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Developing High Performance Coatings

Evaluation of Seven Sealer Systems for Metallized Zinc and Aluminum Coatings in Fresh and Salt Waters

by
Timothy D. Race

A variety of metallizing systems and their recommended sealers are discussed in Civil Works guide specification CW-05036, *Metallizing: Hydraulic Structures and Appurtenant Works*. This study evaluated seven sealer systems for zinc and aluminum metallized coatings exposed to fresh and salt waters.

Based on the results of this study, more specific recommendations for sealing metallized coatings can now be made. For zinc metallizing immersed in fresh water, the recommended sealer systems include epoxy, epoxy with wash primer, aluminum-pigmented urethane, or white-pigmented vinyl. Epoxy and epoxy with wash primer are recommended sealer systems for zinc metallized coatings exposed to salt water. Aluminum metallizing for fresh water applications should be sealed with the vinyl system evaluated in this study. None of the sealer systems evaluated for use on aluminum metallizing exposed to salt water performed adequately.

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FOREWORD

This study was done for the Electrical and Mechanical Branch, Engineering Division, Directorate of Civil Works, Headquarters U.S. Army Corps of Engineers (HQUSACE), under Civil Works Investigations and Studies (CWIS) Work Unit 31205, "Developing High Performance Coatings." The technical monitors were R. Kinsel and J. Gilson, CECW-EE.

This research was performed by the Engineering and Materials Division (FM), of the Infrastructure Laboratory (FL), of the U.S. Army Construction Engineering Research Laboratories (USACERL). The USACERL principal investigator was Mr. Timothy Race. Dr. Michael J. O'Connor is Laboratory Chief, CECER-IF, and Dr. Paul Howdyshell is Division Chief, CECER-FM. The USACERL technical editor was Mr. William J. Wolfe, Information Management Office.

COL Daniel Waldo, Jr., is Commander and Director of USACERL, and Dr. L.R. Shaffer is Technical Director.

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EVALUATION OF SEVEN SEALER SYSTEMS FOR METALLIZED ZINC AND ALUMINUM COATINGS IN FRESH AND SALT WATERS

1 INTRODUCTION

Background

Solution vinyl coatings on U.S. Army Corps of Engineers' (USACE's) hydraulic structures have provided years of superior corrosion protection. Vinyls were first used in the early 1950s on Corps structures along the Mississippi River and are still being widely used. Environmental regulations and special applications requiring abrasion resistance have led to a growing interest in a competing corrosion protection technology known as metallizing.

The origin of metallizing can be traced back to the early 1900s. The growth of this technology has been evolutionary rather than revolutionary. European users were the first to recognize the benefits of metallized coatings, particularly zinc. Metallizing in the United States has recently seen considerable growth especially in the corrosion protection of bridges. The U.S. Navy operates shore repair facilities that apply aluminum metallizing to ship components.

Each user has specific reasons for using metallized coatings instead of the more conventional corrosion protection technology offered by liquid coatings. Initial studies of metallized coatings for the protection of USACE hydraulic structures were conducted in response to the high level of abrasion experienced at some installation sites. Structures located on the Ohio River, for example, have severe abrasion on the downstream skinplates of tainter gates. The abrasion is caused by the backflow of water, debris, and ice. The end result is the total erosion of vinyl paint systems in as little as 1 year (Beitelman 1981). Under normal river flow (i.e., nonabrasive) conditions, vinyls may provide protection for more than 30 years. Metallic coatings are inherently harder and more resistant to abrasion than vinyl coatings (Martell and Yee 1988).

A second and perhaps more compelling reason to use metallized coatings is the implementation of new air pollution regulations aimed at reducing volatile organic compound (VOC) emissions into the atmosphere. Organic coatings account for less than 10 percent of all VOC emissions, but nonetheless are considered a major VOC source. The Corps' current specifications for vinyls, epoxies, and alkyds do not meet many of the regionally implemented VOC regulations. The U.S. Environmental Protection Agency is scheduled to implement a national control technology guideline or national rule for architectural coatings. These guidelines would eliminate using most of the coatings currently accepted by the Corps of Engineers. Metallized coatings are a zero VOC technology and will not be affected by VOC requirements.

In response to the Corps' perceived needs for abrasion resistant coatings and low VOC emissions, the U.S. Army Construction Engineering Research Laboratories (USACERL) conducted an initial panel study and field evaluation of selected metallized coatings. As a result of that study, Civil Works guide specification CW-05036, *Metallizing: Hydraulic Structures and Appurtenant Works*, was prepared for the USACE Directorate of Civil Works (CECW-EE). The guide specification contains a variety of metallizing systems as well as recommended sealers for the metallic coatings. Using sealers in conjunction with metallized coatings is a recognized method of prolonging the life of the coating system. Sealing may also

be used to alter the final appearance of the coating system. Following the initial study, there was a need for a more in-depth analysis of the sealers recommended in the guide specification.

Objective

The objective of this study was to determine the relative merit of selected organic coatings as sealers for metallized zinc and aluminum coatings in salt water and fresh water immersion.

Approach

Sealer selection criteria were established based on a review of available literature and user community experience. Seven sealers selected for evaluation were applied to zinc and aluminum metallized test coupons. Test coupons were then exposed to fresh and salt water for 2 years and periodically evaluated for adhesion, blistering, cracking, and appearance. Test panels were rated for each evaluation category. Sealer systems were then ranked by score for each test exposure and type of metallizing.

Mode of Technology Transfer

The results of this laboratory evaluation of sealers for zinc and aluminum metallized coatings will be incorporated into the Civil Works guide specification CW-05036, *Metallizing: Hydraulic Structures and Appurtenant Works* (Headquarters, U.S. Army Corps of Engineers [HQUSACE], in publication).

2 SELECTION OF SEALERS

Background

Sprayed metallic coatings are formed by individual molten droplets impinging on the substrate and then solidifying. The solidified droplets remain as discrete entities within the newly formed coating. This process of film building by discrete particles produces a relatively porous coating that contains some inclusions or voids. Metallized coatings are typically 85 to 95 percent dense (Burns 1967). Oxides in the sprayed coating account for roughly 0.5 to 3 percent of the coating (Race 1990). The density and oxide content depend on the type of material being applied, the method of application, and the application parameters. In some cases, porosity may be continuous to the substrate. Reportedly, zinc, aluminum, and lead coatings of 5 to 9 mils are sufficiently thick to discount the presence of through porosity (Leclercq 1988). A field study of aluminum bronze alloy and 18-8 stainless steel coatings applied at thicknesses of 15 to 20 mils found these coatings contain porosity that is continuous to the substrate (Race 1990). Figure 1 shows a schematic representation of a cross sectional view of a sprayed metallic coating.

