Overview

• An inhibitor screening approach for corrosion resistant coatings applications.

• Evaluation of lanthanide, transition metal oxoanion, Zn$^{2+}$ inhibitors.

• Assessment of what matters for good corrosion protection from inhibitor pigment additions.

The support SERDP and the DOD is gratefully acknowledged.
**Scientific Understanding of Non-Chromate Inhibitors for Coatings Applications**

Ohio State University, Department of Materials Science and Engineering, Fontana Corrosion Center, Columbus, OH, 43210

Approved for public release; distribution unlimited

ASETSDefense 2009: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 31 - September 3, 2009, Westminster, CO. Sponsored by SERDP/ESTCP.
Paired reduction-oxidation reactions constitute a corrosion reaction, otherwise known as a “corrosion cell”.

**Oxidation:** a reaction that produces electrons.

\[ M \rightarrow M^{n+} + n e^- \]

**Reduction:** a reaction that consumes electrons.

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

Reaction sites must be in electronic and ionic contact:
- electronic - thru metal
- ionic - thru solution
Chromate-Free Inhibitors in Current Organic Coatings

<table>
<thead>
<tr>
<th>Material Characterized</th>
<th>Form</th>
<th>Active corrosion inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytec BR6700-1</td>
<td>Adhesive bond primer, cured film</td>
<td>Calcium silicate, zinc phosphate</td>
</tr>
<tr>
<td>Deft 02GN083</td>
<td>Paint primer, liquid resin</td>
<td>Praseodymium hydroxide, CaCO$_3$</td>
</tr>
<tr>
<td>Deft 02GN084</td>
<td>Paint primer, liquid resin</td>
<td>Praseodymium hydroxide</td>
</tr>
<tr>
<td>Deft 44GN098</td>
<td>Paint primer, liquid resin</td>
<td>Praseodymium hydroxide</td>
</tr>
<tr>
<td>Hentzen 16708/709</td>
<td>Paint primer, liquid resin</td>
<td>Calcium carbonate, magnesium carbonate</td>
</tr>
<tr>
<td>Sherwin Williams cm0481968</td>
<td>Paint primer, liquid resin</td>
<td>Zinc oxide, aluminum phosphate</td>
</tr>
<tr>
<td>PPG RW-4057-64</td>
<td>Paint primer, liquid resin</td>
<td>Magnesium hydroxide</td>
</tr>
<tr>
<td>EcoTuff™</td>
<td>Inhibitive pigment</td>
<td>Cerous citrate, zinc molybdate</td>
</tr>
</tbody>
</table>

Based on these findings, model (reagent grade) inhibitor systems have been selected for solubility testing

Courtesy of Mark Jaworoski, UTRC (2009).
The use of high capacity, synthetic ion exchange compounds as coating pigments is an approach for inhibitor delivery.

- **Cationic clays** (montmorillonites, bentonites)

- **Anionic clays** (hydrotalcites).

**Approaches**

- Exchange anions: transition metal oxoanions for Cl⁻ or SO₄²⁻ in solution.
- Exchange cations: transition metal cations for Na⁺ or K⁺ in solution.
- Exchange both cations and anions using amphoteric exchangers or mixtures of clays.
Bentonite preparation.

25 g of Sodium Bentonite

250 ml of 0.2M REM chloride solution

Washed with water and ethanol

Redispersed and dried @ 40°C

REM Exchanged Bentonite

Exchanged cation release is tracked using UV-Visible spectra of 0.5M NaCl solution in contact with the REM Bentonite
Inhibitor release from pigment slurries in a serial washing experiment.
Preparation of substrate AA2024-T3 and PVA/PVB coatings.

Degreased for 2 minutes

- 32.4 g Sodium Metasilicate
- 48 g Na₂CO₃

1000 ml DI Water (65°C)

Rinsed with DI water

Deoxidized for 3 minutes

- 30 g SANCHEM
- 72 ml HNO₃

928 ml DI Water (55°C)

(4 grams PVA In 200 ml DI water)/ (10 wt% PVB in methanol)

Coated with 4 passes of a roller bar

Dried overnight

Coated Panel
Strontium chromate-pigmented positive control.

Cathodic inhibition by chromate adsorption and reduction.

1000 h SS exposure
PVB neat resin negative control.

Protection by barrier properties.

1000 h SS exposure
Scribed 2024-T3 panels after 1000 hours ASTM B117 Salt Spray Exposure. (5 wt.% pigment in PVB).

Neat:
- 35 ppm Ce$^{3+}$
- 89 ppm Zn$^{2+}$
- <1 ppm PO$_4^{3-}$

Strontium Chromate:
- 10 ppm PO$_4^{3-}$
- 53 ppm Ce$^{3+}$
- <1 ppm PO$_4^{3-}$

132 ppm Zn$^{2+}$
<1 ppm PO$_4^{3-}$
146 ppm MoO$_4^{2-}$

Zn$^{2+}$/PO$_4^{3-}$

Zn$^{2+}$/PO$_4^{3-}$
Pigment screening using a total impedance metric allows the group of pigments to be broken into groups.

EIS carried out on samples subject to salt spray.

