Smart Coatings for Corrosion Protection

Rumbo a los 50 Años
Universidad Autónoma del Carmen
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Luz Marina Calle, Ph.D.
NASA's Corrosion Technology Laboratory
Kennedy Space Center, FL, 32899, USA

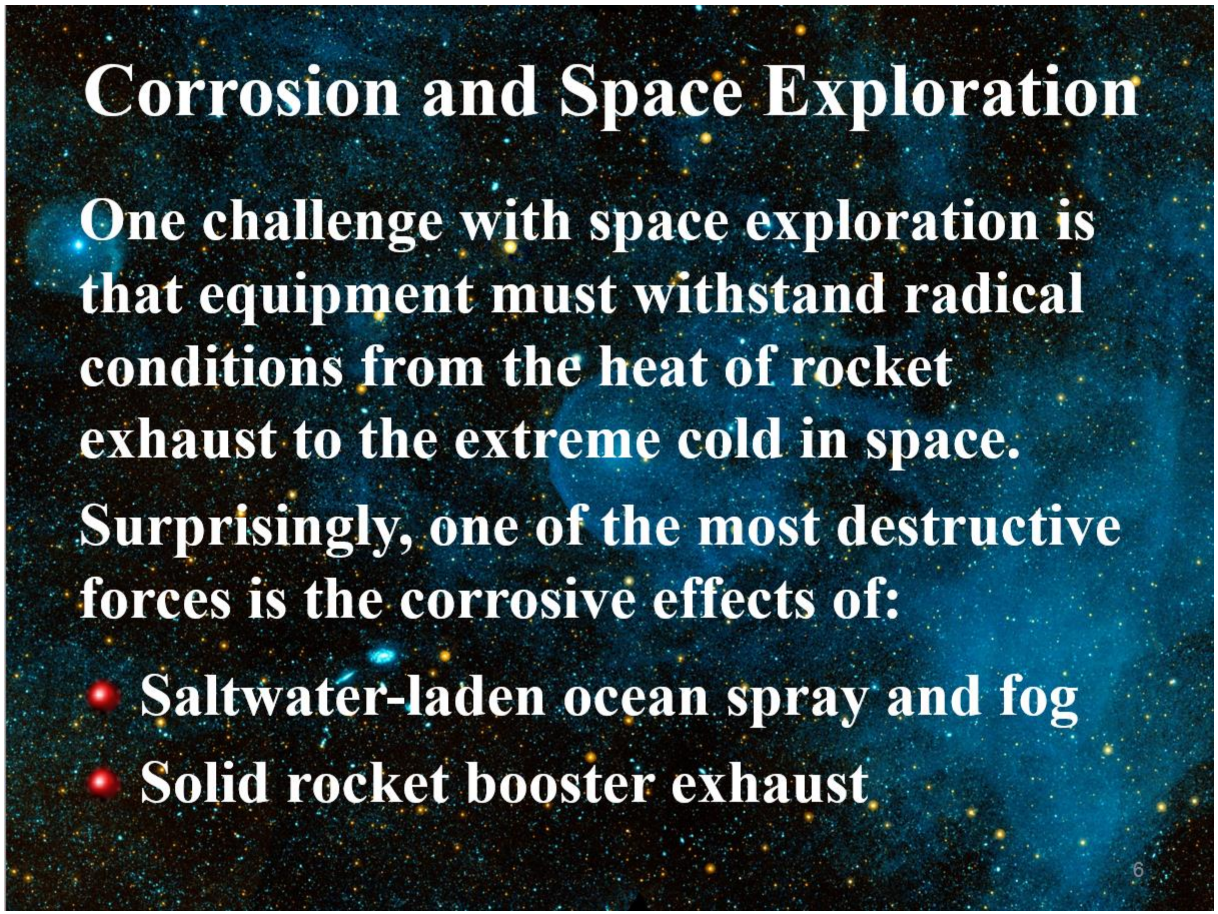
KSC Research Team:
Wendy Li, Ph.D.
Jerry W. Buhrow
Marissa N. Johnsey

Course Outline

- Course objectives
- What is corrosion?
- Why metals corrode?
- Economic, environmental, and safety impact of corrosion
- Forms of corrosion
- Methods to prevent and control corrosion
- Corrosion protective coatings
- Coating types and their mechanism of protection
- Three basic components of coatings
- Generic coating types
- New coating trends
- Coatings testing and selection for NASA
- KSC Natural and Launch Environment
- Examples of Launch Pad Corrosion
- Smart Coatings for Corrosion Control
- Microencapsulation-based Smart Coatings
- Corrosion and pH
- Corrosion Indication
- pH Sensitive Microcapsules for Corrosion Sensing
- Microcapsule Response to pH Increase
- Hidden and early Corrosion Indication
- On-demand corrosion inhibition
- Self-healing
- Summary

Course Objectives

The objective of this short course is to introduce the students to the field of smart coatings for corrosion protection. This will be done in a manner that shows the students how NASA develops technologies to solve problems that affect the accomplishment of its exploration missions.



What is Corrosion?

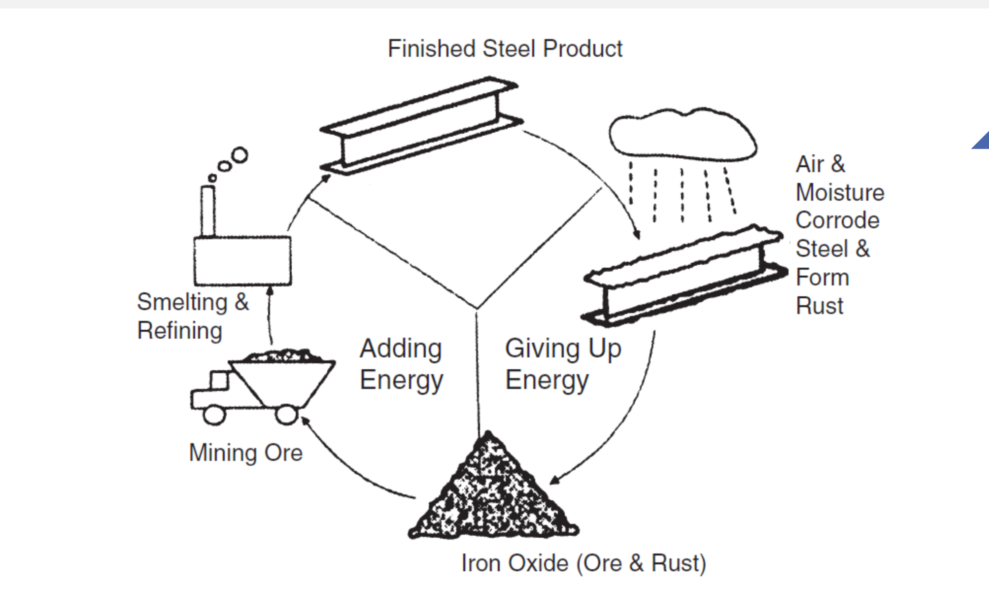
- Corrosion is the deterioration of a material due to reaction with its environment (M.G. Fontana). It literally means to "gnaw away"
- Degradation implies deterioration of the properties of the material.

KSC Launch pad corrosion (after a Space Shuttle launch)

KSC Crawler/Transporter structural steel corrosion

Why Metals Corrode?

- 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.



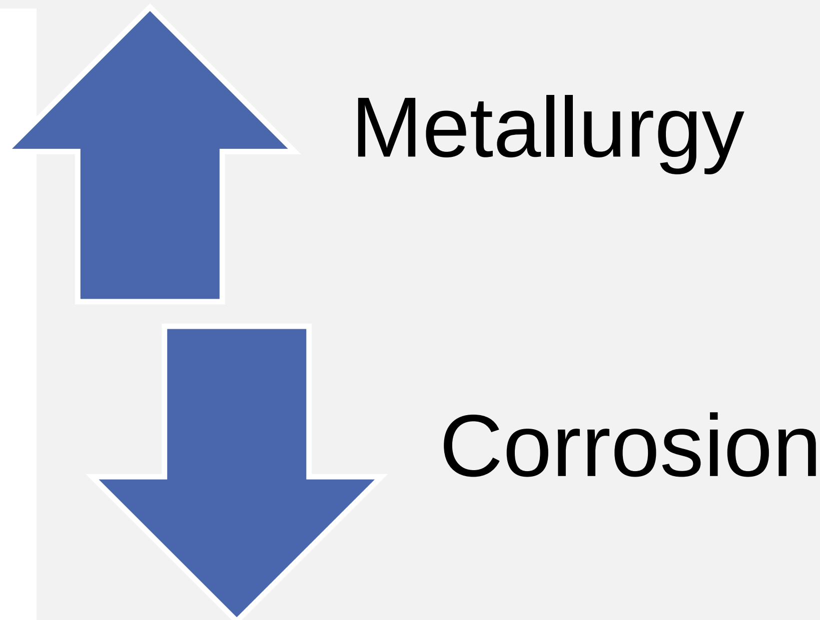


Figure adapted from: http://www.asminternational.org/documents/10192/1849770/06691G_Chapter_1.pdf (accessed 10/20/2016)

Electrochemical Nature of Corrosion

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

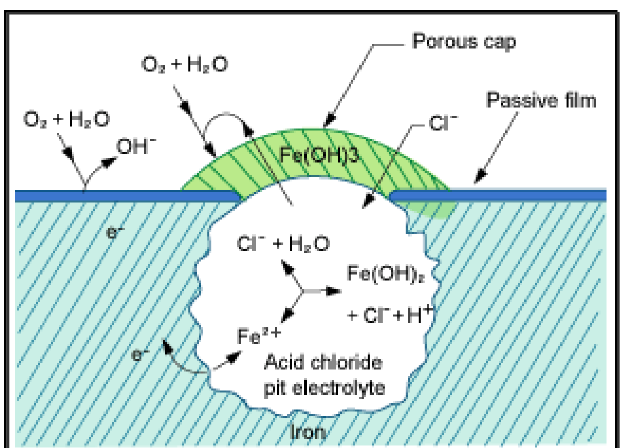
Overall Reaction:

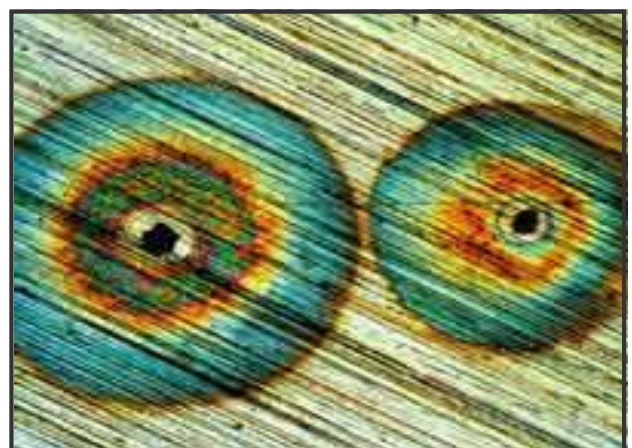
$$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

Anodic: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$



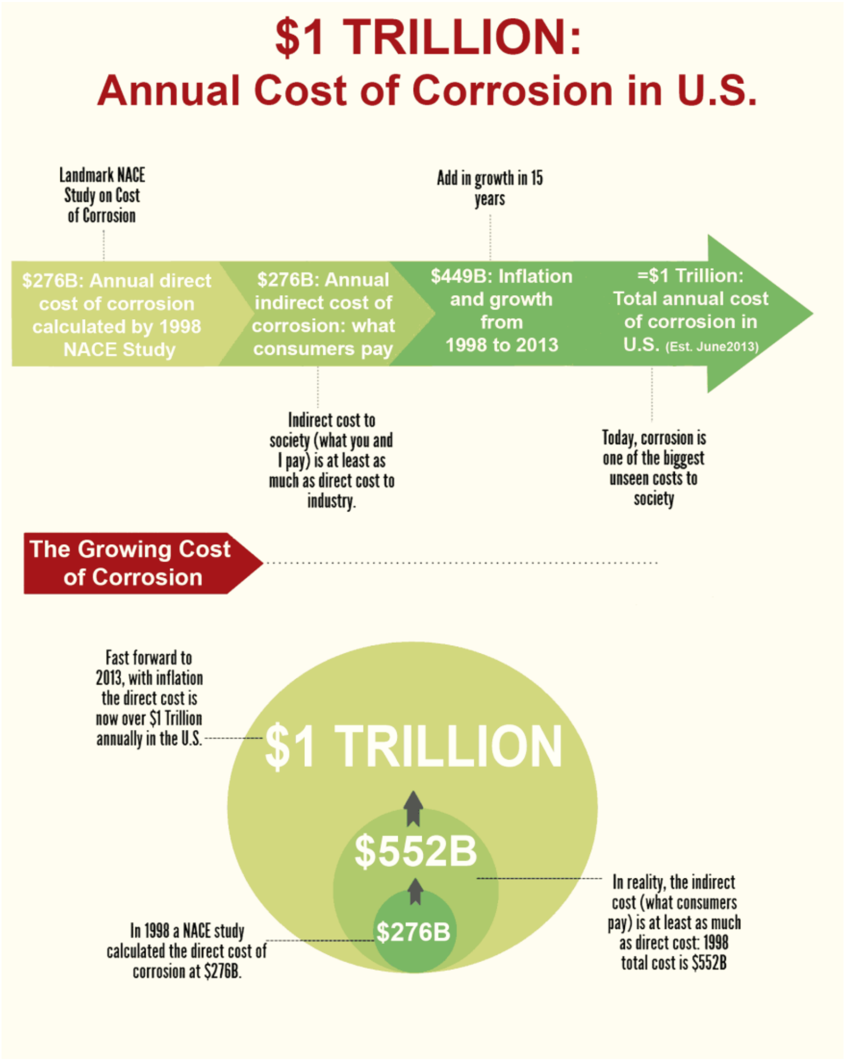


Impact of Corrosion

Repairs will cost about $60 million USD and take about 2 years

Research Opportunities in Science and Engineering, Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council, The National Academies Press, 2011

