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/Images/corrosion_hyperphysics.gif
Delivery System

Inhibitor

Coating compatibility
Inhibitor solubility

Corrosion Protection

Coating
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

Percent 2-MBT Released vs Microparticle Mass

Time (hours)

0 500 1000 1500 2000 2500 3000 3500

0% 5% 10% 15% 20% 25% 30%

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

![Graph showing the percent 2-MBT released vs microparticle mass over time for different batches.]

- Si-MBT-0.23 #4
- Si-MBT-X24 (36% Theo) Batch
- Si-MBT-X25 (33.5% Theo) Batch
- Si-MBT-X28 (38% Theo) Batch
- SiMBT-C23 1
Inorganic: Nitrite
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

[Bar chart showing the effect of different pH levels and compounds on corrosion potential. The x-axis represents pH levels, while the y-axis represents potential in volts. The chart includes data for pH values of 2.0, 7.0, 5.2, 9.2, 3.9, 2.1, 2.8, 6.1, 8.0, 7.7, 4.0, and 5.5, with compounds such as PPA, 8-HQ, 2-MBT, and MBTNa.]
Polarization Resistance

![Graph showing polarization resistance for various conditions and chemicals]

- Control pH 2
- Control pH 4
- Control pH 7
- Control pH 9
- 0.1% PPA
- 0.1% 8-HQ
- 0.1% 2-MBT
- 0.1% MBTNa
- 0.1% PPA
- 0.1% 8-HQ
- 0.1% 2-MBT
- 0.1% MBTNa
- 0.1% PPA
- 0.1% 8-HQ
- 0.1% 2-MBT
- 0.1% MBTNa
- 0.1% PPA
- 0.1% 8-HQ
- 0.1% 2-MBT
- 0.1% MBTNa

Resistance (Ω*cm²)
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>
<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>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="0.1% PPA" /></td>
<td><img src="image3" alt="0.1% PPA and 0.1% 8-HQ" /></td>
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<td><img src="image5" alt="0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image6" alt="0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image7" alt="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="Control" /></td>
<td><img src="image9" alt="0.1% PPA" /></td>
<td><img src="image10" alt="0.1% PPA and 0.1% 8-HQ" /></td>
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<td><img src="image13" alt="0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
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</tr>
<tr>
<td>6 day</td>
<td><img src="image15" alt="Control" /></td>
<td><img src="image16" alt="0.1% PPA" /></td>
<td><img src="image17" alt="0.1% PPA and 0.1% 8-HQ" /></td>
<td><img src="image18" alt="0.1% PPA and 0.002% 2-MBT" /></td>
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<td><img src="image21" alt="0.1% PPA, 0.1% 8-HQ and 0.1% NaMBT" /></td>
</tr>
<tr>
<td>After Wash</td>
<td><img src="image22" alt="Control" /></td>
<td><img src="image23" alt="0.1% PPA" /></td>
<td><img src="image24" alt="0.1% PPA and 0.1% 8-HQ" /></td>
<td><img src="image25" alt="0.1% PPA and 0.002% 2-MBT" /></td>
<td><img src="image26" alt="0.1% PPA and 0.1% NaMBT" /></td>
<td><img src="image27" alt="0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image28" alt="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>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Initial Control" /></td>
<td><img src="image2" alt="Initial 0.1% 8-HQ" /></td>
<td><img src="image3" alt="Initial 0.1% 8-HQ and 0.002% 2-MBT" /></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 and 0.1% 8-HQ" /></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 0.002% NaMBT" /></td>
</tr>
<tr>
<td>5 hour</td>
<td><img src="image8" alt="5 hour Control" /></td>
<td><img src="image9" alt="5 hour 0.1% 8-HQ" /></td>
<td><img src="image10" alt="5 hour 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image11" alt="5 hour 0.1% 8-HQ and 0.1% NaMBT" /></td>
<td><img src="image12" alt="5 hour 0.1% PPA and 0.1% 8-HQ" /></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 0.002% NaMBT" /></td>
</tr>
<tr>
<td>6 day</td>
<td><img src="image15" alt="6 day Control" /></td>
<td><img src="image16" alt="6 day 0.1% 8-HQ" /></td>
<td><img src="image17" alt="6 day 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image18" alt="6 day 0.1% 8-HQ and 0.1% NaMBT" /></td>
<td><img src="image19" alt="6 day 0.1% PPA and 0.1% 8-HQ" /></td>
<td><img src="image20" alt="6 day 0.1% PPA 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image21" alt="6 day 0.1% PPA, 0.1% 8-HQ and 0.002% NaMBT" /></td>
</tr>
<tr>
<td>After Wash</td>
<td><img src="image22" alt="After Wash Control" /></td>
<td><img src="image23" alt="After Wash 0.1% 8-HQ" /></td>
<td><img src="image24" alt="After Wash 0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image25" alt="After Wash 0.1% 8-HQ and 0.1% NaMBT" /></td>
<td><img src="image26" alt="After Wash 0.1% PPA and 0.1% 8-HQ" /></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 0.002% NaMBT" /></td>
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</tbody>
</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>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="0.002% 2-MBT" /></td>
<td><img src="image3" alt="0.1% PPA and 0.002% 2-MBT" /></td>
<td><img src="image4" alt="0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image5" alt="0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
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<tr>
<td>4/5 hour</td>
<td><img src="image6" alt="Control" /></td>
<td><img src="image7" alt="0.002% 2-MBT" /></td>
<td><img src="image8" alt="0.1% PPA and 0.002% 2-MBT" /></td>
<td><img src="image9" alt="0.1% 8-HQ and 0.002% 2-MBT" /></td>
<td><img src="image10" alt="0.1% PPA, 0.1% 8-HQ and 0.002% 2-MBT" /></td>
</tr>
<tr>
<td>1 day</td>
<td><img src="image11" alt="Control" /></td>
<td><img src="image12" alt="0.002% 2-MBT" /></td>
<td><img src="image13" alt="0.1% PPA and 0.002% 2-MBT" /></td>
<td><img src="image14" alt="0.1% 8-HQ and 0.002% 2-MBT" /></td>
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</tr>
<tr>
<td>Steel Piece</td>
<td><img src="image16" alt="Steel Piece" /></td>
<td><img src="image17" alt="Steel Piece" /></td>
<td><img src="image18" alt="Steel Piece" /></td>
<td><img src="image19" alt="Steel Piece" /></td>
<td><img src="image20" 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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</thead>
<tbody>
<tr>
<td>Initial</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>1 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>
</tr>
<tr>
<td>1 day</td>
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<td><img src="image13.png" alt="Image" /></td>
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</tbody>
</table>
### 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>
</tr>
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<tr>
<td>Initial</td>
<td><img src="Image1" alt="Control" /></td>
<td><img src="Image2" alt="0.3% PPA Particles" /></td>
<td><img src="Image3" alt="0.3% PPA Particles 0.25% 8-HQ Particles" /></td>
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<td><img src="Image5" alt="0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles" /></td>
</tr>
<tr>
<td>1 day</td>
<td><img src="Image6" alt="Control" /></td>
<td><img src="Image7" alt="0.3% PPA Particles" /></td>
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<td>6 day</td>
<td><img src="Image11" alt="Control" /></td>
<td><img src="Image12" alt="0.3% PPA Particles" /></td>
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<td><img src="Image15" alt="0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles" /></td>
</tr>
<tr>
<td>Before Wash</td>
<td><img src="Image16" alt="Before Wash" /></td>
<td><img src="Image17" alt="Before Wash" /></td>
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**Particles: 8-HQ**

