Recent Developments on Microencapsulation for Autonomous Corrosion Protection

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Introduction

• NASA has been battling corrosion since the inception of the Space Program.

• NASA launches from the most naturally corrosive environment in North America. Corrosion conditions at the launch pads are even more severe due to solid rocket booster (SRB) exhaust products.

• NASA identified corrosion control technologies as their #1 technology need to lower the cost and improve the sustainability and efficiency of its ground operations in support of future launch activities.

• NASA developed microencapsulation technology specifically designed for corrosion control applications (U.S. Patent No. 7,790,225, 2010).

• These microcapsules are being used to develop a multifunctional coating for autonomous corrosion control.

• This presentation is an overview of the background and progress made to date in the development of a multifunctional coating to indicate corrosion at an early stage and in hidden areas, to deliver corrosion inhibitors on demand, and to self-heal damage, such as a scratch.
Examples of Launch Pad Corrosion

Enclosed / Inaccessible Areas

Dissimilar Metals

KSC Launch tower structural steel corrosion

Under the LC 39B Flame Trench
Examples of Launch Pad Corrosion (cont.)

Pitting of SS 317L Tubing

Micrograph (100X) of pit in SS 304 tubing

SS 304 tubing split caused by pitting
Cost of Corrosion

- Overall direct cost of metallic corrosion in the U.S.: $276B/year (3.1% GDP).¹ $578B (4.2% GDP in 2007)
- Cost of corrosion control at KSC Launch Pads estimated as $1.6M/year²
- Estimated 20 year lifecycle savings from smart coating technology: $132M

² Estimate based on corrosion control cost of launch pads (39A and 39B) and the 3 MLPs in 2001
KSC Natural Environment
KSC Launch Pad Environment

The launch environment at KSC is extremely corrosive:

- Ocean salt spray
- Heat
- Humidity
- Sunlight
- Acidic exhaust from SRBs
Natural Salt Fog Chamber
In 1981 the Space Shuttle introduced acidic deposition (70 tons of HCl) products. NASA plans to use Shuttle-derived SRB rockets in future missions.

\[
\text{NH}_4\text{ClO}_4(s) + \text{Al}(s) \xrightarrow{\text{binder, Fe}_2\text{O}_3} \text{Al}_2\text{O}_3(s) + \text{HCl}(g) + \text{H}_2\text{O}(g) + \text{NO}_x(g)
\]
## Corrosion Rates of Carbon Steel

The table below presents the corrosion rates of carbon steel specimens at various locations.*

<table>
<thead>
<tr>
<th>Location</th>
<th>Type Of Environment</th>
<th>μm/yr</th>
<th>Corrosion rate&lt;sup&gt;a&lt;/sup&gt; mils/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esquimalt, Vancouver Island, BC, Canada</td>
<td>Rural marine</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>Pittsburgh, PA</td>
<td>Industrial</td>
<td>30</td>
<td>1.2</td>
</tr>
<tr>
<td>Cleveland, OH</td>
<td>Industrial</td>
<td>38</td>
<td>1.5</td>
</tr>
<tr>
<td>Limon Bay, Panama, CZ</td>
<td>Tropical marine</td>
<td>61</td>
<td>2.4</td>
</tr>
<tr>
<td>East Chicago, IL</td>
<td>Industrial</td>
<td>84</td>
<td>3.3</td>
</tr>
<tr>
<td>Brazos River, TX</td>
<td>Industrial marine</td>
<td>94</td>
<td>3.7</td>
</tr>
<tr>
<td>Daytona Beach, FL</td>
<td>Marine</td>
<td>295</td>
<td>11.6</td>
</tr>
<tr>
<td>Pont Reyes, CA</td>
<td>Marine</td>
<td>500</td>
<td>19.7</td>
</tr>
<tr>
<td>Kure Beach, NC (80 ft. from ocean)</td>
<td>Marine</td>
<td>533</td>
<td>21.0</td>
</tr>
<tr>
<td>Galeta Point Beach, Panama CZ</td>
<td>Marine</td>
<td>686</td>
<td>27.0</td>
</tr>
<tr>
<td>Kennedy Space Center, FL (beach)</td>
<td>Marine</td>
<td>1070</td>
<td>42.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Two-year average


A mil is one thousandth of an inch
Changes in Corrosion Rate with Distance from the Ocean

Comparison of Average Corrosion Rate (Weight Loss) of UNS G10080 and Atmospheric Salt Content at Various Distances from the Seacoast

- Weight Loss, UNS G10080
- Salt Collection Rate (Funnel Samples)

Distance from Seacoast (Feet)

Weight Loss, grams

Milligrams, NaCl/m²/hr
Corrosion Protective Coatings

• Barrier (passive).