Cost of Corrosion



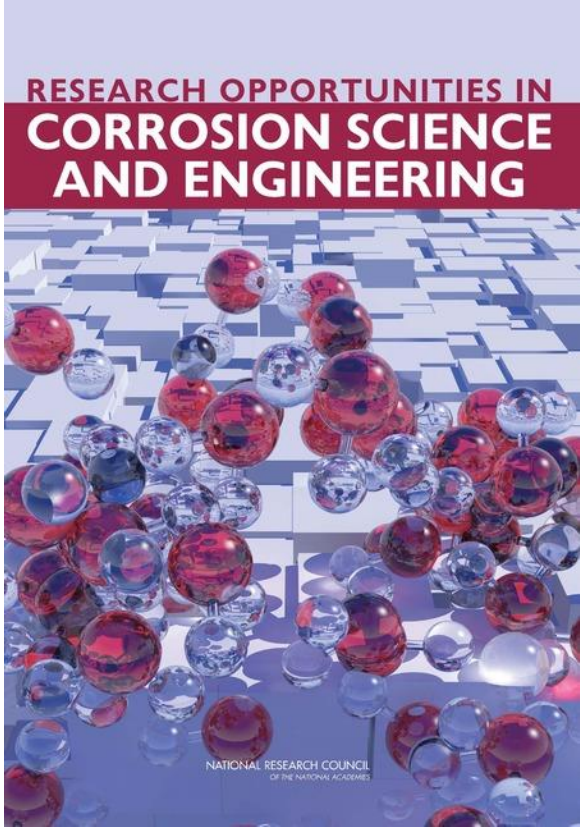
- At US $2.2 (1.6 €) trillion, the annual direct cost of corrosion worldwide is over 3% of the world's GDP.*
- Direct costs do not include the environmental damage, waste of resources, loss of production, or personal injury.

*World Corrosion Organization 2010

(1 Trillion = 10^{12} = 1 billon)

Corrosion Grand Challenges*

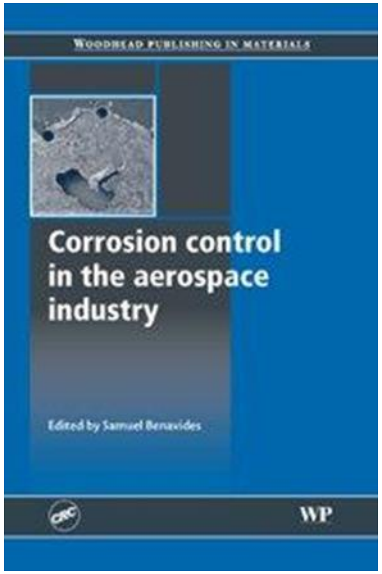
- Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings.
- High-fidelity modeling for the prediction of corrosion degradation in actual service environments.
- Accelerated corrosion testing under controlled laboratory conditions. Such testing would quantitatively 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)

Corrosion in the Aerospace Industry

- 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.



Aloha Airlines Accident, 1988

Associated Press library photo • April 28, 1988 (http://the.honoluluadvertiser.com/2001/Jan/18/118localnews1.html)

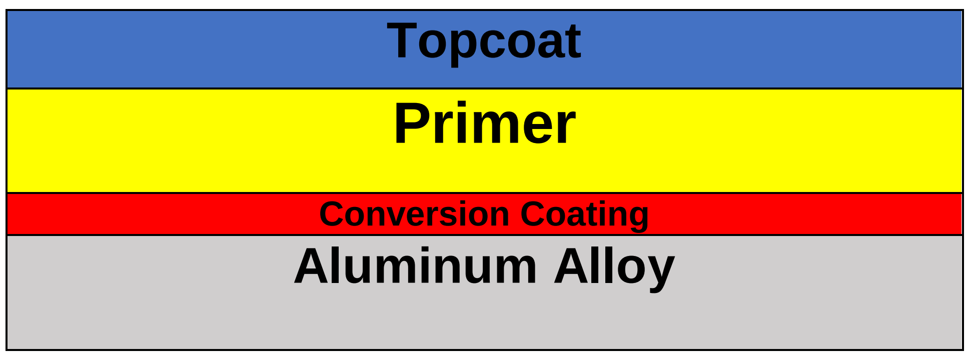
This picture of Aloha Airlines Flight 243, was taken after one-third of the roof flew off of the aircraft while cruising at 24,000 feet. A series of small cracks, caused by corrosion, had grown simultaneously at many nearby rivet holes, the devastating results of which can be seen in this picture. This 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.

New Materials and Coatings to Meet Changing Demands

- **Evolution of aerospace and automotive materials, coatings, and applications processes motivated by:**
  - **Changing environmental regulations**
  - **Demands for better energy efficiency and performance**
  - **Sustainable supply chain**
- **Future systems require smart coatings with on-demand corrosion protection, healing, and corrosion sensing.**
- **Future aerospace and automotive platforms will utilize composites, new alloys and coatings with multifunctional capabilities**

An artist illustration of the Vehicle Assembly Building and NASA's Space Launch System and Orion crew module on the mobile launcher, with Launch Pad 39B in the background.

Introduction

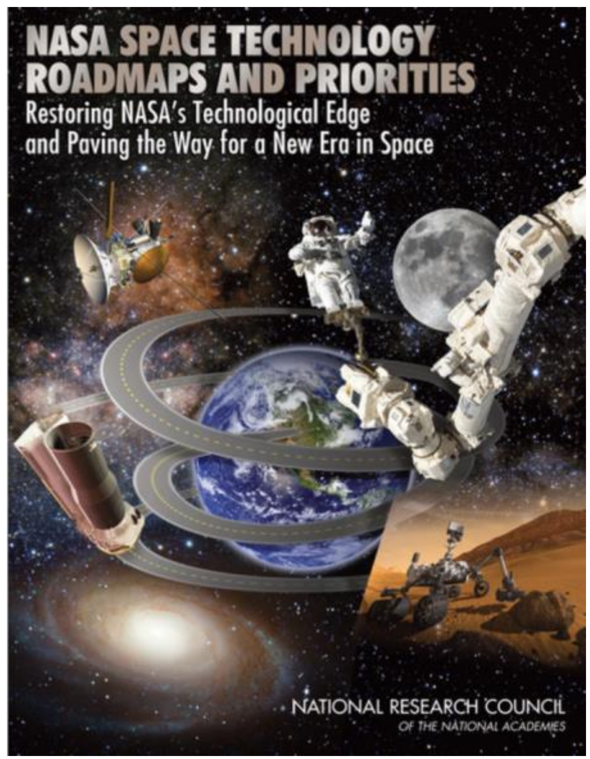
Introduction

NASA Space Technology Roadmap

13.2.1 Corrosion Prevention, Detection and Mitigation

Introduction

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.



Coatings on Orion Spacecraft

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 ^{o}C)

Orion 37 days prior to 1st Test Flight

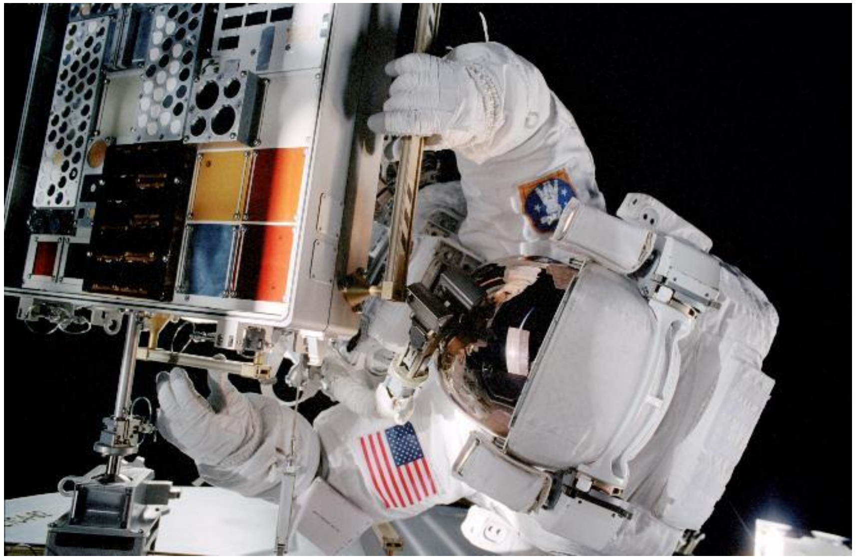
Coatings for the Space Environment

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 Testing for Space

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

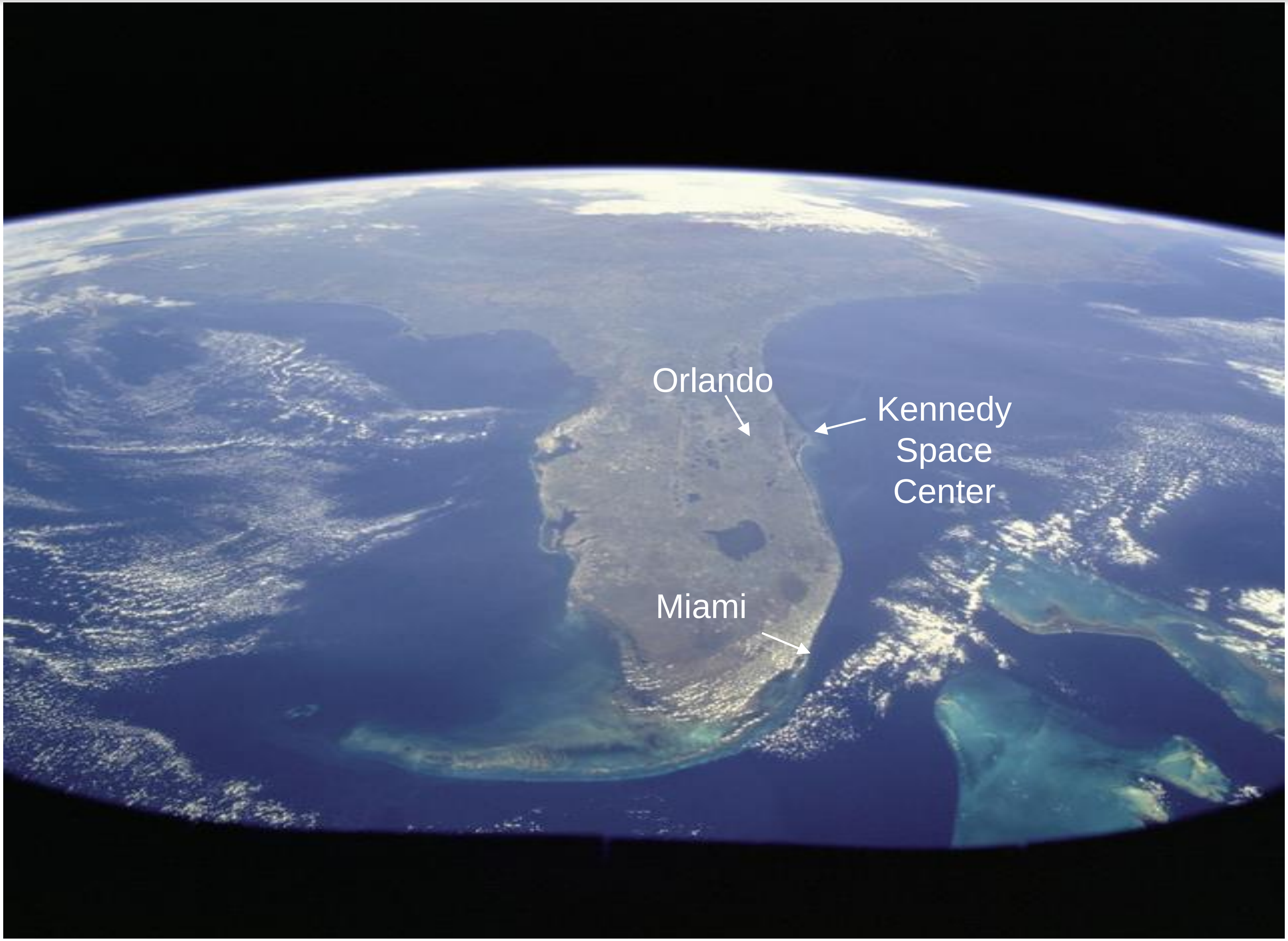
Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night (right photo), in part, due to atomic oxygen.

