Characterization of Encapsulated Corrosion Inhibitors for Environmentally Friendly Smart Coatings

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NASA Kennedy Space Center Corrosion Technology Laboratory
Corrosion

• Worldwide corrosion cost: $2.2 trillion (2010)
• US cost: ~$1 trillion (2013)
• Replace current corrosion inhibitors with environmentally friendly alternatives
  – Coating compatibility issues
  – Solubility issues

http://philipmarshall.net/Images/corrosion_hyperphysics.gif
KSC Approach

- “Smart coating” for corrosion sensing and control
  - Autonomous
  - pH controlled
  - Universal

Microcapsule containing pH indicator (inhibitor, self healing agents)

The shell of the microcapsule breaks down under basic pH (corrosion) conditions

pH indicator changes color and is released from the microcapsule when corrosion starts
Emulsion Polymerization
Release Video
RELEASE STUDIES
Inhibitor Release

• Determine release of inhibitor with time
  – 2-Mercaptobenzothiazole (2-MBT)
  – Nitrite
  – Molybdate

• Method
  – Immersion of particles into 0.01 M base
  – Sampling at regular intervals
MF: 2-MBT Short-term Release

Percent 2-MBT Released vs Microparticle Mass

Time (hours)

Standard MFPTT Formula
No PTT
Higher Formaldehyde
Highest Formaldehyde
Higher Melamine
Highest Melamine
MF: 2-MBT Long-term Release

The graph shows the percent 2-MBT released vs microparticle mass over time (hours) for different MFPTT formulae and conditions.

- Standard MFPTT Formula
- No PTT
- Higher Formaldehyde
- Highest Formaldehyde
- Higher Melamine
- Highest Melamine

The graph indicates a consistent increase in 2-MBT release over time across all conditions, with the highest release observed in the Higher Formaldehyde and Highest Formaldehyde conditions compared to the others.
Inorganic: 2-MBT

![Graph showing the percentage of 2-MBT released vs microparticle mass over time for different batches.]
Inorganic: Nitrite

Percent Nitrite Released vs Microparticle Mass

Time (h)

SiNO2-C13.5 I
SiNO2-C70 I (50%)
SiNO2-C65 I
Inorganic: Molybdate

Percent Molybdate Released vs Microparticle Mass

Time (h)

SiMo-C13.5 Mo I
SiMo-C13.5 Cl- Mo I

0.0% 1.0% 2.0% 3.0% 4.0% 5.0%
Release Studies

• Successful encapsulation and release of inhibitor

• Organic particles
  – Inhibitors can react with particle material
  – Slower, longer-term release

• Inorganic particles
  – Can incorporate a variety of inhibitors, including highly water soluble ionic compounds
  – Quicker, higher amount release
ELECTROCHEMICAL CORROSION TESTING
Accelerated Corrosion Testing

- Carbon steel in 3.5% NaCl solution
- Electrochemical measurements
- Salt immersion
  - Phenylphosphonic acid (PPA)
  - 8-Hydroxyquinoline (8-HQ)
  - 2-MBT & Sodium 2-Mercaptobenzothiazole (2-MBTNa)
Corrosion Potential Increase
Polarization Resistance

![Bar chart showing polarization resistance across different conditions and substances]
SALT IMMERSION TESTING
<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.1% PPA</th>
<th>0.1% PPA and 0.1% 8-HQ</th>
<th>0.1% PPA and 0.002% 2-MBT</th>
<th>0.1% PPA and 0.1% NaMBT</th>
<th>0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT</th>
<th>0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT</th>
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<td>Initial</td>
<td><img src="image1" alt="Initial Control" /></td>
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<td><img src="image5" alt="Initial 0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image6" alt="Initial 0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image7" alt="Initial 0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
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<tr>
<td>5 hour</td>
<td><img src="image8" alt="5 hour Control" /></td>
<td><img src="image9" alt="5 hour 0.1% PPA" /></td>
<td><img src="image10" alt="5 hour 0.1% PPA and 0.1% 8-HQ" /></td>
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<td><img src="image12" alt="5 hour 0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image13" alt="5 hour 0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image14" alt="5 hour 0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
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<tr>
<td>6 day</td>
<td><img src="image15" alt="6 day Control" /></td>
<td><img src="image16" alt="6 day 0.1% PPA" /></td>
<td><img src="image17" alt="6 day 0.1% PPA and 0.1% 8-HQ" /></td>
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<td><img src="image19" alt="6 day 0.1% PPA and 0.1% NaMBT" /></td>
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<td><img src="image21" alt="6 day 0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
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<td>After Wash</td>
<td><img src="image22" alt="After Wash Control" /></td>
<td><img src="image23" alt="After Wash 0.1% PPA" /></td>
<td><img src="image24" alt="After Wash 0.1% PPA and 0.1% 8-HQ" /></td>
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<td><img src="image26" alt="After Wash 0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image27" alt="After Wash 0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image28" alt="After Wash 0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
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# Pure Inhibitor: 8-HQ

