

## **ZINC RICH PRIMERS FOR CORROSION PROTECTION**

J. Peter Ault, P.E., PCS  
*Elzly Technology Corporation*  
*Ocean City, NJ*

Abstract: Various types of zinc-rich coatings are available for corrosion protection. The challenges associated with the proper specification and application of zinc-rich coatings are briefly discussed. The paper then focuses on data from various studies, which quantify the corrosion protection benefits of various types of zinc-rich coatings.

### **ZINC RICH COATING TECHNOLOGIES**

Zinc-rich coatings are used by many industries for the corrosion protection of steel substrates. Uses include highway and infrastructure, industrial and automotive applications. These coating materials have demonstrated improved atmospheric corrosion performance when compared to carbon steels protected only by spray applied organic coatings (such as an epoxy-urethane coating system).

Since the 1800's the practice of hot-dip galvanizing has been used to apply a metallic zinc coating to protect steel from corrosion. Galvanizing provides a metallurgically bonded, pure zinc coating to protect the substrate. Zinc-rich coatings are an attempt to achieve similar protection with liquid materials that can be spray applied at ambient temperatures. Current zinc-rich coatings provide lesser protection than galvanizing, although their protection is typically improved as compared to organically coated carbon steel. As a result, galvanized components are usually preferred for corrosion protection. However, zinc-rich coatings are better suited for large steel components, field applied coatings, repair and touch-up operations (including repair of galvanized components). While they will not provide the same level of protection as galvanizing, zinc-rich coatings effectively improve corrosion performance.

Zinc-rich coatings are described in a number of industry and military specifications. SSPC Paint 20 is an industry specification that categorizes zinc primers according to four vehicle types.

- Type I-A includes water-soluble inorganic post-curing vehicles such as alkali metal silicates, phosphates, and modifications thereof that must be subsequently cured by application of heat or a curing solution.
- Type I-B includes water reducible inorganic self-curing vehicles such as water-soluble alkali metal silicates, quaternary ammonium silicates, phosphates, and modifications thereof. Type I-B coatings cure by a reaction among the zinc, silicate, steel substrate, and naturally occurring carbon dioxide during and after evaporation of water from the coating.

- Type I-C coatings include solvent reducible inorganic self-curing vehicles such as titanates, organic silicates, and polymeric modifications of these silicates. These systems are dependent upon moisture from the atmosphere to complete hydrolysis, forming the titanate- or polysilicate-zinc reaction product.
- Type II coatings involve organic vehicles which may be chemically cured or may dry by solvent evaporation (heat may also be used under certain conditions). Common vehicles for Type 2 coatings include epoxies and moisture cure urethanes.

SSPC Paint 20 defines three levels of zinc in the dried film: Level 1 is equal to or greater than 85%; Level 2 is equal to 77% up to 85% and Level 3 is equal to 65% up to 77%. By this definition, coatings with greater than 65% zinc by weight in the dried film are considered “Zinc-Rich.” It is important to note that zinc content is weight percent. Volume percent will be much lower since the binder is considerably lighter than the zinc. Zinc content is determined in the dried film, so the wet product will likely have a lower zinc content. Finally, note that zinc particle size and purity are also issues, which may impact performance but are not addressed in the specification.

There are a number of military specification for zinc-rich coatings including DOD-PRF-24648, Primer Coating, Zinc Dust Pigmented for Exterior Steel Surfaces (16 July 1985, Canceled 14 January 2008); DOD-P-23236, Type 3 (circa 1982); MIL-DTL-24441, formula 159 (Epoxy zinc-rich with approximately 91% zinc in dry film by weight) and A-A-59745, Commercial Item Description (CID), Zinc-rich Coatings.

Note that inorganic zinc pre-construction primers (PCPs) are a special class of inorganic zinc primers. IOZ PCPs have drastically reduced zinc pigment content (typically in the 28-48% range) with an end-use requirement of 0.6-0.8 mils (15-20  $\mu\text{m}$ ) DFT.<sup>1</sup>

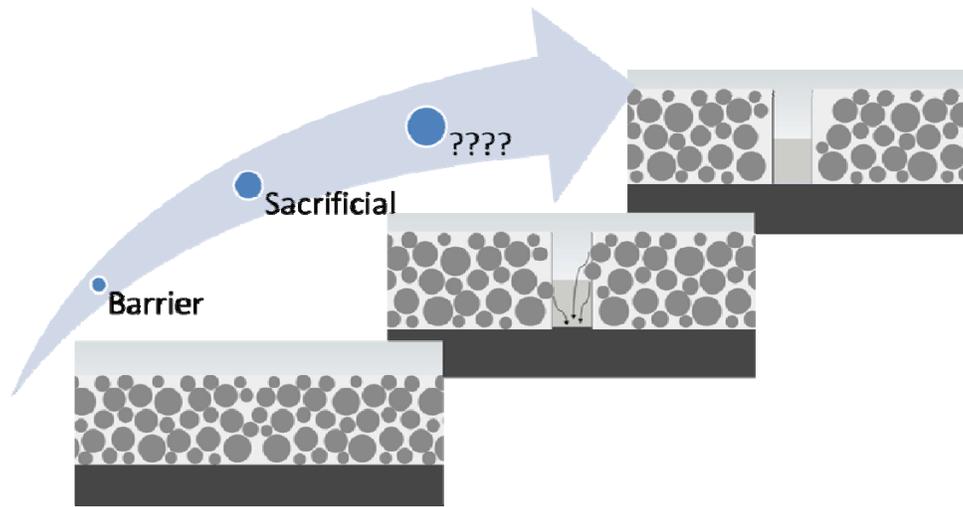
## **MECHANISMS OF PROTECTION**

While the corrosion protective performance of zinc-rich coatings is often attributed to sacrificial protection, it is important to recognize that the protection mechanisms are far more complex. Figure 1 schematically shows three stages in the life of a zinc-rich coating. After application, the zinc-rich coating will be a continuous film, which effectively isolates the substrate from the environment. At this stage, the coating behaves like any other barrier coating; it isolates the substrate from the environment. Once a defect is made in the coating, which exposes the substrate, the zinc-rich coating provides a certain amount of sacrificial protection is provided. This protection depends on the amount and type of moisture present, the electrical connectivity of the zinc particles to each other and the substrate, the purity of the zinc and other factors. After some finite time, the zinc will be depleted and sacrificial protection will cease. Some have suggested that there is still some type of protection provided to the steel after this sacrificial phase,

---

<sup>1</sup> Ault, J. Peter, *Retention of Pre-Construction Primers During Shipbuilding*, Journal of Protective Coatings and Linings, November, 2011.

perhaps due to the inhibitive effects of surface films resulting from the zinc corrosion products.