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 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.

International Space Station Technology – Benefits
Fine Art

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 Natural Environment

KSC Natural Environment

KSC Launch Environment

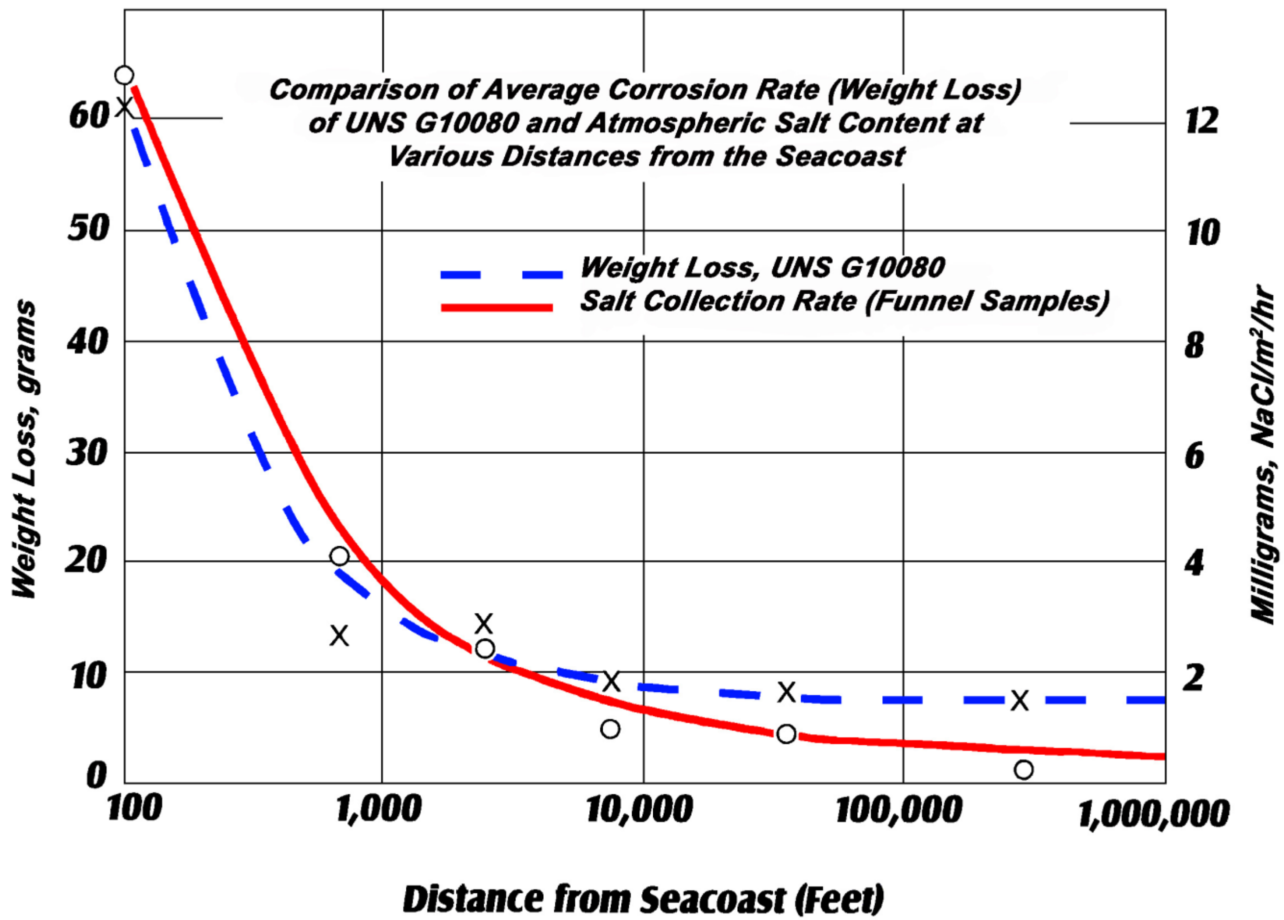
Corrosion Prevention, Detection, and Mitigation Timeline

- 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.
- 2016 4 additional patents allowed. Working on licensing the technology to industry

Atmospheric Exposure Testing

KSC Natural Environment

Changes in Corrosion Rate with Distance from the Ocean



Corrosion Rates of Carbon Steel

Corrosion rates of carbon steel calibrating specimens at various locations*			
Location	**Type Of Environment**	**µm/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*

[a]Two-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

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.

$$NH_4ClO_4(s) + Al(s) \xrightarrow{binder,\ Fe_2O_3} Al_2O_3(s) + HCl(g) + H_2O(g) + NO_x(g)$$

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.

Examples of Launch Pad Corrosion

Enclosed / Inaccessible Areas

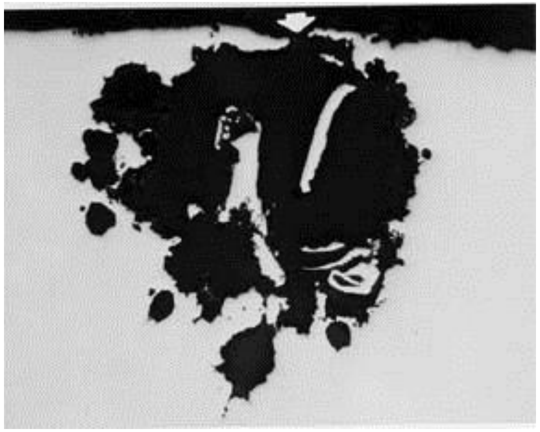
Dissimilar Metals

KSC Launch tower structural steel corrosion

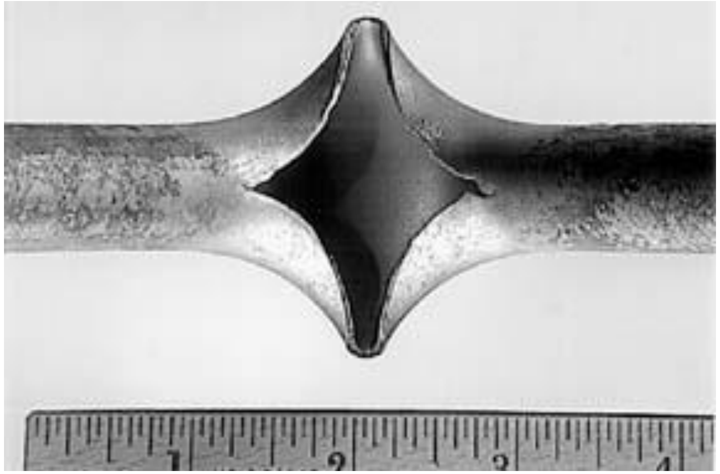
Under the LC 39B Flame Trench

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 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	1966	1981	1985-1987	2000	2004
Space Program starts Corrosion failures begin	Atmospheric exposure testing begins near the launch pads	Space Shuttle introduces acid deposition products that make corrosion worse	Accelerated corrosion testing (salt fog and electrochemical) begins	Corrosion Technology Laboratory is created	The Corrosion Technology Laboratory starts developing smart coatings

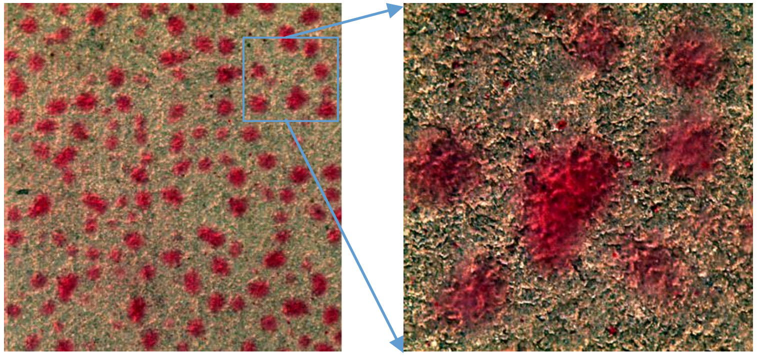
Corrosion testing and failure analysis

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

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 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.

Microencapsulation-based Smart Coatings

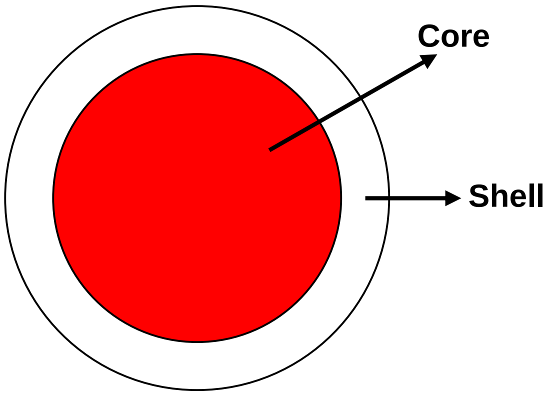
Corrosion indication, detection, and healing of mechanical damage can be achieved using microencapsulation technology

What are microcontainers?

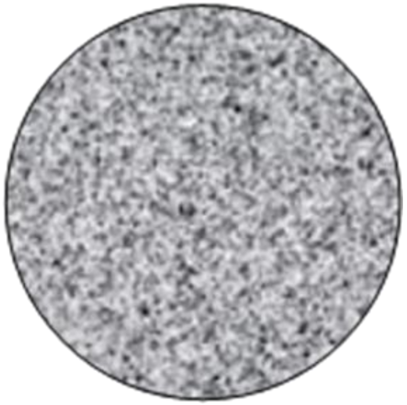
Particles or liquid drops coated in polymers. These microcontainers can carry any material that needs protection or controlled release.

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



Microcapsules



Microparticles

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***

*D. Grigoriev, D. Akcakayiran, M. Schenderlein, and D. Shcukin, Corrosion, 70 (2014): p.446-463.

Electrochemical Nature of Corrosion

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

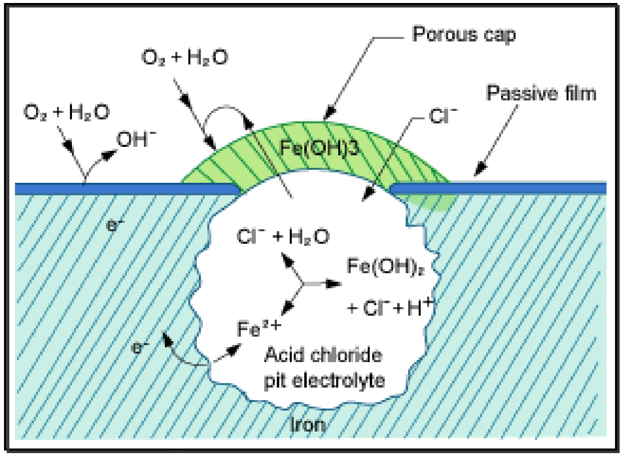
Overall Reaction:

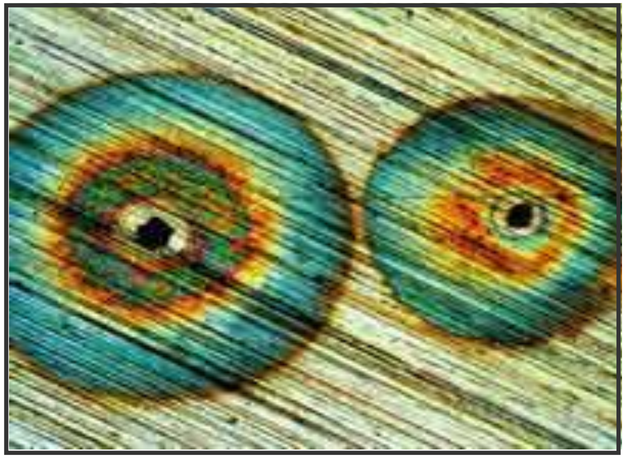
$$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

