Smart Multifunctional Coatings for Corrosion Detection and Control in the Aerospace Industry

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Luz Marina Calle, Ph.D.
NASA’s Corrosion Technology Laboratory
Kennedy Space Center, FL, 32899, USA
Introduction

• NASA has been battling corrosion since the inception of the Space Program in 1962.
• 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’s Space Technology Roadmap includes corrosion control technologies as one of the areas needed to lower the cost and improve the sustainability and efficiency of its ground operations in support of future launch activities.
• NASA has developed microencapsulation technology specifically designed for corrosion control applications (U.S. Patents No. 7,790,225, 2010 and 20130017612, 2014).
• These microcontainers are being used to develop a smart multifunctional coating for autonomous corrosion detection and control.
• This presentation provides an overview of the background and progress made to date in the development of a smart multifunctional coating to indicate corrosion at an early stage and in hidden areas, to deliver corrosion inhibitors on demand, and to self-heal mechanical damage, such as a scratch.
"NASA's Space Launch System (SLS) and Orion will allow human exploration to continue beyond the moon in ways that were once a glimmer in our minds eye. Now we are building the hardware and developing the engineering operations teams that will launch the vehicle that will one day take people to Mars"
Orion/SLS combination is critical to extending human presence beyond low earth orbit.
SLS Architecture Reference Configuration

Launch Abort System
Orion
Interim Cryogenic Propulsion Stage (ICPS)
Interstage

70t 321 ft.

Core Stage
RS-25 Engines
SLS-10002 DAC1

Upper Stage with J-2X Engines
Advanced Boosters
SLS-21002 DAC1

130t 384 ft.
Exploration Mission Timeline

- **2010 PA-1**
- **2014 EFT-1**
- **2017 EM-1**
- **2018 AA2**
- **2021 EM-2**
Orion/SLS are the Basis for Exploration beyond Earth Orbit
HUMAN EXPLORATION
NASA's Journey to Mars

EARTH RELIANT
MISSION: 6 TO 12 MONTHS
RETURN TO EARTH: HOURS

Mastering fundamentals aboard the International Space Station

U.S. companies provide access to low-Earth orbit

PROVING GROUND
MISSION: 1 TO 12 MONTHS
RETURN TO EARTH: DAYS

Expanding capabilities by visiting an asteroid redirected to a lunar distant retrograde orbit

The next step: traveling beyond low-Earth orbit with the Space Launch System rocket and Orion spacecraft

MARS READY
MISSION: 2 TO 3 YEARS
RETURN TO EARTH: MONTHS

Developing planetary independence by exploring Mars, its moons and other deep space destinations

www.nasa.gov
The future of exploration

Space Launch System and Orion enable solar system exploration
One challenge with space exploration is that equipment must withstand radical conditions, from the heat of rocket exhaust to extreme cold in space. Surprisingly, one of the most destructive forces is the corrosive effect of saltwater-laden ocean spray and fog. It rusts launch structures and equipment at the Kennedy Space Center.
What is Corrosion?

Corrosion is the deterioration of a material due to reaction with its environment (M.G. Fontana). It literally means to "gnaw away"

Degradation implies deterioration of the properties of the material.

Metal atoms in nature are present in chemical compounds (i.e. minerals).

Metals in their uncombined state are in a high energy state. The tendency is to corrode and revert to the low energy state. Corrosion has been called metallurgy in reverse.
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:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
Repairs will cost about $60 million USD and take about 2 years.
At US $2.2 (1.6 €) trillion, the annual direct cost of corrosion worldwide is over 3% of the world's GDP.*

Direct costs do not include the environmental damage, waste of resources, loss of production, or personal injury.

*World Corrosion Organization 2010

(1 Trillion = 10^{12} = 1 billon)
Corrosion Grand Challenges*

- Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings.
- High-fidelity modeling for the prediction of corrosion degradation in actual service environments.
- Accelerated corrosion testing under controlled laboratory conditions. Such testing would quantitatively correlate with the long-term behavior observed in service environments.
- Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary. i.e., corrosion prognosis.

*Research Opportunities in Corrosion Science and Engineering, Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council (2010)
The aerospace industry employs high strength aluminum alloys as structural materials for airplanes because of a combination of valuable mechanical properties, strength to weight ratio, good corrosion resistance, easy recyclability, and formability.