In mild exposures, metallized zinc and aluminum coatings may be used without sealers. In more severe exposures, such as coastal or marine atmospheres and immersion in fresh or salt waters, a sealer is usually recommended. The objective of sealer application is to close off pores and prevent the migration of moisture and corrosive ions to the substrate. The sealer also acts as a barrier to protect the metallic coating itself from degradation. A synergism between the sealer and metallic coating has been suggested by some researchers (Leclercq 1988). In some cases, the use of a sealer can reduce the required thickness of the metallized coating without sacrificing performance. The results of the American Welding Society's 19-year corrosion test of metallized steel indicate complete corrosion protection for both a 9 mil unsealed zinc coating and a 3 mil zinc coating treated with a wash primer and sealed with a vinyl coating (American Welding Society 1974).

Most literature references pertain to the sealing of metallized coatings for atmospheric corrosion protection. Polyvinyl butyral wash primers are recommended for applications involving weathering in wet environments. Vinyls have been successfully used on both zinc and aluminum metallized coatings; however, a wash primer should be applied to zinc prior to subsequent vinyl sealer coats (Oechsle 1982). Coatings such as phenolics and oil-based materials should not be used to seal zinc because they will react

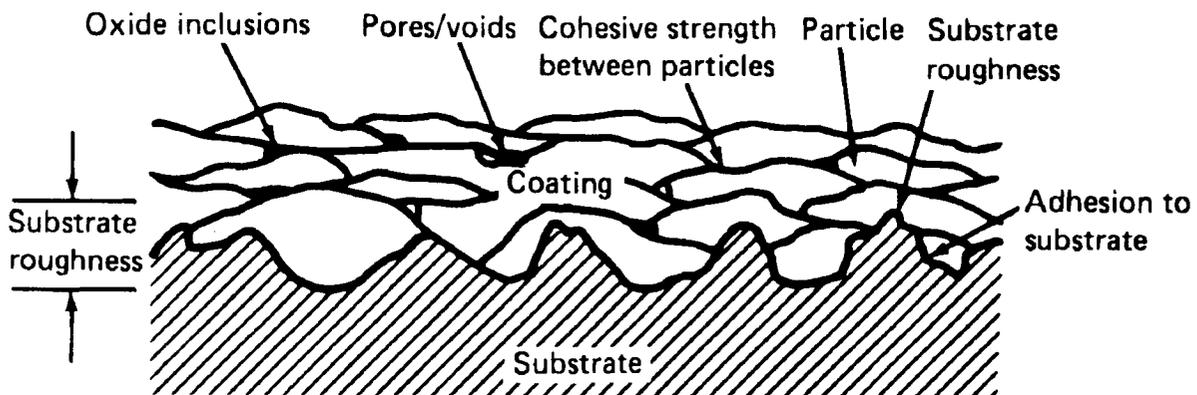


Figure 1. Schematic Representation of a Cross Sectional View of a Metallized Coating.

with the base metal. Metco (a division of the Perkin-Elmer Corp., 1101 Prospect Ave., Westbury, NY 11590), a leader in the metallizing industry, recommends a wash primer and aluminum vinyl sealer system for zinc metallizing. For aluminum metallizing, Metco's recommendation for a sealer depends on the type of exposure. For atmospheric and sea water exposures, wash primer and vinyl sealer are recommended. For fresh water, either wash primer and vinyl or epoxy sealers are recommended. Epoxy sealer is recommended for chemical exposures. The Ministry of Transportation in British Columbia has experimented with vinyl sealers as well as vinyl topcoated with epoxy for use on zinc metallizing. Vinyl topcoated with epoxy proved most effective when used on bridge steel that was subjected to deicing salt and sand (Butler 1987).

Sealer Selection Criteria

Four primary criteria were established for the selection of sealer test materials:

1. Compatibility with metallizing material
2. Known resistance for the intended exposures
3. Relatively low viscosity
4. Existing Military, USACE, or industry specification for the material.

Also of interest was the VOC content of each of the sealer materials. It is not possible at this time to establish a definitive value for VOC content. National guidelines do not exist. Among the more stringent levels required are those issued by the California Air Resources Board (CARB) in the *ARB-CAPCOA Suggested Control Measure (SCM) for Architectural Coatings* (12 May 1989). The CARB recommended SCM for wash primers permits a VOC content of 780 g/L. This number will be lowered to 420 g/L on 1 September 1994. Most other sealing materials qualify as industrial maintenance coatings, which can have a VOC content of 420 g/L. This limit will be lowered to 340 g/L on 1 September 1992.

As stated previously, not all coating materials are chemically compatible with zinc. Sealer materials with known incompatibilities were excluded from this evaluation. As a general rule, the material selected for sealing a metallized coating should be appropriate for the intended exposure environment. For example a coating intended for use on steel subject to atmospheric weathering should not be used as a sealer in immersion.

Low viscosity is an important property for a good sealer. The degree a sealer can penetrate into the pores of the coating depends on its viscosity. The rate a sealer's viscosity increases after application will also affect the degree of penetration into the pores. Solvent evaporation rates and the rate at which the coating cross links should be reduced to the lowest extent possible. For very small pores (less than the size of the pigment particles) the controlling parameter is the viscosity of the pigment-free sealer. Penetration into the pores is very important. If penetration is inadequate due to the rough and porous surface of the metallizing, the result may be poor, wet adhesion of the sealer (Wicks 1987). Voids beneath a sealer will fill with moisture and oxygen, accelerating coating degradation.

Using sealer materials with an existing military, USACE, or industry specification is desirable. Including nonspecification coating materials in USACE guide documents is problematic at best.

Selected Sealers

A broad range of generic types of coatings were chosen for evaluation, including waterborne epoxy, epoxy polyamide, polyurethane, and vinyl. Table 1 lists the seven sealer systems selected. All but system F are described by either a USACE or military specification, and all meet current CARB VOC content requirements except for the vinyl paints.

System A consists of two coats of military specification epoxy polyamide. MIL-P-24441, *Paint, Epoxy, Polyamide, Green Primer, Formula 150, Type 1* (Naval Sea Systems Command 1986), is used extensively by the Navy for salt water immersion and marine atmospheric applications. Civil Works guide specification CW-09940, *Painting: Hydraulic Structures and Appurtenant Works* (HQUSACE 1989), recommends this coating for use on steel and aluminum subject to salt and fresh water immersion. The viscosity of this material may be easily reduced with a suitable thinner. The product applied in this study meets all current VOC restrictions.

System B is essentially the same as System A except for the addition of an initial coat of a zinc chromate vinyl butyral wash primer. This material is described by both a military specification, DOD-P-15328 *Primer (Wash) Pretreatment* (Fort Belvoir Research, Development & Engineering Center 11 April 1983), and by an industry specification, Steel Structures Painting Council (SSPC) Paint Specification No. 27, *Basic Zinc Chromate-Vinyl Butyral Wash Primer* (SSPC 1982). Vinyl butyral wash primer is used primarily to promote adhesion of subsequent coats, especially on nonferrous metals. Its viscosity is much lower than that of conventional paint materials. Under current plans this material is compliant with CARB VOC requirements until September 1994.

Sealer System C consists of a single spray application of the vinyl butyral wash primer.