Anodic: $$Fe \rightarrow Fe^{2+} + 2e^-$$

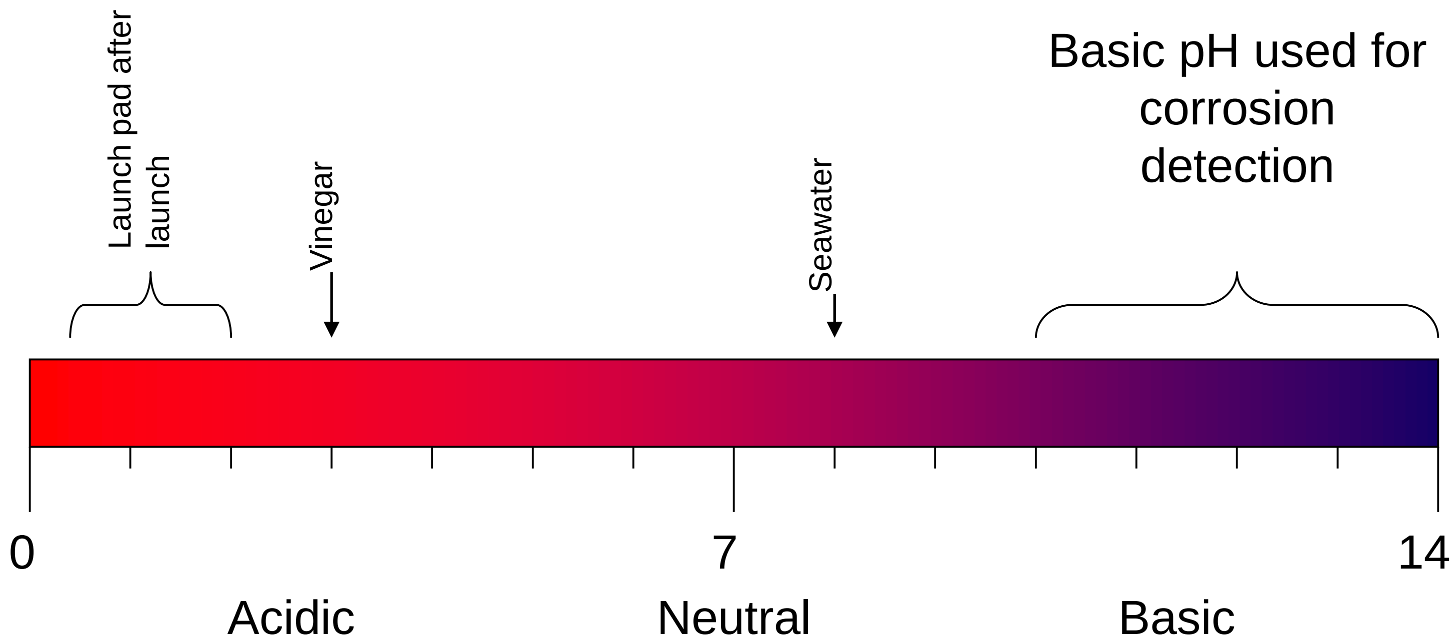
Cathodic:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$





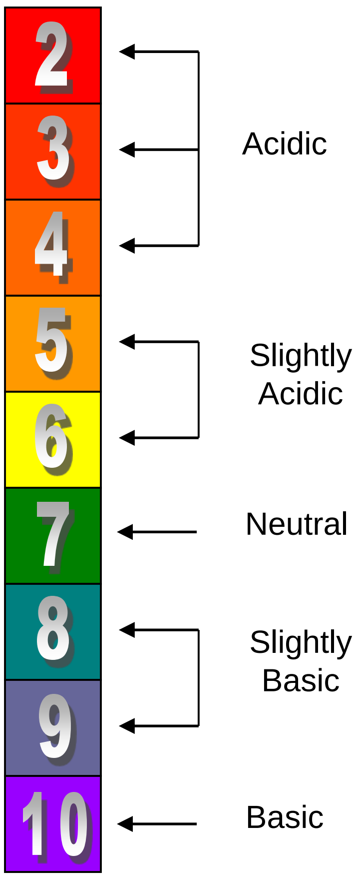
Corrosion and pH

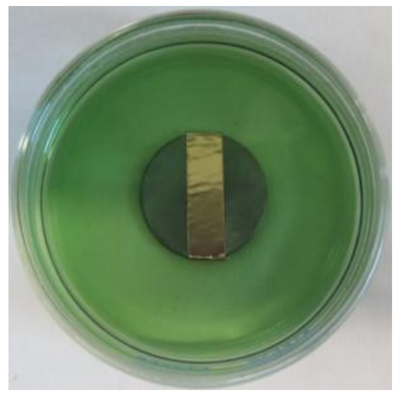


pH Scale

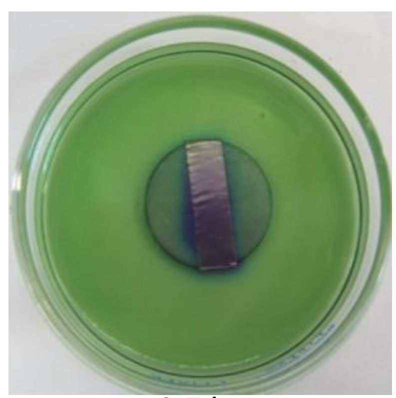
Corrosion Indication

pH changes that occur during corrosion of a metal

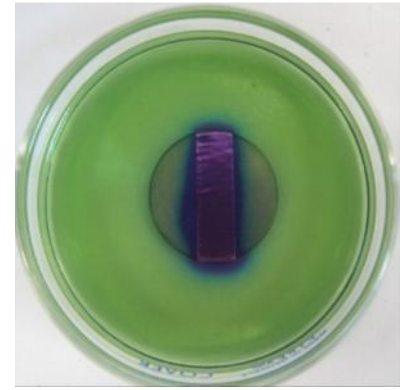




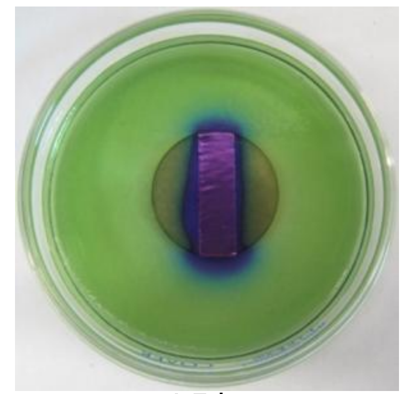
Elapsed Time: 0 hours



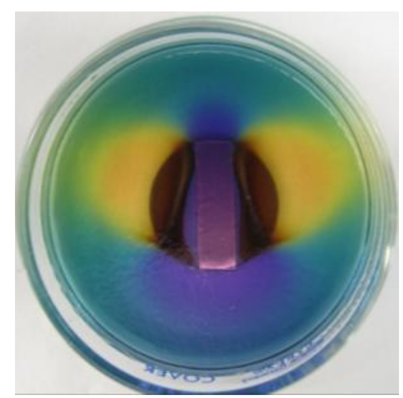
0.5 hours



1.5 hours

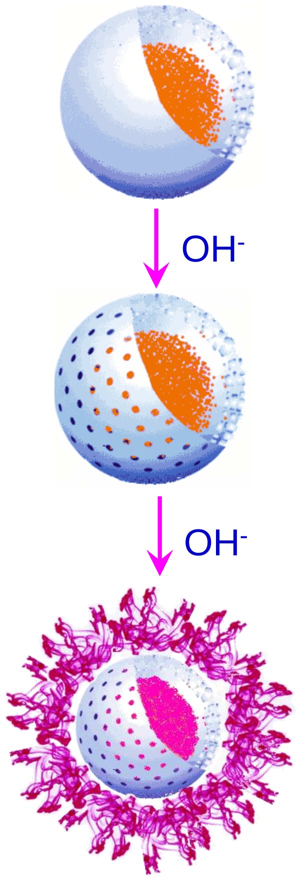


4.5 hours



3 days

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?

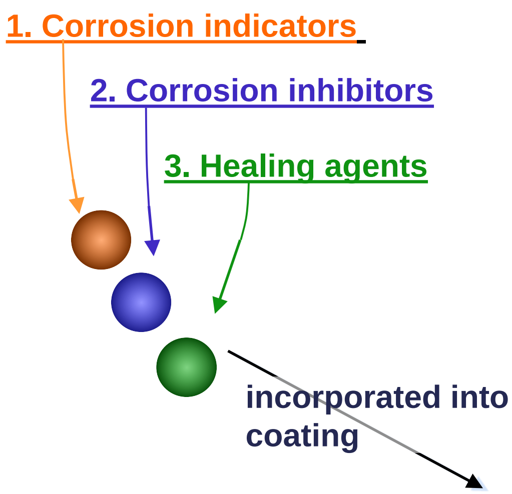
Benefits from corrosion sensing coatings:

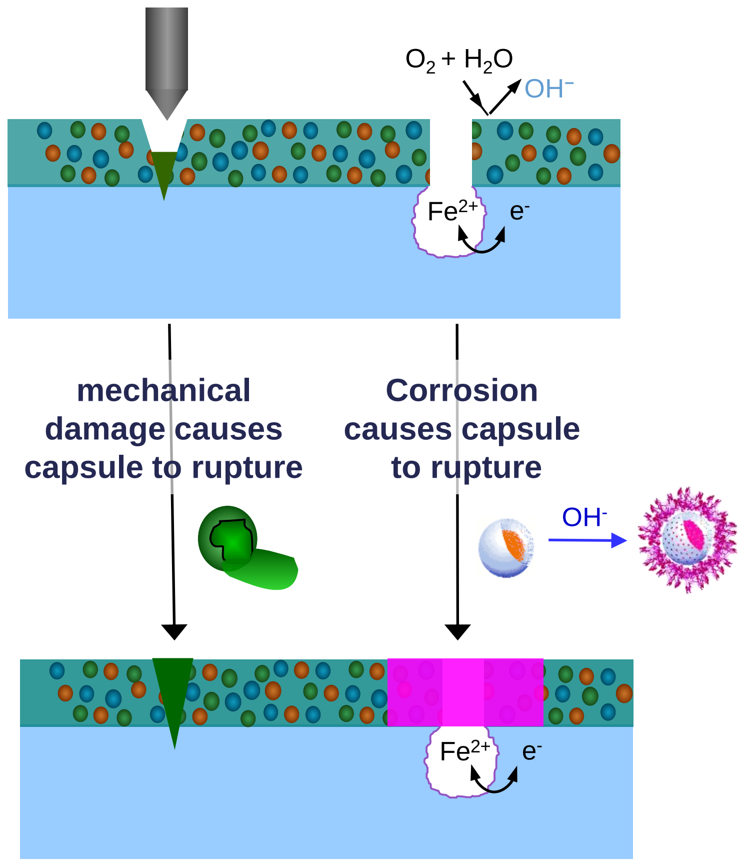
- Overcoming solubility limit of indicators in solvents
- Protecting indicator from coating constituents
- Easy incorporation into different paint systems

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



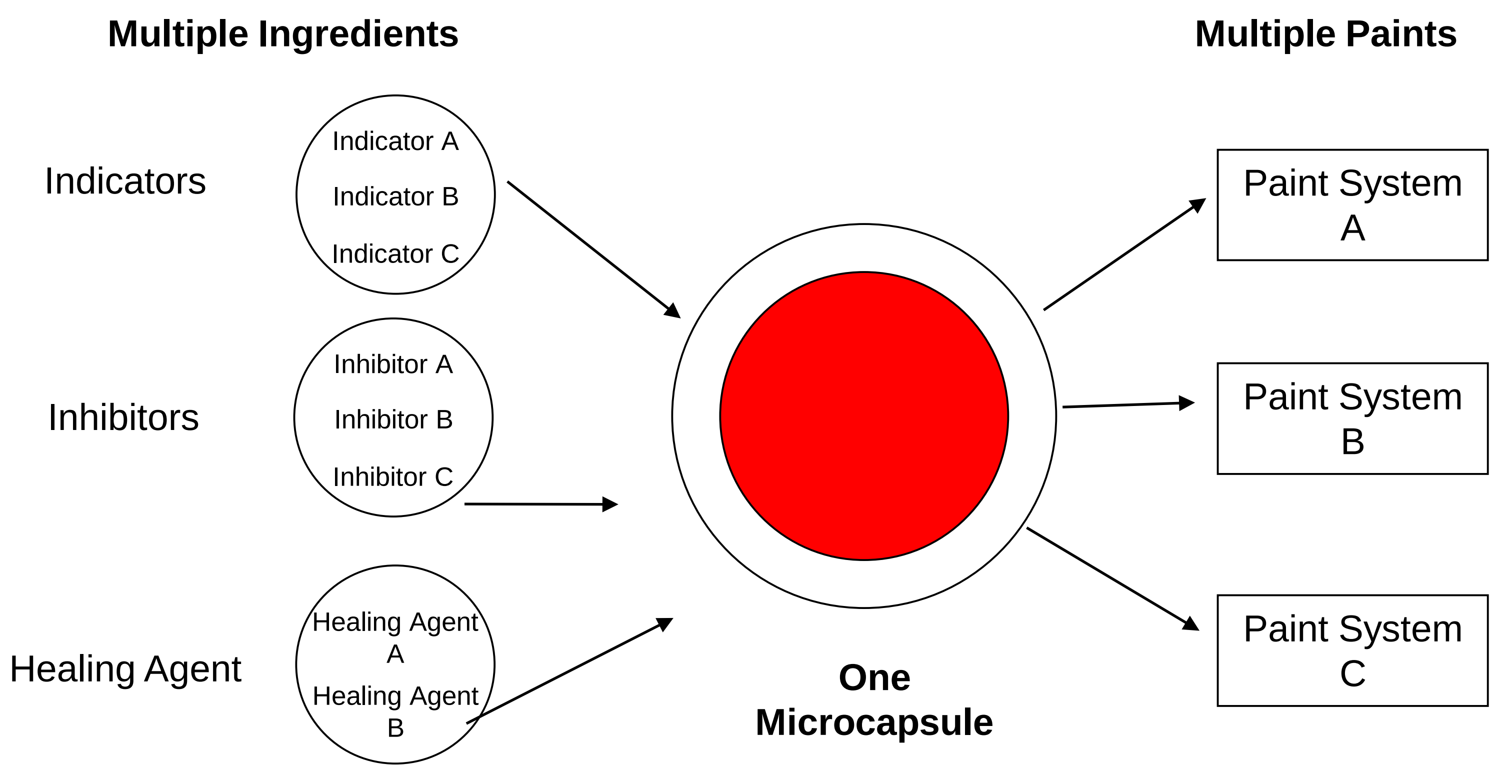


Ruptured Microcapsule:

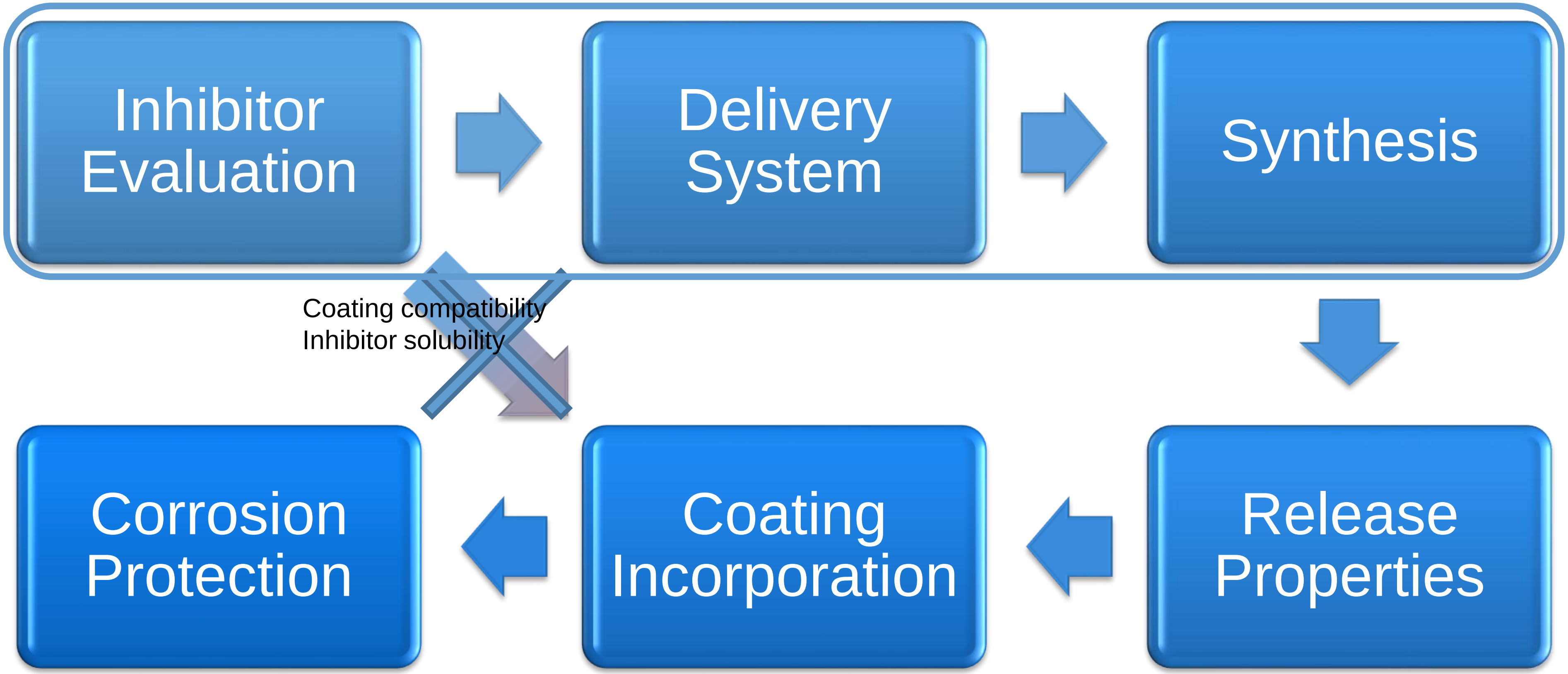
- indicates corrosion
- protects metal from corrosion
- repairs damaged area

Microencapsulation Versatility

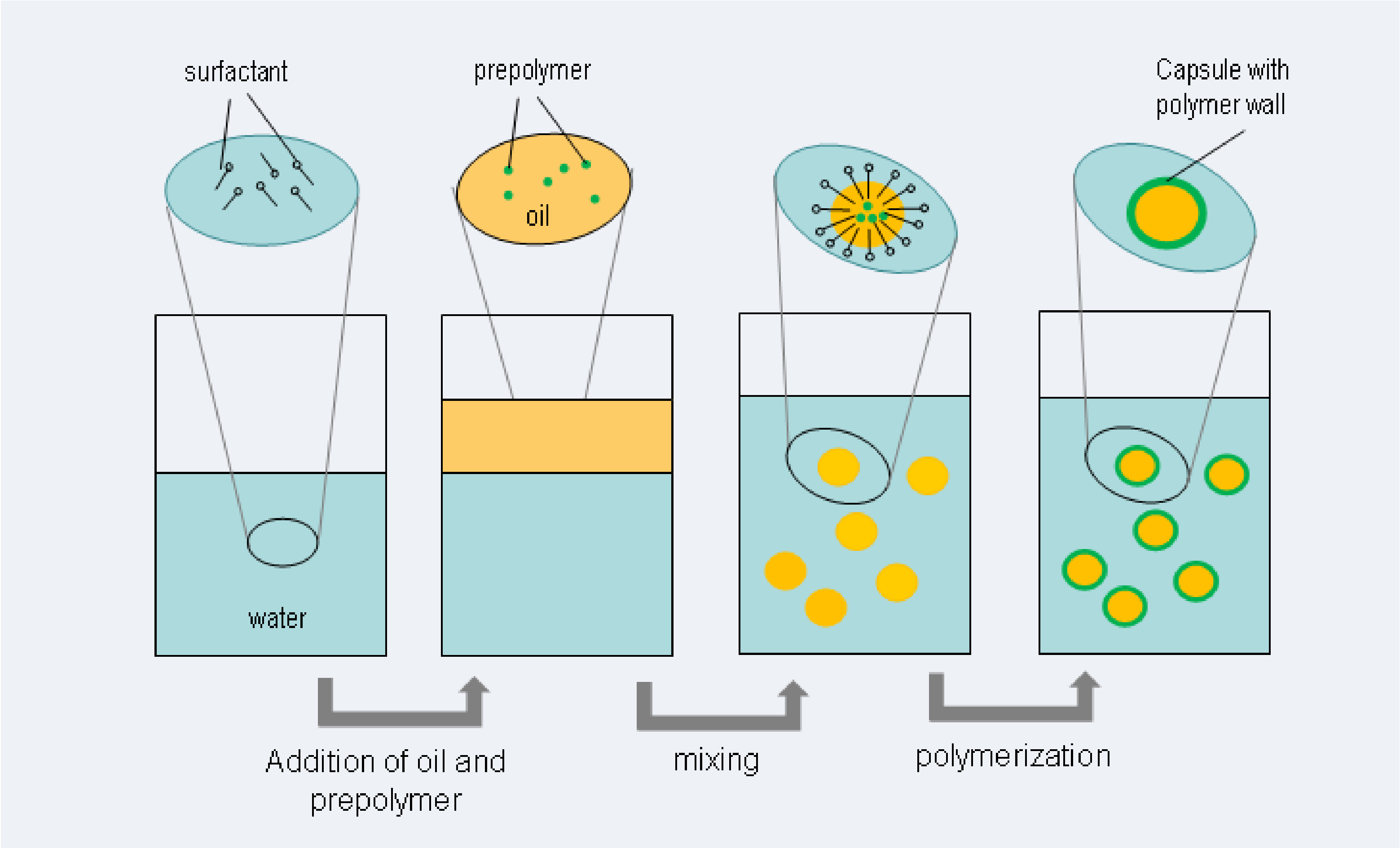
Versatility: Microcapsules can deliver multiple types of contents into different paint systems. The microcapsule wall can be modified to deliver the contents at different rates.



Delivery System

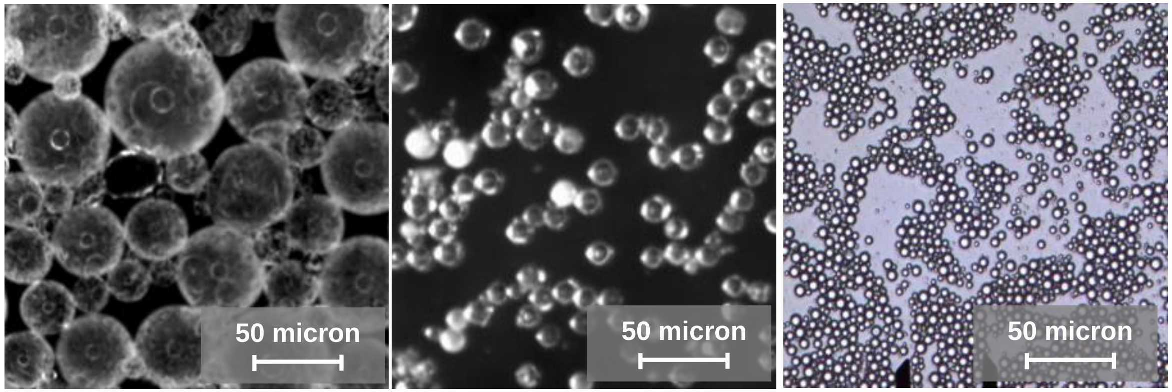


Hydrophobic-Core Microcapsules



Interfacial polymerization of oil-in-water microemulsion process for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.

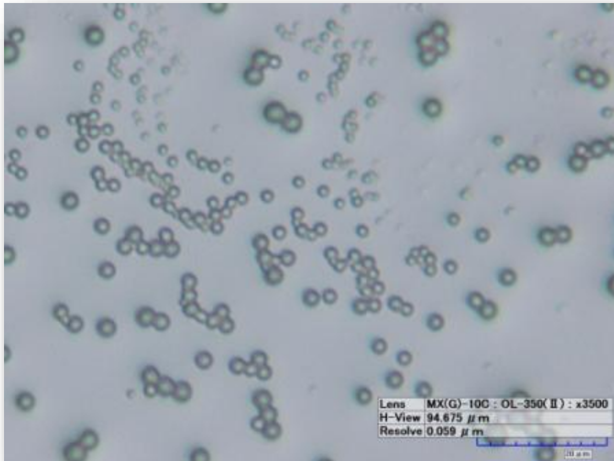
Hydrophobic-core Microcapsules



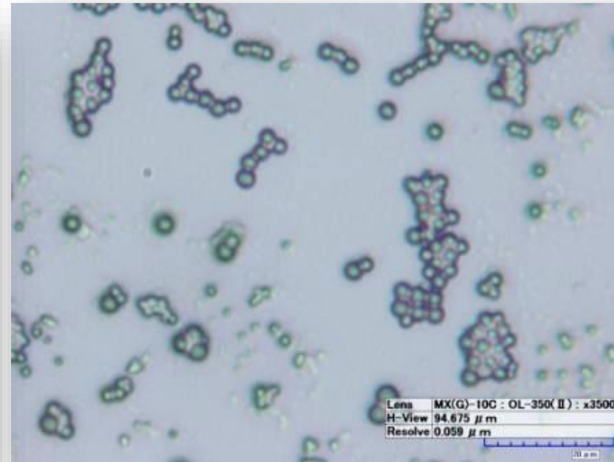
Optical microscopy images of Hydrophobic-core microcapsules of different sizes

