Use of Organic and Inorganic Corrosion Inhibitors in High Performance Coatings

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Overview

1. Corrosion Inhibition Overview
2. Inorganic Corrosion Inhibitors
3. Organic Corrosion Inhibitors
4. Results
5. Conclusions
Metals in their un-combined condition are in high energy states. The tendency is therefore to revert to a lower energy state with a release of energy. This tendency of metals to recombine with components of the environment is **corrosion**.

Why Metals Corrode
1. Oxidation of Fe yields electrons which travel through the metal.
2. Electrons at the Fe (inactive) cathode reduce O₂ to H₂O.
3. The Fe²⁺ migrates through the drop and reacts with O²⁻ and H₂O to form rust.
## Challenges in the Corrosion World

<table>
<thead>
<tr>
<th>Corrosion Inhibitors</th>
<th>Chromate salts</th>
<th>Zinc salts</th>
<th>Barium salts</th>
<th>Nitrites &amp; Nitrates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Risk (Humans)</strong></td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td><strong>Risk (Environment)</strong></td>
<td>High</td>
<td>High</td>
<td>Aquatic toxin Harmful if inhaled or swallowed</td>
<td>High</td>
</tr>
</tbody>
</table>

*Aquatic toxin Harmful if inhaled or swallowed*
### Hazardous Labeling
Zinc Compounds = Sum of Zinc Oxide + Zinc Phosphate

<table>
<thead>
<tr>
<th>Concentration of Zinc Compounds in Product</th>
<th>Labeling (N) (Dangerous to Environment)</th>
<th>Rating (R) (Risk Phrase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 25%</td>
<td>N</td>
<td>R50/53</td>
</tr>
<tr>
<td>24.99 – 2.5%</td>
<td>N</td>
<td>R51/53</td>
</tr>
<tr>
<td>2.499 – 0.2499%</td>
<td>None</td>
<td>R52/53</td>
</tr>
<tr>
<td>&lt; 0.2499%</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>
Types of Corrosion

Of concern in coatings...

Flash Rust
Rapid, widespread corrosion seen during initial application.

Galvanic
Contact between two alloys which promotes oxidation of the less noble metal.

Filiform
Differential aeration promotes this unique form of corrosion.

Corrosion inhibitors - whether inorganic or organic - retard the corrosion rate by affecting the 2 elements of the corrosion process.

1. Anodic reactions – Metal ions pass into solution from anode
2. Cathodic reactions – e⁻ flowing from metal to an acceptor

Corrosion inhibitors perform by:

- Increasing the anodic or cathodic polarization behavior
- Reducing the movement or diffusion of ions to the metallic surface
- Increasing the electrical resistance of the metallic surface
- Interacting with the metallic surface or the environment near it
- Adsorbing themselves on the metallic surface by forming a film
Mixed Metals Passivation

Anodic Reaction
- Slow the reaction rate of anodic dissolution.
- Produce reaction products which form a thin film over anode.

Cathodic Reaction
- Disrupt the flow of electrons from the anode to the cathode.
- Produce reaction products which precipitate selectively at cathodic sites.
## Inorganic Inhibitors

### Commonly Used Inhibitors

- Zinc Phosphate
- Modified Zinc Phosphate
- Complex Phosphosilicate
- Modified Borates
- Complex Borosilicates

### Composition of Inhibitors

- \([\text{Zn}_3 (\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]\)
- \([\text{M}^* \cdot \text{Zn}_3 (\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]\)
- \([\text{M}^* \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2 \cdot \text{XH}_2\text{O}]\)
- \([\text{M}^* \cdot \text{B}_2\text{O}_3 \cdot \text{XH}_2\text{O}]\)
- \([\text{M}^* \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{XH}_2\text{O}]\)

\(\text{M}^*\) may represent one of more of the following metals; Calcium, Barium, Strontium, Molybdenum, Aluminum.
## Inorganic Inhibitors