**Figure 1. Schematic of zinc-rich coating protection mechanisms.**

In an effort to understand the behavior of the zinc-rich coatings, anodic polarization curves were performed on replicate test panels with various products and compared to galvanizing. Figure 2 shows curves run in seawater. Note that the potential of the galvanizing does not shift much over a wide range of current values. This behavior is expected of an effective anode. The curves for the zinc-rich coatings tend to polarize at higher current values, indicating that they are less effective anodes.

Figure 3 attempts to explain the observed phenomena with steel and zinc polarization data from the literature.<sup>2</sup> The polarization curve for zinc agrees fairly well with the galvanized curve shown in Figure 2. A second curve has been developed representing the effect of a smaller zinc to steel area ratio (1:100 versus 1:1). The area ratio change has the effect of shifting the zinc polarization to the left by two decades of current. This curve is consistent with the measured data for the zinc-rich coatings. The analysis suggests that zinc-rich coatings have the capacity to engage a much smaller quantity of zinc in the protective behavior.

---

<sup>2</sup> Based on data in "Atlas of Polarization Diagrams for Naval Materials in Seawater," Harvey P. Hack, April 1995

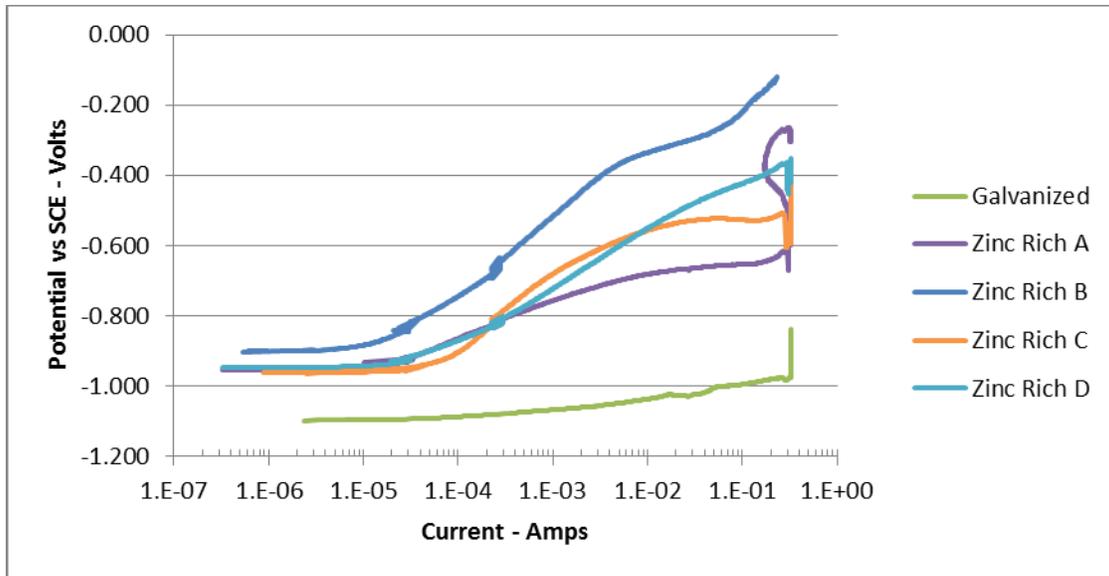


Figure 2. Anodic polarization curves for various zinc-rich coatings and galvanizing.

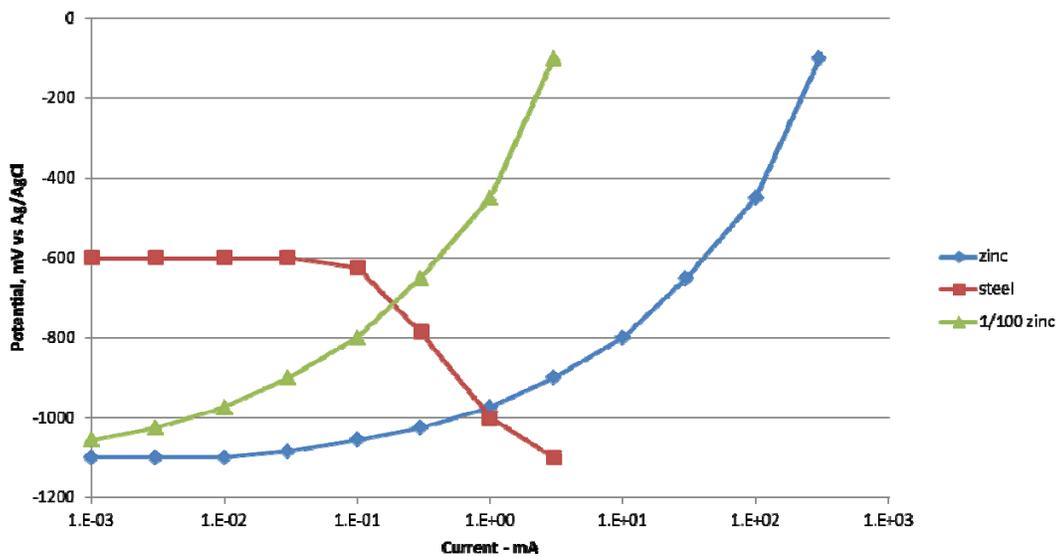
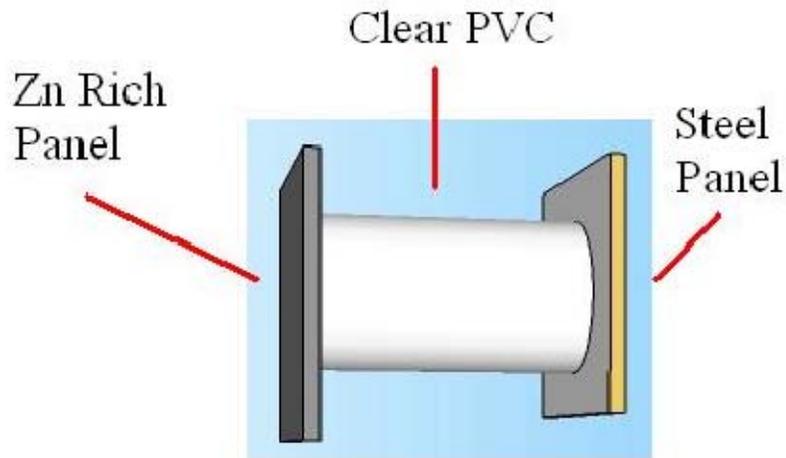