Table 1

Selected Sealers for Evaluation on Zinc and Aluminum Metallized Coatings

Sealer System	1st Coat	2nd Coat	3rd Coat	Type of Material
A	MIL-P-24441 (Form 150)	MIL-P-24441 (Form 152)	--	Epoxy polyamide
B	DOD-P-15328	MIL-P-24441 (Form 150)	MIL-P24441 (Form 152)	Wash primer/ epoxy polyamide
C	DOD-P-15328	--	--	Wash primer
D	MIL-P-53030	MIL-P-53030	--	Waterborne epoxy
E	V-102e	V-102e	V-102e	Vinyl aluminum
F	Urethane	Urethane	--	Moisture cure Aromatic urethane
G	V-766e	V-766e	V-766e	White vinyl

System D consists of two coats of MIL-P-53030, waterborne epoxy. This material is primarily used as a direct-to-metal primer, with or without topcoats, on military equipment such as vehicles. USACE tests have indicated this material can be used in fresh water immersion as a topcoat for zinc-rich primers. This primer can be thinned with water to a low viscosity. MIL-P-53030 meets all current and proposed VOC regulations.

Sealer System E is comprised of three coats of aluminum pigmented vinyl, V-102e, which is described in CW-09940. This material is specified as a topcoat for vinyl primers in CW-09940 and is intended for fresh water immersion applications. V-102e is not VOC compliant in California and some metropolitan areas in other states. It was included in the test program because similar materials have been widely recommended for sealing metallized coatings. There is no limit to the amount of thinner that may be added to this sealer, and therefore very low viscosities may be achieved. Vinyls do, however, show a rapid increase in viscosity after application.

Sealer System F consists of a double coat of a proprietary aromatic moisture-cure urethane. The manufacturer recommends this material for a variety of applications including atmospheric weathering and fresh water immersion for steel and concrete substrates. The product is especially recommended for use on rough or poorly prepared substrates because of its ability to wet and penetrate the surface. It meets all current VOC restrictions for architectural coatings, but will not meet the lower levels established for California by CARB effective September 1992.

Sealer System G is comprised of three coats of white vinyl, V-766e, which is described in CW-09940. CW-09940 recommends this material for painting steel subject to fresh water immersion. The VOC content of this material is nearly the same as that of V-102e and it is subject to the same regional restrictions as that coating. Again, this material can be thinned and applied at quite low viscosities. V-766e has excellent adhesion to most substrate materials.

3 EXPERIMENTAL DESIGN

Metallized Coupon Description

Standard test coupons were prepared from 1/2-in. (1.25 cm), A-36 cold rolled steel. Stock material was cut into 3 (7.5 cm) by 6 in. (15.0 cm) in. test coupons. Coupons were abrasive-blasted using aluminum oxide grit in accordance with SSPC SP-5, *White Metal Blast Cleaning* (SSPC 1989). A minimum profile of 2.5 mils was achieved.

Metallized coatings were applied to coupons using a Metco 12E wire flame-spray gun. Metco application parameters were used to apply 1/8-in. (0.3-cm) diameter wire. Aluminum was applied to an average thickness of 5 to 8 mils. The zinc coating was applied at 6 to 8 mils.

Sealer Application

All sealer materials were applied using conventional air atomization spray. Coatings were thinned using the recommended solvents. The first coat of each sealer system was adjusted to a viscosity of 35 ± 5 seconds on a #4 Ford Cup viscometer. Total dry film thickness of the sealer systems was initially estimated using a magnetic film thickness gage. This magnetic gage was used to ascertain that the sealer system thickness was within the desired range prior to initiating the exposure tests. After completion of the exposure tests, coating thicknesses were measured again using ASTM D 4138, *Measurement of Dry Film Thickness of Protective Coating Systems by Destructive Means* (April 1988). This method produces much more accurate results than a magnetic gage for measuring the thickness of sealers applied to a metallized coating.

Test Exposures and Evaluation Factors

Duplicate panels for each sealer-metallized coating duplex were exposed for 2 years in fresh water and synthetic sea water tanks. The synthetic sea water solution was prepared by dissolving 5 parts, by weight, of low nickel sodium chloride in 95 parts of water conforming to Type IV water in ASTM Specification D 1193, *Standard Specification for Reagent Water* (March 1977). The salt water solution was continuously aerated using an aquarium pump and the temperature was maintained between 70 and 80 °F (21 and 26.4 °C). In the fresh water tests cold tap water at 55 to 65 °F (12.7 to 18.7 °C) was used with continuous flow to prevent stagnation. Fresh water test coupons were evaluated after the first, 6th, 12th, and 24th month of the test. Sea water panels were inspected after the first, 6th, and 24th month of the test.

Panels were rated for each evaluation factor on a numerical scale of zero to 10, with 10 being a perfect rating, or no damage. Evaluation factors included blistering (ASTM D 714, *Evaluating Degree of Blistering of Paints* [1989]), qualitative adhesion, and qualitative appearance (cracking, salt formation, and rust stain). The average of the sum of the evaluation factors was used to assign an overall value for each sealer system.

ASTM D 714 rates blister size on a scale zero to 10. Blistering densities are rated as none, few, medium, medium dense, and dense. For this evaluation, blistering densities were assigned numerical

values from zero to 10, with 10 corresponding to no blistering and zero to dense blistering. The average of the sum of the size and density was recorded as the value for blistering.

Adhesion was evaluated qualitatively by using a knife to make parallel scribes, 1/4 in. (0.625 cm) apart, through the sealer to the base metal. The knife was then used to lift the coating from between the scribed cuts. An experienced technician can use this technique to rapidly assess the relative adhesion of a series of coatings. A perfect score of 10 corresponds to no delamination of the coating. A rating of zero equates to very poor adhesion where the coating readily disbonds from the substrate with no elongation. For simplicity, all intermediate values of adhesion were assigned a rating of 5.

The appearance of the test panels was also assessed qualitatively. Sealers which cracked severely because of subfilm salt deposits were assigned a value of zero. Lesser degrees of cracking were assigned intermediate values. Other surface irregularities, such as rust bleed through, or the formation of salt deposits on the surface of the sealer, were also used to assign a numerical score. The negative sum of the appearance factors, not less than zero, was used to assign an appearance rating.

Sealer system C, vinyl butyral wash primer, could not be evaluated for blistering or adhesion because of its very low film build. The total scores for sealer system C were derived by multiplying the appearance rating by 3.

4 EXPERIMENTAL RESULTS

Table 2 lists the metallized coating-sealer duplexes, indicating the measured dry film thickness of the sealers and the panel numbers assigned to each duplex. Tables 3 and 4 summarize the results for each sealer system applied to zinc metallizing and exposed to fresh and salt water, respectively. Tables 5 and 6 record the results of sealer performance on aluminum metallizing in fresh and salt water, respectively. Figures 2 through 9 show the test effects on the duplexes at the end of 2 years.

