



A Multifunctional Coating for Environmentally Friendly 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 environmentally friendly 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

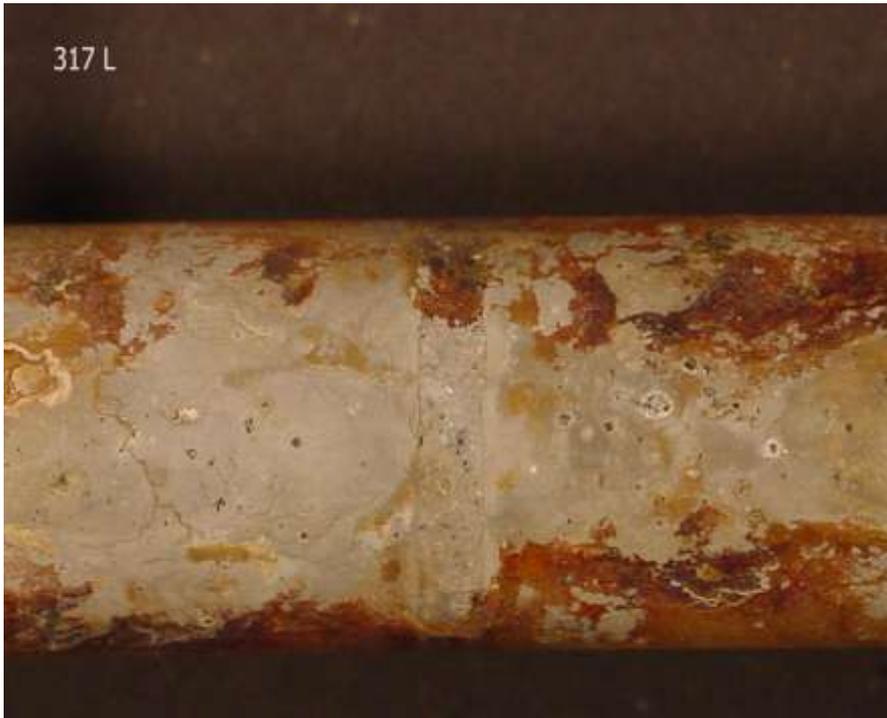


KSC Launch tower structural steel corrosion

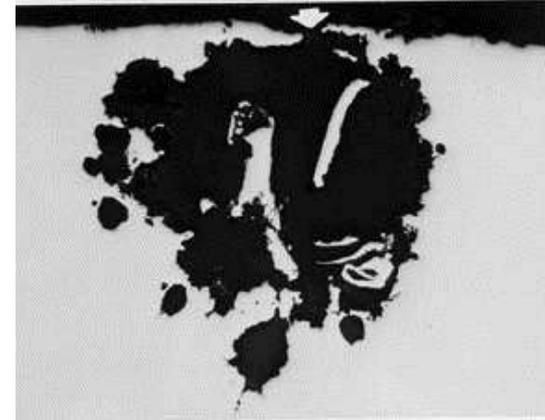


Under the LC 39B Flame Trench

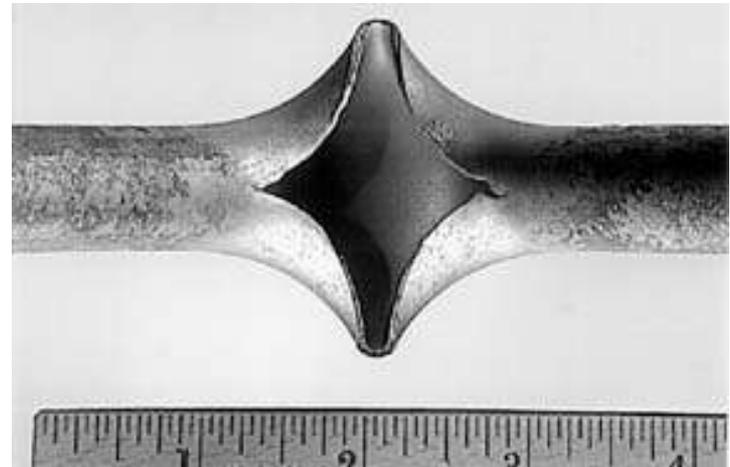
Examples of Launch Pad Corrosion (cont.)



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



¹Corrosion Costs and Preventive Strategies in the United States, Report FHWA-RD-01-156, September 30, 2001

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



A photograph of a Space Shuttle launching from a launch pad. The shuttle is oriented vertically, with its external tank and boosters. Large plumes of white and yellow smoke are visible at the base of the boosters. A red arrow points from the text 'SRB Exhaust' to the base of the right solid rocket booster. The launch pad service structure is visible on the left side of the image.

In 1981 the Space Shuttle introduced acidic deposition (70 tons of HCl) products. NASA plans to use Shuttle-derived SRB rockets in future missions.

SRB Exhaust



Corrosion Rates of Carbon Steel



Corrosion rates of carbon steel calibrating specimens at various locations*

Location	Type Of Environment	$\mu\text{m}/\text{yr}$	Corrosion rate ^a mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	94	3.7
Daytona Beach, FL	Marine	295	11.6
Pont Reyes, CA	Marine	500	19.7
Kure Beach, NC (80 ft. from ocean)	Marine	533	21.0
Galeta Point Beach, Panama CZ	Marine	686	27.0
Kennedy Space Center, FL (beach)	Marine	1070	42.0

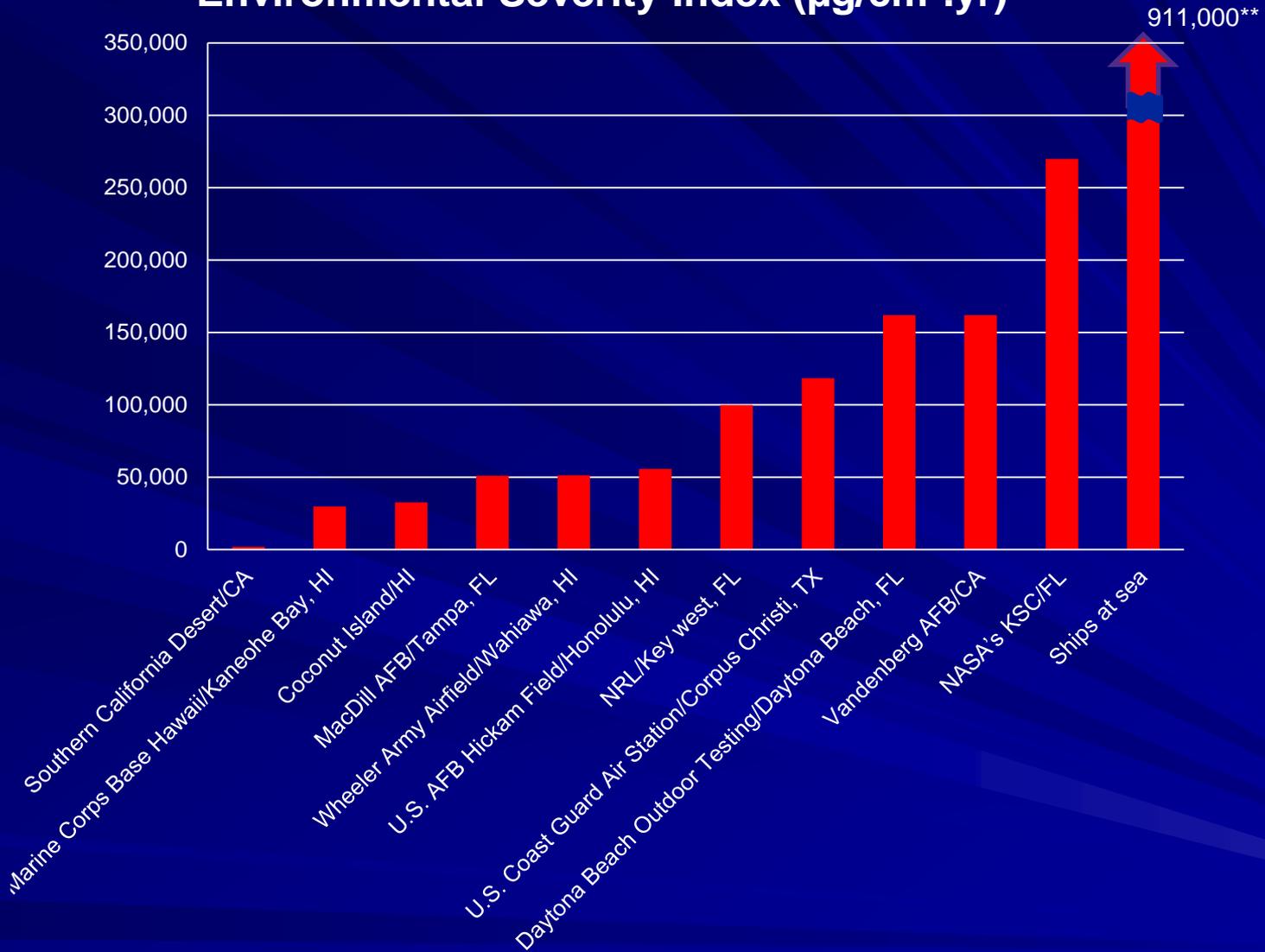
^aTwo-year average

* Data extracted from: S. Coburn, Atmospheric Corrosion, in Metals Handbook, 9th ed, Vol. 1, Properties and Selection, Carbon Steels, American Society for Metals, Metals Park, Ohio, 1978, p.720