Aluminum needs alloying with other elements in order to improve its mechanical strength.

This alloying of aluminum with other metallic elements has a significant effect on its corrosion resistance properties.

Reduction in corrosion resistance occurs as a result of the heterogeneous microstructure attributed to the second phase intermetallic particles of various sizes and compositions in the aluminum alloy matrix.

The presence of these intermetallic particles in the aluminum alloy microstructure is often responsible for localized corrosion in the form of pitting, intergranular corrosion, exfoliation corrosion, etc., depending on the alloy type.

Aluminum alloy surfaces are coated to enhance their corrosion resistance.
This picture of Aloha Airlines Flight 243, was taken after one-third of the roof flew off of the aircraft while cruising at 24,000 feet. A series of small cracks, caused by corrosion, had grown simultaneously at many nearby rivet holes, the devastating results of which can be seen in this picture. This is an extreme example of the damage that corrosion can cause, and an indication of why the protection of aluminum against corrosion is so important in the aerospace industry.

Since this mishap, the aviation community has struggled to accurately predict the onset of corrosion or the extent of structural damage it induces. Despite advances in corrosion algorithms, computation material research, simulation, reliability and maintenance data analysis, a reliable model for prediction corrosion on aging aircraft has yet to be produced. This incident established US civil and military programs for ageing aircraft of which corrosion was a principal area of focus.

Historically, corrosion prevention has not been appreciably designed into an aircraft.
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/Active/Functional/Self-healing

![Schematic of a typical multi-coating system used to protect aluminum alloys from corrosion. The conversion coating provides the first layer of corrosion protection and acts as a base for improved adhesion to the primer. Chromate and chromate-phosphate-based conversion coatings have been used for this purpose for several decades, as they are effective in inhibiting the corrosion of aluminum alloys. However, the use of chromium-containing chemicals has been limited because of harmful carcinogenic effects, and intense research efforts are in progress for finding alternatives.](image-url)
Introduction

NASA Space Technology Roadmap

America is beginning an exciting new chapter in space exploration. To enable the future, NASA has developed a set of roadmaps to define the key new technologies required for our human and robotic explorers to safely venture into deep space, to better understand how our own solar system evolved, and to unravel the mysteries of our universe.

The map you see here is a graphical representation of the NASA Space Technology Roadmaps, serving as a portal to the various technologies that NASA is developing. Let this technology portal serve as a starting point for your adventures beyond the bounds of Earth...

To learn more visit www.nasa.gov/oct

13.2.1 Corrosion Prevention, Detection and Mitigation
Since its inception in 1958, NASA has accomplished many great scientific and technological feats in air and space. NASA technology also has been adapted for many non-aerospace uses by the private sector. NASA remains a leading force in scientific research and in stimulating public interest in aerospace exploration, as well as science and technology in general.
Corrosion protection coating on aluminum lithium alloy (left) and heat shield (right). The heat shield protects the spacecraft from temperatures reaching 4000 degrees Fahrenheit (2204 °C).
Orion 37 days prior to 1\textsuperscript{st} Test Flight
Coatings for the Space Environment

The Space Environment is characterized by:

- Low pressure (vacuum)
- Atomic Oxygen (causes erosion of materials)
- Ultraviolet (UV) radiation
- Charged particles
- Temperature extremes
- Electromagnetic radiation
- Micrometeoroids
- Man-made debris
Materials are tested on the exterior of the International Space Station. The payload container is mounted so one side faces the Earth and the other faces space. The experiments provide a better understanding of material durability, from coatings to electronic sensors, which could be applied to future spacecraft designs.

NASA astronaut Patrick G. Forrester installs exposure experiments designed to collect information on how different materials weather in the environment of space

NASA astronaut Andrew Feustel retrieves long duration materials exposure experiments before installing others during a spacewalk on May 20, 2011.
Orion Heat Shield

Textron technicians apply the Avcoat material by “gunning” the material into each of the 330,000 individual cells of the honeycomb structure
Atomic Oxygen Restoration

Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night (right photo), in part, due to atomic oxygen.

