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

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

Percent 2-MBT Released vs Microparticle Mass

Time (hours)

0 50 100 150 200 250 300 350 400

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
SiMBT-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 vs 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

<table>
<thead>
<tr>
<th>pH</th>
<th>Additive</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.1% PPA</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>0.1% PPA</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>9.2</td>
<td>0.1% PPA</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>0.1% PPA</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>8.2</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0.1% PPA</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>0.1%</td>
<td></td>
</tr>
</tbody>
</table>

- **PPA**: Potassium Phenylenediamine
- **8-HQ**: 8-Hydroxyquinoline
- **2-MBT**: 2-Mercaptobenzothiazole
- **MBTNa**: Sodium 2-Mercaptobenzothiazole

The data shows a significant increase in potential with certain pH levels and additives, indicating adverse effects on corrosion.
Polarization Resistance

![Graph showing polarization resistance for different conditions and compounds. The x-axis represents various conditions such as Control pH 2, Control pH 4, Control pH 7, and various concentrations of PPA, 8-HQ, and 2-MBT with MBTNa. The y-axis represents resistance (Ω cm²) ranging from 0 to 8,000. The graph shows a comparison of resistance under different pH conditions and the effect of the compounds on it.]
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.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>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
</tr>
<tr>
<td>5 hour</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>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
</tr>
<tr>
<td>6 day</td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
</tr>
<tr>
<td>After Wash</td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
<td><img src="image25.png" alt="Image" /></td>
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<td><img src="image27.png" alt="Image" /></td>
<td><img src="image28.png" alt="Image" /></td>
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</table>
## 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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# 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.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>
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<tr>
<td>4/5 hour</td>
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<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="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>
</tr>
<tr>
<td>Steel Piece</td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></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>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="initial_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="initial_0.1%25_PPA_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="initial_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="initial_0.1%25_PPA_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
</tr>
<tr>
<td>1 hour</td>
<td><img src="1_hour_control.png" alt="Image" /></td>
<td><img src="1_hour_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="1_hour_0.1%25_PPA_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="1_hour_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
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<tr>
<td>1 day</td>
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<td><img src="1_day_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="1_day_0.1%25_PPA_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="1_day_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="1_day_0.1%25_PPA_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
</tr>
<tr>
<td>Steel Piece</td>
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<td><img src="steel_piece_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="steel_piece_0.1%25_PPA_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="steel_piece_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
<td><img src="steel_piece_0.1%25_PPA_0.1%25_8-HQ_and_0.1%25_NaMBT.png" alt="Image" /></td>
</tr>
<tr>
<td>Time</td>
<td>Control</td>
<td>0.3% PPA Particles</td>
<td>0.3% PPA Particles 0.25% 8-HQ Particles</td>
<td>0.3% PPA Particles 0.004% 2-MBT Particles</td>
<td>0.3% PPA Particles 0.25% 8-HQ Particles 0.004% 2-MBT Particles</td>
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<tr>
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<tr>
<td>Initial</td>
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<tr>
<td>1 day</td>
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<tr>
<td>6 day</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Before Wash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
### Particles: 8-HQ