A mil is one thousandth of an inch



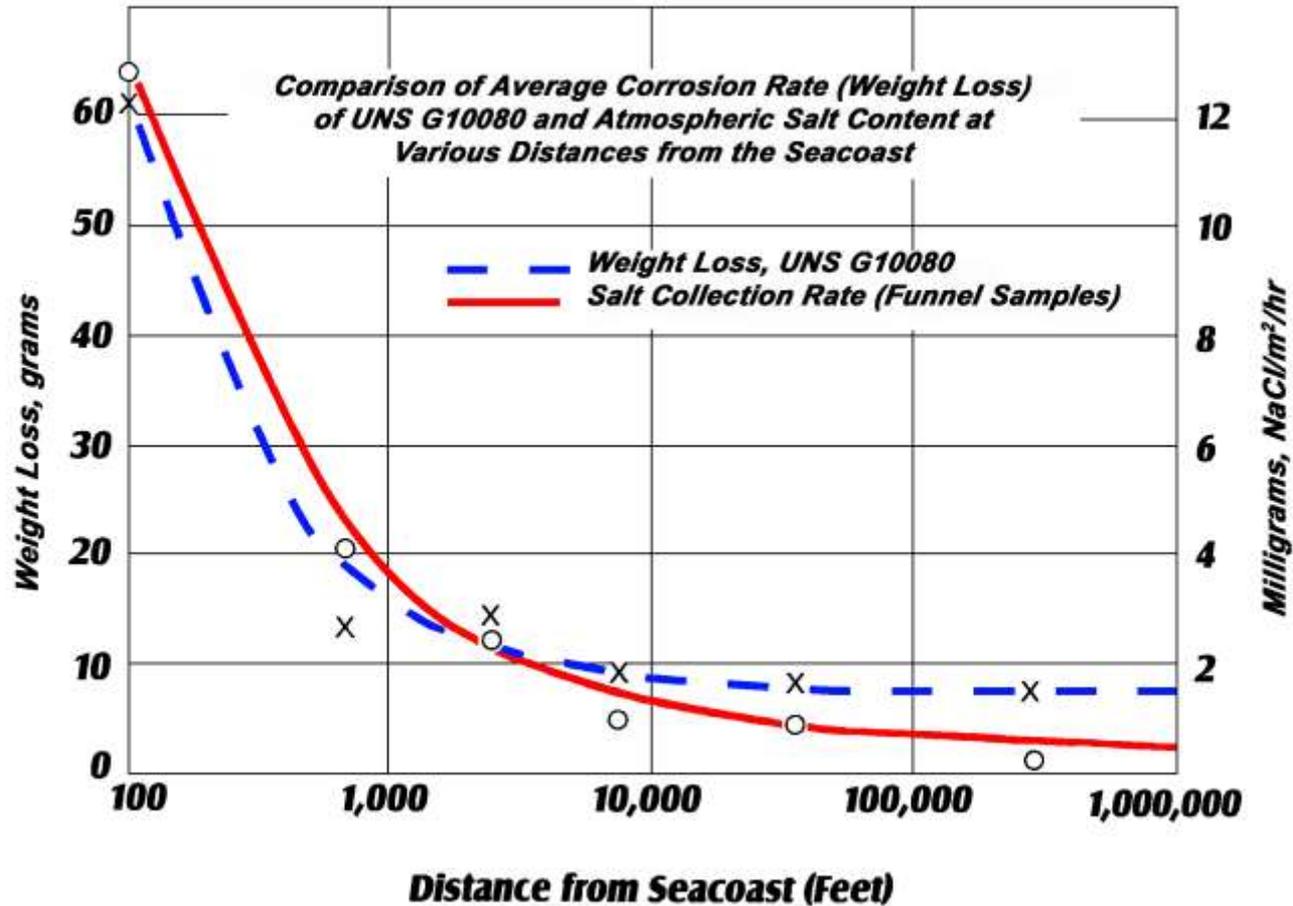
Environmental Severity Index ($\mu\text{g}/\text{cm}^2\cdot\text{yr}$)*



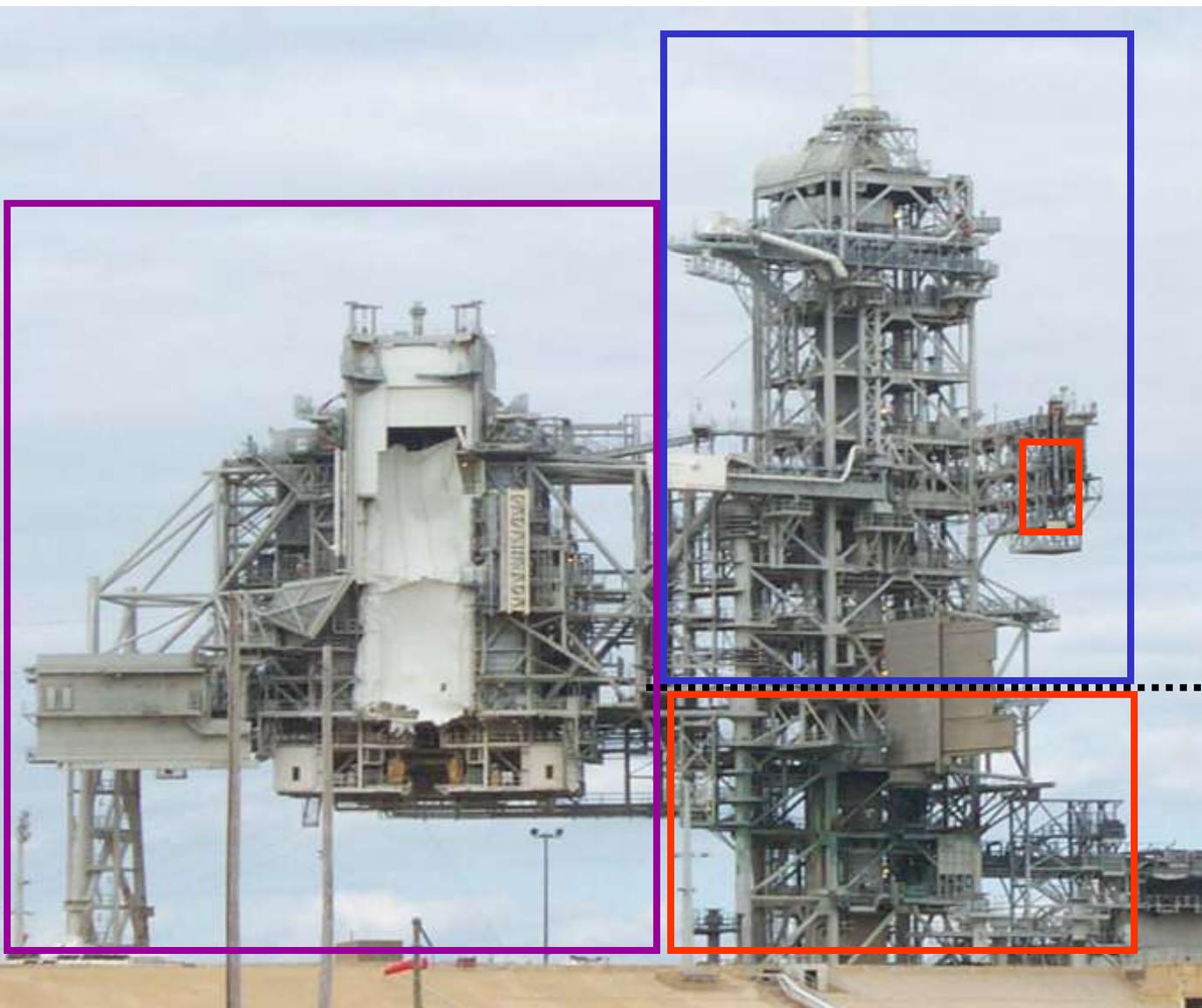
*Corrosion Comprehension: Operating in a Corrosive Environment, DoD Video, March 2012

Determined experimentally using an **Alternating Seawater Spray System at NASA's Beachside Corrosion Test Site at KSC.

