Characterization of Encapsulated Corrosion Inhibitors for Environmentally Friendly Smart Coatings

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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/Imges/corrosion_hyperphysics.gif
Delivery System

- Inhibitor
- Corrosion Protection
- Coating

Coating compatibility
Inhibitor solubility
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
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)

0 50 100 150 200 250 300 350 400

Percent 2-MBT Released vs Microparticle Mass

0% 2% 4% 6% 8% 10% 12% 14% 16%

Standard MFPTT Formula
No PTT
Higher Formaldehyde
Highest Formaldehyde
Higher Melamine
Highest Melamine
Inorganic: 2-MBT

Percent 2-MBT Released vs Microparticle Mass

Time (hours)

Si-MBT-0.23 #4
Si-MBT-0.23 #4
Si-MBT-X24 (36% Theo) Batch
Si-MBT-X25 (33.5% Theo) Batch
Si-MBT-X28 (38% Theo) Batch
SiMT-C23 1
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
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

![Graph showing polarization resistance values for different pH conditions and chemical treatments.](image)
SALT IMMERSION TESTING
### Pure Inhibitor: PPA

<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>
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<td>5 hour</td>
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<td><img src="image" alt="5 hour 0.1% PPA" /></td>
<td><img src="image" alt="5 hour 0.1% PPA and 0.1% 8-HQ" /></td>
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<td>6 day</td>
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</tr>
<tr>
<td>After Wash</td>
<td><img src="image" alt="After Wash Control" /></td>
<td><img src="image" alt="After Wash 0.1% PPA" /></td>
<td><img src="image" alt="After Wash 0.1% PPA and 0.1% 8-HQ" /></td>
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### Pure Inhibitor: 8-HQ

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<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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<tr>
<td>Initial</td>
<td><img src="initial_control.png" alt="Image" /></td>
<td><img src="initial_8-hq.png" alt="Image" /></td>
<td><img src="initial_8-hq_2-mbt.png" alt="Image" /></td>
<td><img src="initial_8-hq_nambt.png" alt="Image" /></td>
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</tr>
<tr>
<td>5 hour</td>
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<td><img src="5-hour_8-hq.png" alt="Image" /></td>
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<td>After Wash</td>
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# Pure Inhibitor: 2-MBT

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<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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<td><img src="image5.png" alt="Image" /></td>
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<tr>
<td>4/5 hour</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
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<tr>
<td>1 day</td>
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<td><img src="image12.png" alt="Image" /></td>
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<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
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<tr>
<td>Steel Piece</td>
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<td><img src="image19.png" alt="Image" /></td>
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## Pure Inhibitor: 2-MBTA

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<th>0.1% NaMBT</th>
<th>0.1% PPA and 0.1% NaMBT</th>
<th>0.1% 8-HQ and 0.1% NaMBT</th>
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### Particles: PPA

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<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>
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<td><img src="image15" alt="0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles" /></td>
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<td>Before Wash</td>
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<th>0.25% 8-HQ Particles</th>
<th>0.3% PPA Particles 0.25% 8-HQ Particles</th>
<th>0.25% 8-HQ Particles 0.004% Z-MBT Particles</th>
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<tr>
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**Particles: 2-MBT**

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<th>Time</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
Pure Inhibitor Solution pH
pH Change during Polarization

- Anodic Polarization
- Cathodic Polarization