<table>
<thead>
<tr>
<th>Time</th>
<th>Control</th>
<th>0.25% 8-HQ Particles</th>
<th>0.3% PPA Particles</th>
<th>0.25% 8-HQ Particles</th>
<th>0.004% 2-MBT Particles</th>
<th>0.3% PPA Particles</th>
<th>0.25% 8-HQ Particles</th>
<th>0.004% 2-MBT Particles</th>
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</thead>
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<tr>
<td>Initial</td>
<td><img src="image1" alt="Initial Control" /></td>
<td><img src="image2" alt="Initial 0.25% 8-HQ Particles" /></td>
<td><img src="image3" alt="Initial 0.3% PPA Particles" /></td>
<td><img src="image4" alt="Initial 0.25% 8-HQ Particles" /></td>
<td><img src="image5" alt="Initial 0.004% 2-MBT Particles" /></td>
<td><img src="image6" alt="Initial 0.3% PPA Particles" /></td>
<td><img src="image7" alt="Initial 0.25% 8-HQ Particles" /></td>
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<tr>
<td>1 day</td>
<td><img src="image9" alt="1 day Control" /></td>
<td><img src="image10" alt="1 day 0.25% 8-HQ Particles" /></td>
<td><img src="image11" alt="1 day 0.3% PPA Particles" /></td>
<td><img src="image12" alt="1 day 0.25% 8-HQ Particles" /></td>
<td><img src="image13" alt="1 day 0.004% 2-MBT Particles" /></td>
<td><img src="image14" alt="1 day 0.3% PPA Particles" /></td>
<td><img src="image15" alt="1 day 0.25% 8-HQ Particles" /></td>
<td><img src="image16" alt="1 day 0.004% 2-MBT Particles" /></td>
</tr>
<tr>
<td>6 day</td>
<td><img src="image17" alt="6 day Control" /></td>
<td><img src="image18" alt="6 day 0.25% 8-HQ Particles" /></td>
<td><img src="image19" alt="6 day 0.3% PPA Particles" /></td>
<td><img src="image20" alt="6 day 0.25% 8-HQ Particles" /></td>
<td><img src="image21" alt="6 day 0.004% 2-MBT Particles" /></td>
<td><img src="image22" alt="6 day 0.3% PPA Particles" /></td>
<td><img src="image23" alt="6 day 0.25% 8-HQ Particles" /></td>
<td><img src="image24" alt="6 day 0.004% 2-MBT Particles" /></td>
</tr>
<tr>
<td>Before Wash</td>
<td><img src="image25" alt="Before Wash Control" /></td>
<td><img src="image26" alt="Before Wash 0.25% 8-HQ Particles" /></td>
<td><img src="image27" alt="Before Wash 0.3% PPA Particles" /></td>
<td><img src="image28" alt="Before Wash 0.25% 8-HQ Particles" /></td>
<td><img src="image29" alt="Before Wash 0.004% 2-MBT Particles" /></td>
<td><img src="image30" alt="Before Wash 0.3% PPA Particles" /></td>
<td><img src="image31" alt="Before Wash 0.25% 8-HQ Particles" /></td>
<td><img src="image32" alt="Before Wash 0.004% 2-MBT Particles" /></td>
</tr>
</tbody>
</table>
### 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>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="2-MBT Particles" /></td>
<td><img src="image3" alt="PPA Particles" /></td>
<td><img src="image4" alt="8-HQ Particles" /></td>
<td><img src="image5" alt="PPA Particles, 8-HQ Particles, 2-MBT Particles" /></td>
</tr>
<tr>
<td>1 day</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="2-MBT Particles" /></td>
<td><img src="image3" alt="PPA Particles" /></td>
<td><img src="image4" alt="8-HQ Particles" /></td>
<td><img src="image5" alt="PPA Particles, 8-HQ Particles, 2-MBT Particles" /></td>
</tr>
<tr>
<td>6 day</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="2-MBT Particles" /></td>
<td><img src="image3" alt="PPA Particles" /></td>
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<tr>
<td>Before Wash</td>
<td><img src="image1" alt="Control" /></td>
<td><img src="image2" alt="2-MBT Particles" /></td>
<td><img src="image3" alt="PPA Particles" /></td>
<td><img src="image4" alt="8-HQ Particles" /></td>
<td><img src="image5" alt="PPA Particles, 8-HQ Particles, 2-MBT Particles" /></td>
</tr>
</tbody>
</table>
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 + Formaldehyde → Methylol melamine (MM)

Methylol melamine (MM) + Base → Melamineformaldehyde (MF)

Melamineformaldehyde Pentaerythritol tetrakis (MF-PTT)
Pure Inhibitor Solution pH

The bar chart illustrates the pH values before polarization for various inhibitor solutions at different pH levels. The pH values range from 0 to 10, with each bar representing a specific concentration and pH condition. The chart includes control samples at pH 2, 4, 7, and 9, as well as solutions containing 0.1% PPA, 8-HQ, 2-MBT, and MBTNa.

- **Control pH 2**: pH before polarization at pH 2.
- **Control pH 4**: pH before polarization at pH 4.
- **Control pH 7**: pH before polarization at pH 7.
- **Control pH 9**: pH before polarization at pH 9.
- **0.1% PPA**: pH before polarization for 0.1% PPA solutions at various pH levels.
- **8-HQ**: pH before polarization for 8-HQ solutions at various pH levels.
- **2-MBT**: pH before polarization for 2-MBT solutions at various pH levels.
- **MBTNa**: pH before polarization for MBTNa solutions at various pH levels.

The chart indicates the effectiveness of these inhibitors in maintaining a stable pH before polarization, which is crucial for understanding their corrosion inhibition properties.
pH Change during Polarization

![Graph showing pH changes during polarization.](image-url)