Cure Mechanism and Corrosion Protection of Organic and Inorganic Zinc Rich Coatings

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Benefits of Zinc Rich Coatings

• More active than steel, sacrificial under most normal conditions
• Relatively economical, performance measured in decades
• Proven steel corrosion prevention track record
• Can self-heal minor damage
• Minimal human toxicity
# Electrochemical series:

<table>
<thead>
<tr>
<th>Potential (volts)</th>
<th>Element</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>gold</td>
<td>Noble</td>
</tr>
<tr>
<td>1.2</td>
<td>platinum</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>silver</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>hydrogen (acid)</td>
<td></td>
</tr>
<tr>
<td>-0.44</td>
<td>iron</td>
<td></td>
</tr>
<tr>
<td>-0.77</td>
<td>zinc</td>
<td></td>
</tr>
<tr>
<td>-1.67</td>
<td>aluminum</td>
<td></td>
</tr>
<tr>
<td>-2.5</td>
<td>magnesium</td>
<td>Active</td>
</tr>
</tbody>
</table>
Zinc/iron galvanic cell:

\[
\text{Zinc (Anode)}: \quad \text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^{-}
\]

\[
\text{Iron (Cathode)}: \quad \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}
\]
Desired Coating Properties for Effective Cathodic Protection:

• Freedom to sacrifice
• Intimate zinc/zinc and zinc/steel contact
• A binder that glues the zinc particles together and is resistant to the environment
Desired Coating Properties for Effective Cathodic Protection:

- High zinc loading, greater than 65%

<table>
<thead>
<tr>
<th>Wgt. % Zn in dry film:</th>
<th>SSPC designation:</th>
<th>Corrosion protection:</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥ 85%</td>
<td>Level 1</td>
<td>Best</td>
</tr>
<tr>
<td>≥ 77% and &lt;85%</td>
<td>Level 2</td>
<td>Better</td>
</tr>
<tr>
<td>≥ 65% and &lt;77%</td>
<td>Level 3</td>
<td>Good</td>
</tr>
</tbody>
</table>

- Conductive polymers and/or pigments can reduce the required amount of zinc in the dry film for the same corrosion protection
Additional Desired Coating Properties:

- VOC compliance
- Ease of application and acceptable cure time to topcoat and/or put into service
- Low lead content:
  - ASTM D520 type I – not specified
  - ASTM D520 type II – maximum 0.01%
  - ASTM D520 type III – maximum 0.002%
Types of Zinc Rich Coatings:

• Inorganic
  – Water-based
  – Solvent-based

• Organic
  – Epoxy
  – Urethane
  – Others such as epoxy ester, phenoxy, and chlorinated rubber
Types of Inorganic Zinc Rich Coatings:

• Water-based:
  – Alkali silicates, post-cured
  – Alkali silicates, self-cured
  – High ratio silicates, self-cured

• Solvent-based:
  – Alkyl silicates, self-cured
  – High solids alkyl silicates, self-cured
Alkali Silicates, post-cured:

• Sodium silicates, water-based chemistry
  \[ \text{Na}_2\text{O} \cdot \text{xSiO}_2 \]
  
  • \( \text{x} \) represents some number larger than 1, typically around 3
  
  • Commercial grades differentiated by mole ratio (silica to alkali metal) and alkali metal
  
  • In general air drying is faster as the mole ratio / silica concentration increases
Alkali Silicates, post-cured:

• 3 package (alkali silicate, zinc dust, & post cure solution)
• Requires white metal blast
• Excellent performance
• Limited film thickness
• Minimal topcoat bubbling

• High tendency to cause topcoat blistering in wet environments
• Dries fast in low humidity
• Cannot be applied at freezing temperatures
Alkali Silicates, post-cured
Cure Mechanisms:

Two step process:

1. Solvent/water evaporation
   - Film, although dry to touch, is sensitive to water before post-curing

2. Neutralization of the alkali silicate binder with weakly acidic solutions (i.e. application of a post cure solution) or heat cure
   - Organic acids, acidic phosphate salt solutions and other weak mineral acids
Alkali Silicates, self-cured:

- Potassium and lithium silicate water-based chemistries are the most common
  - $\text{K}_2\text{O} \cdot x\text{SiO}_2$
  - $\text{Li}_2\text{O} \cdot x\text{SiO}_2$
- $x$ represents some number larger than 1 and higher than 3
- Commercial grades differentiated by mole ratio (silica to alkali metal) and alkali metal
- In general air drying is faster as the mole ratio / silica concentration increases
Alkali Silicates, self-cured:

- NASA and Schutt patents, mole ratios of potassium silicate solutions of 5:1 or higher
- Water based, 2 package
- High zinc loading
- Reduced salting of high mole ratio self-cured alkali silicates
- Requires white metal blast
- Sensitive to organic contaminants
Alkali Silicates, self-cured:

- Excellent performance
- Cures fast in low humidity
- Water insensitive within hours of application
- Topcoat bubbling can be a problem
- Tendency to form salts in mild environments and cause topcoat blistering in wet environments
- Cannot be applied at freezing temperatures
Alkali Silicates, self-cured Cure Mechanisms:

Two step process:
1. Solvent/water evaporation
2. No need for the application of a post cure solution or heat. Silicate binder reacts with atmospheric CO$_2$ in the form of HCO$_3^-$

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+
\]
Alkyl Silicates, self-cured:

- Alcohol solvent based, 2 package
- Based upon TEOS (tetraethyl orthosilicate) and other alkyl silicates

\[
\text{Si(OC}_2\text{H}_5)_4
\]

- TEOS reacts with moisture/water releasing ethanol forming a three dimensional Si-O network

\[
\text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{SiO network} + \text{EtOH}
\]
Alkyl Silicates, self-cured:

- Typically acid catalyzed
- More tolerant of surface contamination than water based inorganic silicates
- Excellent performance
- Can be applied below freezing
- Cures best in high humidity
- Better physical properties than water-based silicates
- VOC issues, 400 g/l or higher
High Solids Alkyl Silicates

- Alcohol solvent based, 3 package
- Based upon oligomers of TEOS (tetraethyl orthosilicate) and other alkyl silicates
- Oligomers reacts with moisture/water releasing ethanol forming a three dimensional Si-O network

\[
\text{Si oligomers} + \text{H}_2\text{O} \rightarrow \text{SiO network} + \text{EtOH}
\]

- Separate catalyst package needed for proper cure
High Solids Alkyl Silicates:

- Low VOC at $\leq 300$ g/l
- More tolerant of surface contamination than water based inorganic silicates
- Excellent performance
- Can be applied below freezing
- Cures best in high humidity
- Better physical properties than water-based silicates
Types of Organic Zinc Rich Coatings:

• Epoxy
• Urethane
• Others such as epoxy ester, phenoxy, and chlorinated rubber
Organic Zinc Primer Advantages:

- Non-porous film
- Good adhesion to substrate, varies with generic type
- Easier to apply and no topcoat bubbling
- Can be used to repair inorganic zinc rich coatings
- As few as one component
Organic Zinc Primer Advantages:

• Better physical properties (impact resistance, pull-off strength, etc.) than IOZ
• Can handle more abuse due to better impact resistance and adhesion
• Can be topcoated quickly
• More resistant to acidic environments than IOZ
• Can cure under adverse conditions
Organic Zinc Primer Disadvantages:

- Limited recoat window for some
- Performance very good but not quite as good as IOZ without very high zinc loadings
- More expensive than IOZ with very high zinc loadings.
- Moisture cured zinscs are plagued by poor can stability. Very sensitive to moisture contamination.
Epoxy Zinc Primer Cure Mechanism:
Bisphenol-A epoxy + aliphatic amine reaction:

\[
\begin{align*}
\text{Bisphenol-A epoxy} & \quad \text{aliphatic amine} \\
\end{align*}
\]
Moisture Urethane Cure Mechanism:

\[
\text{Reaction site}
\]
Moisture Urethane Cure Mechanism: Continued:

Reaction site

CO₂ gas
Questions?

Thank you.