Table 2
Metallized Coating Sealer Duplexes

Sealer System	Metallized Coating	Panel Number	Sealer Dry Film Thickness (mils)
A	Zinc	2892	9
B	Zinc	2893	9-10
C	Zinc	2894	<1
D	Zinc	2895	1.5
E	Zinc	2896	5
F	Zinc	2897	8-9
G	Zinc	2898	8
A	Aluminum	2899	7.5
B	Aluminum	2900	8
C	Aluminum	2905	<1
D	Aluminum	2901	1.5
E	Aluminum	2902	6.5
F	Aluminum	2903	8
G	Aluminum	2904	9

Table 3

Performance of Sealer-Zinc Metallizing Duplexes in Fresh Water

Sealer System	Number of Months	Blistering	Adhesion	Appearance	Total
A	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	10	10	10	30
B	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	10	10	10	30
C	1	N/A	N/A	10	30
	6	N/A	N/A	9	27
	12	N/A	N/A	8	24
	24	N/A	N/A	8	24
D	1	10	10	10	30
	6	10	10	9	29
	12	10	10	8	29
	24	10	10	8	28
E	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	6	10	10	26
F	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	10	10	10	30
G	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	10	10	10	30

Table 4
Performance of Sealer-Zinc Metallizing Duplexes in Salt Water

Sealer System	Number of Months	Blistering	Adhesion	Appearance	Total
A	1	10	10	10	30
	6	10	10	10	30
	24	10	10	10	30
B	1	10	10	10	30
	6	10	10	10	30
	24	10	10	10	30
C	1	N/A	N/A	8	24
	6	N/A	N/A	8	24
	24	N/A	N/A	0	0
D	1	10	10	8	28
	6	10	10	8	28
	24	10	5	0	15
E	1	10	10	10	30
	6	10	10	9	29
	24	6	10	9	25
F	1	10	10	10	30
	6	10	10	9	29
	24	6	10	8	24
G	1	6	10	10	26
	6	4	10	9	23
	24	4	5	7	16

Table 5

Performance of Sealer-Aluminum Metallizing Duplexes in Fresh Water

Sealer System	Number of Months	Blistering	Adhesion	Appearance	Total
A	1	10	10	10	30
	6	10	10	8	28
	12	10	10	8	28
	24	6	5	0	11
B	1	10	10	10	30
	6	10	10	10	30
	12	10	10	10	30
	24	6	5	0	11
C	1	N/A	N/A	10	30
	6	N/A	N/A	5	15
	12	N/A	N/A	0	0
	24	N/A	N/A	0	0
D	1	10	10	10	30
	6	10	10	5	25
	12	10	10	5	25
	24	10	10	5	25
E	1	10	10	10	30
	6	10	10	9	29
	12	8	10	9	27
	24	8	10	9	27
F	1	10	10	10	30
	6	10	10	10	30
	12	10	10	9	29
	24	8	10	9	27
G	1	10	10	10	30
	6	10	10	9	29
	12	10	10	9	29
	24	8	10	9	27

Table 6**Performance of Sealer-Aluminum Metallizing Duplexes in Salt Water**

Sealer System	Number of Months	Blistering	Adhesion	Appearance	Total
A	1	10	10	10	30
	6	4	10	5	19
	24	0	0	0	0
B	1	10	10	10	30
	6	10	10	6	26
	24	0	0	0	0
C	1	N/A	N/A	5	15
	6	N/A	N/A	0	0
	24	N/A	N/A	0	0
D	1	6	5	8	19
	6	N/A	0	0	0
	24	N/A	0	0	0
E	1	6	10	10	26
	6	4	10	10	24
	24	1	0	0	1
F	1	4	10	10	24
	6	0	0	0	0
	24	0	0	0	0
G	10	10	10	10	30
	6	2	5	5	12
	24	1	5	5	11

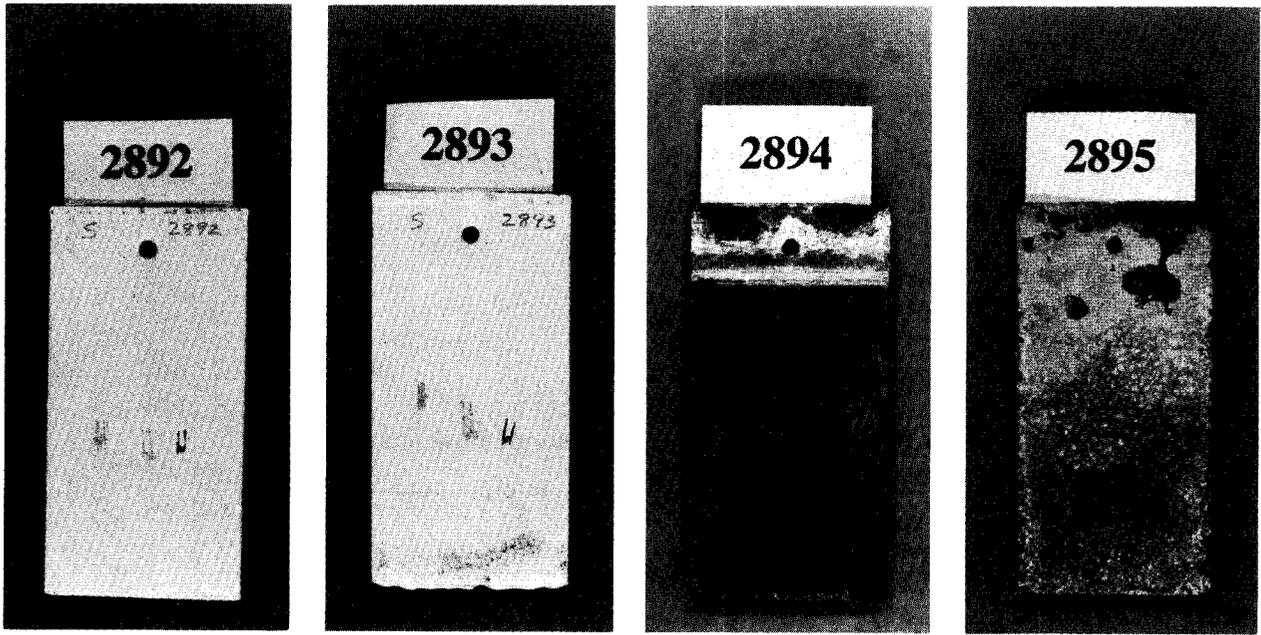


Figure 2. Sealer-Zinc Duplexes After 2 Years' Fresh Water Immersion: 2892 System A, 2893 System B, 2894 System C, 2895 System D.

