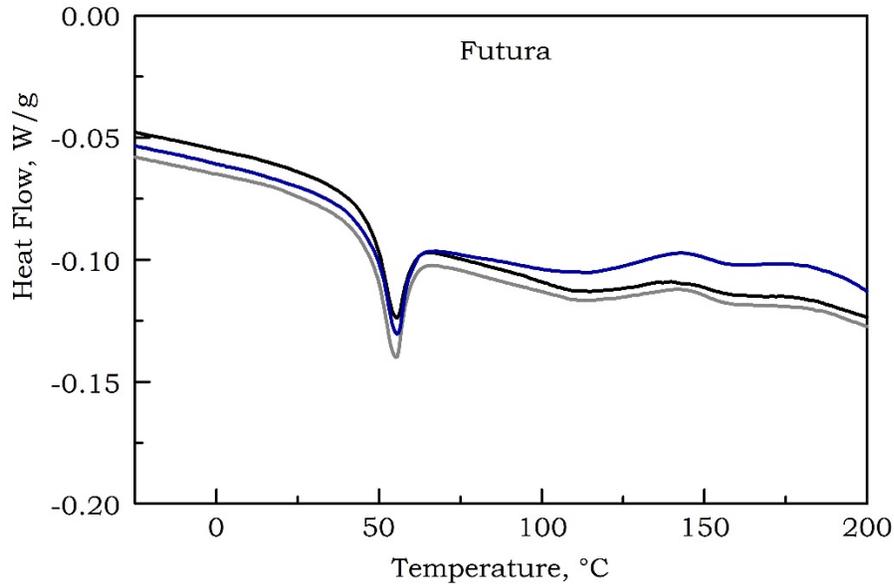
6. Futura Protec II. Aromatic polyurethane

Thermogravimetric Analysis



The weight loss with temperature shows several processes as the temperature increases which is a typical pattern for a crosslinked polymer with a complex structure.