<table>
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<tr>
<th>Time</th>
<th>Control</th>
<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% 2-MBT Particles</th>
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<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="0.25% 8-HQ Particles" /></td>
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<td><img src="image5" alt="0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles" /></td>
</tr>
<tr>
<td>1 day</td>
<td><img src="image6" alt="Control" /></td>
<td><img src="image7" alt="0.25% 8-HQ Particles" /></td>
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**Particles: 2-MBT**

<table>
<thead>
<tr>
<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>
<th>0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles</th>
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<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="0.009% Inorg 2-MBT Part" /></td>
<td><img src="image3" alt="0.3% PPA Part 0.004% 2-MBT Part" /></td>
<td><img src="image4" alt="0.25% 8-HQ Part 0.004% 2-MBT Part" /></td>
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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 long-term 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

The synthesis process involves the following steps:

1. **Melamine** reacts with **Formaldehyde** in the presence of a Base to form **Methylol melamine (MM)**.
   
   \[
   \text{H}_2\text{N} - \text{N} - \text{N} - \text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N} - \text{N} - \text{N} - \text{NH} \quad \text{Base} \quad \Delta \quad \text{H}_2\text{O} \rightarrow \text{H}_2\text{N} - \text{N} - \text{N} - \text{NH} \quad \text{MM}
   \]

2. **Methylol melamine (MM)** undergoes reaction with **Melamineformaldehyde (MF)** to form **Melamineformaldehyde Pentaerythritol tetrakis (MF-PTT)**.
   
   \[
   \text{R} - \text{OH} + \text{R} - \text{NH} - \text{N} - \text{NH} - \text{OH} \rightarrow \text{R} - \text{O} - \text{NH} - \text{N} - \text{NH} - \text{O} - \text{R} \quad \text{MF-PTT}
   \]

3. **Melamineformaldehyde (MF)** reacts with **2-Mercaptobenzothiazole (2-MBT)** to form a different compound.
   
   \[
   \text{R} - \text{O} - \text{NH} - \text{N} - \text{NH} - \text{O} - \text{R} + \text{S} - \text{NH} - \text{N} - \text{NH} - \text{SH} \rightarrow \text{R} - \text{O} - \text{NH} - \text{N} - \text{NH} - \text{SH} - \text{S} - \text{NH} - \text{N} - \text{NH} - \text{SH} - \text{R} \quad \text{MF-2-MBT}
   \]
pH Change during Polarization

The graph illustrates the pH change during anodic and cathodic polarization at different pH levels. The pH values are shown for Control pH 2, Control pH 4, Control pH 7, Control pH 9, 0.1% PPA, 0.1% 8-HQ, 0.1% 2-MBT, 0.1% MBTNa, 0.1% PPA, 0.1% 8-HQ, 0.1% 2-MBT, 0.1% MBTNa, 0.1% PPA, 0.1% 8-HQ, 0.1% 2-MBT, 0.1% MBTNa, 0.1% PPA, 0.1% 8-HQ, 0.1% 2-MBT, 0.1% MBTNa, 0.1% PPA, 0.1% 8-HQ, 0.1% 2-MBT, 0.1% MBTNa.

Anodic Polarization is represented by red bars, and Cathodic Polarization by green bars.