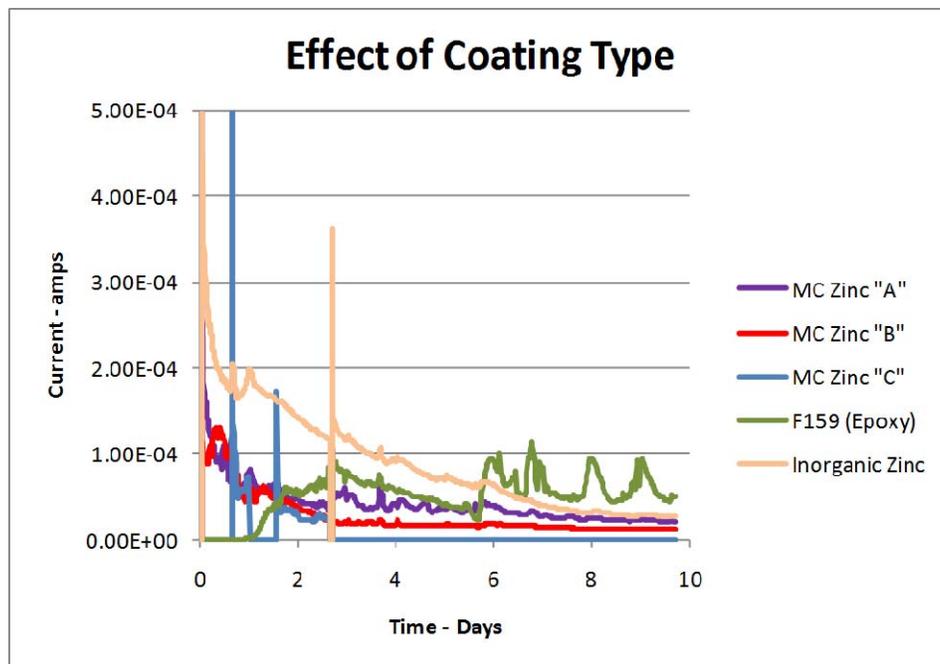
Figure 3. Interaction of couples with different zinc:steel area ratios.

An experiment was designed to quantify the level of sacrificial protection provided to steel by a zinc-rich coating. The test setup used a zinc coated and bare steel test panel separated by a clear section of PVC pipe between that could be filled with an electrolyte and the electrical current flowing from the zinc coated panel to the steel was monitored. Provisions were made so that the protected and unprotected electrochemical potential of the steel panels could also be determined. Figure 4 shows a schematic of the test setup.



**Figure 4. Schematic of galvanic experimental setup.**

Figure 5 shows the current provided by each of the coatings as a function of time. Figure 6 shows the potential of the couple as a function of time. At the end of the 10-day exposure, the steel panels coupled to the Inorganic zinc, MC Zinc A and MC Zinc B had minimal corrosion while the panels coupled to the other two coatings had corrosion over the entire steel surface, these were the samples with couple potentials nominally between -0.8 and -0.7 volts versus saturated calomel electrode (SCE).



**Figure 5. Galvanic current provided by various zinc-rich coatings.**

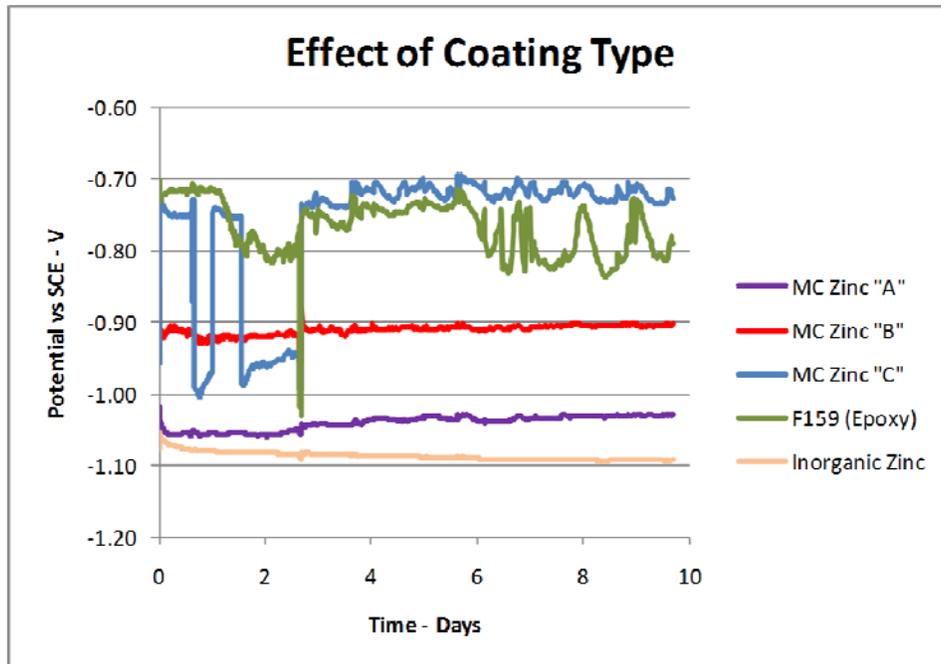


Figure 6. Couple potential versus time for various coating-steel couples.