In the upper reaches of the atmosphere, about 200-500 miles, an elemental form of oxygen is created from exposure to intense solar ultraviolet light. Oxygen molecules are decomposed from $\text{O}_2$ into two separate oxygen atoms. This form of elemental oxygen is highly reactive and exposes a spacecraft to corrosion that shortens its life. While developing methods to prevent damage from atomic oxygen, it was discovered that it could also remove layers of soot or other organic material from a surface. Atomic oxygen will not react with oxides, so most paint pigments will not be affected by the reaction.
The left photo was taken after the Cleveland Museum of Art's staff attempted to clean and restore it using acetone and methylene chloride. The right photo is after cleaning by the atomic oxygen technique.
Coatings for NASA’s Launch Environment
The Kennedy Space Center in Florida, USA, is a special place where we launch rockets from a wild life refuge in one of the most corrosive areas in the world.
KSC Launch Environment
What is Corrosion?

Corrosion is the deterioration of a material due to reaction with its environment (M.G. Fontana). It literally means to "gnaw away"

Degradation implies deterioration of the properties of the material.

Metal atoms in nature are present (i.e. minerals).
Corrosion Prevention, Detection, and Mitigation Timeline

- In May 1961, President John F. Kennedy challenged America to go to the Moon.
- On July 1, 1962 NASA’s launch facilities in Florida became the Launch Operations Center. In 1963 the Center's name was changed to the John F. Kennedy Space Center (KSC).
- In 1966 NASA establishes atmospheric exposure testing at KSC.
- 1985 Electrochemical corrosion testing begins.
- 1989 Electrochemical Impedance Spectroscopy (EIS) is introduced as a research tool to evaluate Shuttle alloys and zinc-rich primers.
- 2000 The Corrosion Technology Laboratory is created to achieve KSC’s goal of increased participation in research and development.
- 2004 Research on smart coatings for corrosion detection and mitigation begins.
- 2005 First patent application on “Coatings and methods for corrosion detection and/or reduction” filed.
- 2010 First patent granted (US 7790225). Subsequent patent applications are filed.
- 2010 NASA seeks industry partners interested in the commercial applications of the smart coating for corrosion detection and protection technology.
Atmospheric Exposure Testing

Beachside atmospheric exposure testing
1.6 km
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 Rates of Carbon Steel

<table>
<thead>
<tr>
<th>Location</th>
<th>Type Of Environment</th>
<th>µm/yr</th>
<th>Corrosion rate(^a) 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><strong>Marine</strong></td>
<td><strong>1070</strong></td>
<td><strong>42.0</strong></td>
</tr>
</tbody>
</table>

\(^a\)Two-year average


A mil is one thousandth of an inch
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.

\[
\text{NH}_4\text{ClO}_4(s) + \text{Al}(s) \xrightarrow{\text{binder, Fe}_2\text{O}_3} \text{Al}_2\text{O}_3(s) + \text{HCl}(g) + \text{H}_2\text{O}(g) + \text{NO}_x(g)
\]
Launch Complex 39 Zones of Exposure

**Zone 1:** Surfaces that receive direct rocket engine exhaust impingement and External Tank/Intertank access point.

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

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

FSS 115” Level
Examples of Launch Pad Corrosion

Enclosed / Inaccessible Areas

Dissimilar Metals

KSC Launch tower structural steel corrosion

Under the LC 39B Flame Trench
Pitting of SS 317L Tubing

Micrograph (100X) of pit in SS 304 tubing

SS 304 tubing split caused by pitting
At US $2.2 (1.6 €) trillion, the annual direct cost of corrosion worldwide is over 3% of the world's GDP.*

Direct costs do not include the environmental damage, waste of resources, loss of production, or personal injury.

*World Corrosion Organization 2010

(1 Trillion = $10^{12} = 1 billon)
Cost of Corrosion Control at KSC Launch Pads

$1.6M/year\(^1\)

\(^1\) Estimate based on corrosion control cost of launch pads (39A and 39B) and the 3 Mobile Launch Platforms (MLPs) in 2001
Corrosion Technology Laboratory at KSC

Timeline

1962
Space Program starts
Corrosion failures begin

1966
Atmospheric exposure testing begins near the launch pads

1981
Space Shuttle introduces acid deposition products that make corrosion worse

1985-1987
Accelerated corrosion testing (salt fog and electrochemical) begins

2000
Corrosion Technology Laboratory is created

2004
The Corrosion Technology Laboratory starts developing smart coatings

Corrosion testing and failure analysis
Corrosion testing and technical innovation
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 (Intelligent, self-healing, active or feedback active)**

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. These coatings are also referred to in the literature as intelligent, self-healing, and active or feedback active, to distinguish them from barrier or passive coatings.