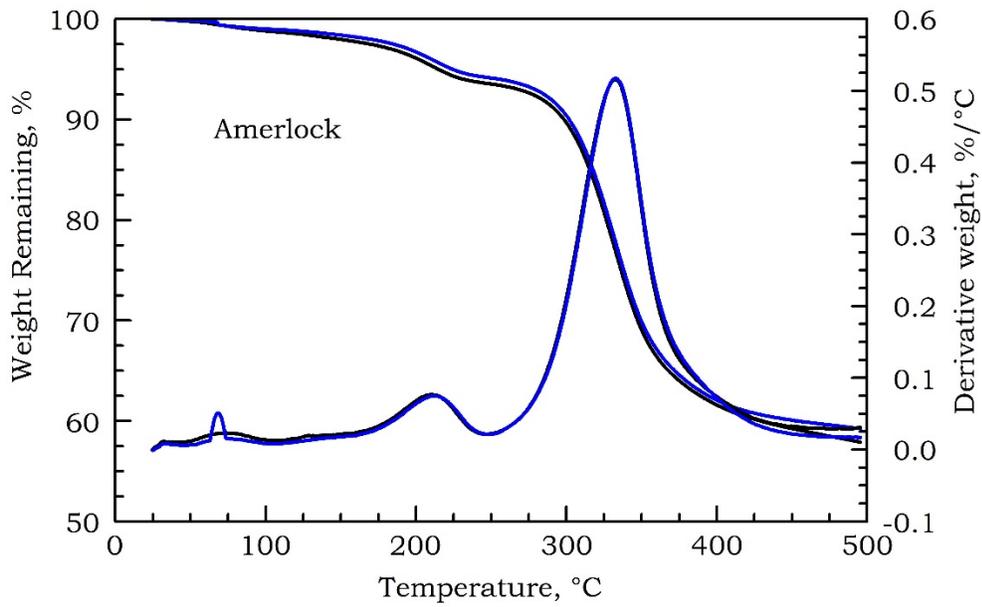
Differential Scanning Calorimetry



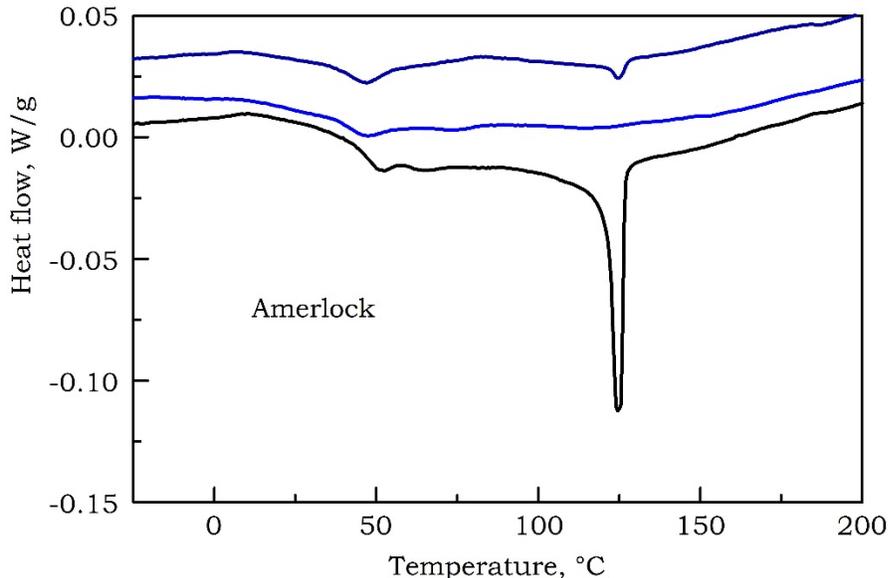
The T_g of this material is at 53 °C.

7. PPG Amerlock 2 GF. High Solids epoxy.

Thermogravimetric Analysis



Differential Scanning Calorimetry



The T_g is at 45 °C but there is also material present that shows a (probable) melting endotherm at 125 °C, approximately. This is probably contamination found in this sample only. If this is a melting point, it may indicate contamination by polyethylene. This was the only material to show this. The razor blade that was used to scrape material from the coated panel is supposedly itself coated with PTFE, which has a much higher melting point, 326 °C, than polyethylene.

Other work

The data here was available from other sources at NDSU, but was not requested in the solicitation from the Bureau of Reclamation.

Weight loss

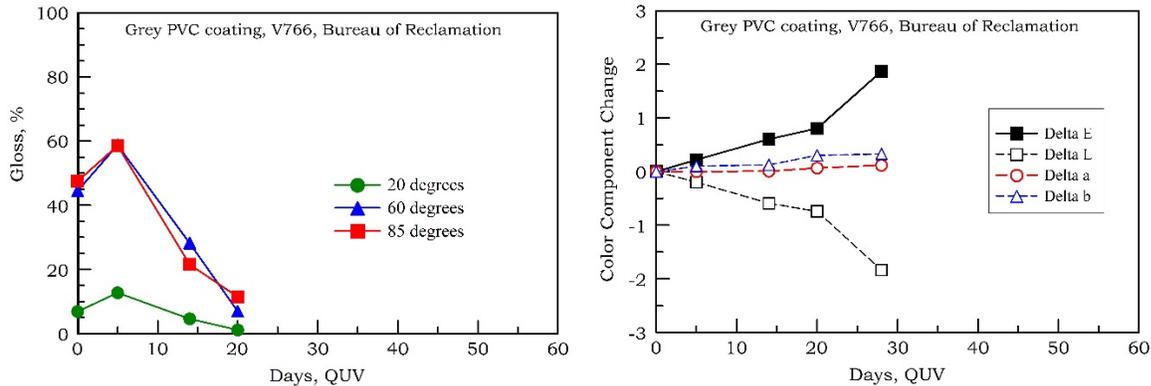
Approximately half of the remaining free film that was V766 alone was weighed then immersed in DI water for 3 whole days continuously. Before immersion, the weight was 13.601 g. Immediately after removing from immersion and removal of surface water, the weight was 13.495 g, a loss of 0.8%, approximately. There must be material that was leached out in aqueous immersion. After 3 days further drying at room temperature the weight had reduced to 13.406 g, a further weight loss of 0.66%. This second increment of weight loss is probably water that had been absorbed while immersed.

This is in contrast to most coatings, e.g. polyurethane, which typically gain 2-3% of absorbed water, or epoxies which can gain 5% or more water. The vinyl coatings, by comparison, must be rather hydrophobic.