### **PERFORMANCE BENEFITS OF ZINC RICH COATINGS**

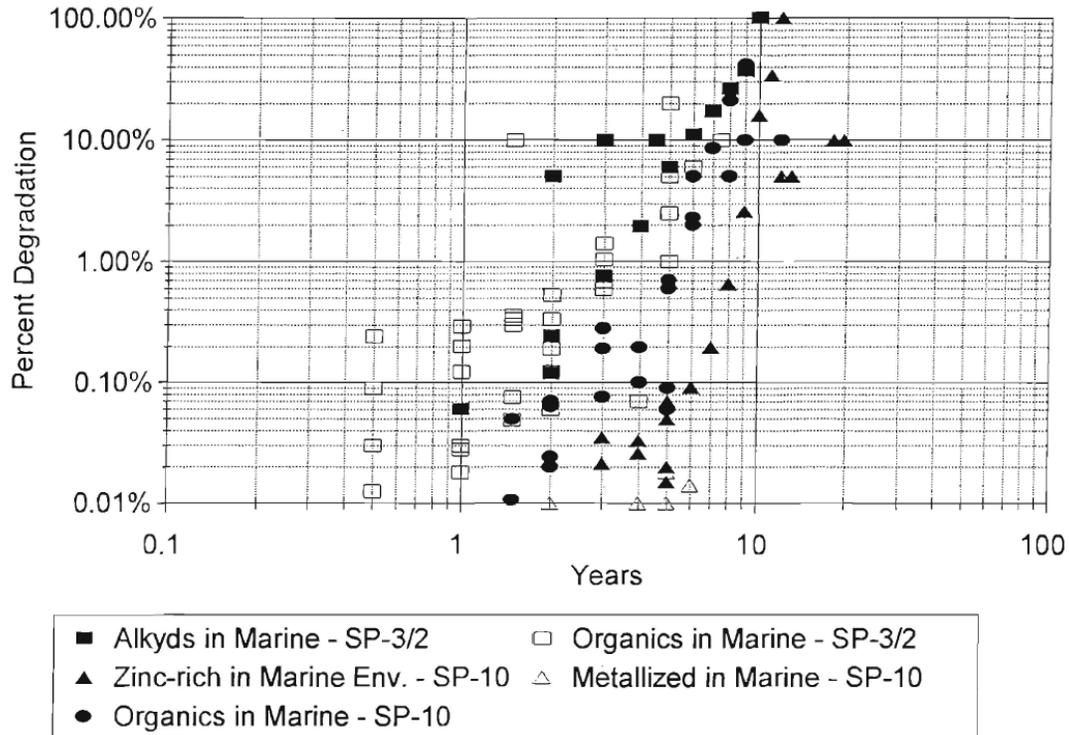
Numerous studies have been performed on the performance of zinc-rich coatings in a wide range of environments. In general, the studies document the benefit of zinc-rich coatings at preventing underfilm corrosion of steel substrates in accelerated or severe natural environments. Several of the studies are reviewed in this section.

#### **Zinc Rich Coatings on Bridges**

A Federal Highway Administration report<sup>3</sup> documents the 5-year performance of thirteen generically different coating systems applied to four bridges in different environments. The systems were selected based on the performance of 34 different systems in a battery of accelerated corrosion tests. The report concluded that the best performing liquid-applied systems were those incorporating zinc-rich primers. While both organic and inorganic zinc primers shows good corrosion protection, the inorganic zinc primer had better resistance to undercutting at the scribe. The organic zinc coatings did perform better than the remaining systems without zinc-rich primers.

<sup>3</sup>Kogler, R.A., Ault, J. Peter and Farschon, C.L.; *Environmentally Acceptable Materials for the Corrosion Protection of Steel Bridges*, Report No. FHWA-RD-96-058, Federal Highway Administration, Washington, DC, January 1997.

In the 1980's, FHWA sponsored a program called Performance of Alternative Coatings in the Environment (PACE).<sup>4</sup> This program generated an abundance of coatings data over a long timeframe. Figure 7 (reproduced from reference 2) shows the deterioration rate (percent rust-through) versus time for Alkyd coatings, other organic coatings (epoxies, urethanes, etc.), zinc-rich systems and metallized systems in a marine environment. The data clearly show improved performance of the zinc-rich coatings versus other organic coatings over and SP-10 surface. The data suggest at least 2-5 years of added life to any particular failure condition.



**Figure 7. Coating deterioration versus time in a marine environment. Reproduced from reference 2. Note log scales.**

The New Jersey DOT has an ongoing evaluation of various bridge coatings on the Thomas Mathis Bridge, which carries State Route 37 over Barnegat Bay in central New Jersey.<sup>5</sup> This project involved application of a different coating system to each span of the bridge. Each span was entirely painted with the test coating system (bearings, stringers, diaphragms, etc.). The author has participated in several inspections of these structures.

<sup>4</sup> B.R. Appleman, J.A. Bruno and R.E. Weaver; *Performance of Alternative Coatings in the Environment (PACE)*, Report Nos. FHWA-RD-89-127, FHWA-RD-89-235 and FHWA-RD-89-236, Federal Highway Administration, Washington, DC, September 1990.

<sup>5</sup> A. Chmiel, V. Mottloa, and J. Kauffman, *Structural Coating Evaluation in New Jersey*, Research News, Journal of Protective Coatings and Linings, January 1989, pp. 23-26.

Eight systems with an inorganic zinc (IOZ) primer were tested. The inorganic zinc systems performed quite well as a class. Only one system performed unacceptably – water-based inorganic zinc with a silicone topcoat applied over a SP-6 (Commercial Blast) surface. The performance of the inorganic zinc systems is quite interesting because of the variety of systems evaluated. Figure 8 shows the ratings over time for each of the individual systems. The dark blue lines correspond to systems applied over an SP-10 surface and the pink lines correspond to systems applied over an SP-6 surface. Comparable coating systems have similar symbols. It is interesting to note that the waterborne inorganic zinc performed poorly over the SP-6 surface while the solvent based systems performed as well or better over the SP-6 versus the SP-10 surfaces. This is in contrast to the standard industry requirement that an inorganic zinc coating should be applied over an SP-10 surface.

