CORROSION INHIBITORS FOR WATERBORNE ALKYDS
Outline

- Part 1: Corrosion Inhibitors
  - Background, Mechanisms

- Part 2: Applications & formulating strategies
  - Waterborne Alkyds
Part 1:
Corrosion Inhibitors
What is corrosion?

The electrochemical deterioration of a metal due to the reaction with its environment involving the oxidation of a metal and the reduction of another material.

Fe$_2$O$_3$ . H$_2$O

2Fe + nH$_2$O + 2H$_2$O$^+$ + 2e$^-$ \[ \rightarrow \]
2Fe$^{2+}$ + 2OH$^-$ \[ \rightarrow \] Fe(OH)$_2$

4Fe(OH)$_2$ + O$_2$ \[ \rightarrow \] 2Fe$_2$O$_3$ + 4H$_2$O
Electrochemistry

**Anode**
- High potential to oxidize (lose electrons)
  - Fe → Fe$^{2+}$ + 2e$^{-}$
- Stressed region (scratch, crack, grain boundary)

**Cathode**
- High potential for reduction (gain electrons)
  - O$_2$ + 2H$_2$O + 4e$^{-}$ → 4OH$^{-}$
  - 4H$^+$ + O$_2$ + 4e$^{-}$ → 2H$_2$O
  - 2H$^+$ + 2e$^{-}$ → H$_2$
- Unstressed region
Coating failure mechanisms

Water draws in by osmotic pressure
Methods of combating corrosion

**Passive**
Protect through the barrier properties of resin or pigment having low H$_2$O transmission. (i.e. epoxies, chlorinated rubbers)

**Active**
- Inorganic Inhibitive Pigments
- Organic Corrosion Inhibitors
- Ion Exchange
- Vapor Phase

**Sacrificial**
Zinc-rich primers protect through the preferential oxidation of zinc metal
Zinc Phosphate Mechanism

$\text{Zn}_3(\text{PO}_4)_2$

Hydrolysis

$\text{FePO}_4$

Precipitate $\text{Zn(OH)}_2$

$\text{H}_2\text{O}$

$\text{Fe}^{2+}$

$\text{Fe}^{2+}$

Anode

Cathode

Paint Film

Substrate
Part 2: Applications and Formulating Strategies
Water Reducible Alkyds
Water Based Alkyd Uses

- Low cost corrosion protection
- Light duty industrial maintenance
  - Moderate performance (e.g. machinery, propane tanks)
  - Lower volatile organic compounds (VOC)
  - Fast drying
  - Good adhesion to steel, aluminium, plastic
Water Based Alkyds

- Water Reducible
  - Modified Polyesters with COOH pendant groups

- Water Dispersible
  - Core shell technology
# Water Based Alkyds

<table>
<thead>
<tr>
<th>Feature</th>
<th>Water Reducible Alkyd (WRA)</th>
<th>Water Dispersible Alkyd (WDA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ability to achieve low VOC</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>High gloss</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Hydrolysis resistance</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Shear stability</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>Gloss retention</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Dry time (wet edge/open time)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alkaline resistance</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Moisture resistance</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gelling with basic pigments</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Drier kick-out resistance</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Yellowing</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Hydrolysis of Alkyds (Reverse)

 Acid regeneration leads to pH drop
## Typical Formulation
(Water Reducible Epoxy Ester)