All experiments and measurements were carried out at room temperature and humidity.

Appearance Changes

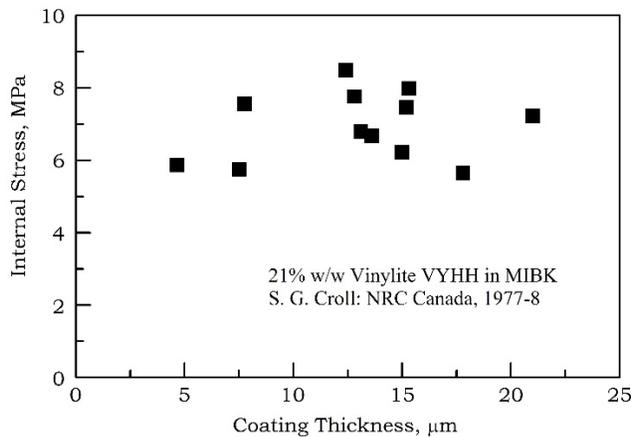
The V766 free film was subjected to the same accelerated weathering as polyurethane pipeline coatings [7] have in other work: ASTM 4587 (UVA type), cycle 1: UV + condensing humidity: 8 h UV of $0.83 \text{ W}/(\text{m}^2 \cdot \text{nm})$ at $70 \pm 2.5 \text{ }^\circ\text{C}$ ($158 \pm 5 \text{ }^\circ\text{F}$) and 4 h condensation (dark) at $50 \pm 2.5 \text{ }^\circ\text{C}$ ($122 \pm 5 \text{ }^\circ\text{F}$).



Gloss loss occurred over approximately the same time frame as for the aromatic polyurethanes, however, color changes were much less over this period and took place more slowly. Both the titanium dioxide and carbon black pigments used in the gray PVC topcoat will protect the resin from degradation, whereas the pipeline coatings were made using aromatic polyurethanes that degrade and yellow quickly and were formulated without protective pigments. Weight loss due to degradation over the period of the testing here was too small to measure reliably although it was appreciable in the aromatic polyurethane coatings [7].

Internal Stress

In 1977-8, the internal stress of Vinylite VYHH (Union Carbide) deposited from solutions at 21 weight percent in methyl isobutyl ketone was measured using the overhanging beam method [8]. The temperature was maintained at $23 \text{ }^\circ\text{C}$ at a relative humidity of 50%. In each case the film was allowed to dry for 6 weeks, or longer until the internal stress became constant. These results were not published at the time due to availability of data from other homopolymers and the rather narrow range of thicknesses achievable.



The internal stress, caused by solvent loss after the films solidified, is constant with film thickness (average 6.9 MPa, standard deviation 0.9 MPa) which is a behavior characteristic of thermoplastic coatings.

Discussion

The discussion is in sections that summarize the results and then provide some speculative thoughts.

The EIS data (from a separate report) show that the vinyl and coal tar enamel coatings exhibit much less systematic reduction in performance, than the epoxy coating, the coal tar epoxy coating and the polyurethane coating. However, within that lesser group, the polyurethane coating changes much less than the epoxy or coal tar epoxy and thus is the best candidate for a barrier coating from within this group. This paragraph is repeated almost verbatim from the report on the EIS results.

The analytical results here shed a little light on that behavior. The analyses requested by the Bureau show that all the coatings have a glass transition temperature at, or a little above, the temperature at which they will see service. This usually the choice for coatings that must have tough mechanical properties. The measured values of modulus are very typical of thermoplastic and thermoset materials and the results from the DSC are consistent with those from DMTA. The TGA results were useful in clarifying some features seen in the DSC traces.

PVC is a thermoplastic polymer that may form crystals. However, XRD results on the simplest vinyl resin revealed peaks only corresponding to amorphous material, so no further XRD was performed on the other materials which all had less likelihood of exhibiting crystallinity. Electron diffraction measurements also failed to find characteristics of PVC crystals in any of the materials.

