

Zinc Rich Coatings In Immersion Service, where to use them and where not to

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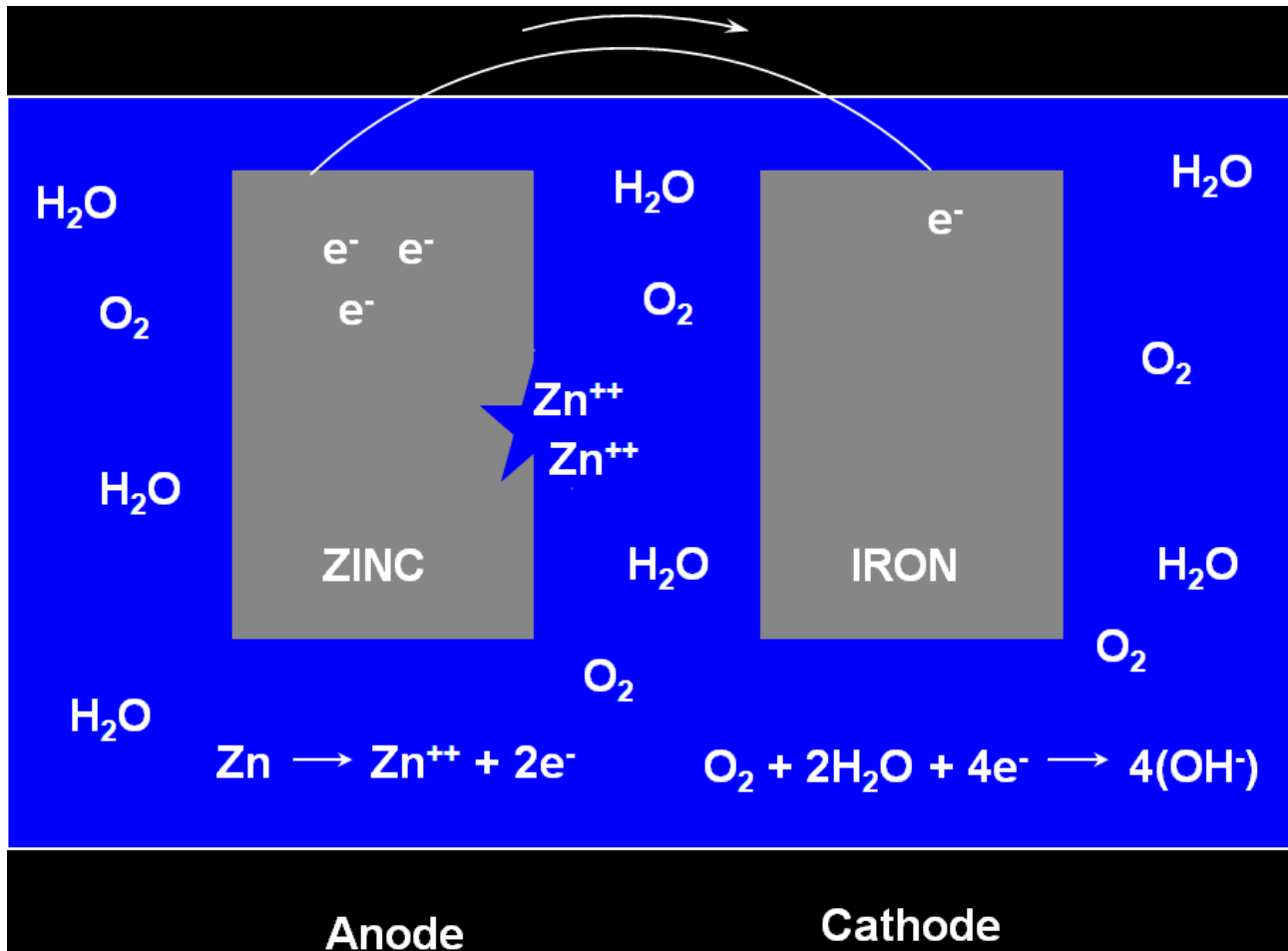
Background:

- The first zinc rich primers with zinc particles held together with a polymer were utilized in the 1930s.
- This worked by cathodic protection resulting from the sacrifice of the zinc metal in the coating in preference to oxidation of the carbon steel substrate.