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 microcontainers 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.
Corrosion indication, detection, and healing of mechanical damage can be achieved using microencapsulation technology.

What are microcontainers?
Particles or liquid drops coated in polymers. These microcontainers can carry any material that needs protection or controlled release.

Why microencapsulate a material?
- Incorporate active materials while maintaining coating integrity
- Achieve controlled-release
- Make active materials easier/safer to handle.
- Incorporate multiple component systems.
- Prevent undesired leaching
- Versatility
Types of Feedback-Active Microcontainers for Corrosion Detection and Control

- Containers with an active ingredient-rich core and stimuli-responsive shell (microcapsules)

- Containers with an active ingredient incorporated into a stimuli-responsive matrix (microparticles)

- Containers with a porous ceramic core impregnated by inhibitor and enveloped by a stimuli-responsive polyelectrolyte (PE) shell*

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

- Acidic
- Neutral
- Basic

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>Elapsed Time</th>
<th>Image</th>
<th>pH Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 hours</td>
<td><img src="image" alt="0.5 hours" /></td>
<td>Slightly Acidic</td>
</tr>
<tr>
<td>1.5 hours</td>
<td><img src="image" alt="1.5 hours" /></td>
<td>Acidic</td>
</tr>
<tr>
<td>4.5 hours</td>
<td><img src="image" alt="4.5 hours" /></td>
<td>Acidic</td>
</tr>
<tr>
<td>3 days</td>
<td><img src="image" alt="3 days" /></td>
<td>Basic</td>
</tr>
</tbody>
</table>

- Acidic
- Slightly Acidic
- Neutral
- Slightly Basic
- Basic
pH Sensitive Microcapsules for Corrosion Indication

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
Why pH-Sensitive Microcapsules?

Benefits from corrosion sensing coatings:

- Overcoming solubility limit of indicators in solvents
- Protecting indicator from coating constituents
- Easy incorporation into different paint systems

Benefits from corrosion-controlled inhibitor release:

**Smart:**
- Corrosion-controlled release on demand at tailorable rate.
- Minimization of inhibitor loss by leaching or diffusion if desired.
- Inhibitor release can be maximized when corrosion occurs.
- Inhibitor delivery when and where needed.

**Green:**
- Reduction of the detrimental impact of inhibitors on the environment.

**Enabling:**
- Inhibitor isolation avoids incompatibility with other coating components.
- Allows incorporation of water-soluble inhibitor into paint formulation without blistering.
Smart Coating for Corrosion Detection and Control

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

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

Chemical reactions:
\[ \text{Fe}^{2+} + e^- \rightarrow \text{Fe} \]
\[ \text{Fe}^{2+} + \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 4\text{OH}^- \]
Versatility: Microcapsules can deliver multiple types of contents into different paint systems. The microcapsule wall can be modified to deliver the contents at different rates.
Delivery System

Inhibitor Evaluation -> Delivery System -> Synthesis

Coating compatibility
Inhibitor solubility

Corrosion Protection <- Coating Incorporation <- Release Properties
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.
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).
Hydrophobic-Core Inhibitor Microcapsules

oil-in-water emulsion

microcapsule formed

SEM of hydrophobic-core microcapsules containing an organic inhibitor
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 hydrophilic-core microcapsules
When corrosion begins, the microcapsule will release the contents of the core (indicator or inhibitor) in close proximity to the corrosion.

SEM images of microcapsules with corrosion indicator (top) and inhibitor (bottom).
Microparticle Formation

Addition of active agents in solution
Mixing & Ouzo effect
Solvent Diffusion & polymerization
Further Polymerization
Corrosion Indicating Microparticles

SEM image of microparticles with color changing indicator (left) and with fluorescent indicator (right)
Microparticles with Inhibitors

SEM and EDS of microparticles with corrosion inhibitor phenylphosphonic acid (PPA)
Inorganic Carriers with Hierarchical Architecture for Controllable Delivery of Corrosion Inhibitors
From Concept to Reality

- Initial concept: a simple pH-sensitive microcapsule
- Reality: a portfolio of delivery systems (micro-containers) including
  - Hydrophobic-core and hydrophilic-core pH-sensitive microcapsules
  - pH-sensitive micro-particles
  - Inorganic micro-containers
Microcapsules for Self-Healing Coatings

Optical micrographs of spherical and elongated microcapsules for self-healing of mechanical scratches
Oil-core microcapsules developed using interfacial polymerization

The pH sensitivity of the microcapsules was tested.