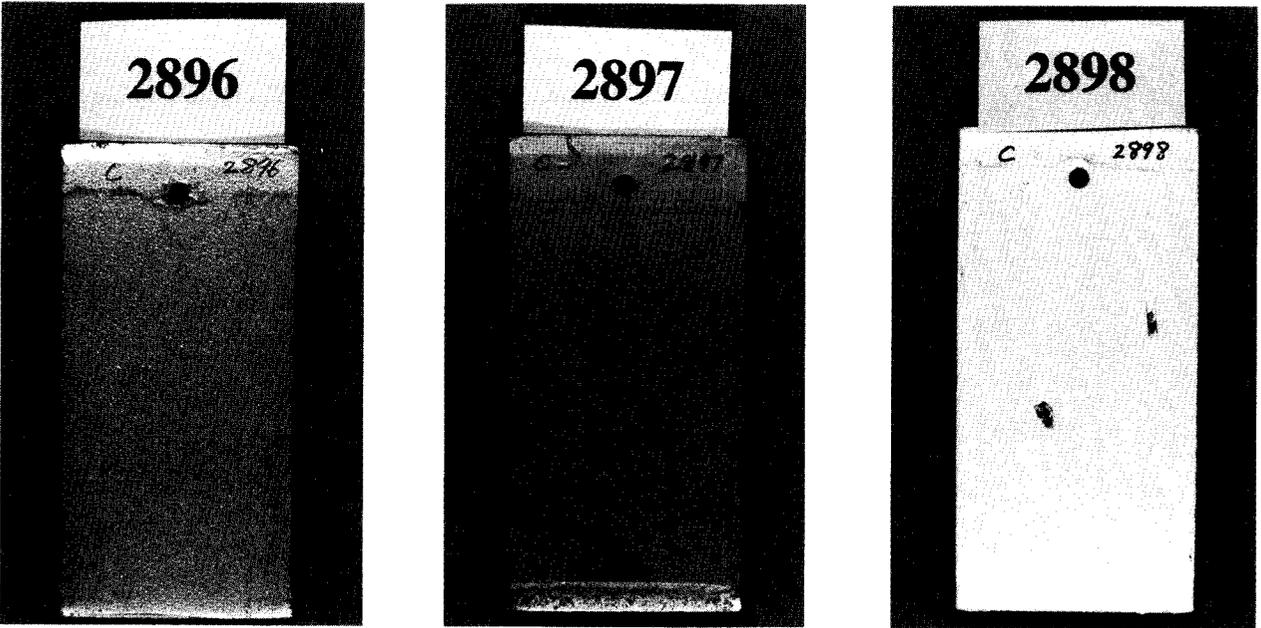


Figure 3. Sealer-Zinc Duplexes After 2 Years' Immersion in Fresh Water: 2896 System E, 2897 System F, 2898 System G.

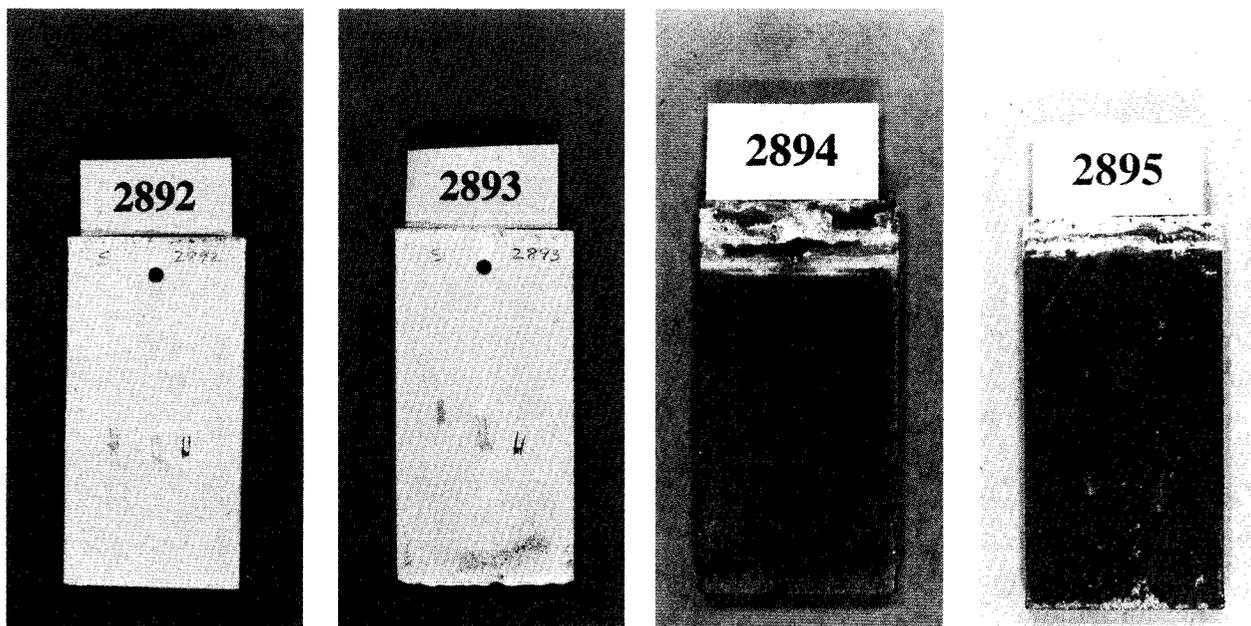


Figure 4. Sealer-Zinc Duplexes After 2 Years' Immersion in Salt Water: 2892 System A, 2893 System B, 2894 System C, 2895 System D.

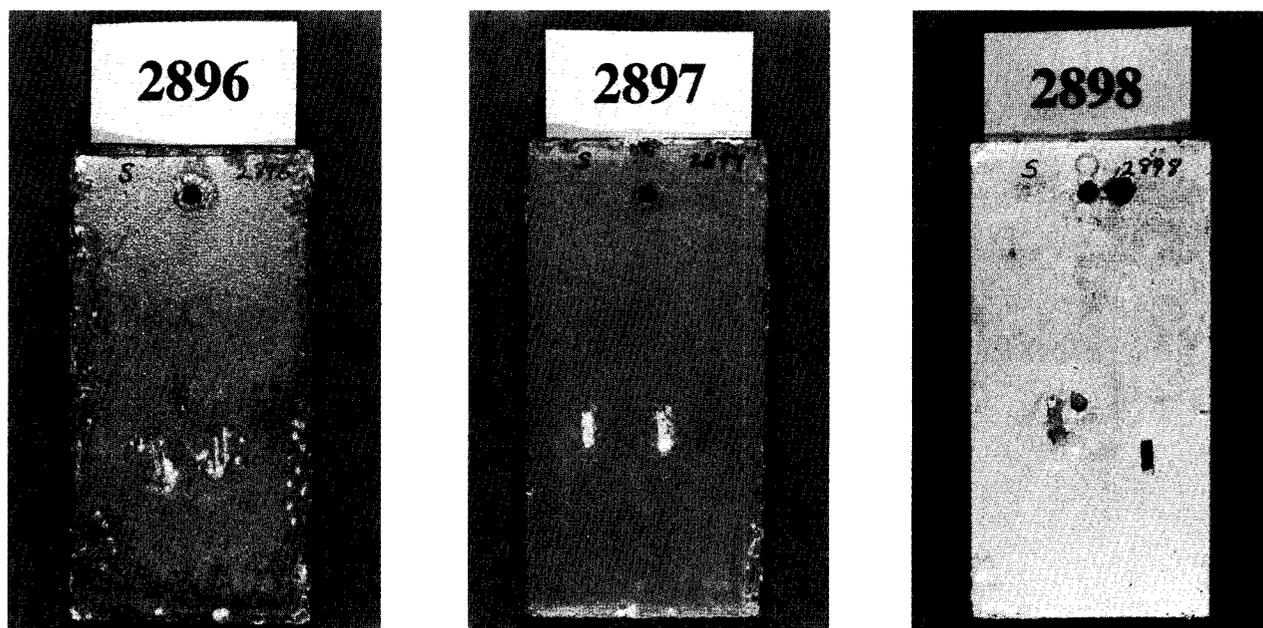


Figure 5. Sealer-Zinc Duplexes After 2 Years' Immersion in Salt Water: 2896 System E, 2897 System F, 2898 System G.