Background:

- Zinc, under most conditions, is more active than carbon steel and will actively keep carbon steel protected from corrosion provided:
 1. There is intimate contact between the zinc and carbon steel.
 2. Free zinc available to sacrifice itself.
- Zinc is somewhat self healing and will bridge small gaps of damaged or uncoated areas.

Zinc/iron galvanic cell:



Some of the variables affecting the corrosion rate of zinc rich primers:

- Water content
- pH, high or low
- Dissolved oxygen and carbon dioxide content
- Water purity and salt content

Zinc corrosion products:

- Zinc in the presence of water and dissolved gases (oxygen and carbon dioxide) forms:
 1. Zinc hydroxide and zinc oxide
 2. Zinc carbonate, a stable zinc salt
- A layer of zinc oxide and zinc carbonate effectively stabilize the surface to further corrosion and continued sacrifice of zinc

Zinc corrosion products:

- In the presence of Cl^- ions, as is the case with substrate contamination with residual NaCl, zinc chloride salts develop
- These zinc chloride salts are hygroscopic and when present under a topcoat result in osmotic blistering

Types of Zinc Rich Coatings:

- Inorganic
 - Water-based
 - Solvent-based
- Organic
 - Epoxy
 - Urethane
 - Others such as epoxy ester, phenoxy, and chlorinated rubber

The silicate binders used in inorganic zinc coatings, IOZ, are unaffected by most alcohols, solvents and hydrocarbons and have been successfully used for immersion service for nearly a century.

Inorganic zinc rich coatings will be the primary focus of this discussion as organic zinc rich coatings are not commonly used in immersion service.

Where to use them in immersion service:

- Hydrocarbon products
- Solvents
- Near pH-neutral aqueous solutions
- Zinc is amphoteric in nature and performs well at pH ranging from 5.5-10 however the duration of corrosion protection is optimum at pH of 7

Where to use them:

- Hydrocarbon products and solvents
 - Fuels:
 - Gasoline
 - Diesel and kerosene
 - Sweet crude oil
 - Fuel ethanol / denatured ethanol
 - Aliphatic hydrocarbons
 - Naphthalene solvents
 - Mineral spirits

Where to use them:

- Hydrocarbon products and solvents
 - Aromatic hydrocarbons
 - Toluene
 - Xylene
 - Phenol
 - Styrene
 - Aromatic hydrocarbon mixes such as Aromatic 100
 - Strong organic polymer solvents such as MEK

Where to use them:

- Hydrocarbon products and solvents
 - Ketones
 - MEK
 - MIBK
 - Alcohols
 - Methanol
 - Ethanol
 - Fresh water with a pH near neutral, 7

Where not to use them in immersion service:

- Aqueous solutions below pH of 5.5 or above 10
 - Very dilute concentrations of acids and bases rapidly accelerate the corrosion rate of zinc. However consumption of zinc is higher in dilute acids than dilute bases.
 - Strong acids and bases readily dissolve zinc

Where not to use them:

- Storage of high purity water where water purity must be preserved
- Service temperatures at or above 140 F due to accelerated consumption of the zinc
- Any service where slight zinc pickup would pose a problem

Where not to use them:

- As a primer in potable water applications
 - Although there are some successful case histories, penetration of water and dissolved gases can cause the formation of zinc salts and blistering beneath the topcoat.
 - All organic topcoats are permeable to water, its only a matter of time and rate of diffusion

Topcoat blistering:

- Topcoat blistering is the primary mode of failure when zinc primers are top-coated and placed in water immersion service
- The blisters manifested in topcoats applied over zinc primers are typically the result of:
 - Osmosis
 - Electro-osmosis
 - Volumetric expansion

Osmosis:

The diffusion of water through a semi permeable membrane. More specifically, it is the movement of water across a semi-permeable membrane (the topcoat) from an area of high water potential (low solute concentration) to an area of low water potential (high solute concentration).

Electro-osmosis:

The movement of water through a semi-permeable membrane as a result of a potential gradient.