Oil-core microcapsules developed using interfacial polymerization

Oil-core microcapsules with corrosion indicator phph (2wt%) were synthesized.

Oil-core corrosion indicator microcapsules obtained in free flowing powder.

Water-core microcapsules developed using interfacial polymerization

Water-core microcapsules optimized to reduce capsule size.

Water-core microcapsules optimized to reduce cluster formation. The synthesis was modified to use environmentally friendly reagents.

Water-core microcapsules with corrosion indicator phph (5wt%) were synthesized.

Water-core microcapsules with incorporated phph (30wt%) were synthesized.

MFPTT Melamine Formaldehyde Pentaerythritol Tetra (3-Mercaptopropionate)
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.
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

Indication of hidden corrosion by color change
Coating systems used for hidden corrosion indication testing.

<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 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.

Early Onset of Corrosion Detection

Fluorescent Indicator

Center scribed 3” x 2” R type Q-panels coated with Solvent-based 2k acrylic-urethane clear coat with encapsulated fluorescein (0.05 wt%). A scan was taken every 15 minutes for 12 hours examined via digital microscopy with a Keyence VHX-600 digital microscope at 100X magnification to correlate areas of high fluorescence intensity to corrosion spots on the panel visually observed and observed via fluorescence spectroscopy.

<table>
<thead>
<tr>
<th>Device</th>
<th>Tecan Infinite M1000 Pro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>1536 Flat Bottom Transparent Polystyrene Well Plate</td>
</tr>
<tr>
<td>Mode</td>
<td>Fluorescence Top Reading</td>
</tr>
<tr>
<td>Excitation Wavelength</td>
<td>494 nm</td>
</tr>
<tr>
<td>Emission Wavelength</td>
<td>525 nm</td>
</tr>
<tr>
<td>Excitation Bandwidth</td>
<td>5 nm</td>
</tr>
<tr>
<td>Emission Bandwidth</td>
<td>5 nm</td>
</tr>
<tr>
<td>Gain</td>
<td>100 Manual</td>
</tr>
<tr>
<td>Flash Frequency</td>
<td>400 Hz</td>
</tr>
<tr>
<td>Integration Time</td>
<td>20 µs</td>
</tr>
<tr>
<td>Lag Time</td>
<td>0 µs</td>
</tr>
<tr>
<td>Settle Time</td>
<td>100 ms</td>
</tr>
<tr>
<td>Z-Position (Manual)</td>
<td>100 ms</td>
</tr>
</tbody>
</table>

Fluorescence Spectroscopy Instrument Parameters
Diamond Clad with Fluorescein

Laser Scanning Microscopy (LSM) confocal fluorescece microscopy image
Diamond Clad with Fluorescein
Diamond Clad with Fluorescein

Good dispersion of particles in coating

Florescent corrosion indicators provide very sensitive detection at very low indicator particle loading (0.05-0.5%) in coatings.
Confocal scanning laser microscopy 2D images of fluorescent corrosion sensing coating on steel. Unexposed panel (left) and near scribe after 15 hours of immersion in 5% NaCl (right).
Deft 02GN084 + 0.25% Microparticles on AA2024-T3 at Scribe – 6 hrs. Immersion in 5% NaCl, 488 nm Confocal LSM

Master Gain 446

Scaling X: 0.791 μm
Scaling Y: 0.791 μm
Scaling Z: 5.117 μm
Dimensions: x=512, y=512, z=12, 8-bit
Image size: x=404.06 μm, y=404.06 μm, z=56.29 μm
Scan Mode: stack
Zoom: 2.1
Objective: EC Epiplan-Apochromat 10x/0.3 HD DIC M27
Pixel dwell: 1.58 μs
Average: 1
Master gain: 446
Digital gain: 1.24
Digital offset: 0.00
Pinhole: 45 μm
Filters: 493 - 625
Beam splitters: MBS : MBS 488
MBS_InVis : Plate
Lasers: 488 nm : 2.0 %
TECAN reflectance fluorescence spectroscopy scanning composite image of a coated cold rolled steel panel during salt immersion exposure up to 5.5 hours, with an artificial defect in the middle. While the main corrosion event is at the defect site, there are many other corrosion events occurring as early as 1 hour.
Fluorescent corrosion sensing coating for early corrosion detection. TECAN scan image after 5.5 hours salt water immersion testing is in the middle, while a picture and optical microscopy images (100X) of the panel after 15 hours of salt water immersion testing are shown on the left and right respectively.
Oil-core microcapsule developed using interfacial polymerization

The pH sensitivity of the microcapsules was tested.