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>% WEIGHT</th>
<th>FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resydrol AX237w/70BG</td>
<td>33.16</td>
<td>Resin</td>
</tr>
<tr>
<td><strong>Ammonium hydroxide</strong></td>
<td>0.62</td>
<td>Amine</td>
</tr>
<tr>
<td><strong>Triethylamine</strong></td>
<td>1.86</td>
<td>Amine</td>
</tr>
<tr>
<td>Additol VXW-6206</td>
<td>0.38</td>
<td>Drier</td>
</tr>
<tr>
<td>Troymax Antiskin B</td>
<td>0.18</td>
<td>Antiskin</td>
</tr>
<tr>
<td>Patcote 577</td>
<td>0.09</td>
<td>Defoamer</td>
</tr>
<tr>
<td>De-Ionized Water</td>
<td>9.22</td>
<td></td>
</tr>
<tr>
<td>RO-4097 Kroma Red</td>
<td>8.32</td>
<td>Pigment</td>
</tr>
<tr>
<td><strong>Anticorrosive Pigment</strong>*</td>
<td>6.02</td>
<td>Corrosion Inhibitor</td>
</tr>
<tr>
<td>Micro Talc AT Extra</td>
<td>5.23</td>
<td>Filler</td>
</tr>
<tr>
<td>Millicarb</td>
<td>6.52</td>
<td>Filler</td>
</tr>
<tr>
<td>Bartex 65</td>
<td>6.62</td>
<td>Filler</td>
</tr>
<tr>
<td>Aerosil 200</td>
<td>0.37</td>
<td>Rheology modifier</td>
</tr>
<tr>
<td>De-Ionized Water</td>
<td>21.41</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100.0</strong></td>
<td></td>
</tr>
</tbody>
</table>

Typical Formulation (Water Reducible Epoxy Ester)  

Amine Package  

Fast (25%)  

Amine  

Slow (75%)  

Anticorrosive Pigment
Formulating with W/R Alkylds

Effect of:

- **Neutralizing Agent**
  - Critical for Stability and Performance (pH: 8.5-9.0)
  - Use 100% Triethylamine (TEA) for excellent stability and good Salt Spray
  - Use a blend of TEA and Ammonia hydroxide for good stability and excellent Salt Spray
Changes to the Amine Package

Water Epoxy Ester - Cold Rolled Steel – 2.0 mils - 336 hrs SS

Best Performance

Best Stability

100% Triethylamine

75:25 TEA and Ammonium Hydroxide
Stability vs. Amine Package

Heat Aged Stability

Graph showing stability over weeks at 50°C for different TEA to Ammonium Hydroxide ratios (100, 75/25, 50/50, 25/75).

TEA to Ammonium Hydroxide Ratio
Formulating with W/R alkylds

Effect of:

- **Corrosion inhibitor**
  - Zinc phosphate with low levels of ZnO showed better corrosion performance
  - MEK double rubs: saw better solvent resistance with Zn than Ca
  - EIS showed higher electrochemical impedance with Zn than Ca
  - Organic corrosion inhibitor synergy
Role of Zinc Oxide

- Improved cross link density (higher Z)
- ZnO is an active “cathodic” inhibitor with synergistic effects with traditional zinc phosphate
- Can react with mono- & di-carboxylic acid binder breakdown products
## Corrosion Performance

<table>
<thead>
<tr>
<th>ZnO</th>
<th>0%</th>
<th>0%</th>
<th>2%</th>
<th>17%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEK</td>
<td>6</td>
<td>8</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>

- Blank Control (no inhibitor)
- Zinc phosphate 6 wt%
- Calcium phosphosilicate 6 wt%
- Strontium zinc phosphosilicate 6 wt%
Impedance Spectra (Bode plots)

- Strontium zinc phosphosilicate
- Calcium phosphosilicate
- Zinc phosphate
- Blank
Synergy: Inorganic and Organic Corrosion Inhibitors

Water Reducible Alkyd - Cold Rolled Steel – 1.0 mil - 500 hrs SS

Blank 6% Mod ZnPO4 6% Mod ZnPO4
6% Mod ZnPO4 2% Organic Cl

Even Better!!
Summary

- Balancing the amine package is key to formulating hydrolytically stable WR alkyd primers
- Modified (i.e., containing ZnO) zinc phosphate pigments provide excellent corrosion resistance compared to non-zinc or traditional zinc phosphate corrosion inhibitors
- Salt spray and electrochemical impedance corrosion testing correlated well
QUESTION & ANSWERS
SESSION