• Barrier plus active corrosion inhibiting components:
  ▪ Sacrificial (zinc-rich primers)
  ▪ Corrosion inhibitors (can have detrimental effects on the coating properties and the environment; most expensive additive; subject to progressively stricter environmental regulations)

• Smart

A smart coating detects and responds actively to changes in its environment in a functional and predictable manner and is capable of adapting its properties dynamically.

Smart coating responding to changing pH conditions
The use of "smart coatings" for corrosion sensing and control relies on the changes that occur when a material degrades as a result of its interaction with a corrosive environment.

Such transformations can be used for detecting and repairing corrosion damage.

NASA’s Corrosion Technology Laboratory is developing a coating that can detect and repair corrosion at an early stage.

This coating is being developed using pH sensitive microcapsules that deliver the contents of their core when corrosion starts to:

- Detect and indicate the corrosion location
- Deliver environmentally friendly corrosion inhibitors
- Deliver healing agents to repair mechanical coating damage.
Electrochemical Nature of Corrosion

Metal is oxidized (anodic reaction); something else is reduced (cathodic reaction)

Overall Reaction:

\[ 2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^- \]

Anodic:

\[ Fe \rightarrow Fe^{2+} + 2e^- \]

Cathodic:

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

pH Scale

Basic pH used for corrosion detection

Launch pad after launch

Vinegar

Seawater

0 7 14

Acidic Neutral Basic

pH Scale
Corrosion Indication

pH changes that occur during corrosion of a metal

Elapsed Time: 0 hours

1.5 hours

4.5 hours

0.5 hours

3 days
Corrosion indication, detection, and healing of mechanical damage can be achieved using microencapsulation technology

**What are microcapsules?**

Particles or liquid drops coated in polymers. These microcapsules can carry any material that needs protection or controlled release.

**Why microencapsulate a material?**

- To achieve controlled-release.
- Make active materials easier/safer to handle.
- Compartmentalize multiple component systems.
- Protect sensitive materials from their environment.
- Versatility
Microencapsulation Versatility

- Versatility: Microcapsules can deliver multiple types of contents into different paint systems shortening the time to a new coating formulation when one of the components becomes unavailable.

![Diagram of Microcapsules](image)
**pH Sensitive Microcapsules for Corrosion Sensing**

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
Smart Coating Response to Corrosion

1. Corrosion indicators
2. Corrosion inhibitors
3. Healing agents

Ruptured Microcapsule:
- indicates corrosion
- protects metal from corrosion
- repairs damaged area

Corrosion causes capsule to rupture

Mechanical damage causes capsule to rupture

\[
\begin{align*}
\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{OH}^- \\
\text{Fe}^{2+} + \text{e}^- & \rightarrow \text{Fe}^{0}
\end{align*}
\]
Interfacial polymerization of oil-in-water microemulsion process for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.
Hydrophobic-core Microcapsules

Optical microscopy images of Hydrophobic-core microcapsules of different sizes

Free flowing powder samples of hydrophobic-core microcapsules. The core contents of these microcapsules are Rhodamine B (on the left), Phenolphthalein (in the middle), and a universal pH indicator (on the right).
Hydrophilic Core Microcapsules

Interfacial polymerization of water in oil microemulsion process for hydrophilic-core microcapsules. Oil is shown in yellow and water in blue.
Hydrophilic-core Microcapsules

SEM images of the hydrophilic-core microcapsules
When corrosion begins, the microcapsule will release the contents of the core (indicator, inhibitor, and self healing agent) in close proximity to the corrosion.

SEM images of microcapsules with corrosion indicator (top) and inhibitor (bottom).
Microcapsule Response to pH Increase
pH sensitive microcapsules with corrosion indicator for corrosion detection

Significance:
Damage responsive coatings provide visual indication of corrosion in hard to maintain/inaccessible areas (on towers) prior to failure of structural elements.