Oil-core microcapsules with organic and some inorganic inhibitors, such as CeCl₃, were synthesized.

Oil-core microcapsules optimized to reduce the emulsion stability for easy microcapsule separation. This process yields a free-flowing powder.

Water-core microcapsule developed using interfacial polymerization

Water core microcapsule modified to reduce microcapsule cluster formation. The new formulation uses environmental friendly reagents. Various water soluble inhibitors were encapsulated: cerium nitrate, sodium molybdate, sodium phosphate, calcium metaborate, and phenyl phosphonic acid.

Water core microcapsule synthesis was optimized by using a water soluble wall forming pre-polymer. The synthesis time was also reduced, and the microcapsule wall properties were improved.

Different inorganic inhibitors were encapsulated at different concentrations. These microcapsules were then heat treated at different conditions to achieve various release rates. They were incorporated into coatings for testing.

Corrosion tests showed the need to control the permeability of the capsule wall to avoid the leaching of inhibitor into the coating when the encapsulated inhibitor concentration is too high. To address this problem, MFPTT microparticles containing various corrosion inhibitors were synthesized.
Improve Existing System: Inorganic Zinc

• Inorganic zinc is being watched for its environmental impact.
• Provides excellent protection when steel is sand-blasted to white metal - difficult for hard to access area.
• Inhibitor particles can improve adhesion - reduce cost and improve protection.

Develop New System: Polymer Coating

• Environmentally friendly corrosion protective coating through controlled release of inhibitors.
• Partner with commercial companies for product development.
• Improved protection for steel.

Next Generation: Waterborne

• While solvent-based coatings still dominate in areas requiring the heavy corrosion protection, the next generation will be solvent free systems: waterborne and powder coating.
• New particle formulas are being developed to target these systems.

Corrosion Protection Function Development

Controlled release inhibitors have been used in three areas of coating development for steel protection: improved inorganic zinc, new Cr(VI) free organic coating, and effective solvent-free coatings.
Organic coating formulations being developed with industry partners for steel protection. Steel panels after accelerated cyclic corrosion testing (left), and coated steel panels being tested at beachside atmospheric exposure test site.
New inorganic delivery systems being developed (left) shows great promise for improving corrosion protection of waterborne system (right).
## Corrosion Protection: Aluminum Alloys

<table>
<thead>
<tr>
<th>Method</th>
<th>System</th>
<th>Al 7XXX (0.3% Cu)</th>
<th>Al7XXX (0.6% Cu)</th>
<th>Al7XXX (0.9% Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual</td>
<td>Without Inhibitor</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>
</tr>
<tr>
<td></td>
<td>With Inhibitor</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>
</tr>
<tr>
<td>SEM (LABE)</td>
<td>without inhibitor</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>
</tr>
<tr>
<td></td>
<td>With inhibitor</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>
</tr>
</tbody>
</table>

- Further testing and development to extend the protection benefits to Aluminum alloys.
- Some encapsulated inhibitors proven to be effective for protecting Aluminum alloy substrates as well.
- The inhibitor particles will be used to develop Cr(VI) free paints for different Aluminum alloys.
Several self-healing coating systems have been developed:

- One and two capsule systems
- Self-sealing system using flowable polymers
- Elongated microcapsules
Self-Healing Coatings (2 Capsule System)

Siloxane (top) and tin catalyst (bottom) microcapsules

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%.
Self Healing (1 Capsule System)

Microscopy image of self-healing microcapsule.

Control and self healing paint coated steel panels after 1000 hours of salt fog testing.
Summary

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

The corrosion indicating function has been demonstrated by incorporating encapsulated color changing and fluorescent indicators into clear coatings. 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.

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