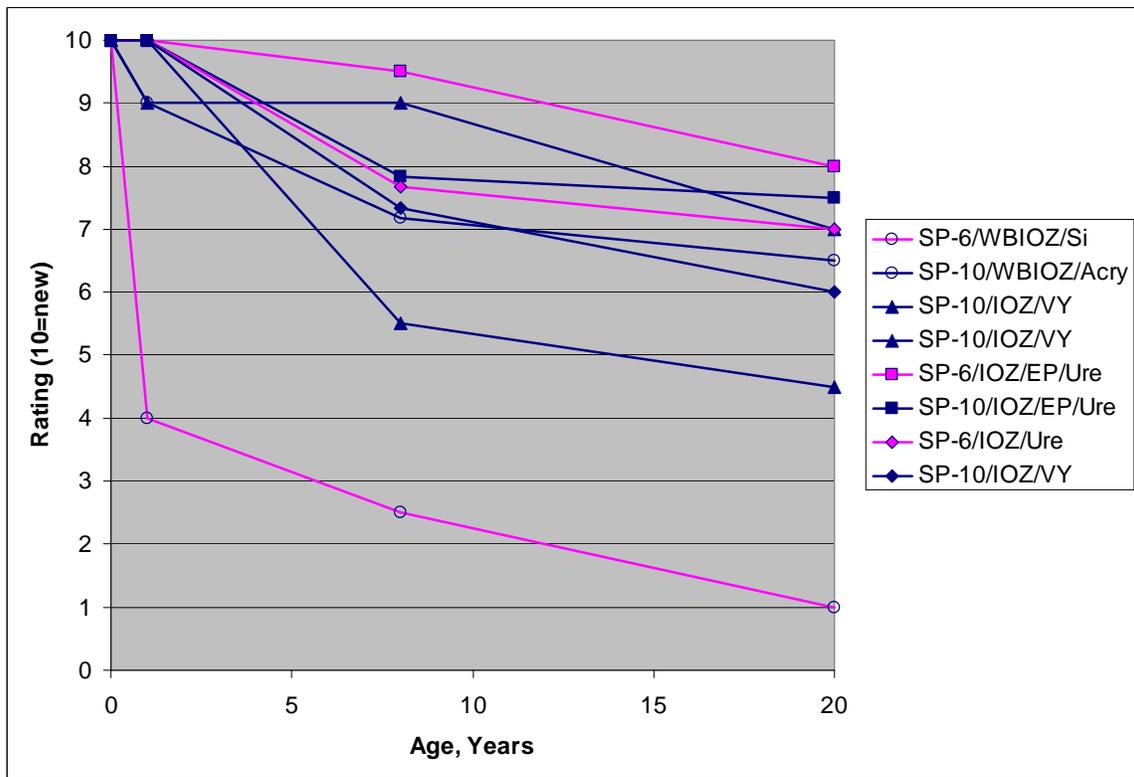


Figure 8. 20-year performance of inorganic zinc systems.

The test program included seven organic zinc systems (OZ). The organic zinc systems performed quite well as a class. The only system that did not perform well was one of the organic zinc systems with a urethane topcoat over an SP-6 prepared surface. Figure 9 shows the performance versus time of the individual organic zinc systems. Again, the dark blue lines represent systems over an SP-10 surface while the pink lines represent systems over an SP-6 surface. Excepting the organic zinc/urethane system, the data suggest that equivalent performance can be achieved over an SP-6 and SP-10 surface.

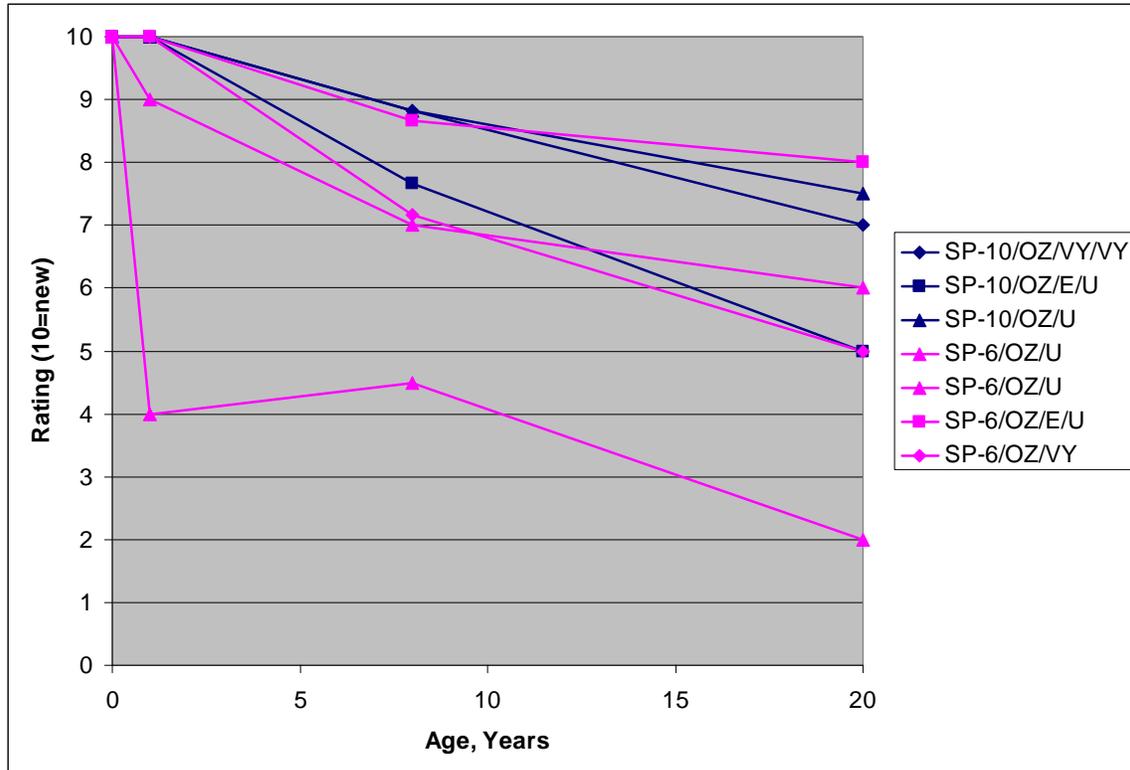


Figure 9. 20-year performance of organic zinc systems.