Volumetric expansion:

- The zinc salts that are your coatings ally when un-top coated are your coating systems enemy when top-coated.
- Under the right conditions the aforementioned zinc salt reaction products, $\text{Zn}(\text{OH})_2$, ZnO , ZnCO_3 , and ZnCl develop at the zinc primer/topcoat inter-phase and are the primary cause for topcoat blistering by osmosis and or volumetric expansion

Top-coating Zinc Primers used in Immersion Service is a Ticking Time Bomb

- All topcoats are semipermeable
- Water will permeate through the topcoat
- Zinc will chemically react with water once it permeates the topcoat
- Zinc salts will form at the zinc primer/topcoat inter-phase which will likely
 - Attract more water by osmosis
 - Result in localized areas of significant volumetric expansion
- Blistering of the top coat is only a matter of time

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**Overcoating of Inorganic Zinc Primers
for Underwater Service**

Not all topcoats are created equally

- Topcoats providing sufficient barrier protection allowing little to no water permeability could work. However, if that's the case then you probably don't need zinc.
- Topcoats with a very high PVC (pigment volume concentration) result in porous films that allow water, some salts, and gasses to pass through easily significantly reducing the likely-hood of blistering

How do we know the coating system works or how do we find out?

- Lab testing
- Case history
- Chemistry

Chemical resistance testing for immersion service (NACE TM0174-02):

Procedure A:

- One sided exposure comparable to ASTM C868 and commonly referred to as atlas cell testing
- Provides an excellent representation of the cold-wall effect
- Permeation of the test solution is accelerated versus procedure B

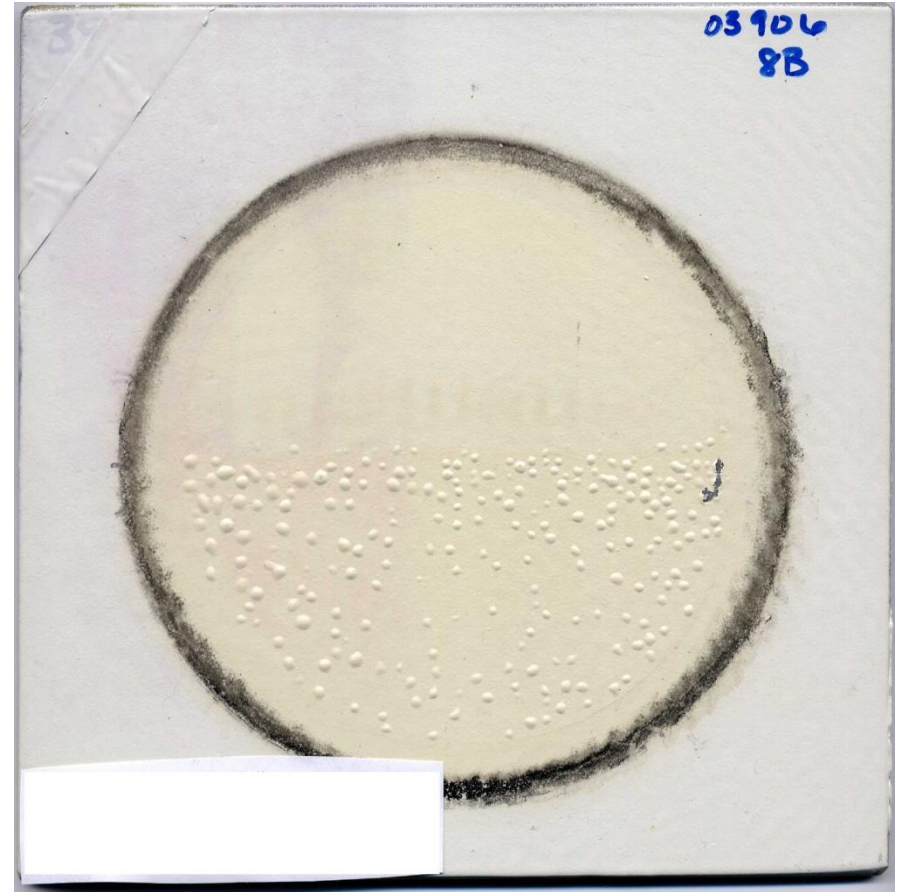
NACE TM0174-02

Procedure A



NACE TM0174-02

Procedure A



Chemical resistance Testing for immersion service (NACE TM0174-02):

Procedure B:

- Partial or complete immersion of a coated coupon
- Simple, easy to setup and run
- Somewhat less realistic than Procedure A but still valid where no cold wall condition exists