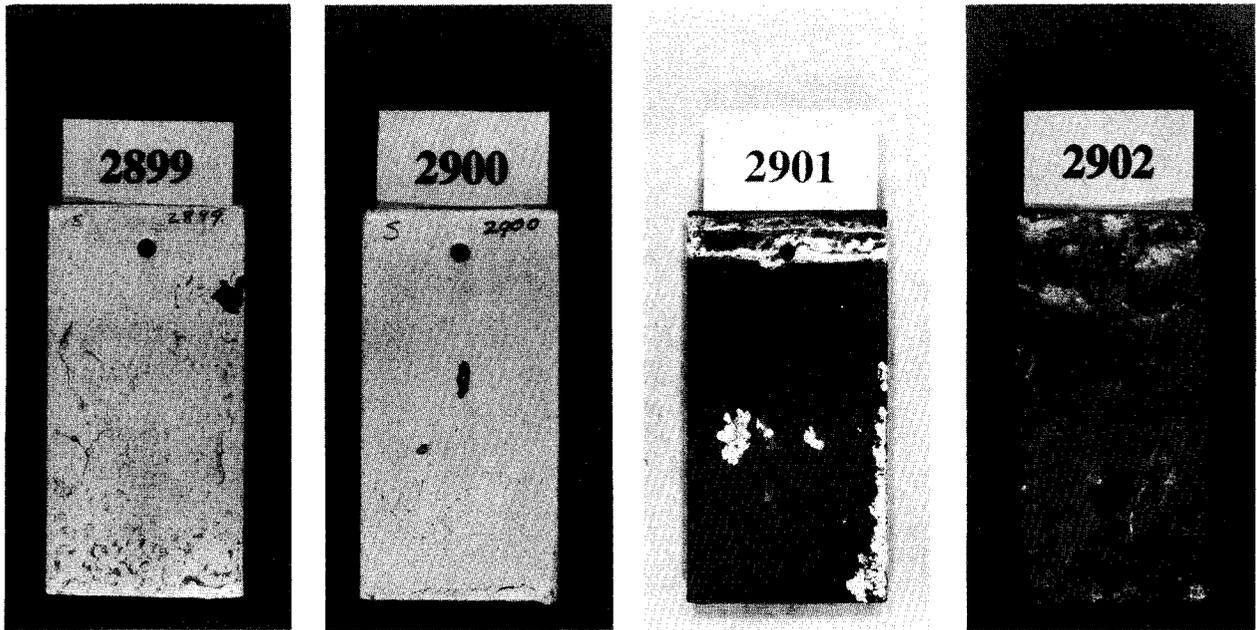


Figure 6. Sealer-Aluminum Duplexes After 2 Years' Immersion in Fresh Water: 2899 System A, 2900 System B, 2901 System D, 2902 System E.

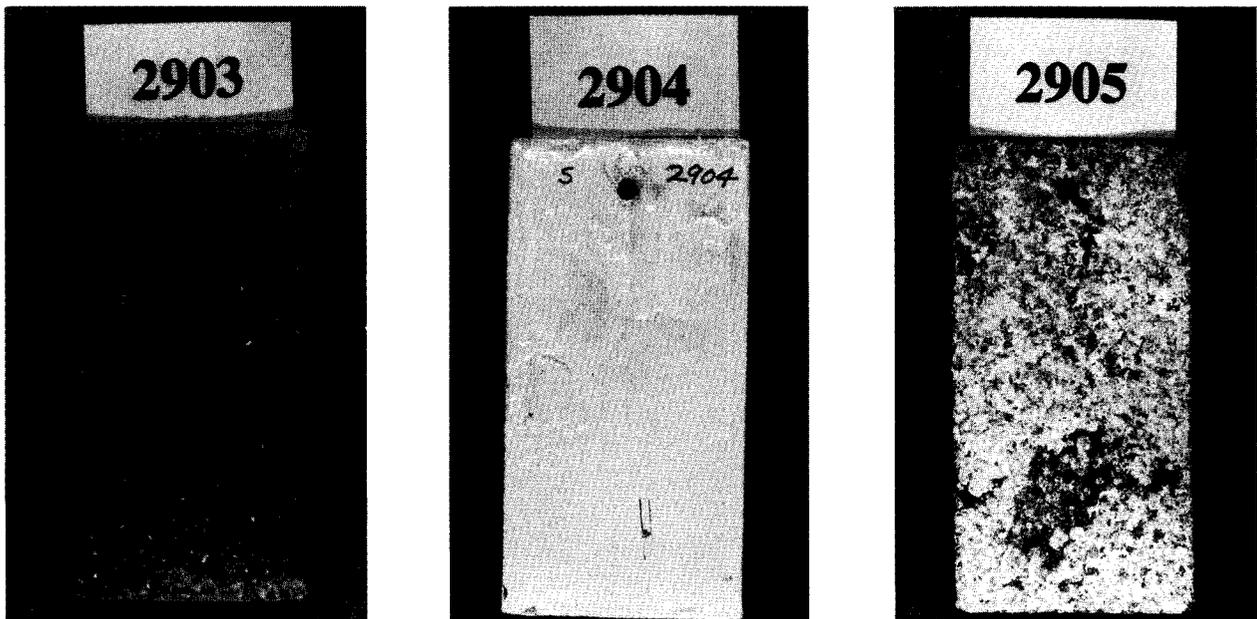


Figure 7. Sealer-Aluminum Duplexes After 2 Years' Immersion in Fresh Water: 2903 System F, 2904 System G, 2905 System C.