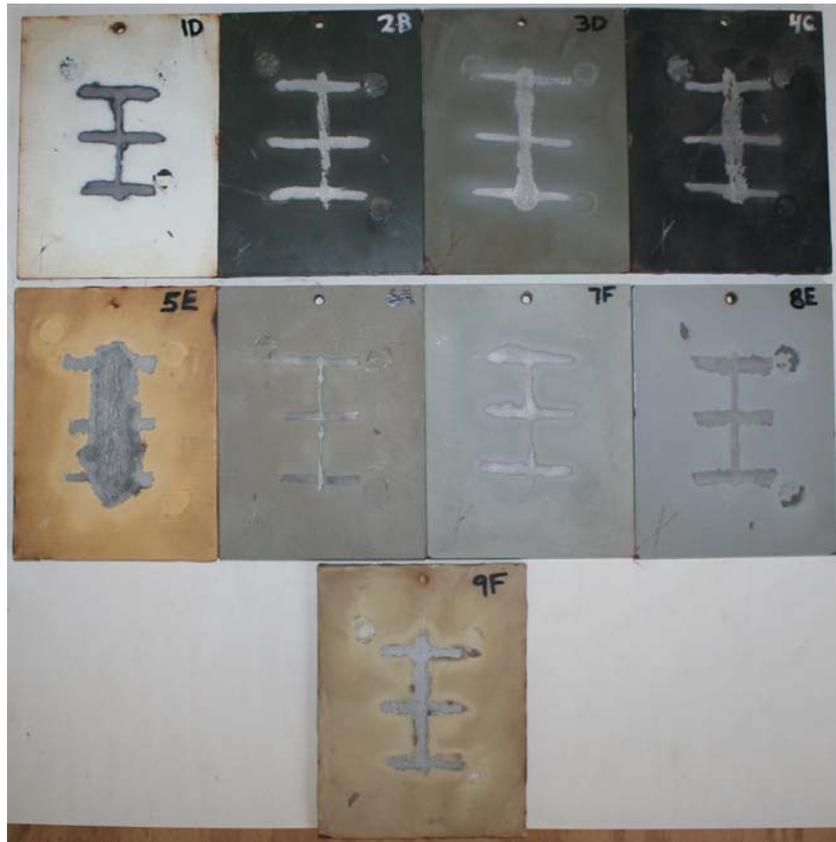
### Zinc Rich Coatings for Shipbuilding and Marine Uses

Ships and marine structures contain a variety of corrosive microenvironments. One particularly corrosive environment includes bilges and troughs, which are intermittently wetted (with seawater) and dried, may undergo large temperature fluctuations and typically have high humidity. A test program was conducted to investigate the performance of alternative coating systems in this type of environment. Several 6- by 9-inch test panels with each of the coating systems shown in Table 1 was exposed in an accelerated corrosion test designed to simulate a marine trough environment. After 19 months, one test panel with each coating was destructively inspected to determine the actual extent of corrosion from the intentional scribe in the panel.

To determine the extent of section loss, the coating and corrosion was carefully removed from the panel to create the pattern shown in Figure 10. The pattern chosen to remove the paint facilitated measurement of the pit depths. After the coating and corrosion was removed, the panels were then cleaned and wiped down with acetone. Once cleaned, a Pit & Crack Depth Gauge (Albuquerque Industrial, Inc) was used to measure the pit depth. The instrument has a measuring range of 0 to 500 mils and a resolution of 0.5 mils. Three measurements were made in each of the three designated spots (top, middle, and bottom). Figure 3 shows the maximum pit depth for each panel in the designated spots.

**Table 1 - Coating Systems Tested**

Number	Coating System
1	Conversion Coat: TT-C-490, Type I, Zinc Phosphate Primer: MIL-P-23377J, Class C, High Solids Epoxy, 0.6 to 0.9 mil Topcoat: MIL-PRF-22750F, High Solids Epoxy, 1.7 to 2.3 mils
2	Primer: MIL-P-23377J, Class C, High Solids Epoxy, 0.6 to 0.9 mil Topcoat: MIL-PRF-85285, Type II, Class H, Polyurethane, 2-3 mils
3	Powder Coat: MIL-PRF-23236, Type VIII, Epoxy Powder, 6-8 mils
4	Powder Coat: MIL-P-23236, Type VIIIa, two coats Primer: Zinc-rich Epoxy @ 3-4 mils Topcoat: TGIC-Polyester @ 3-4 mils
5	MIL-PRF-23236C, Type VII, Class 5, Phenolic-modified High Solids Epoxy, 2 coats @ 9-11 mils each coat
6	MIL-DTL-24441, Type III Polyamide Epoxy Primer: Zinc-rich Epoxy, Formula 159, 4 mils Midcoat: Epoxy, Formula 150, 4 mils Topcoat: Epoxy, Formula 151, 4 mils
7	Primer: Inorganic Zinc, 2-4 mils Topcoat: High Solids Epoxy, 4 to 8 mils
8	Primer: Inorganic Zinc, 2-4 mils Topcoat: Epoxy Siloxane, 5 mils
9	MIL-PRF-24667A Epoxy Polysulfide, 2 coats @ 10-12 mils each coat



**Figure 10. All test panels after cleaning.**

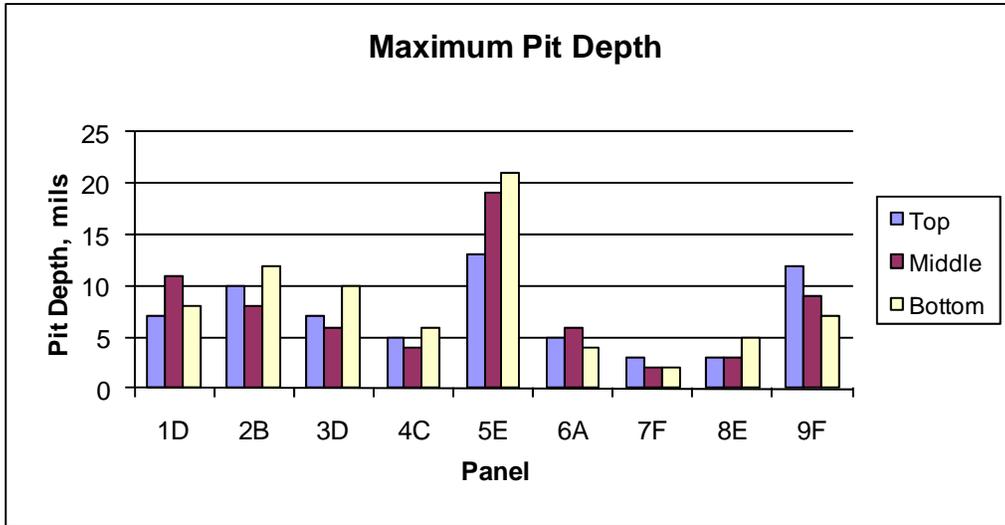


Figure 11. Maximum measured pit depth.

