A Multifunctional Coating for Autonomous Corrosion Control

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What is Corrosion?

- "Corrosion is the environmentally induced degradation of a material that involves a chemical reaction.
- Degradation implies deterioration of the structural properties of the material.
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 $1.6M/year$^2$
- 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
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

#### Corrosion rates of carbon steel calibrating 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><strong>Kennedy Space Center, FL (beach)</strong></td>
<td>Marine</td>
<td>1070</td>
<td>42.0</td>
</tr>
</tbody>
</table>

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


<sup>1</sup>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
Zone 3: Surfaces, other than those located in Zones 1 or 2, that receive acid deposition from solid rocket booster exhaust products.

Zone 2: Surfaces that receive elevated temperatures and acid deposition from solid rocket booster exhaust with no exhaust impingement.

FSS 115” Level

Zone 1: Surfaces that receive direct rocket engine exhaust impingement and ET/IT Attachment point
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.

[Image of a 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

Acidic

Neutral

Basic

pH Scale

Launch pad after launch

Vinegar

Seawater

Basic pH used for corrosion detection
Corrosion Indication

**pH changes that occur during corrosion of a metal**

<table>
<thead>
<tr>
<th>pH Level</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>0 hours</td>
</tr>
<tr>
<td>Slightly Acidic</td>
<td>4.5 hours</td>
</tr>
<tr>
<td>Neutral</td>
<td>0.5 hours</td>
</tr>
<tr>
<td>Slightly Basic</td>
<td></td>
</tr>
<tr>
<td>Basic</td>
<td></td>
</tr>
</tbody>
</table>

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

Microcapsules developed at KSC
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 showing multiple ingredients and multiple paints connected to a single microcapsule](image-url)
**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
1. Corrosion indicators
2. Corrosion inhibitors
3. Healing agents

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

Mechanical damage causes capsule to rupture
Corrosion causes capsule to rupture

O₂ + H₂O → OH⁻
Fe²⁺ + e⁻
Hydrophobic Core Microcapsules

Interfacial polymerization of oil-in-water microemulsion process for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.
Polymeric wall formation involves using a cross-linking agent that has one or more ester and mercapto groups such as pentaerythritol tetrakis (3-mercaptopropionate) (PTT):

- Film-forming monomers and pre-polymers such as urea formaldehyde and melamine formaldehyde are used to provide structural integrity to the wall
- Wall break down occurs by base-catalyzed ester hydrolysis
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.
Microcapsule Response to pH Increase

Capsule wall breakdown and indicator color change under basic conditions: NaOH, (pH of 12)

- Frames a-d: the basic solution starts to penetrate the microcapsule wall and the indicator inside changes color.
- Frame e: the microcapsule begins to slowly release its contents (as evidenced by the small droplet that begins to form on the bottom left quadrant of the frame).
- Frames f-h: oil droplets are observed as the aqueous solution penetrates the hydrophobic microcapsule core.
- Frame i: The content continues to be released until it dissipates into the solution.
- Frames j-n: The microcapsule wall eventually breaks down completely.
Microcapsules for Corrosion Indication

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.

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

Indication of hidden corrosion by color change

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>

Coating systems used for hidden corrosion indication testing.

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 test\(^1\) 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.

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.

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