Changes in Corrosion Rate with Distance from the Ocean



Launch Complex 39 Zones of Exposure



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

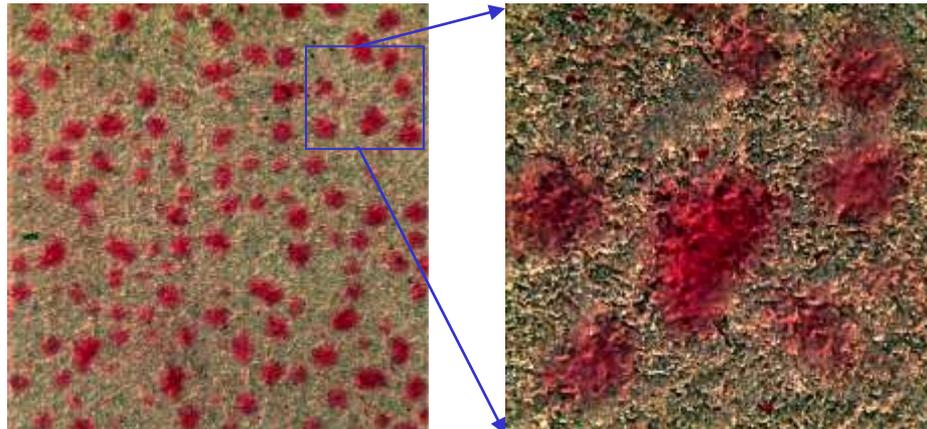
Zone 1: Surfaces that receive direct rocket engine exhaust impingement and External Tank/Intertank access point.

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.



Smart coating responding to changing pH conditions

Smart Coatings for Corrosion Control



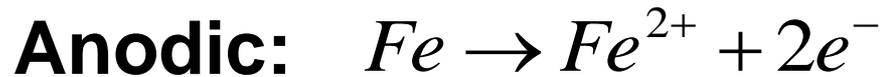
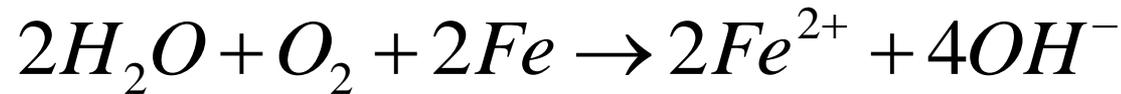
- **The use of "smart coatings" for corrosion sensing and control relies on the changes that occur when a material degrades as a result of its interaction with a corrosive environment.**
- **Such transformations can be used for detecting and repairing corrosion damage.**
- **NASA's Corrosion Technology 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

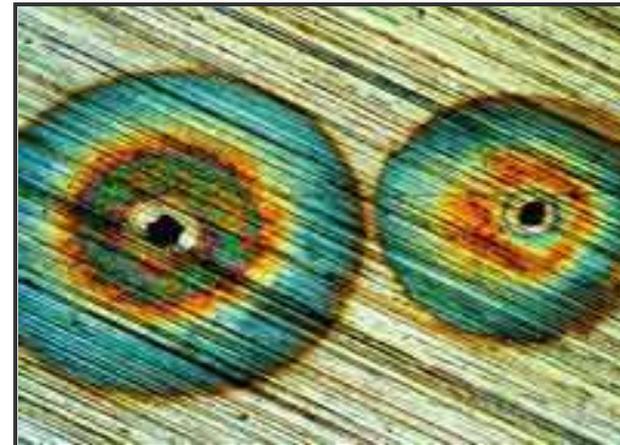
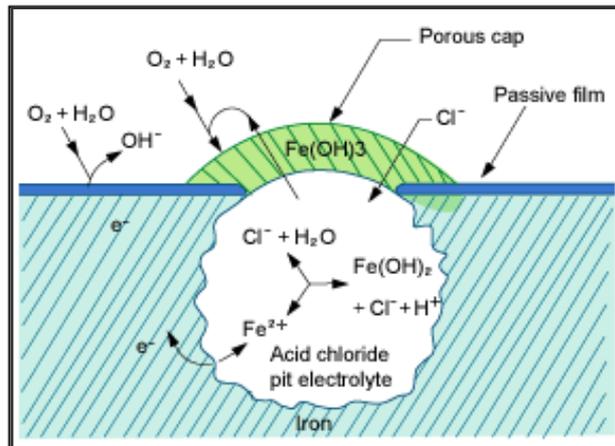
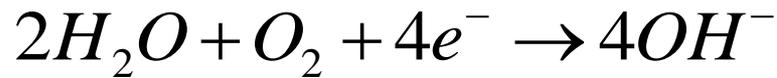


Metal is oxidized (anodic reaction); something else is reduced (cathodic reaction)

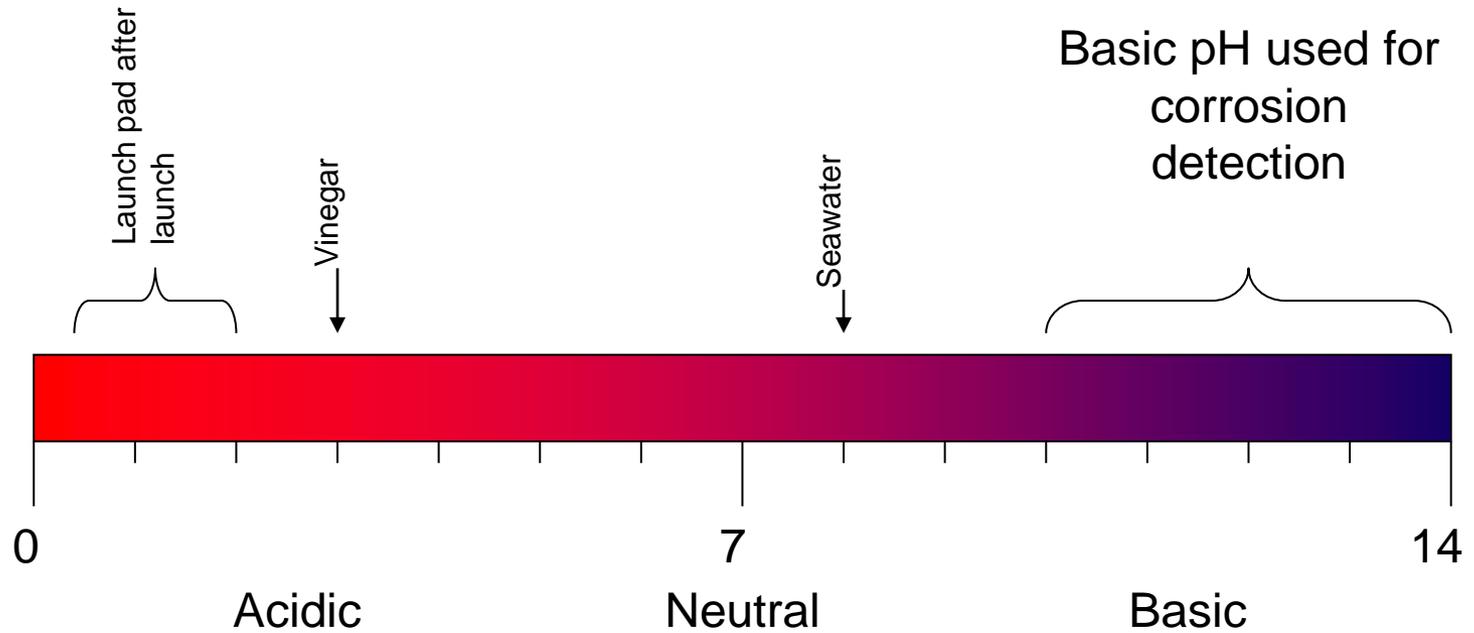
Overall Reaction:



Cathodic:



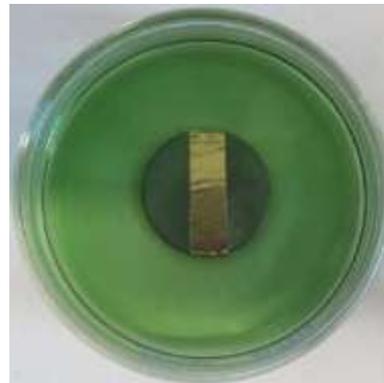
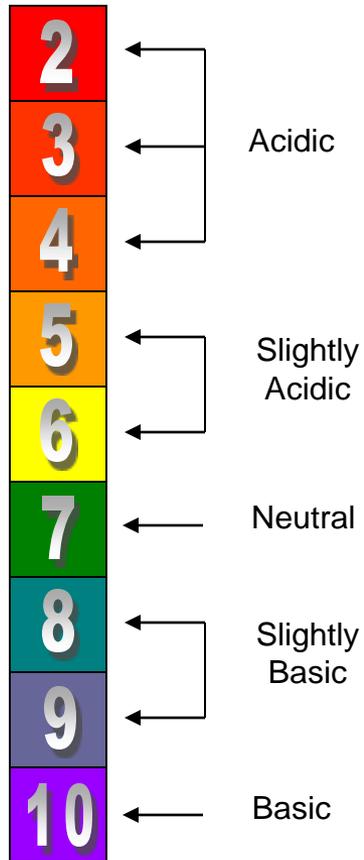
Corrosion and pH



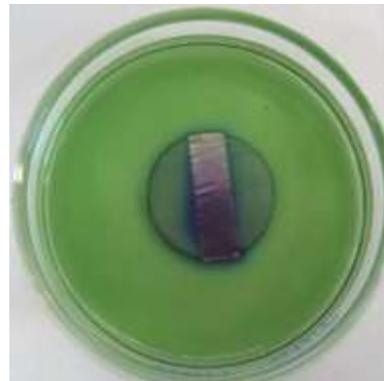
pH Scale

Corrosion Indication

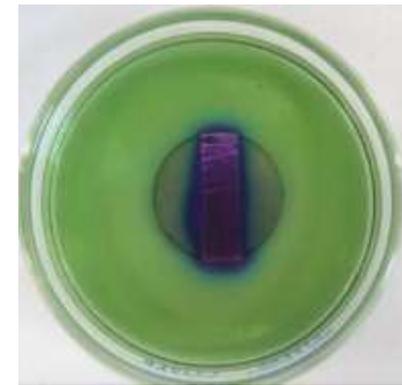
pH changes that occur during corrosion of a metal



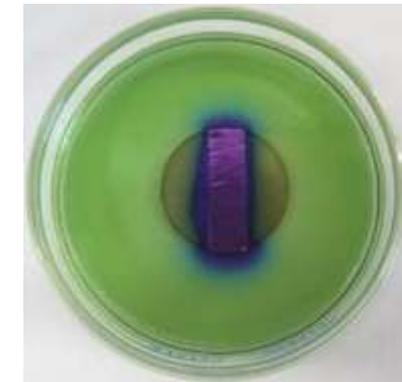
Elapsed Time: 0 hours



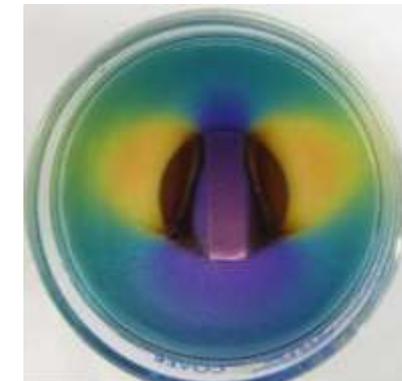
0.5 hours



1.5 hours



4.5 hours



3 days

Smart Coating "Brain"



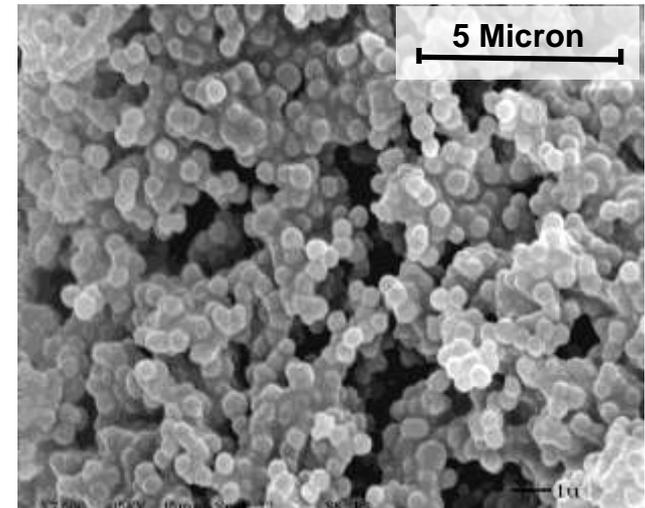
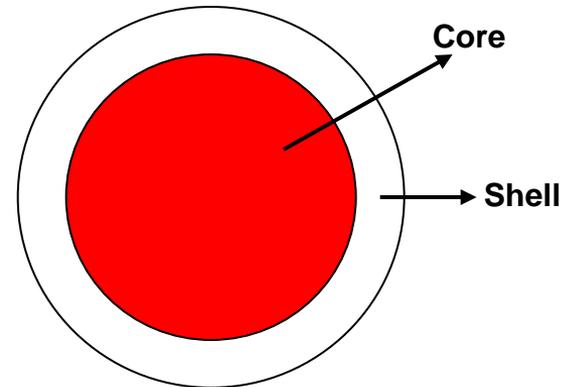
Corrosion indication, detection, and healing of mechanical damage can be achieved using microencapsulation technology