<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.1% 8-HQ</th>
<th>0.1% 8-HQ and 0.002% 2-MBT</th>
<th>0.1% 8-HQ and 0.1% NaMBT</th>
<th>0.1% PPA and 0.1% 8-HQ</th>
<th>0.1% PPA 0.1% 8-HQ and 0.002% 2-MBT</th>
<th>0.1% PPA, 0.1% 8-HQ and 0.002% NaMBT</th>
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<tbody>
<tr>
<td>Initial</td>
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<tr>
<td>After Wash</td>
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</table>
## Pure Inhibitor: 2-MBT

<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.002% 2-MBT</th>
<th>0.1% PPA and 0.002% 2-MBT</th>
<th>0.1% 8-HQ and 0.002% 2-MBT</th>
<th>0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT</th>
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<tr>
<td>Initial</td>
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<td><img src="image" alt="Initial" /></td>
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<tr>
<td>4/5 hour</td>
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<tr>
<td>1 day</td>
<td><img src="image" alt="1 day" /></td>
<td><img src="image" alt="1 day" /></td>
<td><img src="image" alt="1 day" /></td>
<td><img src="image" alt="1 day" /></td>
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<tr>
<td>Steel Piece</td>
<td><img src="image" alt="Steel Piece" /></td>
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</table>
**Pure Inhibitor: 2-MBTNa**

<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.1% NaMBT</th>
<th>0.1% PPA and 0.1% NaMBT</th>
<th>0.1% 8-HQ and 0.1% NaMBT</th>
<th>0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT</th>
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<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Initial Control" /></td>
<td><img src="image2" alt="Initial 0.1% NaMBT" /></td>
<td><img src="image3" alt="Initial 0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image4" alt="Initial 0.1% 8-HQ and 0.1% NaMBT" /></td>
<td><img src="image5" alt="Initial 0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
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<tr>
<td>1 hour</td>
<td><img src="image6" alt="1 hour Control" /></td>
<td><img src="image7" alt="1 hour 0.1% NaMBT" /></td>
<td><img src="image8" alt="1 hour 0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image9" alt="1 hour 0.1% 8-HQ and 0.1% NaMBT" /></td>
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<td><img src="image11" alt="1 day Control" /></td>
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## Particles: PPA

<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.3% PPA Particles</th>
<th>0.3% PPA Particles 0.25% 8-HQ Particles</th>
<th>0.3% PPA Particles 0.004% 2-MBT Particles</th>
<th>0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles</th>
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<tr>
<td>Initial</td>
<td><img src="image" alt="Control" /></td>
<td><img src="image" alt="0.3% PPA Particles" /></td>
<td><img src="image" alt="0.3% PPA Particles 0.25% 8-HQ Particles" /></td>
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<td>1 day</td>
<td><img src="image" alt="Control" /></td>
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<tr>
<td>6 day</td>
<td><img src="image" alt="Control" /></td>
<td><img src="image" alt="0.3% PPA Particles" /></td>
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<tr>
<td>Before Wash</td>
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### Particles: 8-HQ

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<th>Control</th>
<th>0.25% 8-HQ Particles</th>
<th>0.3% PPA Particles</th>
<th>0.25% 8-HQ Particles</th>
<th>0.25% 8-HQ Particles</th>
<th>0.004% 2-MBT Particles</th>
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<tbody>
<tr>
<td>Initial</td>
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<td><img src="image2" alt="0.25% 8-HQ Particles" /></td>
<td><img src="image3" alt="0.3% PPA Particles" /></td>
<td><img src="image4" alt="0.25% 8-HQ Particles" /></td>
<td><img src="image4" alt="0.25% 8-HQ Particles" /></td>
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</tr>
<tr>
<td>1 day</td>
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<td><img src="image2" alt="0.25% 8-HQ Particles" /></td>
<td><img src="image3" alt="0.3% PPA Particles" /></td>
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## Particles: 2-MBT

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<th>Time</th>
<th>Control</th>
<th>0.009% Inorganic 2-MBT Particles</th>
<th>0.3% PPA Particles 0.004% 2-MBT Particles</th>
<th>0.25% 8-HQ Particles 0.004% 2-MBT Particles</th>
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Conclusion

- Successful encapsulation of various inhibitors into organic & inorganic microparticles
- Release of inhibitor monitored over long periods of time → short- and longterm controlled release
- Corrosion protection of pure materials confirmed through electrochemical testing
- Particles effective at preventing corrosion in salt immersion testing
- Inhibitors combinations showing high corrosion inhibition efficiency
Synthesis: Organic Particles

Melamine $\rightarrow$ Formaldehyde $\rightarrow$ Methylol melamine (MM) $\rightarrow$ Melamineformaldehyde (MF) $\rightarrow$ Melamineformaldehyde Pentaerythritol tetrakis (MF-PTT)

Methylol melamine (MM)

Melamineformaldehyde (MF)

2-Mercaptobenzothiazole (2-MBT)
pH Change during Polarization

[Bar chart showing pH changes during anodic and cathodic polarization for different pH values and chemicals.]

0.1% PPA 0.1% 8-HQ 0.1% 2-MBT 0.1% MBTNa

Control pH 2  Control pH 4  Control pH 7  Control pH 9

Anodic Polarization  Cathodic Polarization