Electron microscope images show that the vinyl and coal tar enamel coating formulations are very continuous without obvious flaws that would have resulted from poor formulation so they make good use of the properties intrinsic to the ingredients. Some structured regions were observed in the coal tar enamel coatings that suggest the various polycyclic hydrocarbon

molecules may be able to form some volumes with fairly regular packing and electron diffraction measurements detected molecular spacings that are close to those of graphite. This is not surprising in such a material.

Neither the coal tar enamel nor the vinyl coatings are crosslinked. Modern, environmentally friendly replacements are highly crosslinked polymers, for a variety of reasons (but including the assumption that high degrees of crosslinking provide good barrier properties).

All are high performance, well formulated, coatings, but evidently some last longer than others.

Speculation.

Cross-linked coatings fill many niches and have a number of advantages in terms of mechanical properties, chemical and thermal resistance depending on their use. They also are very useful in limiting VOC and/or HAPs because the precursor compounds are usually liquid which means that the material can be easily applied, but then they react to form the solid polymer, thus avoiding the need for much of the solvent that was necessary to deliver a thermoplastic polymer as a coating.

Recent studies have shown that network polymers, like epoxies and polyurethanes, may have large (on a molecular level) intrinsic defects that are formed and preserved by the crosslinking process [9 - 11]. These defects are extensive regions of no, or low, crosslinking which would be locations where water and ions might accumulate or they might combine to form paths via which water and ionic species might pass. Although they might have other drawbacks, thermoplastic polymers do not have such defects and their inter-molecular “free” volume would not have such large volumes where water and salt might gather or pass to the same extent. Vinyl coatings and coal tar enamels are thermoplastic. Thermoplastic polymer molecules, provided that their T_g is suitable, can relax around defects so there is the chance that any larger defects would shrink.

PVC is not compatible with water, see weight loss data, being rather non-polar; it only suffers a water-aided attack under acidic conditions [2]. Since ionic material is even more polar than water, it is probably a decent barrier to corrosive salts. Coal Tar enamel is hydrophobic and thus would act as a good barrier to polar and ionic species.

The features that these coal tar enamel and vinyl coatings have in common are that they are hydrophobic and probably quite continuous at the molecular level. The search for improved materials with improved environmental and health impacts might focus on retaining these features. One might either look for novel materials or seek to use current materials with ingredients that provide these features, e.g. impermeable flake pigments, although there is very little unequivocal data that shows any large improvement coming from the use of flake pigments.

Modern epoxy and polyurethane coatings can easily be applied at suitable thicknesses, they have adequate environmental and performance properties and they are reasonably economical and versatile, but they do not last for sufficiently long periods and so must be replaced or repaired. Lifecycle analysis should be performed rigorously in order to determine whether these modern

materials should be used or whether it is more economical and environmentally more responsible to return to the old technologies instead.

Additional Information

These notes are not intended to be a comprehensive review.

(i) "Vinyl" Coatings

The term "vinyl" is for polyvinylchloride (PVC), as it is in the many other products that are labelled in the same way. PVC is not easily soluble in the solvents common to paints and coatings and has been restricted in use as a coating due to the large quantity of VOC solvent that must be used especially since several applications are necessary to form a usefully thick coating. However, vinyl coatings are very tough and survive as corrosion protective coatings, where impact damage is likely, for longer than modern, less problematic materials. The history and use of vinyl coatings has been well studied and reported [12] and will not be reiterated here.

Vinyl coatings are thermoplastic, not crosslinked. The glass transition temperature of pure unplasticized PVC ("uPVC" or "rigid PVC") is approximately 80 °C, so it would be somewhat brittle in use, especially where it may be immersed in cool water. The most common usage is as a resin in which it is copolymerized, e.g. with ~ 14% vinyl acetate, to make it more flexible (polyvinylacetate has a glass transition temperature of 30 °C, although the T_g of the copolymer is usually ~70 °C). A copolymer is also a little more soluble in common solvents, e.g. ketones. Additional softening is commonly achieved by using plasticizers that have low volatility and so remain in the coating. In common with other flexible vinyl products (hoses, luggage etc.) vinyl coatings used compounds such as di-isodecyl phthalate or tricresyl phosphate as plasticizers which add to their potential health hazards during application.