To further explore the relationship between undercutting and pitting, the maximum pit depth was plotted as a function of the maximum destructively determined undercutting. Figure 12 and Table 2 show the results. The correlation between undercutting and pit depth is not strong, but generally shows a positive relationship.

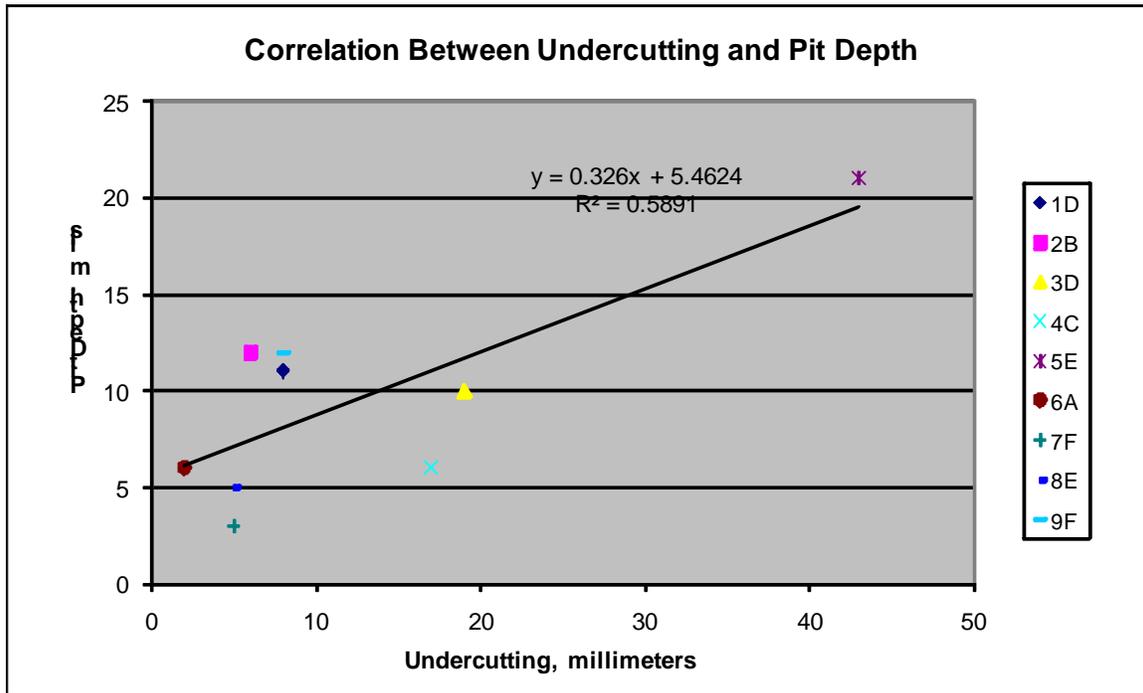


Figure 12. Correlation between pitting and Undercutting.

**Table 2- Maximum Undercutting and Maximum Pit Depth after 19 Months Exposure**

Panel	Undercutting, mm	Pit Depth, mils
1D	8	11
2B	6	12
3D	19	10
4C	17	6
5E	43	21
6A	2	6
7F	5	3
8E	5	5
9F	8	12

The deepest pitting was observed on coating system 5, a high solids, high build epoxy applied direct to metal. This was also the panel with the largest undercutting. Systems with inorganic zinc primers (7 and 8) had the least depth of pitting. Figure 13 compares the pitting under system 5 and system 7 after cleaning. Organic zinc-rich systems (4 and 6) had the next lowest observed pit depths.



**Figure 13. Pitting under system 5 (left) and 7 (right) after cleaning.**

### **Armor Steel on Military Vehicles**

A current US Marine Corps project includes testing to demonstrate the ability of zinc-rich coatings to provide corrosion protection to armor grade steel where coating damage (e.g., a scribe) has occurred.<sup>6</sup> Painted test panels are exposed in natural atmospheric exposure (Ft. Lauderdale, FL) while a duplicate set has completed 120 cycles of exposure in an accelerated corrosion test (GM9540P).

---

<sup>6</sup> J. Peter Ault, John Repp, and Andrew Sheetz, *Zinc-rich Coatings - How They Work and How to Check If They'll Work*, paper presented at the DoD Corrosion Conference, August 2011.

Test samples are 4-inch by 6-inch by 1/8-inch MIL-A-46100 armor steel panels. Panels were prepared by abrasive blasting to a nominal 1-mil (25.4- $\mu$ m) profile prior to coating. The control coating was MIL-P-53030 epoxy primer with MIL-C-64159 CARC topcoat.

The primary series of test panels was prepared to investigate the effectiveness of a zinc-rich coating conforming to Commercial Item Description (CID) A-A-59745. Three products meeting the CID were evaluated untopcoated and as part of the CARC system. All three products employed a moisture cure urethane binder. The zinc-rich primer was applied direct to metal with a CARC system applied over the primed surface (MIL-DTL-53030 epoxy primer and MIL-DTL-64159 CARC topcoat).

A second series of test panels was prepared with untopcoated alternatives to the zinc-rich products meeting the CID. Specifically, a commercially available ethyl silicate inorganic zinc coating and a zinc-rich epoxy meeting the requirements of MIL-DTL-24441, formula 159 were compared to the CID products in an untopcoated condition.

During this testing all samples were visually evaluated at regular intervals for visible corrosion (ASTM D610), coating blistering (ASTM D714) and scribe creepage (mm of visible underfilm cutback from the scribe). For natural exposure samples this is nominally every quarter (three months) through one (1) year of exposure. For accelerated corrosion samples this was every 20 cycles through 120 cycles of testing. At each inspection interval samples were photographed.

The natural exposure samples are still in test; this paper will focus on the accelerated test results. At the completion of accelerated testing the panels were destructively evaluated for corrosion beneath the coating. The destructive inspection included removing coating and corrosion product such that the extent of metal loss could be measured with a pit gage.

Figure 14 shows a representative test panel before and after cleaning for analysis. The extent of undercutting was determined by measuring the extent that the coating could easily be removed using a controlled amount of pressure. The maximum pit depth was the deepest pit measured in the corroded area using a Pit & Crack Depth Gauge with a resolution of 0.5 mils.