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



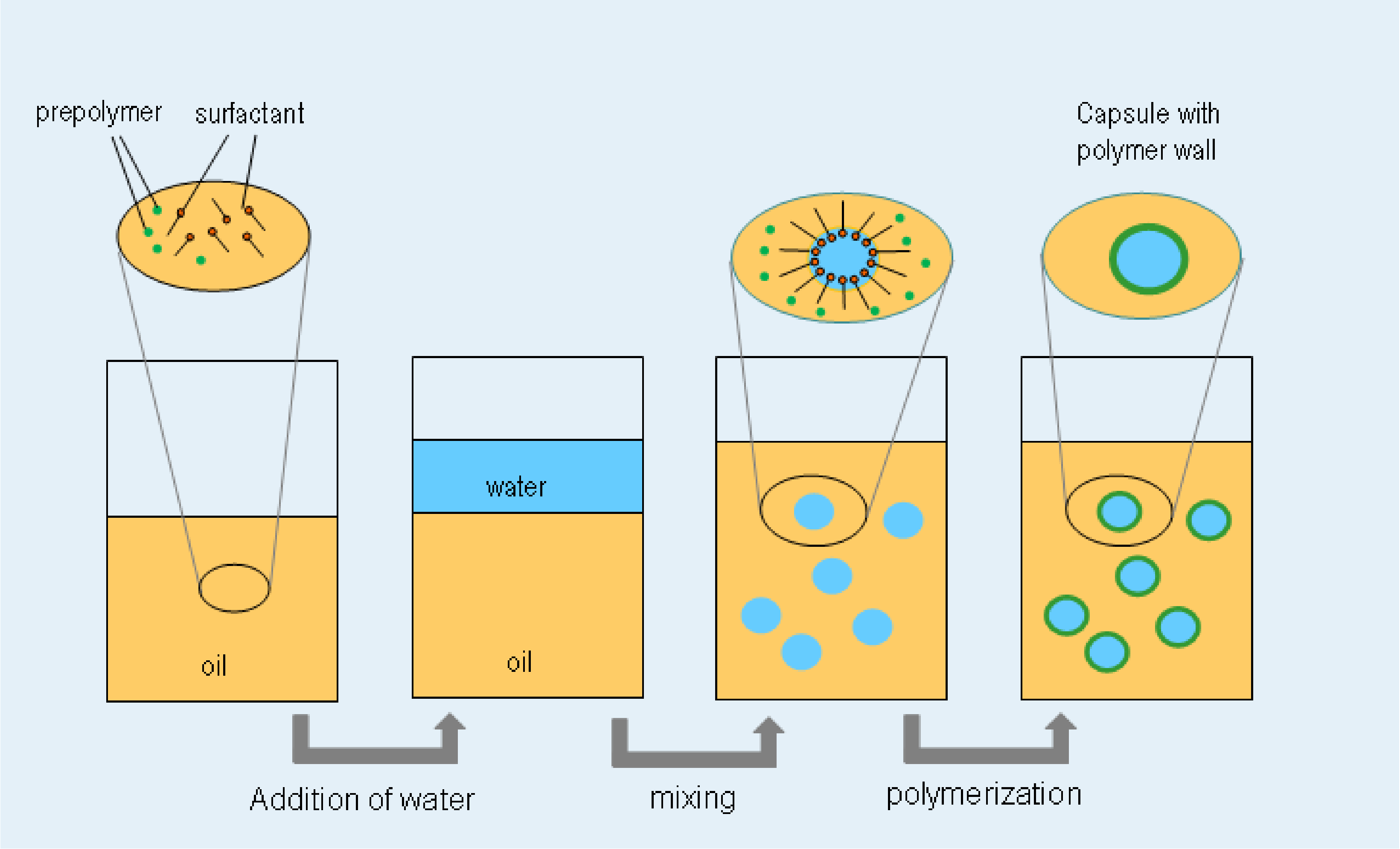
oil-in-water emulsion



microcapsule formed

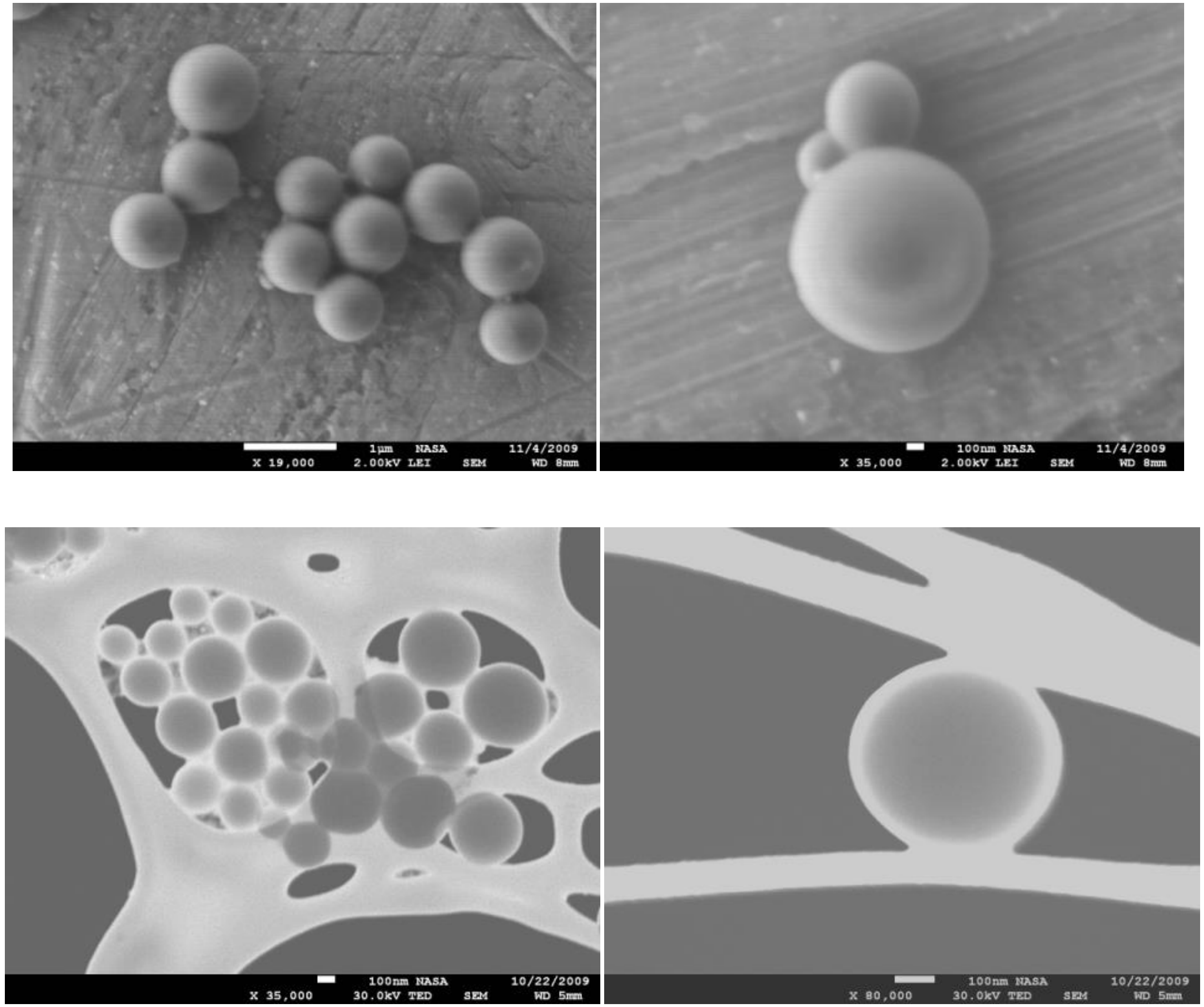
SEM of hydrophobic-core microcapsules containing an organic inhibitor

Hydrophilic-Core Microcapsules



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

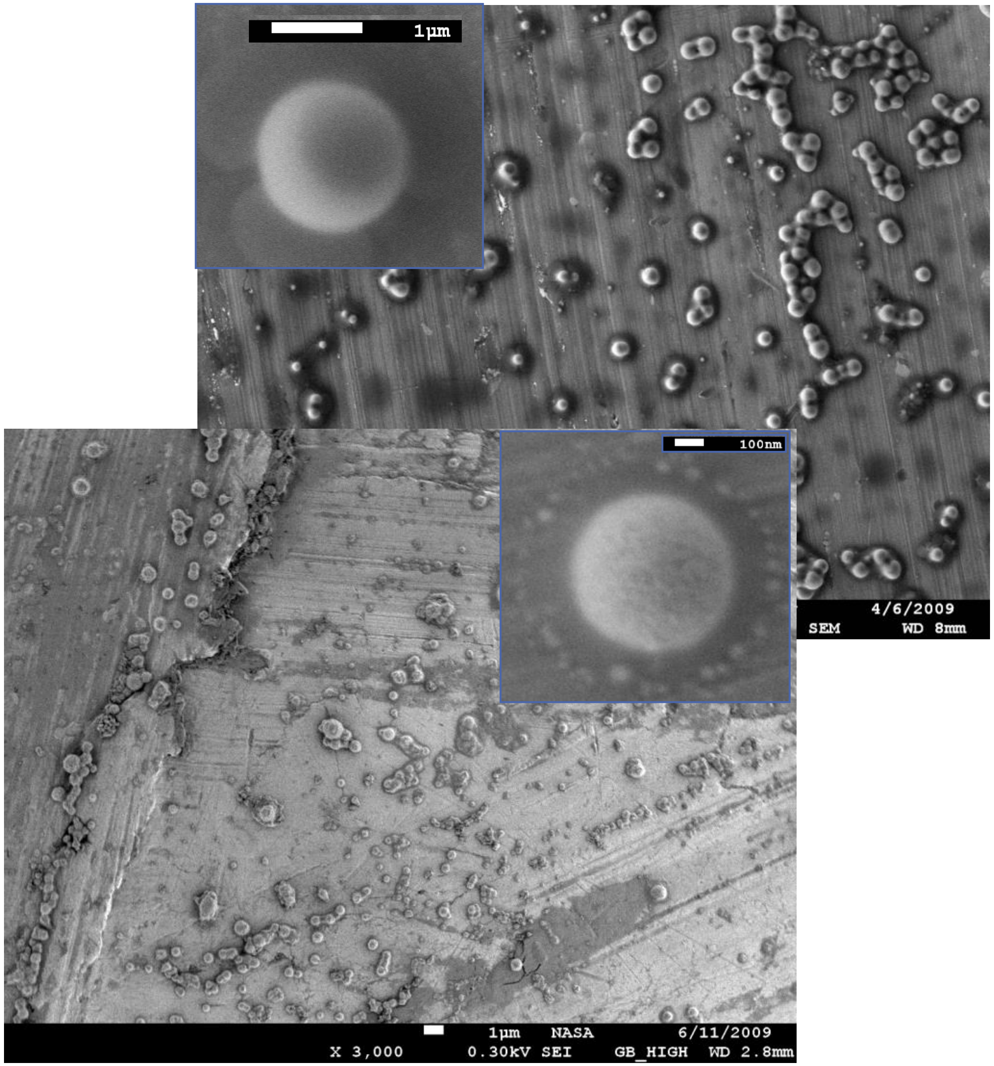
Hydrophilic-core Microcapsules



SEM images of hydrophilic-core microcapsules

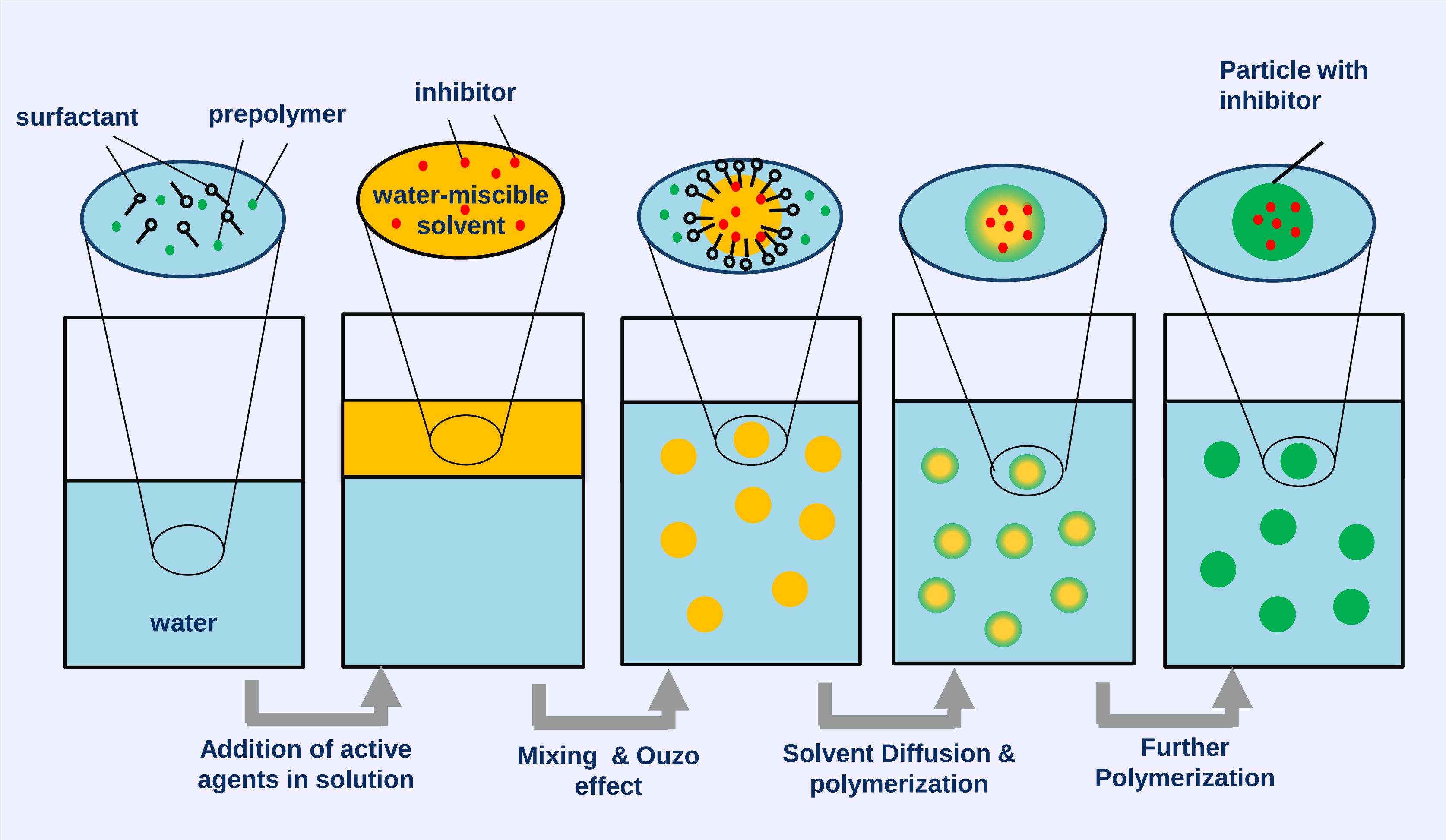
Microcapsules for Corrosion Indication and Inhibition

When corrosion begins, the microcapsule will release the contents of the core (indicator or inhibitor) in close proximity to the corrosion.