Time lapse pictures of a microcapsule with indicator breaking down under basic pH conditions.

A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was immersed in gel with microcapsules containing a corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and progress of corrosion.
Indication of Hidden Corrosion

Pad 39B MLP-1: Bolt from Victaulic joint on center upper shield

Conceptual illustration of corrosion indication in structural bolts at the launch pad
## Hidden Corrosion Indication

<table>
<thead>
<tr>
<th>System label</th>
<th>Metal Substrate</th>
<th>Coating systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc galvanized nut and bolt</td>
<td>Clear urethane coating containing 10% phenolphthalein (phph) microcapsules.</td>
</tr>
<tr>
<td>2</td>
<td>Zinc galvanized nut and bolt</td>
<td>First coated with epoxy, then top coated with clear urethane containing 10% phph microcapsules.</td>
</tr>
<tr>
<td>3</td>
<td>Sand blasted nut and bolt</td>
<td>The ends of the nut and bolt were coated with inorganic zinc coating; the entire nut and bolt was coated with urethane containing 10% phph microcapsules.</td>
</tr>
<tr>
<td>4</td>
<td>Sand blasted nut and bolt</td>
<td>The ends of the nut and bolt were coated with inorganic zinc coating. The entire nut and bolt was coated with epoxy and then top coated with a clear urethane containing 10% phph microcapsules.</td>
</tr>
<tr>
<td>5</td>
<td>Zinc galvanized nut and bolt</td>
<td>The ends of the nut and bolt were coated with urethane containing 10% phph microcapsules.</td>
</tr>
<tr>
<td>6</td>
<td>Zinc galvanized nut and bolt</td>
<td>The ends of the nut and bolt were coated with epoxy and then top coated with urethane containing 10% phph microcapsules.</td>
</tr>
</tbody>
</table>

Nut and bolt set up for crevice corrosion testing. The pictures show results after 600 hour of salt fog exposure.
Experimental Corrosion Indicating Coating

Salt fog test¹ results of panels coated with a clear polyurethane coating loaded with 20% oil core microcapsules with corrosion indicator in their core. The coating detects corrosion in the scribed area at a very early stage (0 seconds) before the appearance of rust is visible.

Encapsulated inhibitors were tested in an epoxy mastic coating. Rust rating is higher for coating with encapsulated inhibitor when compared to the control.

<table>
<thead>
<tr>
<th>Carbomastic 15 FC Coating Systems</th>
<th>Sample #</th>
<th>Rust Grade</th>
<th>Scribe Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>10% (w/v) PA inhibitor microcapsule</td>
<td>1</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>
Corrosion Inhibition: 6 month Salt Fog

Inhibitor capsules were tested in inorganic zinc coating on steel substrate without surface preparation.

It is known that inorganic zinc provides excellent corrosion protection when surface preparation is sufficient to provide good adhesion. This test was done on steel without surface preparation.

The encapsulated inhibitor improved the adhesion and the rust grade of the coating on steel.

<table>
<thead>
<tr>
<th>Cathacoat 304V Coating Systems</th>
<th>Sample #</th>
<th>Rust Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>10% water-core inhibitor microcapsule slurries</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>
Self Healing

Siloxane microcapsules synthesized by *in situ* polymerization reaction procedure.

Control and 2-Part siloxane capsule system (siloxane and tin catalyst), blended into an epoxy primer coating, after 700 hrs of salt fog exposure testing. Coating thickness is about 400μm and microcapsule content is 20 wt%.
Summary

KSC is developing a smart coating, based on pH-sensitive microcapsules and particles, for early corrosion detection, corrosion inhibition, and self-healing.

The corrosion indicating function has been demonstrated by incorporating an encapsulated corrosion indicator into a clear polyurethane coating. Salt fog test results showed that the coating detects corrosion at a very early stage before the appearance of rust is visible.

Salt fog test results showed the effectiveness of the encapsulated corrosion indicator in detecting hidden corrosion in an epoxy coating with urethane as a top coat.

Salt fog test results showed the effectiveness of an encapsulated corrosion inhibitor.

Salt fog test results showed the effectiveness of an encapsulated self-healing system.