Figure 15 shows the maximum measured pit depth and maximum measured undercutting respectively for the control Epoxy/CARC system, the untopcoated zinc-rich coatings meeting the CID and the same zinc-rich coatings with the control epoxy/CARC system applied over the CID primer. Note that the zinc-rich primer with or without a topcoat resists undercutting and pitting better than the control system. Deepest pits were 2-3 times deeper under the control versus the systems with zinc-rich primer.

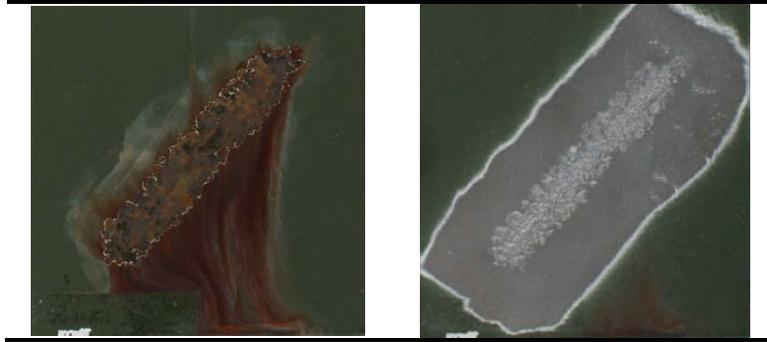


Figure 14. Test panels after exposure (left) and cleaned for evaluation (right).

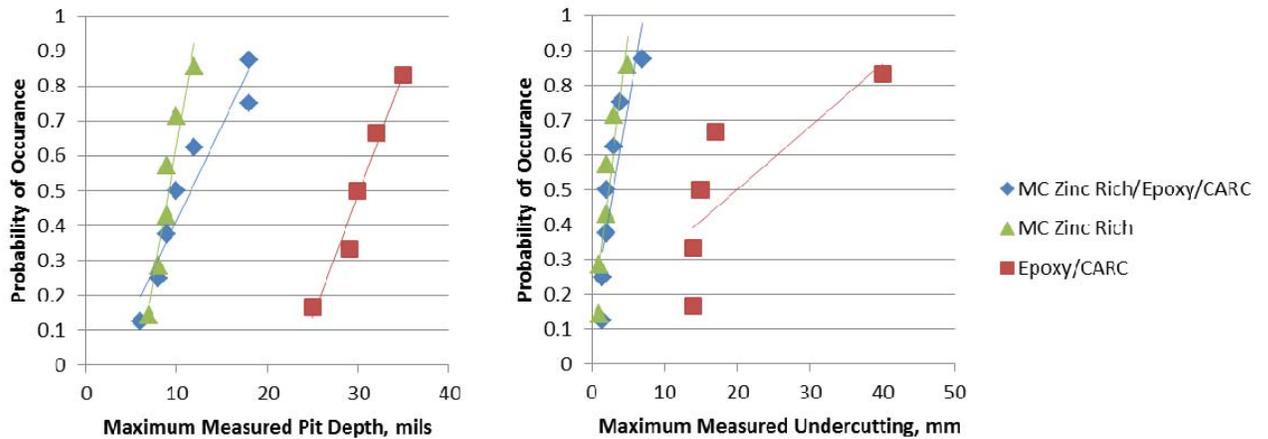


Figure 15. Corrosion observed on test panels after 120 Cycles GM 9540P exposure.

Figure 16 shows the maximum measured pit depth and maximum measured undercutting respectively for the control Epoxy/CARC system and the three classes of zinc-rich coatings without a topcoat. As would be expected, the inorganic zinc coating performed considerably better than either type of organic zinc material. However, both organic zinc materials performed better than the control system. Finally it is worth noting that the zinc-rich meeting the CID performed better both from an undercutting and pitting perspective than the zinc-rich epoxy.

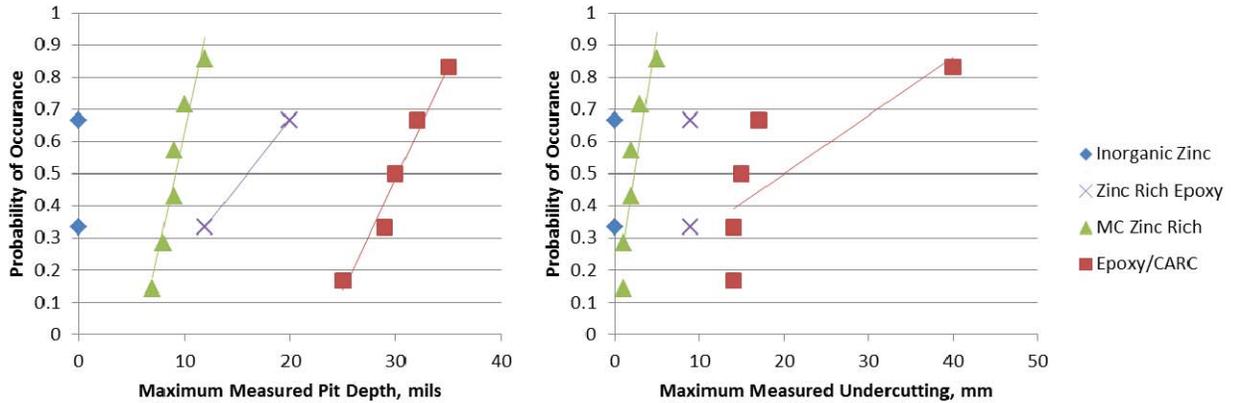


Figure 16. Corrosion observed on test panels after 120 cycles of GM 9540P exposure.

## CONCLUSIONS

A review of past research and available literature supports the following conclusions with respect to the use and performance of zinc-rich coatings.

1. Zinc rich coatings provide substantially improved corrosion protection versus most organic barrier coatings. This improvement is manifested as reduced underfilm corrosion and reduced pit depths at coating defects. Both phenomena can increase the coating and/or structure service life.
2. A range in performance of zinc-rich coatings can be expected. Formulation and application details can impact performance. Generally, inorganic zinc coatings can provide better corrosion protection than organic zinc coatings.
3. Sacrificial cathodic protection is likely not the only mechanism by which zinc-rich coating protect the substrate based on their long-term benefits as compared to a lesser amount of zinc participating in the sacrificial protection process (as compared to galvanizing).