Non-Toxic Corrosion Inhibitors

Optimization, Evaluation, and Qualification

“Bust the Rust”
Outline

- Definition of Corrosion and Mechanisms of Corrosion Inhibitors
- Formulating with Non-toxic Corrosion inhibitors
- Evaluation and Qualification of Anticorrosive coatings
Corrosion and Mechanisms of Corrosion Inhibitors
Definition of Corrosion

The electrochemical deterioration of a metal due to the reaction with its environment.

$$
2 \text{ Fe} \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ e}^- \\
3/2 \text{ O}_2 + 2 \text{ Fe}^{2+} + 2 \text{ e}^- \rightarrow \text{ Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}
$$

Fe$^{2+}$ + 2 OH$^-$ $\rightarrow$ Fe(OH)$_2$

4Fe(OH)$_2$ + O$_2$ $\rightarrow$ 2Fe$_2$O$_3$ + 4H$_2$O
How do corrosion inhibitors work?

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

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

\[ \text{Paint Film} \]

\[ \text{Substrate} \]

\[ \text{Anode} \quad \text{Fe} \quad \text{FePO}_4 \]

\[ + \quad - \]

\[ \text{Cathode} \quad \text{H}_2\text{O} \quad \text{M(OH)}_x \]

\[ \text{Precipitate} \]

\[ \text{Hydrolysis} \quad M_x(\text{PO}_4)_y \]
Organic C.I. Mechanism

1. **Interfacial activity**: Improve coating wet adhesion
2. **Anodic activity**: formation of insoluble complex salts at anodic defect sites
3. **Barrier activity**: Reduce porosity & permeability in coating
Using Inorganic Inhibitors

- Order of Addition – Grind phase
- Ensure proper level and type of dispersant
- Use manufacturer recommend inhibitor chemistry and loading level
- Do not do equal weight replacement
Using Organic Inhibitors

- If in liquid form, may be added to letdown or post-added to paint
- Usage level is low, usually ≤ 2% t.f.w.
- Used a sole inhibitor or in conjunction with inorganic corrosion inhibitors
- Soluble in a variety of solvents
Other Considerations:

- **EXTENDER PIGMENT MORPHOLOGY**
  Platy or lamellar shaped extender pigments are the best for corrosion resistant formulas.

- **OTHER ADDITIVES IN YOUR FORMULA**
  Minimal levels of hydrophobic additives are typically the best for corrosion resistant formulas.

- **COMBINING OTHER NON-TOXIC INHIBITOR MECHANISMS**
  Explore SYNERGIES between different Non-Toxic Inhibitor Mechanisms (e.g. If you do not obtain the desired performance with a certain inorganic inhibitor, try blending with another inorganic inhibitor or possibly an organic inhibitor. Organic Inhibitors can greatly improve corrosion resistance in combination with inorganic inhibitors at minimal use levels – typically, < 3% on total formula weight).
Formulating with W/B Acrylic Latex

- Dispersant Choice and Amount
- Utilize organic with inorganic corrosion inhibitors – Synergy
- Proper coalescent / plasticizer selection and loading level
- Remove additives at high levels that may cause water sensitivity.
Dispersant Choice

Water Base Acrylic Latex Primer
336 hours SS - Cold Rolled Steel - 2.0 to 2.5 mils

5% Inorganic Corrosion with Different Dispersants
Synergy – Inorganic & Organic

Water Base Acrylic Latex Primer
Cold Rolled Steel - 2.0-2.5 mils - 500 hrs SS

Blank Control
5% Calcium Phosphate
5% Calcium Phosphate + 2% Organic Acid Amine
Coalescent / Plasticizer Selection

Self-Crosslinking Stryene Acrylic Primer
Cold Rolled Steel - 2.0-2.5 mils - 500 hrs SS

5% Inorganic Corrosion Inhibitor

Original Coalescent Package
Increased Plasticizer Only
Added Texanol & Plasticizer
Formulating with W/R Alkyds

- **Stability/Separation**
  - Increase strong amine level (Triethylamine)
  - Add coupling solvent (glycol ether, alcohol.)