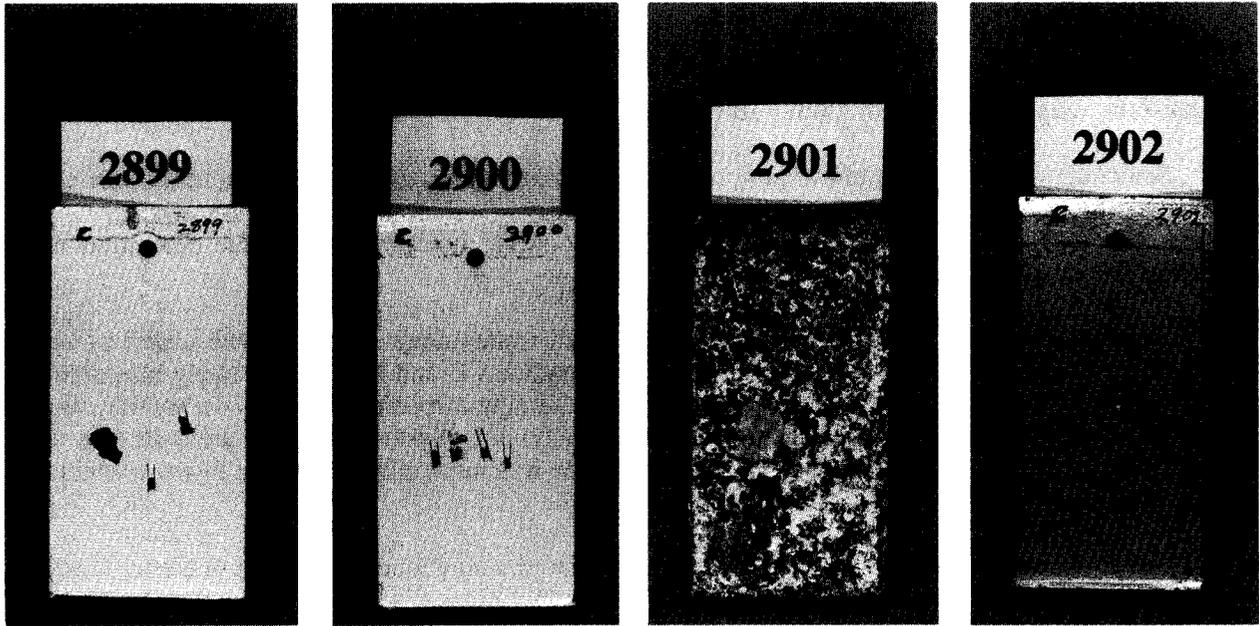


Figure 8. Sealer-Aluminum Duplexes After 2 Years' Immersion in Salt Water: 2899 System A, 2900 System B, 2901 System D, 2902 System E.

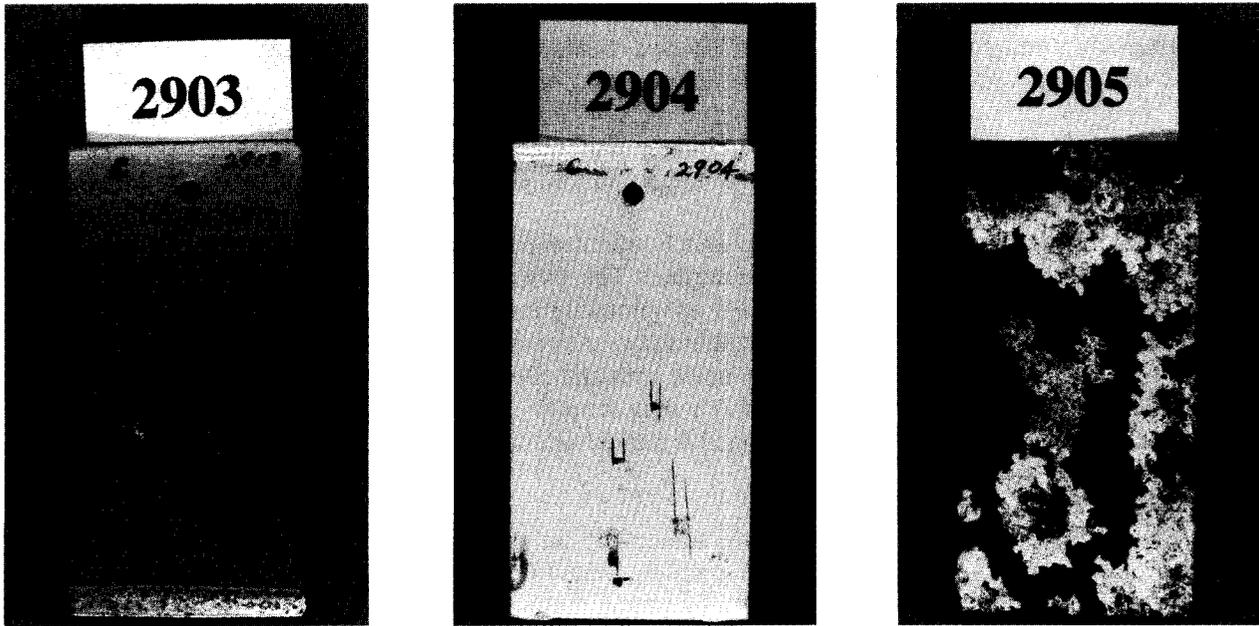


Figure 9. Sealer-Aluminum Duplexes After Two Years' Immersion in Salt Water: 2903 System F, 2904 System G, 2905 System C.

5 DISCUSSION OF RESULTS

Sealer-Zinc Duplexes in Fresh Water Immersion

Sealer systems A, B, F, and G (epoxy, epoxy with wash primer, aluminum-pigmented urethane, and white vinyl), were in near perfect condition after 2 years of fresh water immersion. System C, wash primer, developed a light coating of zinc corrosion products, indicating incomplete protection of the metallic zinc coating.

Sealer system D, waterborne epoxy, exhibited small white eruptions through the sealer, as well as white deposits at the waterline. The deposits found on systems C and D are most likely insoluble zinc hydroxide, $Zn(OH)_2$. Waterline deposits are probably basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$, formed by the reaction of zinc hydroxide and atmospheric carbon dioxide. Systems C and D are quite thin. Most likely coverage of the relatively rough metallizing profile was incomplete, resulting in the formation of zinc corrosion products.

Sealer system E, aluminum pigmented vinyl, performed well with the exception of blister formation adjacent to the scribes made during an adhesion test. The blisters were water-filled rather than salt containing. Water-filled blisters often result from osmosis, caused by the presence of soluble salt deposits beneath a paint. Zinc corrosion products, however, are not sufficiently soluble to cause osmotic blistering. The blistering was probably caused by the formation of an oxygen concentration cell at the scribe. The oxygen concentration differential developing because of the ready access of oxygen to zinc at the scribe. The white vinyl and epoxy systems probably did not blister by this mechanism because of better adhesion to the zinc.

Sealer-Zinc Duplexes in Salt Water Immersion

Sealer systems A and B, epoxy and epoxy with wash primer, provided superior protection of the zinc metallizing immersed in salt water for 2 years. Sealer system C, wash primer, was totally obscured by zinc corrosion products at the end of the 2-year test period.

System D, waterborne epoxy, was severely disfigured by eruptions of zinc corrosion products through the sealer. Holes in the sealer were clearly discernable after removal of the white tubercles.