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

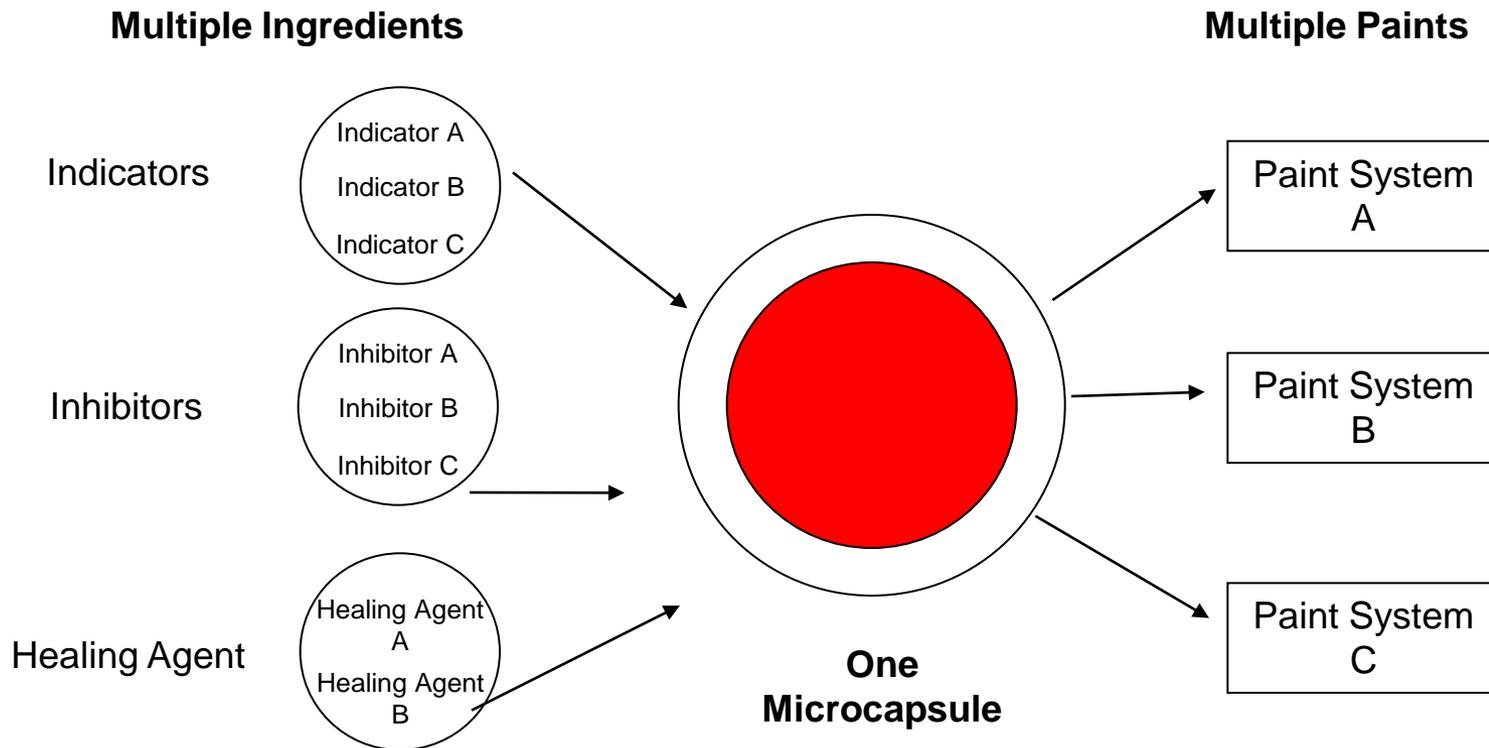


Microcapsules developed at KSC

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.**



pH Sensitive Microcapsules for Corrosion Sensing

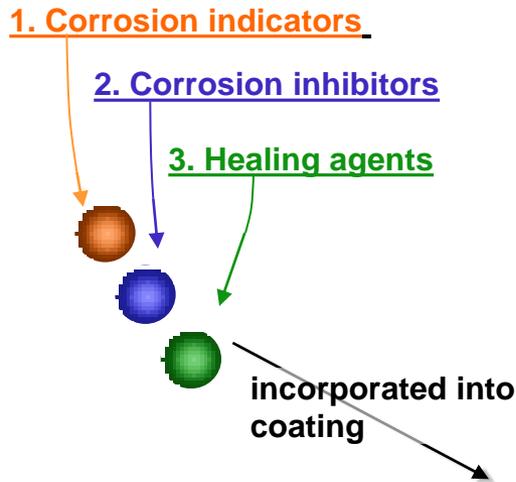


Microcapsule containing pH indicator (inhibitor, self healing agents)

The shell of the microcapsule breaks down under basic pH (corrosion) conditions

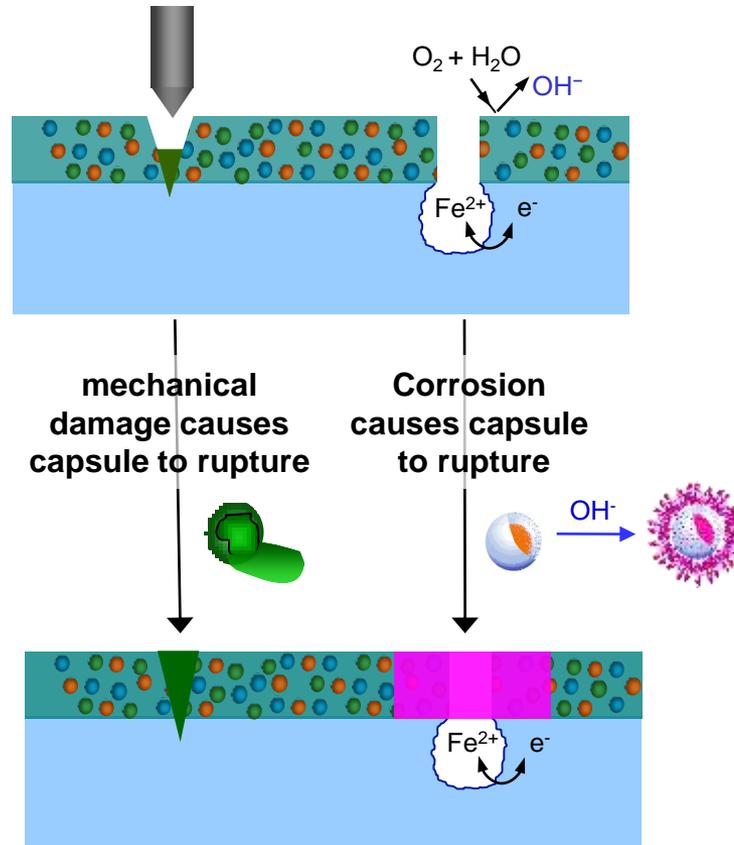
pH indicator changes color and is released from the microcapsule when corrosion starts

Smart Coating Response to Corrosion

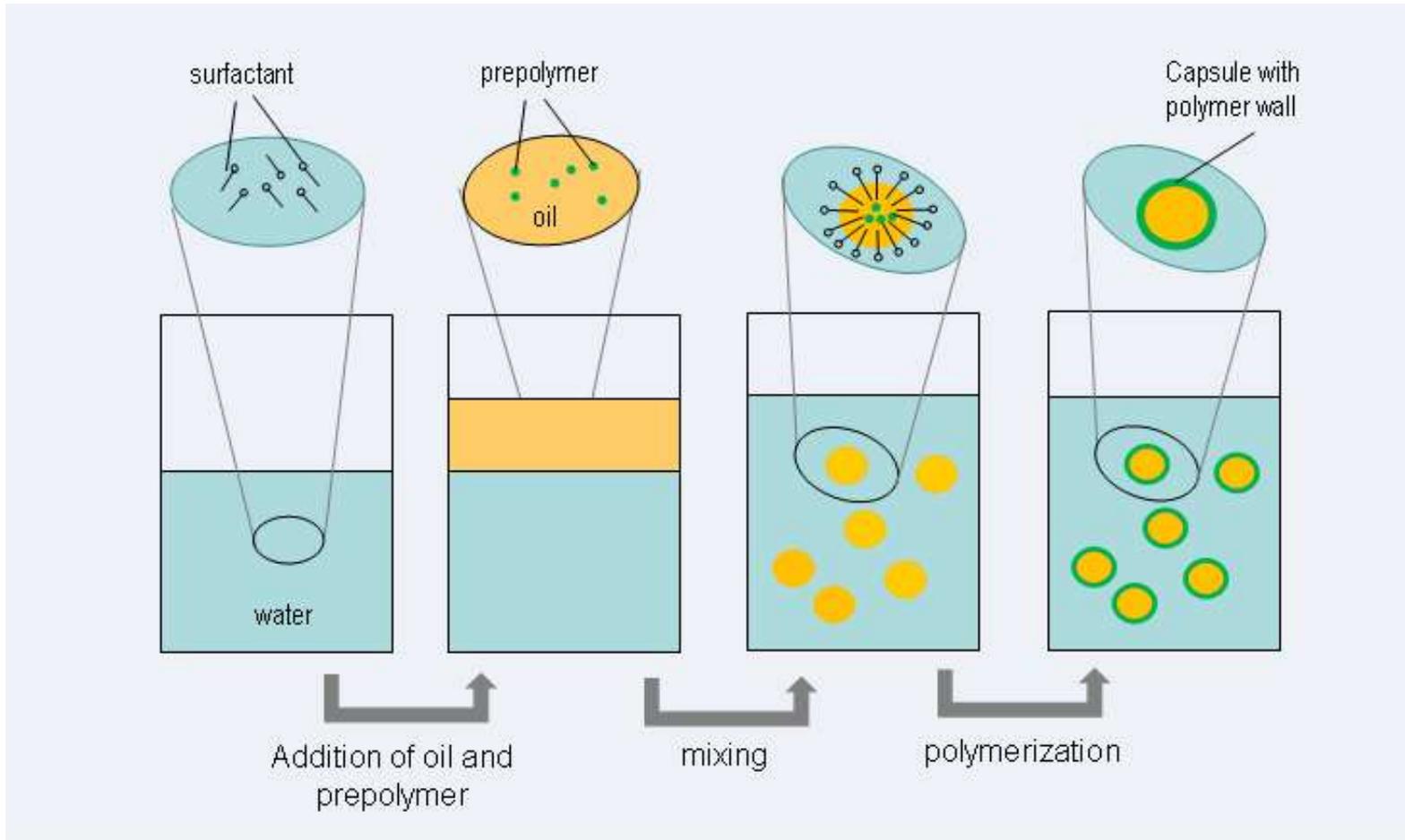


Ruptured Microcapsule:

- indicates corrosion
- protects metal from corrosion
- repairs damaged area

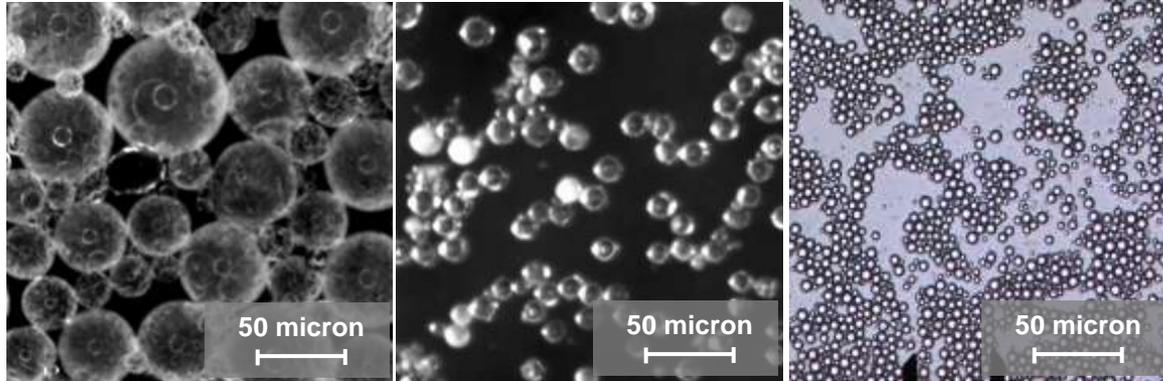


Hydrophobic Core Microcapsules



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

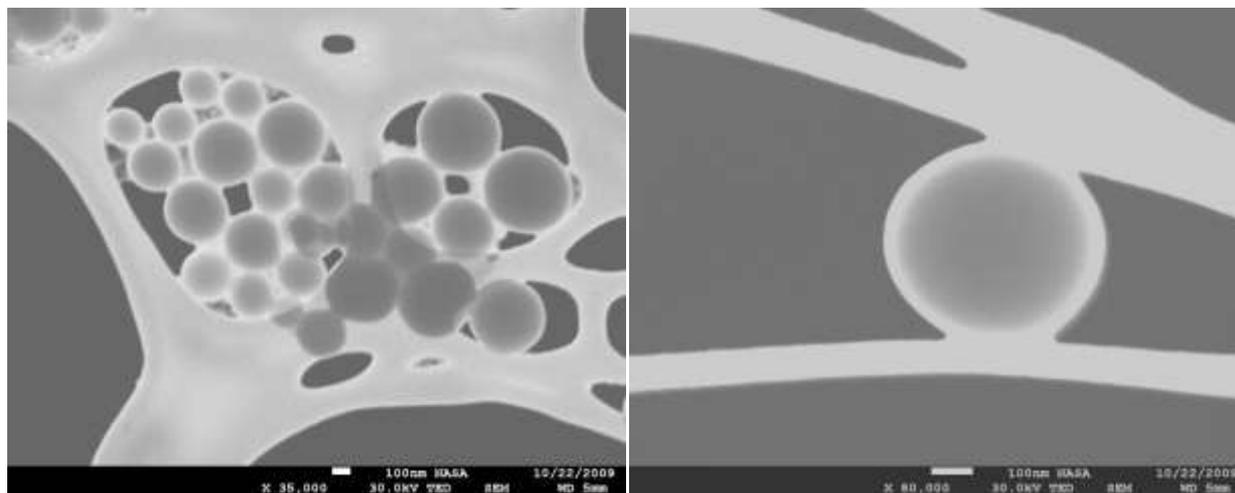
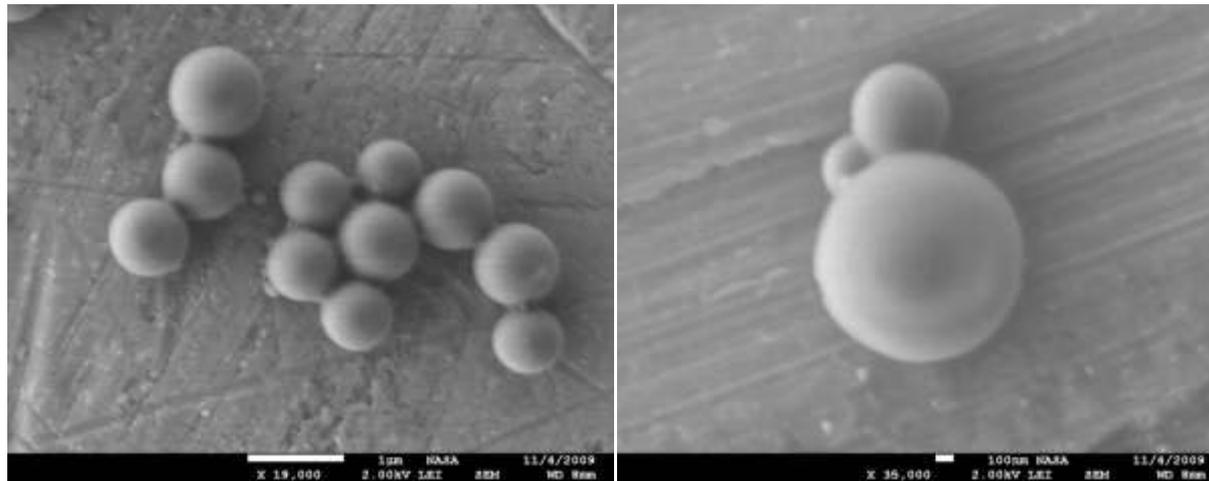


Optical microscopy images of Hydrophobic-core microcapsules of different sizes



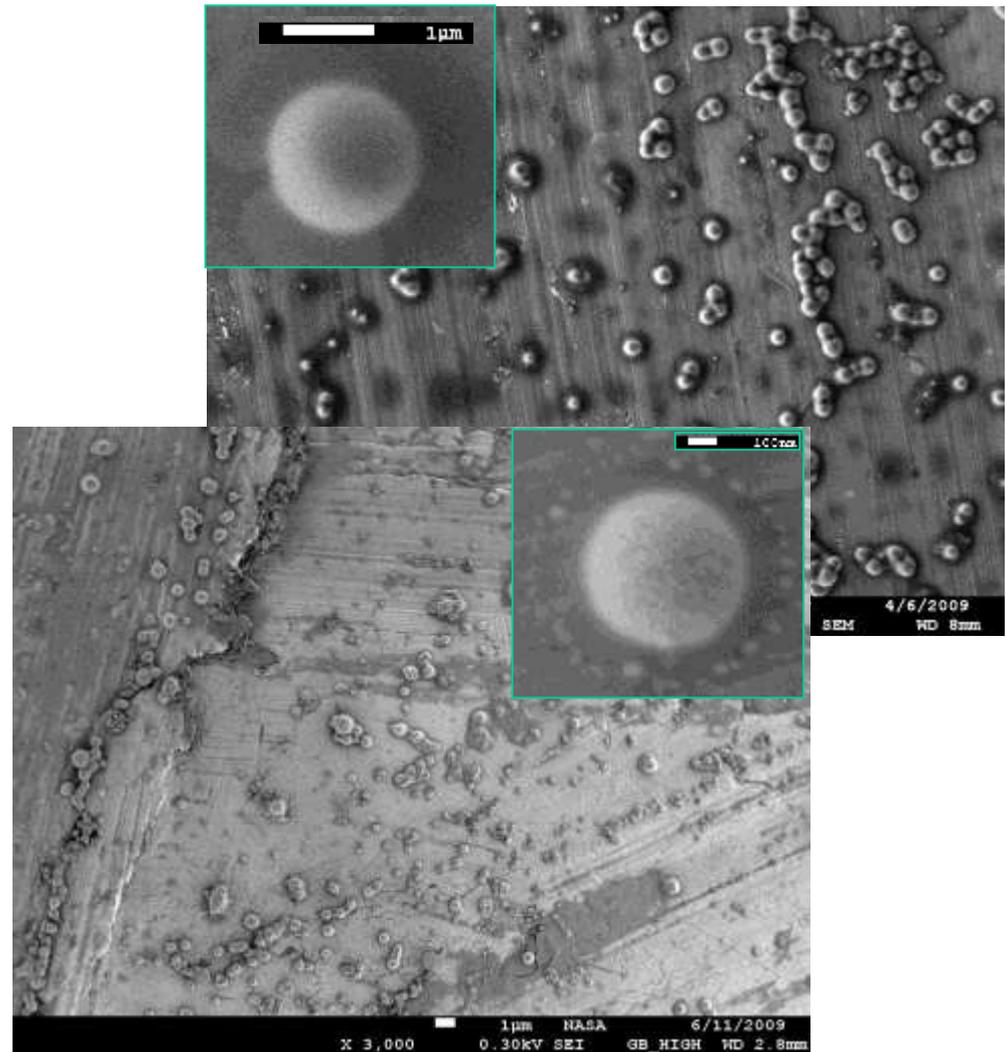
Free flowing powder samples of hydrophobic-core microcapsules. The core contents of these microcapsules are Rhodamine B (on the left), Phenolphthalein (in the middle), and a universal pH indicator (on the right).