<table>
<thead>
<tr>
<th>Description</th>
<th>Composition</th>
<th>Anticorrosive Mechanism</th>
<th>Ions released</th>
<th>End Use Coatings Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZP</td>
<td>Zinc Phosphate</td>
<td>Anodic passivation</td>
<td>Zinc and Phosphate</td>
<td>Water-borne, Solvent borne</td>
</tr>
<tr>
<td>SZP</td>
<td>Strontium Zinc Phosphosilicate</td>
<td>Anodic passivation</td>
<td>Strontium Zinc Phosphate</td>
<td>Water-borne, Solvent borne</td>
</tr>
<tr>
<td>SP</td>
<td>Strontium phosphosilicate</td>
<td>Anodic passivation</td>
<td>Strontium Phosphate</td>
<td>Epoxy</td>
</tr>
<tr>
<td>CP</td>
<td>Calcium Phosphate Magnesium, Aluminum Double Layer Hydroxide</td>
<td>Cathodic passivation &amp; anion exchange</td>
<td>Calcium, Phosphate &amp; Carbonate</td>
<td>Water-borne, Solvent borne, High Solids, 100% solids, Powder coatings</td>
</tr>
<tr>
<td>CB</td>
<td>Calcium Borosilicate</td>
<td>Anodic passivation       &amp; Saponification</td>
<td>Calcium &amp; Borate</td>
<td>Solvent borne, High Solids, 100% solids</td>
</tr>
</tbody>
</table>
1. **Interfacial activity**: Improve coating wet adhesion
2. **Anodic activity**: formation of insoluble complex salts at anodic defect sites
3. **Cathodic activity**: precipitate formation due to increased alkalinity at cathodic sites
4. **Barrier activity**: Reduce porosity & permeability in coating
5. **Adsorption activity**: protective layer formation
Organic Corrosion Inhibitors

Azoles, Calcium Alkyl-aryl Sulfonates, diamines, metal salts of dinonylnaphthalene sulphonates, etc.

\[
\begin{align*}
R & \quad \text{SO}_3 \quad \text{Ca. n CaCO}_3 \\
\text{R} & \\
\text{N} & \quad \text{S} \\
\text{R} & \\
\text{N} & \quad \text{O} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
\end{align*}
\]
Water and corrosion products can cause adhesion loss, delamination, blistering.

- Coatings adhere by mechanical AND polar interactions, (e.g. hydrogen bonding). These can be displaced by water.
- Fe$_2$O$_3$ nH$_2$O is 2.16 times more voluminous than Fe metal, therefore a stable, continuous metal oxide film cannot form, leading to “bulging” rust.
Organic Corrosion Inhibitors

- Anodic passivation
  - Reduced uniform corrosion & flash rusting
- Improve adhesion
  - Reduced blistering
- Increase water resistance
- Form protective films
  - Adsorption mechanism
- Increase coating flexibility
- Increase chemical resistance
Galvanic Corrosion Inhibition