NACE TM0174-02

Procedure B



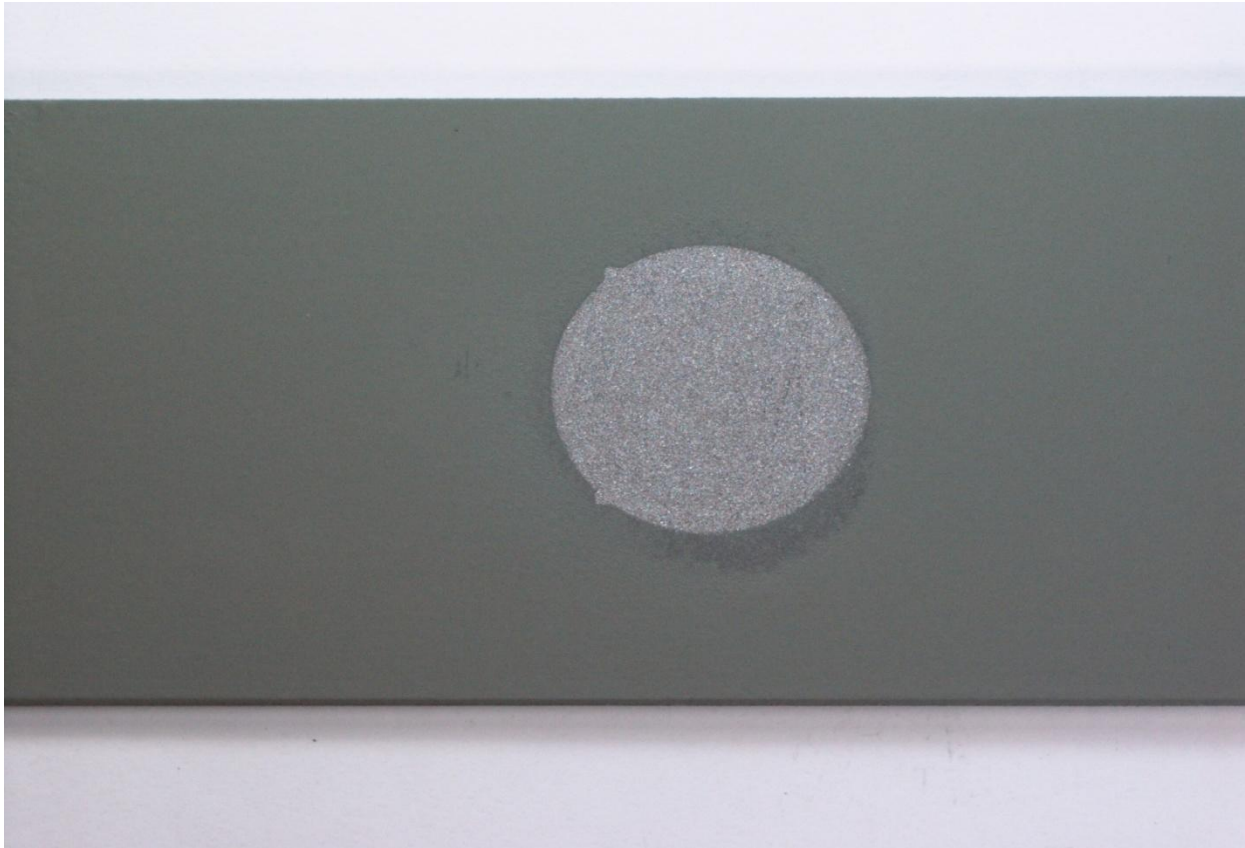
Typical chemical and corrosion resistance tests:

- After exposure to chemical and corrosion resistance tests, exposed samples are typically evaluated for:
 - Rusting (ASTM D610)
 - Blistering (ASTM D714, size and frequency)
 - Coating discoloration
 - Softening and degradation of the film

Additional chemical resistance testing:

- Weight gain or loss evaluations
- Wet adhesion and/or post exposure adhesion
- Chemical analysis of the exposed immersion solution

AASHTO M300 bullet hole testing:



Bullet hole testing parameters:

- 1.5 inch diameter uncoated blasted steel surface
- 5% NaCl immersion solution
- 650 hours in immersion
- No rusting allowed on the coated or uncoated surface of the test panel

Case History





Questions?

Thank you.