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).

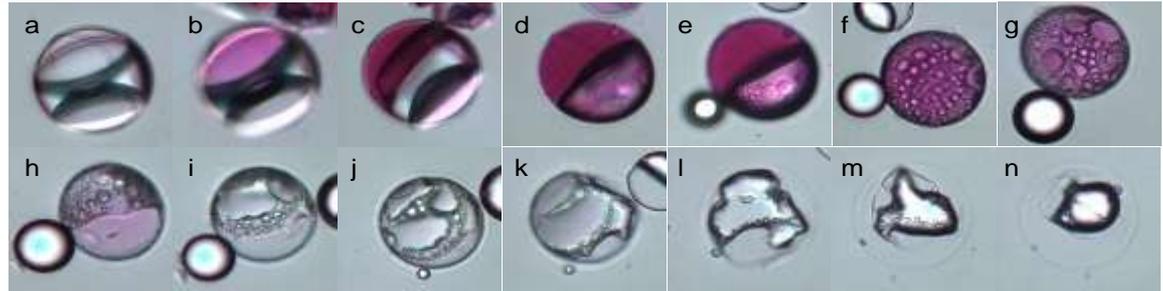
Microcapsule Response to pH Increase



Microcapsules for Corrosion Indication



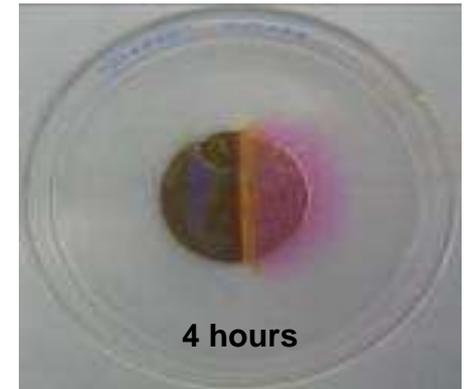
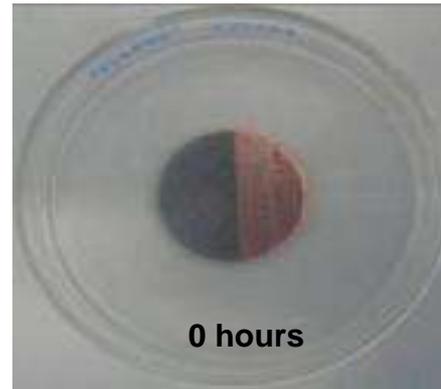
pH sensitive
microcapsules with
corrosion indicator for
corrosion detection



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

Significance:

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

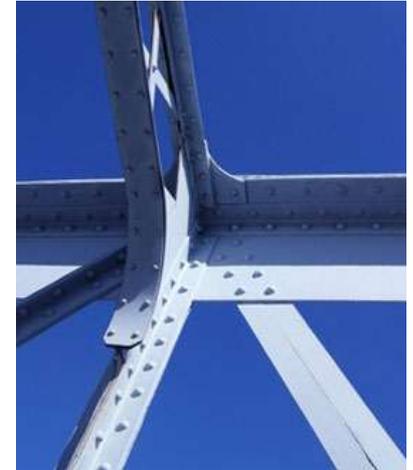


A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was immersed in gel with microcapsules containing a corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and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

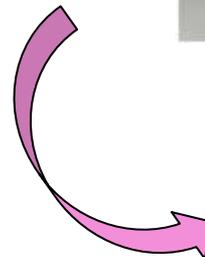
Indication of Hidden Corrosion



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



Indication of hidden corrosion by color change

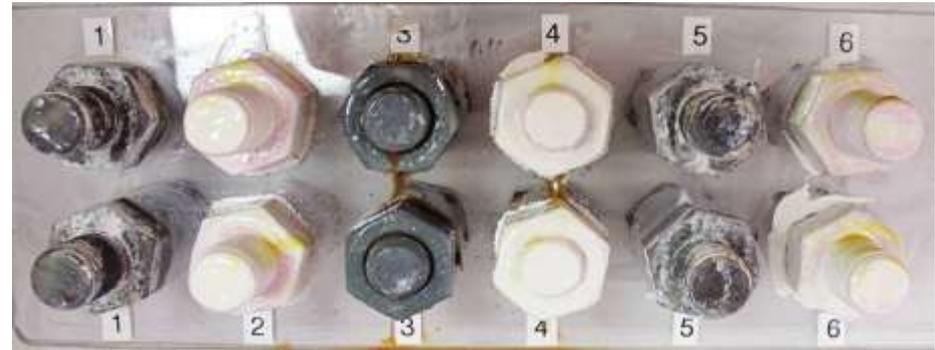


Conceptual illustration of corrosion indication in structural bolts at the launch pad

Hidden Corrosion Indication



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



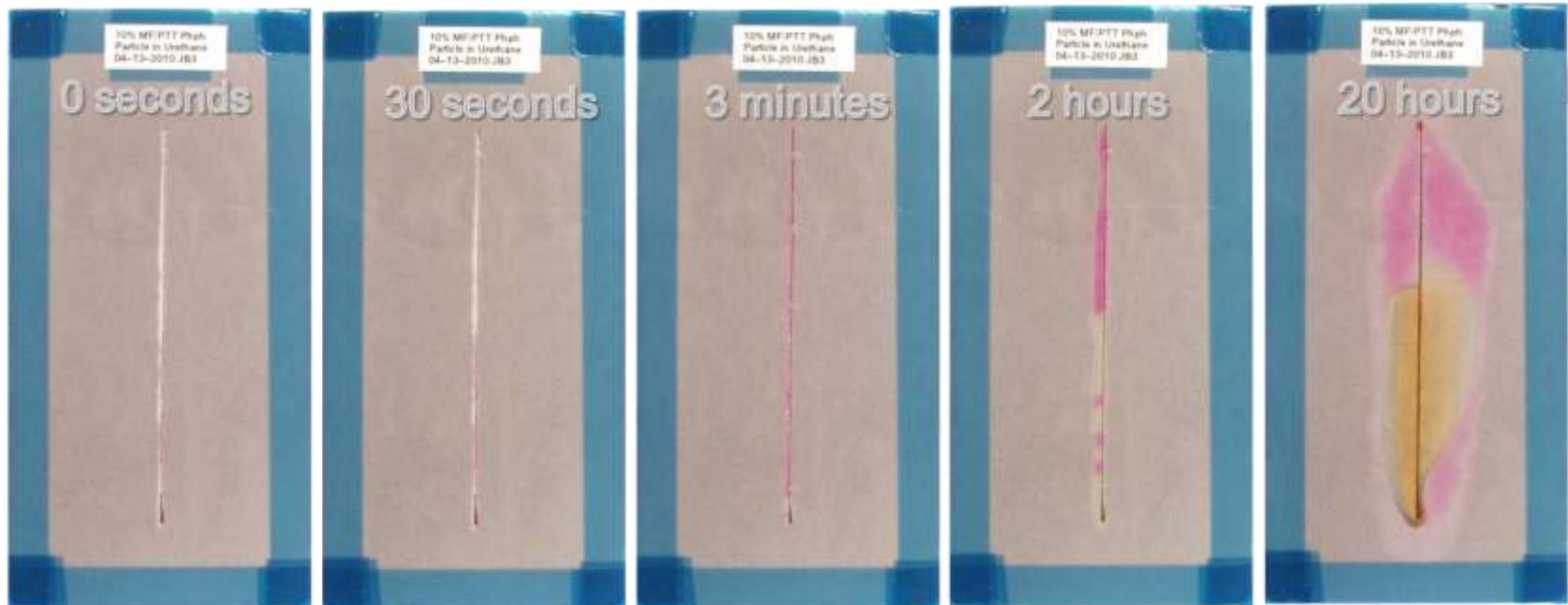
Coating systems used for hidden corrosion indication testing.