Weld Seams

- Uninhibited
  - Galvanic & Uniform Corrosion

- Sodium Nitrite
  - Flash Rust Inhibited

- Organic CI's
  - Galvanic & Flash Rust Inhibition
### Standard Reduction Potentials at 25°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Half Reaction</th>
<th>$E^0$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>$Au^{3+}<em>{(aq)} + 3e^- \rightarrow Au</em>{(s)}$</td>
<td>+1.50</td>
</tr>
<tr>
<td>Platinium</td>
<td>$Pt^{2+}<em>{(aq)} + 2e^- \rightarrow Pt</em>{(s)}$</td>
<td>+1.18</td>
</tr>
<tr>
<td>Silver</td>
<td>$Aq^+<em>{(aq)} + e^- \rightarrow Ag</em>{(s)}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>Iron</td>
<td>$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}$</td>
<td>+0.77</td>
</tr>
<tr>
<td>Copper</td>
<td>$Cu^{2+}<em>{(aq)} + 2e^- \rightarrow Cu</em>{(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>Tin</td>
<td>$Sn^{4+}<em>{(aq)} + 2e^- \rightarrow Sn^{2+}</em>{(aq)}$</td>
<td>+0.13</td>
</tr>
<tr>
<td>Nickel</td>
<td>$Ni^{2+}<em>{(aq)} + 2e^- \rightarrow Ni</em>{(s)}$</td>
<td>-0.25</td>
</tr>
<tr>
<td>Iron</td>
<td>$Fe^{2+}<em>{(aq)} + 2e^- \rightarrow Fe</em>{(s)}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>Chromium</td>
<td>$Cr^{3+}<em>{(aq)} + 3e^- \rightarrow Cr</em>{(s)}$</td>
<td>-0.74</td>
</tr>
<tr>
<td>Zinc</td>
<td>$Zn^{2+}<em>{(aq)} + 2e^- \rightarrow Zn</em>{(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>Manganese</td>
<td>$Mn^{2+}<em>{(aq)} + 2e^- \rightarrow Mn</em>{(s)}$</td>
<td>-1.18</td>
</tr>
<tr>
<td>Titanium</td>
<td>$Ti^{2+}<em>{(aq)} + 2e^- \rightarrow Ti</em>{(s)}$</td>
<td>-1.37</td>
</tr>
<tr>
<td>Aluminium</td>
<td>$Al^{3+}<em>{(aq)} + 3e^- \rightarrow Al</em>{(s)}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>Magnesium</td>
<td>$Mg^{2+}<em>{(aq)} + 2e^- \rightarrow Mg</em>{(s)}$</td>
<td>-2.27</td>
</tr>
<tr>
<td>Cerium</td>
<td>$Ce^{3+}<em>{(aq)} + 3e^- \rightarrow Ce</em>{(s)}$</td>
<td>-2.34</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>$Pr^{3+}<em>{(aq)} + 3e^- \rightarrow Pr</em>{(s)}$</td>
<td>-2.35</td>
</tr>
<tr>
<td>Sodium</td>
<td>$Na^+<em>{(aq)} + e^- \rightarrow Na</em>{(s)}$</td>
<td>-2.71</td>
</tr>
<tr>
<td>Calcium</td>
<td>$Ca^{2+}<em>{(aq)} + 2e^- \rightarrow Ca</em>{(s)}$</td>
<td>-2.87</td>
</tr>
</tbody>
</table>
1. SILICONE ESTER HYDROLYZES TO FORMS SILANOL

\[ \text{RO-Si-OR} + \text{H}_2\text{O} \rightarrow \text{RO-Si-OH} + \text{ROH} \]

2. SILOXANE BOND FORMS

\[ \text{RO-Si-OH} + \text{OH-} \rightarrow \text{RO-Si-OR} \]

3. GELATION (CROSS-LINKING)

\[ \text{POLYMER} \ 	ext{SUBSTRATE} + \text{H}_2\text{O} + \text{ROH} \]
Inorganic pigments can be trapped both within and underneath the network formed, thus providing excellent corrosion resistance – SYNERGY!
<table>
<thead>
<tr>
<th>Description</th>
<th>Composition</th>
<th>Anticorrosive Mechanisms</th>
<th>Function</th>
<th>End Use Coatings Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Amino Carboxylate</td>
<td>Anodic</td>
<td>Long-term, flash rust &amp; in can rust inhibitor, adhesion</td>
<td>Water-based Acrylics, Polyurethane, Alkyds</td>
</tr>
<tr>
<td>OAAC</td>
<td>Organic Acid Amine Complex</td>
<td>Anodic</td>
<td>Long-term, flash rust, adhesion</td>
<td>Water-based Acrylics, UV, Polyurethanes, Polyester Alkyds</td>
</tr>
<tr>
<td>ODA salt</td>
<td>Alkyl ammonium Salt of an organic di acid</td>
<td>Anodic</td>
<td>Humidity resistance, barrier properties, adhesion on poorly prepped surfaces</td>
<td>Solvent borne Epoxy Systems, Alkyds Polyurethane</td>
</tr>
<tr>
<td>S-G</td>
<td>Silane based sol-gel</td>
<td>Adhesion</td>
<td>Humidity resistance, barrier properties, adhesion</td>
<td>Water-based Acrylics, UV, Polyurethanes, Polyester Alkyds</td>
</tr>
</tbody>
</table>