Some blistering of sealer systems E and F, aluminum vinyl and aluminum urethane, was visible along the panel edges and adjacent to the scribe. The blisters were filled with clear to white colored gelatinous deposits. These subfilm deposits are probably insoluble zinc hydroxide. The deposits may have filled an existing blister by displacing the water. Alternatively the blister may have been formed by the expanding volume of zinc hydroxide beneath the paint film. On an equal molar basis, zinc hydroxide is approximately 7 to 8 times more voluminous than metallic zinc. Both sealer systems E and F are quite flexible and will expand and contain trapped water or salts to a greater extent than other less flexible coating materials which may crack.

Sealer system G, white vinyl, blistered adjacent to the scribe, along the panel edges, and at random spots on the surface. The blisters near the scribe were filled with zinc corrosion products. Random blisters along the surface were water filled. Removal of the coating at the water filled blisters revealed an absence of zinc corrosion products and that zinc is grey in color. The white vinyl declined in adhesion between the 6-month and 2-year evaluations. The appearance of random blisters on the surface of the panel is consistent with the drop in adhesion. Coatings with poor wet adhesion typically exhibit blistering.

Sealer-Aluminum Duplexes in Fresh Water Immersion

Sealer systems A and B, epoxy and epoxy with wash primer over aluminium metallizing, did not perform well in fresh water immersion. Both systems exhibited blistering that appeared to progress through a filiform type mechanism. The tubular shaped blisters formed an interconnected network of subfilm deposits of aluminum corrosion products. Corrosion of aluminum in water progresses from alumina (Al_2O_3), to hydrated forms of alumina, boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) (deS. Brasunas, 1984). Alumina is only 1.3 to 1.5 times more voluminous than metallic aluminum. The hydrated forms of alumina are significantly more voluminous than alumina and are probably responsible for the blistering observed with the epoxy sealer systems. Epoxy coatings are generally more brittle than other types of organic coatings such as vinyls and urethanes. The epoxy sealers on aluminum were not able to contain the blistering and consequently cracked.

Firmly adherent white aluminum corrosion products covered approximately 50 percent of sealer system C, wash primer, after 2 years in fresh water immersion. Removal of these deposits with a razor blade revealed small dark grey spots that were probably alumina. Removal of the grey deposits indicated the presence of small pits, below which the aluminum metallizing was still intact. This process of pitting would have eventually progressed to the point of rust breakthrough.

Sealer systems D, E, F, and G (waterborne epoxy, aluminum vinyl, aluminum urethane, and white vinyl) all had similar performance characteristics. The waterborne epoxy showed some white rust breakthrough along one edge and adjacent to the scribe. Each of the other sealer systems exhibited slight blistering and formation of white aluminum corrosion products adjacent to the scribes. Removal of these white corrosion products revealed pitting of the aluminum and minor red rust staining in the pits. With the exception of mechanically damaged areas, each of these sealer systems protected the metallized aluminum coating in fresh water immersion.

Sealer-Aluminum Duplexes in Salt Water Immersion

Epoxy sealer systems A and B on aluminum suffered the same types of failures they experienced in fresh water. Subfilm aluminum corrosion product deposits led to cracking of the epoxy coating. Sealer system F (urethane) failed by the same mode as the epoxy sealers for this exposure. Pitting and red rust breakthrough was exposed upon removal of the sealer and white aluminum corrosion products.

Systems C and D (wash primer and waterborne epoxy) developed heavy surface deposits of white aluminum corrosion products. Some of the tubercles protruded nearly 1/4 in. (0.625 cm) from the surface of the test panels. The waterborne epoxy also experienced subfilm salt deposition. Removal of corrosion products revealed that, for both of these systems, the aluminum had considerable pitting. Red rust stain was also visible on the aluminum metallizing.

Sealer systems E and G (aluminum and white vinyls) experienced similar forms of deterioration. Large blisters, up to 2 in. (5 cm) in diameter, covered most of each coating duplex. The damage was somewhat more severe with the aluminum vinyl sealer. Blisters on both sealer systems were filled with white aluminum corrosion products. Removal of the sealer and corrosion deposits exposed a rough and pitted aluminum coating. Red rust stain was clearly visible on the aluminum metallizing.

6 CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this study, more specific recommendations can be added to guide specification CW-05036, *Metallizing: Hydraulic and Appurtenant Works*, regarding zinc and aluminum metallized coatings immersed in fresh and salt water.

Several sealers are compatible with zinc metallizing for exposure in fresh water. Sealer systems composed of epoxy, wash primer and epoxy, aluminum pigmented moisture cured aromatic urethane, and white pigmented vinyl, adhere well to, and protect zinc metallizing from early deterioration. The guide specification recommends that zinc metallizing that will be immersed in fresh water should be sealed with one of several vinyl paint systems or with epoxy system A, evaluated in this study. These guide specification recommendations are consistent with the results of this study. In geographic locations mandating the use of lower VOC sealers and coatings, the epoxy sealer system is recommended.

Sealer-Zinc Duplexes in Fresh Water Immersion

The two epoxy sealer systems (epoxy and epoxy with wash primer) exhibited superior performance as sealers for metallized zinc exposed to salt water immersion. These epoxies performed somewhat better than the vinyls, waterborne epoxy, and urethane sealers. This result is consistent with the known performance of the materials when used to protect steel surfaces in salt water immersion. Civil works guide specification CW-09940, *Painting: Hydraulic Structures and Appurtenant Works*, recommends the coatings used in sealer system A, for the protection of steel in salt water. Zinc-metallized sprayed coatings, are not the primary recommendation found in CW-05036 for salt water immersion. Sealer recommendations are not provided in that document for zinc metallizing in salt water immersion. The epoxy sealer system A, without the wash primer, is recommended for sealing zinc metallizing intended for use in salt water. The wash primer contains materials that are objectional from a standpoint of health and safety. Also, the wash primer does not appear to enhance the performance of the epoxy sealer system.

Sealer-Aluminum Duplexes in Fresh Water Immersion

Aluminum and white pigmented vinyls and urethane sealers all provided adequate protection of aluminum in fresh water. CW-05036 does not address the use of aluminum metallizing for fresh water immersion. However, literature sources and manufacturers' information do describe the use of aluminum metallizing for fresh water immersion applications. These sources indicate the acceptability of both vinyls and epoxies. This study found that at least some epoxies are not acceptable for this application. Sealing of aluminum metallizing for fresh water applications should be performed with one of the vinyl systems evaluated in this study. For applications requiring a sealer material with a lower VOC content, the use of the urethane system should be considered.

Sealer-Aluminum Duplexes in Salt Water Immersion

None of the sealer systems evaluated for use on aluminum metallizing exposed to salt water performed adequately. USACE guidance CW-05036 calls for the use of sealer system A (epoxy) evaluated in this study. The use of this sealer system may potentially accelerate the degradation of the

sprayed aluminum coating as well as the steel substrate. Further work is needed to identify an appropriate sealer system for aluminum metallizing for use in salt water immersion.

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