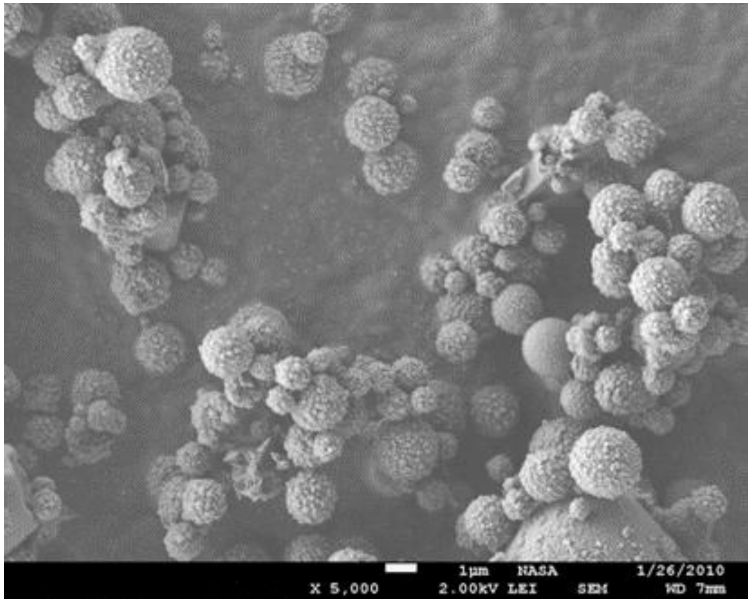


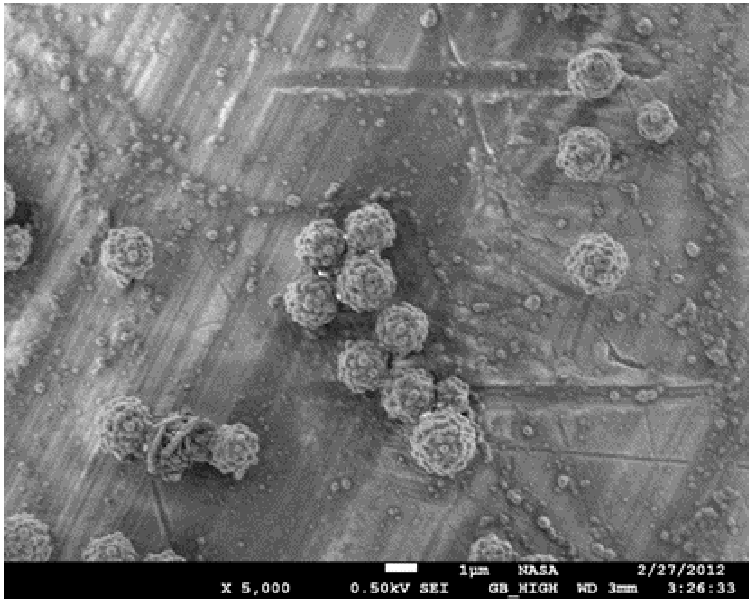
SEM images of microcapsules with corrosion indicator (top) and inhibitor (bottom).

Microparticle Formation



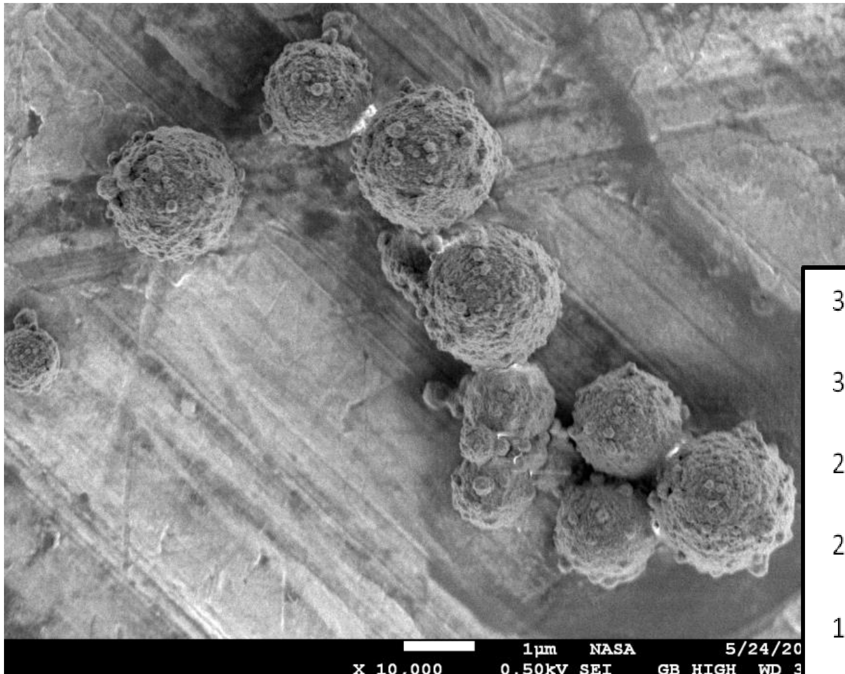
Corrosion Indicating Microparticles

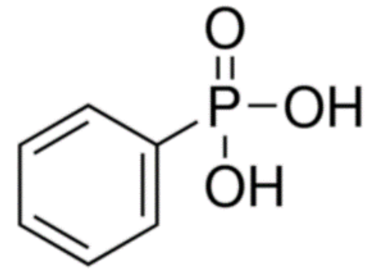


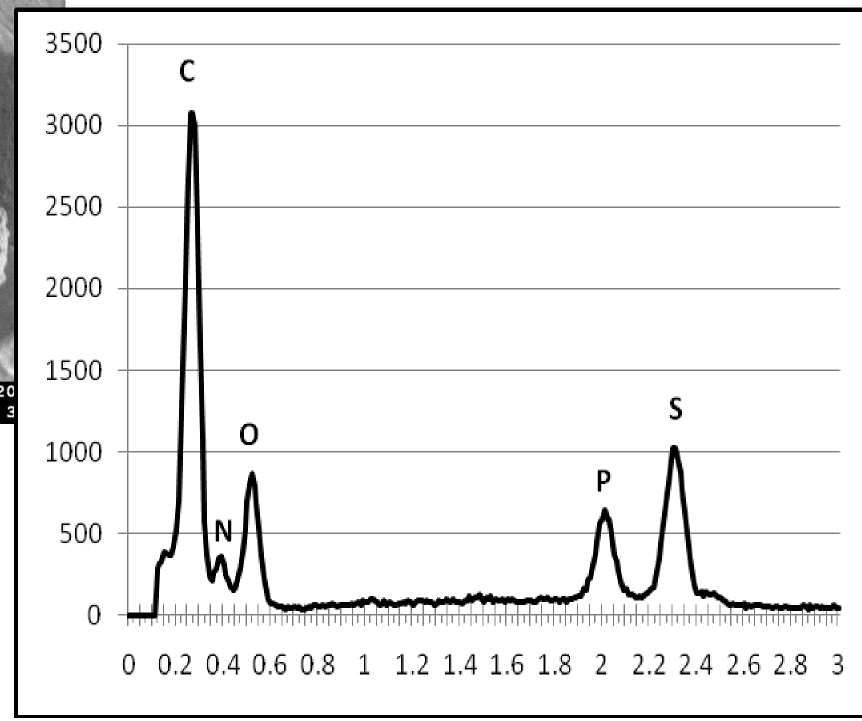


SEM image of microparticles with color changing indicator (left) and with fluorescent indicator (right)

Microparticles with Inhibitors

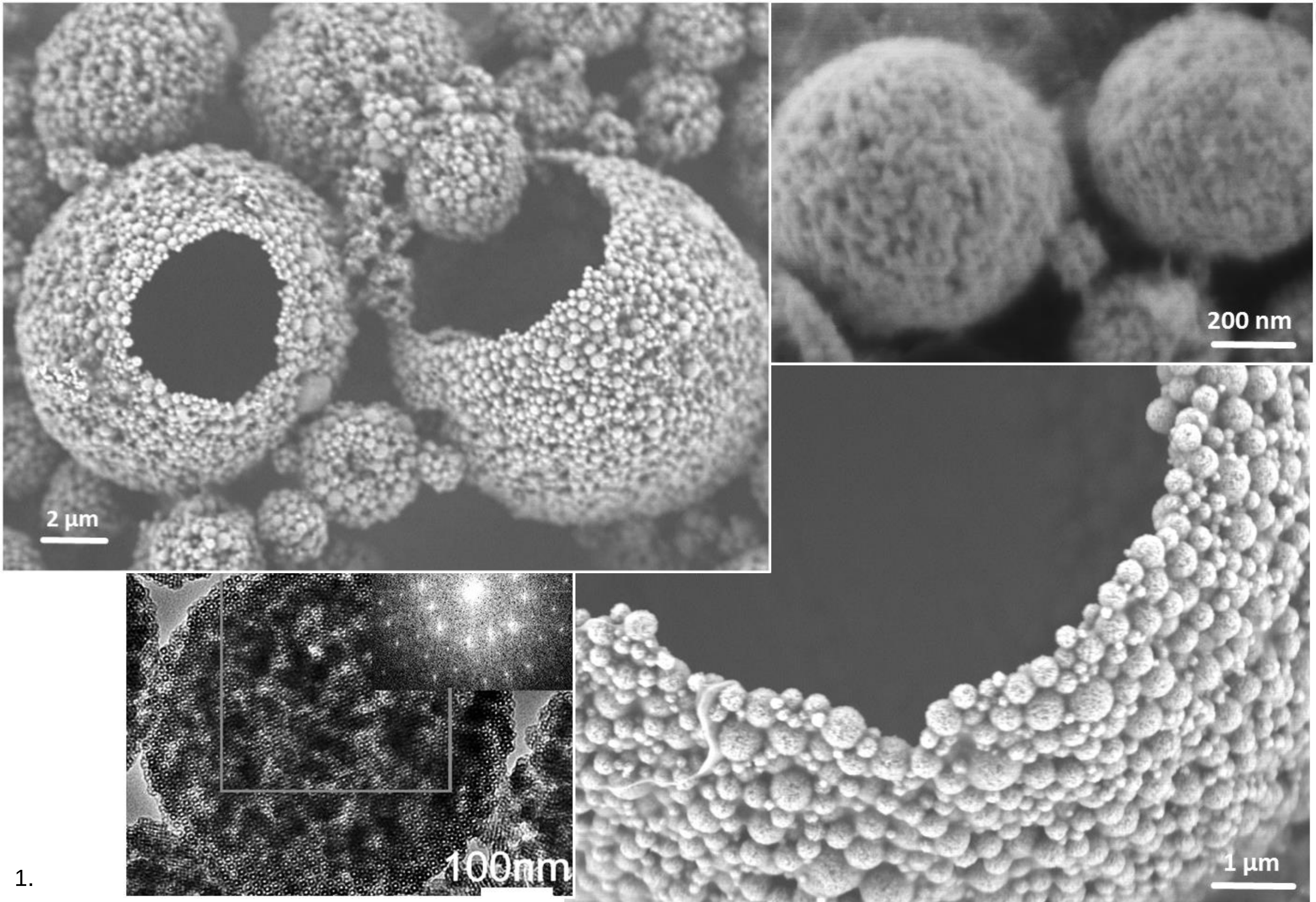






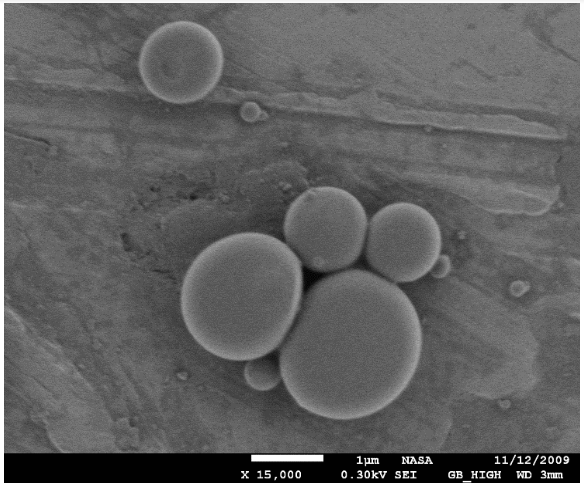
SEM and EDS of microparticles with corrosion inhibitor phenylphosphonic acid (PPA)

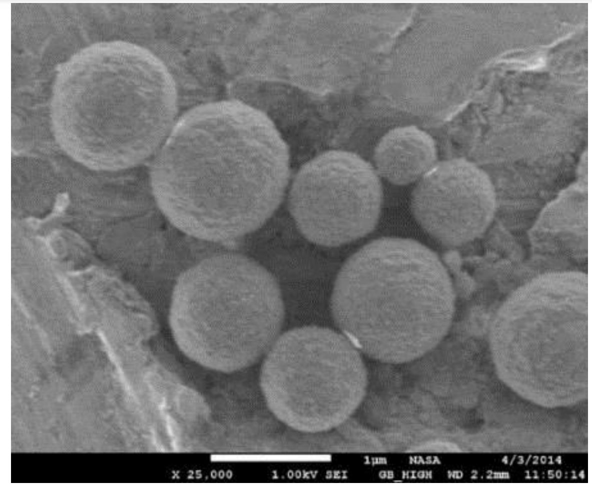
Inorganic Carriers with Hierarchical Architecture for Controllable Delivery of Corrosion Inhibitors

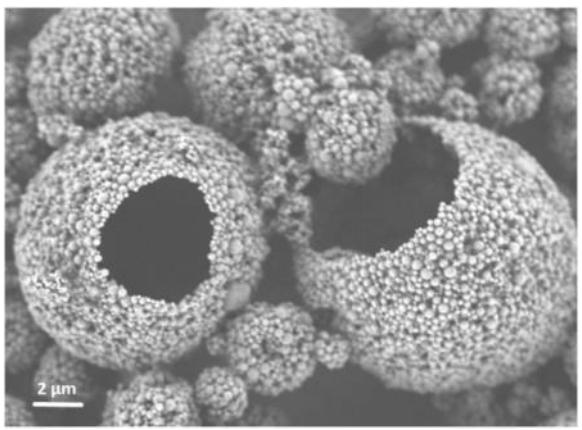


1.