Organic Corrosion Inhibitors
• Combine the inhibitors
  • Higher solubility $\rightarrow$ short-term protection via passivation e.g. flash rust resistance
  • Lower solubility $\rightarrow$ long-term protection via sustained release

• Add other pigments, additives, or organic inhibitors
  • To reinforce impermeability with extenders (e.g. mica)
  • To increase efficiency of inhibitor (basic pigments like calcium metasilicate, zinc oxide)
  • Organic inhibitors preferentially adsorb onto the metal surface and keep corrosive (de-passivating) ions out
Improving the Coating Performance

Higher solubility pigments

Lower solubility pigments

Passivation

<table>
<thead>
<tr>
<th></th>
<th>AIPO₄</th>
<th>Ba₃(PO₄)₂</th>
<th>Ca₃(PO₄)₂</th>
<th>Sr₃(PO₄)₂</th>
<th>Zn₃(PO₄)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{sp}</td>
<td>10 x 10^{-21}</td>
<td>3 x 10^{-23}</td>
<td>1 x 10^{-26}</td>
<td>1 x 10^{-31}</td>
<td>9 x 10^{-33}</td>
</tr>
</tbody>
</table>

Olmsted, J & Williams, G; *CRC Handbook of Chemistry and Physics: 5° ed.*, 2007.
Synergy: Inorganic-Organic

Mechanism I

Inorganic

Organic

Anodic Passivation
Ion Scavenging

Adhesion
Hydrophobicity

Synergy
Increased focus on Analytical Analysis

Positive potential shift (anodic)
EIS Principles

- Rapidly provides info on physical and electro chemical behavior of coatings
- Monitors permeability of electrolyte through ionic conduction
- Good wet adhesion is paramount for good protection
- Changes in coating resistance correlate to penetration of ionic species
HEAVY METAL FREE CORROSION INHIBITORS

Water Base Acrylic Latex Primer based on Maincote HG-86ER
Salt Spray - 500 hours - Matte CRS - 50 microns - % on tfw

Control
Inorganic CP @ 5%
Inorganic CP @ 5%
Organic AC @ 1%
ASTM B117  3000 Hours

2K Water Based Polyurethane on Bare Aluminum 3003
Dry Film Thickness: 3.0-4.5  mils (75-113 microns)

Blank  Competitor  2% - Inorganic CP 0.5% - S-G  2% - Inorganic CP 1.0% - S-G
ASTM B117: WB Epoxy – 168 Hours

Blank

Inorganic SP

Inorganic SP/Organic S-G
ASTM B117: WB Epoxy – 336 Hours

Terminated at 168 Hrs

Blank

Inorganic SP

Inorganic SP/Organic S-G
Bode Plots of 2K Epoxy

- Time zero to 168 hours

Inorganic, CP + Organic AC

No Inhibitor
The change in Capacitance can be used to calculate the water uptake in a coating under immersion conditions.

\[
\%v = 100 \frac{\log(C_{C,0} / C_{C,24})}{\log(80)}
\]

Volume fraction of water
ASTM B117: Medium Oil Alkyd – 504 Hrs.

Blank

Inorganic SZP

Inorganic SZP/Organic, ODA Salt
Bode Plot of Medium Oil Alkyd

• Time zero and 168 hours

Inorganic, SZP + Organic, ODA Salt

Control
Identifying the correct inhibitor quickly can save you time and money.
Thank You!

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