Use of Organic Corrosion Inhibitors in High Performance Coatings

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### 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>

- Chromate salts are harmful if inhaled or swallowed.
- Zinc salts have low risk for humans and high risk for the environment.
- Barium salts are low risk for both humans and the environment.
- Nitrites & Nitrates are high risk for both humans and the environment.
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.

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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.
• **Indirect Inhibitors:** Requires a reaction between the inhibitive pigment and the resin system. It is the reaction by-products which are inhibitive in nature not the pigment.

• **Direct Inhibitors:** The soluble ions of the pigment are inhibitive in nature. They usually require no reaction within the resin system.
Inorganic Inhibitors

<table>
<thead>
<tr>
<th>Commonly Used Inhibitors</th>
<th>Composition of Inhibitors</th>
</tr>
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<tbody>
<tr>
<td>• Zinc Phosphate</td>
<td>• ([\text{Zn}_3\text{(PO}_4\text{)}_2\cdot 2\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>• Modified Zinc Phosphate</td>
<td>• ([\text{M}^*\cdot \text{Zn}_3\text{(PO}_4\text{)}_2\cdot 2\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>• Complex Phosphosilicate</td>
<td>• ([\text{M}^*\cdot \text{P}_2\text{O}_5\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>• Modified Borates</td>
<td>• ([\text{M}^*\cdot \text{B}_2\text{O}_3\cdot x\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>• Complex Borosilicates</td>
<td>• ([\text{M}^*\cdot \text{B}_2\text{O}_3\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}])</td>
</tr>
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</table>

\(\text{M}^*\) 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>Inorganic</td>
<td>Zinc Phosphate</td>
<td>Anodic passivation</td>
<td>Zinc and Phosphate</td>
<td>Water-borne, Solvent borne,</td>
</tr>
<tr>
<td>Inorganic A</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>
<tr>
<td>Inorganic B</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>
</tbody>
</table>
Mechanism(s) of Organic Inhibitors

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
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
1. SILICONE ESTER HYDROLYZES TO FORMS SILANOL

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

2. SILOXANE BOND FORMS

\[
\text{RO-}[\text{Si}-\text{OH}]+\text{OH}+\text{OH}+\text{OH}+\text{OH} \rightarrow \text{RO}_4-\text{Si}_4\text{OR}_4 + \text{ROH}
\]

3. GELATION (CROSS-LINKING)

\[
\text{RO}_4-\text{Si}_4\text{OR}_4 \rightarrow \text{POLYMER} + \text{H}_2\text{O} + \text{ROH}
\]
Inorganic pigments can be trapped both within and underneath the network formed, thus providing excellent corrosion resistance – **SYNERGY!**
## Organic Corrosion Inhibitors

<table>
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<tr>
<th>Description</th>
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<th>Anticorrosive Mechanisms</th>
<th>Function</th>
<th>End Use Coatings Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic A</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>Organic B</td>
<td>Organic Acid Amine Complex</td>
<td>Anodic</td>
<td>Long-term, flash rust, adhesion</td>
<td>Water-based Acrylics, Polyurethanes, UV, Polyester Alkyds</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Silane based sol-gel</td>
<td>Adhesion</td>
<td>Humidity resistance, barrier properties, adhesion</td>
<td>Water-based Acrylics, Polyurethanes, UV, Polyester Alkyds</td>
</tr>
</tbody>
</table>
Tips to Formulating

• 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
Synergy: Inorganic-Organic

Mechanism I

Inorganic → Anodic Passivation
Ion Scavenging

Organic → Adhesion
Hydrophobicity

Mechanism II

Synergy
Accelerated Test Methods

- Salt Spray (ASTM B-117)
- QUV (ASTM 6154)
- Prohesion (ASTM G85 – Annex A5)
- QUV/Prohesion (ASTM 5894 -5)
- Humidity (ASTM 2247)
- SAE J2334
- Filiform Corrosion (Controlled Humidity)
  ASTM D 2803
- EIS (Electrochemical Impedance Spectroscopy)
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 B @ 5%
Inorganic B @ 5%
Organic B @ 1%

ASTM B117  Water Base Acrylic
2K Water Based Polyurethane on Bare Aluminum 3003
Dry Film Thickness: 3.0-4.5 mils (75-113 microns)

- Blank
- Competitor
- 2% - Inorganic B
- 0.5% - Hybrid
- 2% - Inorganic B
- 1.0% - Hybrid
ASTM B117: WB Epoxy – 168 Hours

Blank

Inorganic

Inorganic/Organic
ASTM B117: WB Epoxy – 336 Hours

Terminated at 168 Hrs

Blank
Inorganic
Inorganic/Organic
Bode Plots of 2K Epoxy

- Inorganic + Organic A
- Inorganic + Hybrid
- Inorganic
- Control
Bode Plots of 2K Epoxy

• Time zero to 168 hours
Bode Plots of 2K Epoxy

- Time zero and 168 hours
The change in Capacitance can be used to calculate the water uptake in a coating under immersion conditions.

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

Volume fraction of water

<table>
<thead>
<tr>
<th>TIME (days)</th>
<th>WATER PERMEATION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No Inhibitor</td>
</tr>
<tr>
<td>4% organic corrosion inhibitor</td>
<td></td>
</tr>
</tbody>
</table>
Blank

Inorganic

Inorganic/Organic
Bode Plot of Medium Oil Alkyd

- Time zero and 168 hours

Inorganic + Organic B

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