Although there has long been an interest in PVC crystals [3], it is very difficult to make well defined crystals of any size [13] and there has been some discussion about the possibility of crystals forming in PVC melts at all [14]. PVC, unless special synthesis procedures are used, is mostly atactic and will not form crystals. Typical lengths of syndiotactic polymer are very short (< 5 - 6 repeat units) so that crystallites can only be very thin [15]. The commonly used values for the PVC crystal unit cell are $a = 1.06$ nm, $b = 0.54$ nm, $c = 0.51$ nm and commonly seen spacings in amorphous PVC are 0.36 nm and 0.50 nm [16] which are similar to values seen in crystals [3]. PVC does degrade slowly in sunlight and suffers similar decay processes in thermal and photodegradation [16], but can be stabilized readily.

Vinnol H 15/50 is a close analogue of the Union Carbide VYHH grade and the H 15/45M is close to the Union Carbide VMCH. According to the current manufacturer of these polymers, Wacker Chemie AG, Vinnol H 15/50 has a weight average molecular weight of 60-80, 000; Union Carbide literature had the number average molecular weight as 27,000. It contains 85% vinyl chloride and 15% vinyl acetate by weight. Vinnol H 15/45M (same molecular weight) contains 84% vinyl chloride, 15% vinyl acetate and 1% of "other monomers" (dicarboxylic acid

according to Wacker but maleic acid according to previous Union Carbide literature) that give it an acid value of 7 (mg KOH per gram of polymer).

(ii) Coal Tar Enamel

Early coal tar coatings were a mixtures of pitch from coke ovens. More modern variants are somewhat refined to use compounds that are less brittle at low temperatures but often use powdered coal as a filler to raise their softening point, along with mineral talc or other fillers. Some of the heavy oils obtained from the process are used to plasticize the product to the required extent, i.e. control its brittleness. Coal Tar enamels are best used in circumstances where they will not lose the plasticizer otherwise they become brittle.

Coal Tar pitch has a varied composition containing many ingredients [17 - 19] that depend on the original source of coal. Many of the compounds found are polycyclic in their structure and may have molecular weights as high as 5000 or 10,000 u [18, 20, 21] or much higher]. A current assertion is that polycyclic aromatic hydrocarbons (PAHs) and other heterocycle compounds pack in planar layers approximately 4.5 Angstrom units (Å) apart [22] which is a little wider than the alternating layers in a graphite crystal, 3.354 Å [23]. However, previous X-ray diffraction results have that the interlayer spacing in coal pitch as approximately 3.4 Å [24] and asphaltenes as 3.5 Å [25] i.e. close to graphite. Forms of Coal Tar pitch called mesophases (an intermediary for forming carbon fibers) exhibit some liquid crystal behavior [26]. Thus there is value in exploring the ways in which such a mixture might organize itself in a film. Related research is seen in other technologies, e.g. asphaltenes may precipitate from petroleum fluids which causes problems in pipelines and ancillary equipment, but has caused some studies to be made of what effects the aggregation of such ring containing compounds [27, 28]. Graphene is the subject of much current research and a feature that attracts much attention is its very high impermeability [29]. Polycyclic aromatic hydrocarbons are carcinogenic which means there is considerable reluctance to use coal tar in ways that humans can suffer exposure.

Coal tar pitch is also used to make general purpose graphite fiber for use in composites as well as forming the basis of the binder in carbon-carbon composites [30]. The modern interest in fullerenes, graphene etc. and improving the environmental impact of coal as a fuel has ensured that journals, such as "Carbon" are flourishing, with considerable interest in characterizing possible pre-cursors for these modern materials. Thus there is a current literature that may be useful in thinking about coal tar, or similar, coatings.

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Data Sets that Support the Final Report

If there are any data sets with your research, please note:

- Share Drive folder name and path where data are stored:
T:\ENGLAB\MERL\COATINGS_Coal Tar Enamel\Publications\Merten_S&T Final Report
- Point of Contact name, email, and phone: Bobbi Jo Merten, bmerten@usbr.gov, 303-445-2380
- Short description of the data: lab testing data, field testing data, literature, and reports
- Keywords: coatings, corrosion protection, coal tar enamel, coal tar epoxy, epoxy, polyurethane, penstocks
- Approximate total size of all files: 800 MB