Nut and bolt set up for crevice corrosion testing. The pictures show results after 600 hour of salt fog exposure 31



Early Indication of Corrosion

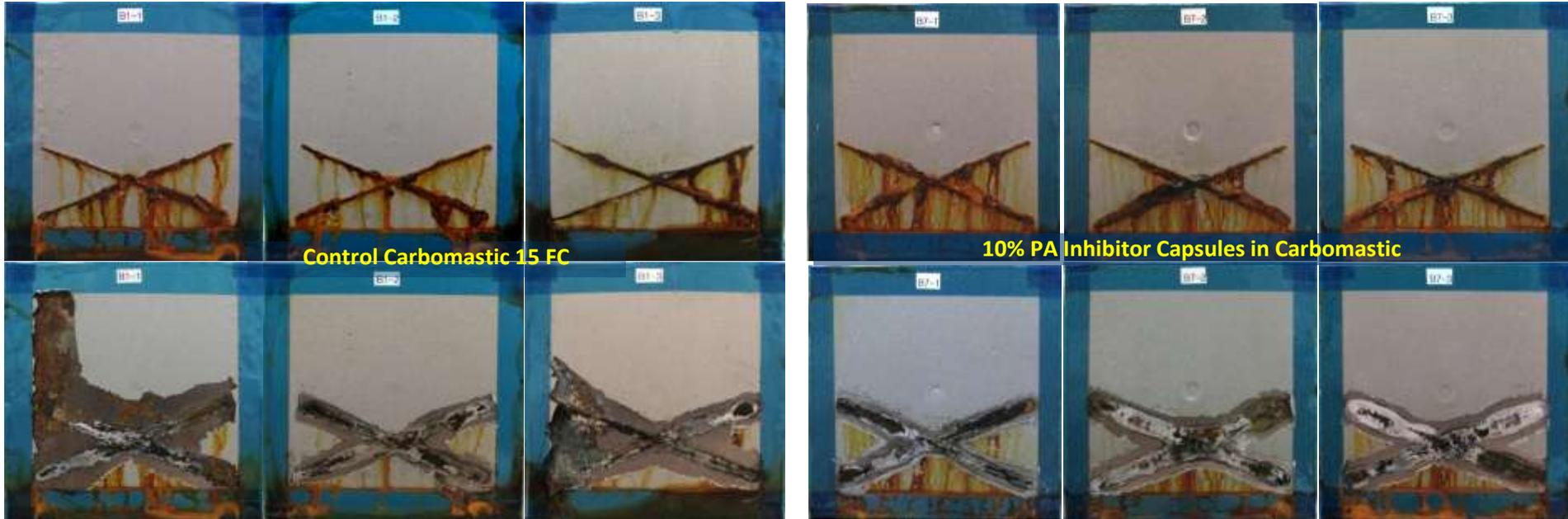
Experimental Corrosion Indicating Coating



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.

¹ASTM B 117-97, Standard Practice for Operating Salt Spray (Fog) Apparatus, ASTM International, 1997

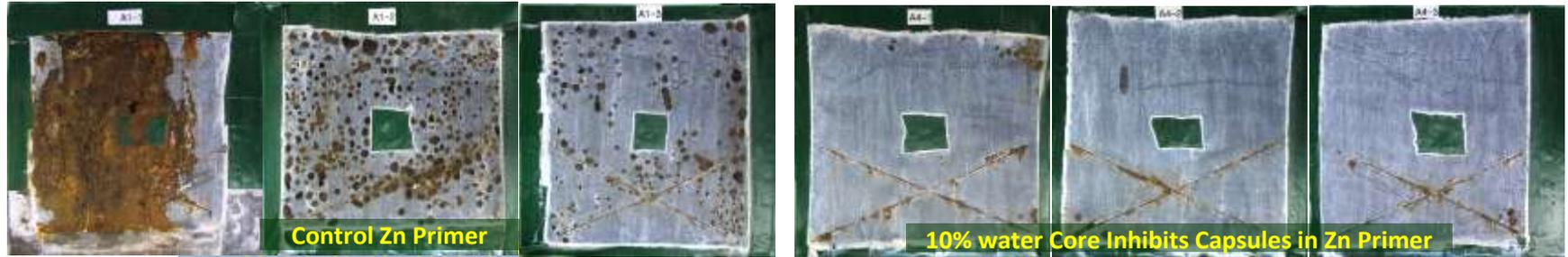
Corrosion Inhibition: 6 month Salt Fog



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

Carbomastic 15 FC Coating Systems	Sample #	Rust Grade	Scribe Rating
Control	1	5	5
	2	10	5
	3	6	5
10% (w/v) PA inhibitor microcapsule	1	10	5
	2	10	5
	3	10	5

Corrosion Inhibition: 6 month Salt Fog



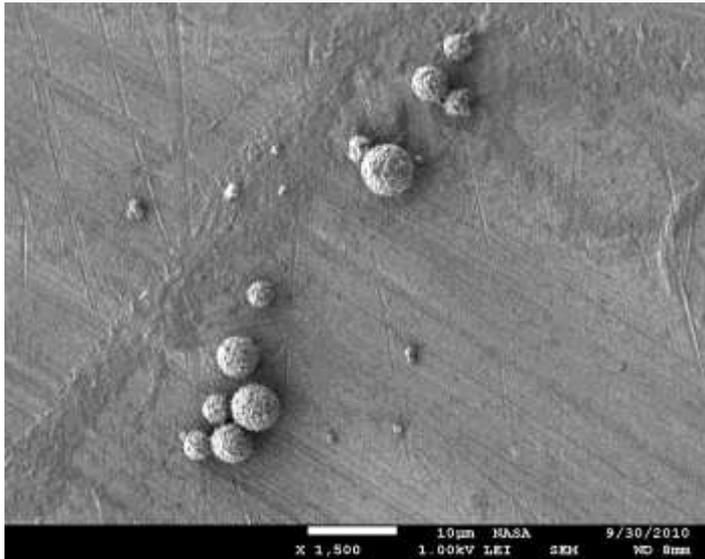
Inhibitor capsules were tested in inorganic zinc coating on steel substrate without surface preparation.

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.

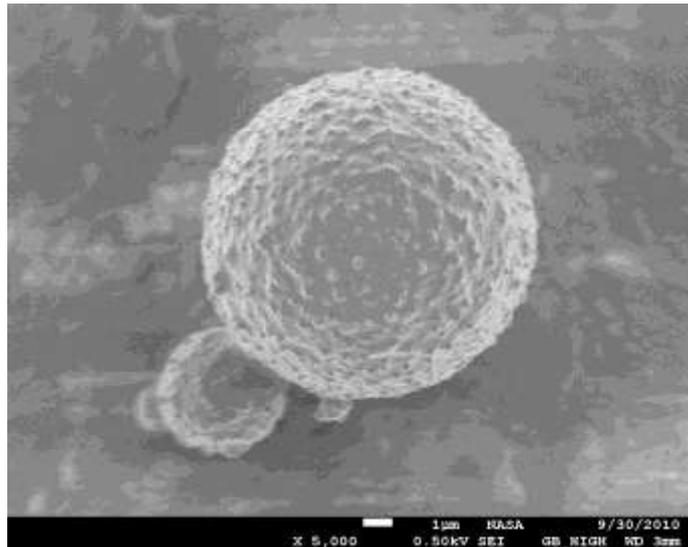
The encapsulated inhibitor improved the adhesion and the rust grade of the coating on steel.

Cathacoat 304V Coating Systems	Sample #	Rust Grade
Control	1	1
	2	2
	3	3
10% water-core inhibitor microcapsule slurries	1	6
	2	7
	3	7

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%.

NASA's Corrosion Technology Laboratory Team





- **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.**

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SMART COATINGS DEVELOPMENT TEAM

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