- **Seedy/Gelling**
  - Use a dispersant (Tamol 681, BYK, W-33)
  - Less reactive inhibitor (non zinc)
  - Increase strong amine level

- **Poor Salt Spray Performance**
  - Too much of strong amine (blend with NH$_4$OH)
  - Add organic corrosion inhibitor
  - Drier package
Changes to the Amine Package

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

Equal Loading Level of Corrosion Inhibitor

Better Performance

Best Stability

100% Triethylamine

75:25 TEA and Ammonium Hydroxide
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

2% Organic Cl

Even Better!!
Evaluation and Qualification of Anticorrosive Coatings

Common Accelerated Corrosion Tests
Accelerated Corrosion Testing

Weathering factors that are accelerated in the laboratory which cause coatings to fail.

- Light – UV (short wavelength)
- Temperature
- Moisture
- Other contributing factors: electrolytes
Common Accelerated Tests used for Qualification of Coatings

Static Tests:
- Salt Spray (ASTM B117)
- Humidity Testing (ASTM D2247)
- Immersion Test (ASTM D870)
- EIS

Cyclic Tests:
- Filiform Corrosion Test (ASTM D2803)
- QUV Condensation, QUV/Prohesion (ASTM D5894)
- Xenon Arc (ASTM D2568, G26)
Salt Spray (ASTM B-117)

- Samples are placed in racks at an acute tilt angle.
- A 5% NaCl solution (6.50-7.20 pH) is mixed with humidified air at a spray nozzle in center of cabinet.
- The temperature of the cabinet is maintained at 95°F.
- Panels are subjected to static fog until failure or desired number of hours is obtained.
Example of Salt Spray Failure

100 hours salt spray – Water based Acrylic – Substrate: CRS – 2.0 mils D.F.T
Humidity Test (ASTM D2247)

- Also referred to as Water Resistance Test
- Samples are exposed to 100% relative humidity
- Water vapor condenses on surface
- Failure can occur in many forms
Humidity Testing Example

336 Hours Humidity

Long Oil Alkyd – CRS - 2.0 mils D.F.T
Common Cyclic Tests

QUV (ASTM G154)
- QUV cycle – UV light – 4 hr followed by condensation cycle – 4 hr
- Fluorescent UV lamps
- Condensation Cycle – chamber maintains 100% RH, 50°C

Prohesion Cycle (ASTM G85 A5)
- Samples exposed to an electrolyte solution (0.05% NaCl + 0.35% Ammonium Sulfate) at 35°C for one hour, then exposed to a dry cycle for one hour at 40°C, the cycle repeats
Example of QUV/Prohesion Failure

Initial

5 Cycles – 1680 Hours
Example Test Comparisons

Salt Spray vs QUV/Prohesion

500 Hours Salt Spray

2 Cycles QUV/Prohesion

2K Water-base Polyurethane – CRS – 2.25 mils D.F.T
Exterior Exposure

- Location – Worst Case Environments: South Florida, and Arizona
- Type of test rack (unbacked, backed, and under glass)
- Orientation of test sample (examples 90° South, 45° South)
- Natural Marine Atmospheric Conditions – very aggressive environments. Example: Kure Beach N.C. (increases in temperature, chloride content, moisture, wind).
Comparison of Accelerated Laboratory Tests to Real World Exterior Exposure

Exterior Exposure vs Salt Spray

2.5 Years– Industrial Site

500 Hours Salt Spray
Comparison of Corrosion Testing

Solvent Based Polyurethane – CRS- 2.0 mils D.F.T

2000 Hrs SS  2000 Hrs Prohesion  2 Years Ocean City, FL 45\(^{\circ}\)S
Comparison Industrial vs. Marine Environment Exposure

3 Years Exposure – Substrate: Cold Rolled Steel – 2 mils D.F.T

Industrial Site  45° South  Ocean City, Florida 45° South
Does Accelerated Testing Correlate to Exterior Exposure?

- Predicting the unpredictable - the actual weather
- Multiple weather factors influence the life of the coating
- Laboratory tests are more controlled
- Sample size
- There is no factor between salt spray hours and real world exposure (i.e. $X$ # hours of salt spray $\approx X$ # years of exterior exposure)
So many tests.....

- The more accelerated tests, the better
- Cyclic testing more indicative of “real world”
- There is little correlation of test results between lab test methods and natural conditions
- Natural weathering is not a controlled process
- Lab tests are simply an effort to incorporate natural stresses (temp, time, humidity, UV, salts) into a controlled environment
THANK YOU

Questions??

“Bust the Rust”