- **Group 1**
  - $35\text{Ce}^{3+}/89\text{Zn}^{2+}/<\text{PO}_4^{3-}$
  - $\text{SrCrO}_4$

- **Group 2**
  - $\text{Zn}^{2+}/\text{PO}_4^{3-}(1:4)$
  - Neat PVB resin
  - $347\text{Zn}^{2+}$

- **Group 3**
  - $10\text{PO}_4^{3-}$
  - $\text{Zn}^{2+}/\text{PO}_3^{4-}(1:1)$
  - $132\text{Zn}^{2+}/<\text{PO}_4^{3-}/146\text{MoO}_4^{2-}$
  - $53\text{Ce}^{3+}/<\text{PO}_4^{3-}$

**|Z| at 0.01Hz (ohm-cm²)**

**Exposure time in salt spray (days)**
For coatings on Al alloys, high corrosion protection is strongly correlated with inhibition of oxygen reduction reaction.

\[
\text{Potential (V}_{\text{SCE}}) \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad 0.001 \quad 0.01
\]

\[
\text{Current density (A/cm}^2) \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad 0.001 \quad 0.01
\]

Ce\(^{3+}\) and Zn\(^{2+}\) are good cathodic inhibitors.

MoO\(_4^{2-}\) and phosphates are not.
In immersion experiments, coating corrosion protection scales with Ce or Zn dose.

43 days in aerated 0.5M NaCl solution.

- B-Ce
  - 24.4 ppm Ce
  - pH 6.22

- HT-P/B-Zn (1:1)
  - 4 ppm Zn
  - pH 7.63

- HT-P/B-Zn (4:1)
  - 0.2 ppm Zn
  - pH 7.94

1g pigment in 50 mL solution 30 days
Some take-away points.

• The effectiveness of an inhibitor in a coating application correlates with its ability to inhibit the oxygen reduction reaction.

• Inhibitor effectiveness is concentration dependent.
  - critical minimum concentrations needed
  - critical concentration ranges may exist.

• Inhibitor effectiveness may depend on pH.
Lanthanides suppress oxygen reduction, but to varying extents.

Cathodic polarization on 2024-T3 substrates in aerated 0.1 M NaCl solution with chloride salts in various concentrations.
Free corrosion experiment and SEM analysis

The decreasing order of corrosion inhibition is Ce, Pr, La and Zn as inferred by inspection.

• Al2024-T3 sample is immersed in solution of 100 mM NaCl solution and 300 ppm of the inhibitor (as a chloride salt) for 48 hours

• SEM, mapping and spot EDAX analysis was done to study the mechanism of inhibition
Time-dependent EIS for PVB coatings with 10 wt.% Ce³⁺- and Pr³⁺-exchanged bentonites on 2024-T3
Time-dependent EIS for PVB coatings with 10 wt.% Ce$^{3+}$- and Pr$^{3+}$-exchanged bentonites on 2024-T3
Some take-away points.

• $\text{Ce}^{3+}$ and $\text{Pr}^{3+}$ inhibit oxygen reduction to a similar extent, and protect to a similar degree in our screening experiments.

• $\text{Zn}^{2+}$ is an intriguing, but inconsistent inhibitor for Al alloys in our experiments.

• None of the lanthanides or $\text{Zn}^{2+}$ inhibit the ORR as effectively as chromate and corrosion protection in coatings where these inhibitors are present scale accordingly in our experiments.
Vanadates are potent inhibitors of oxygen reduction.

How can we get vanadate inhibitors into coatings?

50 mM NaCl solution
We use a rapid screening test to identify pigments for further development.
Rudimentary primers--epoxy plus IEC pigment give good scribe corrosion resistance.

1008 hours ASTM B117 salt spray exposure.

HT-V primer 25% loading applied by drawdown bar on silane pre-treated 2024-T3

HT-V primer 25% loading applied by drawdown bar on deoxidized 2024-T3
Summary--some answers to the core questions.

• What is the basis for selecting combinations?
  - Cathodic inhibition—specifically inhibition of oxygen reduction.
  - pH where effective.
  - Concentration where effective.

• What inhibitor combinations should be examined?
  - Focus on cathodic inhibition and account for substrate, environment, and transport.

• How are inhibitor combinations to be evaluated?
  - Electrochemical approaches for screening (hard to discriminate exposure results).
  - Exposure plus electrochemical approaches for evaluation.

• How are inhibitor combinations delivered?
  - Ion exchanging pigments and polymers.
  - Sparingly soluble salts (limited).
  - Triggered release (ICPs).
Pigments and pigment combinations

- Hydrotalcite pigments were synthesized by co-precipitation.
- Bentonite pigments were synthesized by ion exchange.
- Synthesis was verified by XRD.

Inhibitor concentrations developed by soaking 1g of pigment or pigment mixture in 50 mL 0.5M NaCl for 2 days.
Inhibitors and combinations for this discussion.

Anion exchangers
- Phosphate-bearing hydrotalcite  HT-P
- Molybdate-bearing hydrotalcite  HT-Mo

Cation exchangers
- Zinc-bearing bentonite  B-Zn
- Cerium-bearing bentonite  B-Ce

Mixtures
- Cerium and phosphate  B-Ce + HT-P
- Cerium-zinc-phosphate  B-Ce + B-Zn + HT-P
- Zinc-phosphate-molybdate  B-Zn + HT-P + HT-Mo
Pigment corrosion protection is assessed in high permeability coatings.

**Coating Application**

- 5 wt. % pigment loading in polyvinyl butyral (PVB) (15 wt% in ethanol) on clean AA2024-T3

- Drawdown bar application; air cure.

**Evaluations**

- Salt spray exposure per ASTM B117 and periodic removal for EIS in 5% NaCl solution.

- Static immersion in aerated 0.5M NaCl solution.
Shift in the (001) peak in the sodium bentonite indicates cation exchange.