From Concept to Reality

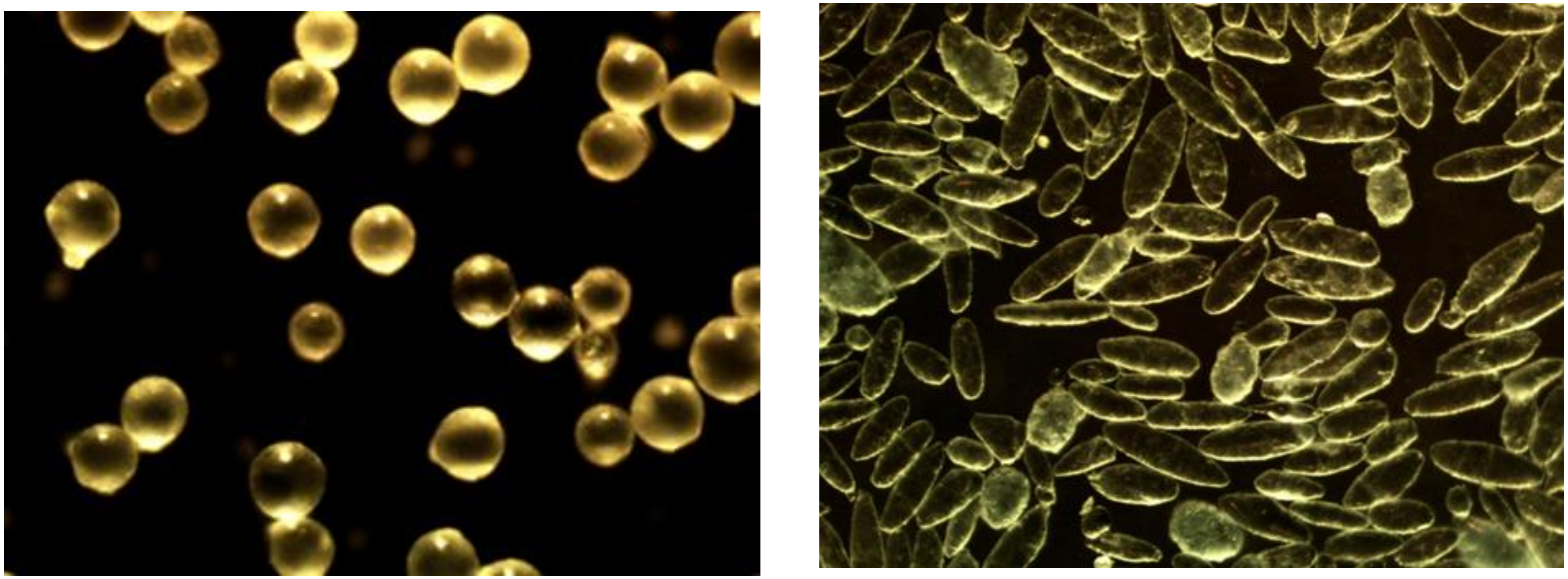






- Initial concept: a simple pH-sensitive microcapsule
- Reality: a portfolio of delivery systems (micro-containers) including
  - Hydrophobic-core and hydrophilic-core pH-sensitive microcapsules
  - pH-sensitive micro-particles
  - Inorganic micro-containers

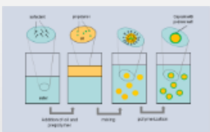
Microcapsules for Self-Healing Coatings



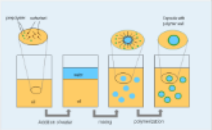
Optical micrographs of spherical and elongated microcapsules for self-healing of mechanical scratches

Development and Optimization: Indication

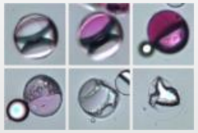
Oil-core microcapsules developed using interfacial polymerization



Water-core microcapsules developed using interfacial polymerization

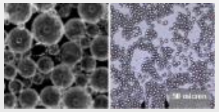


The pH sensitivity of the microcapsules was tested.

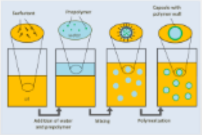


Water-core microcapsules optimized to reduce cluster formation. The synthesis was modified to use environmentally friendly reagents.

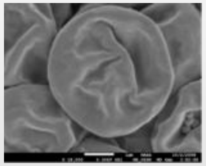
Oil-core microcapsules optimized to reduce capsule size.



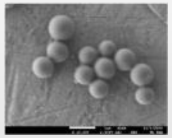
Water-core microcapsules optimized by using a water soluble wall forming prepolymer. The synthesis time was reduced and the microcapsule wall properties were improved.



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

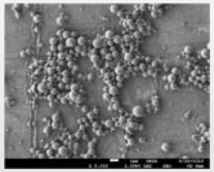


Water-core microcapsules with corrosion indicator phph (5wt%) were synthesized.



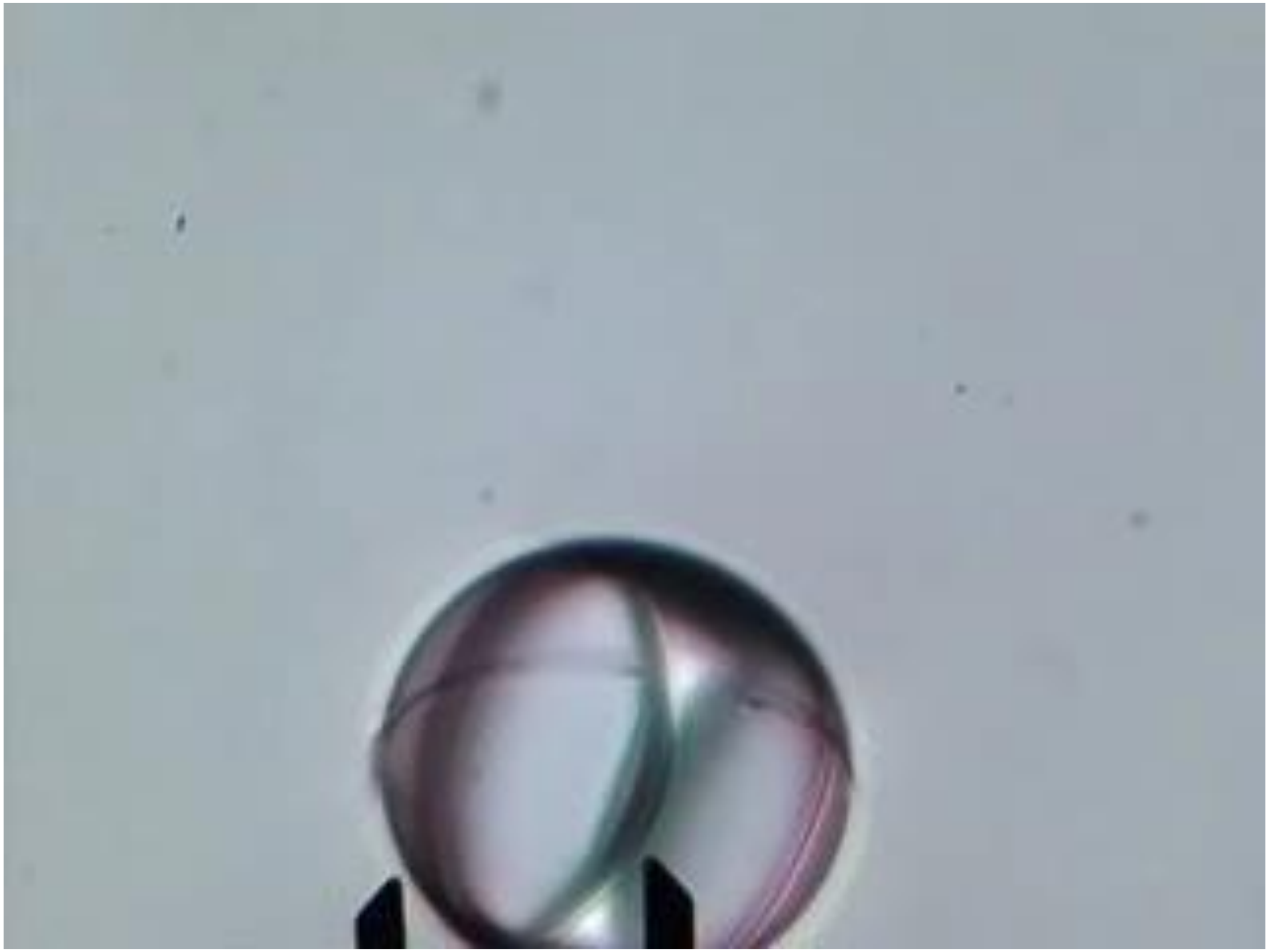
Oil-core corrosion indicator microcapsules obtained in free flowing powder.

MFPTT* microparticles with incorporated phph (30wt%) were synthesized.



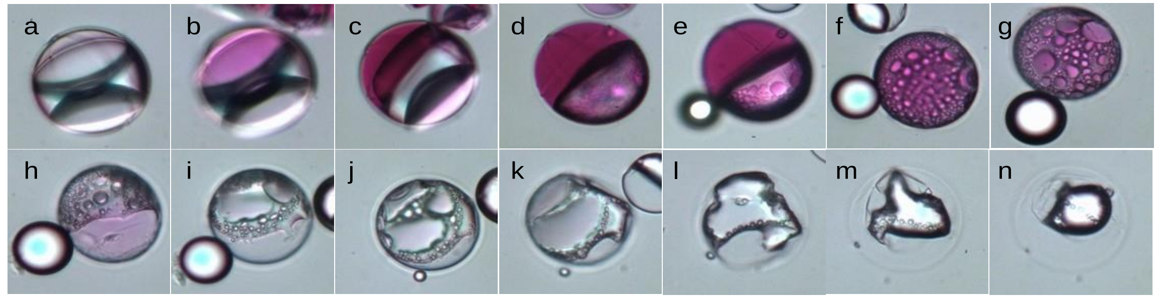
MFPTT Melamine Formaldehyde Pentaerythritol Tetra (3-Mercaptopropionate)

Microcapsule Response to pH Increase



Microcapsules for Corrosion Indication

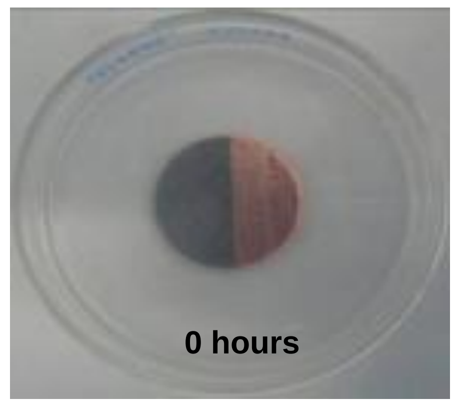
pH sensitive microcapsules with corrosion indicator for corrosion detection

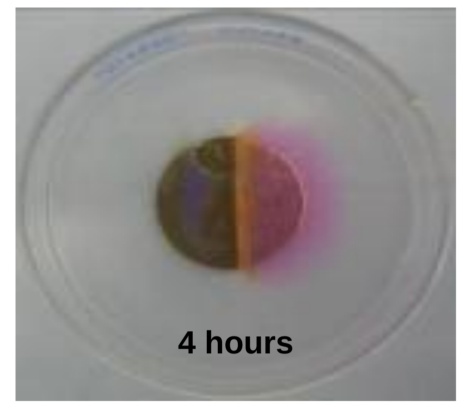


Time lapse pictures of a microcapsule with indicator breaking down under basic pH conditions.

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 (phph) microcapsules.
2	Zinc galvanized nut and bolt	First coated with epoxy, then top coated with clear urethane containing 10% phph 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% phph 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% phph microcapsules.
5	Zinc galvanized nut and bolt	The ends of the nut and bolt were coated with urethane containing 10% phph 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% phph microcapsules.

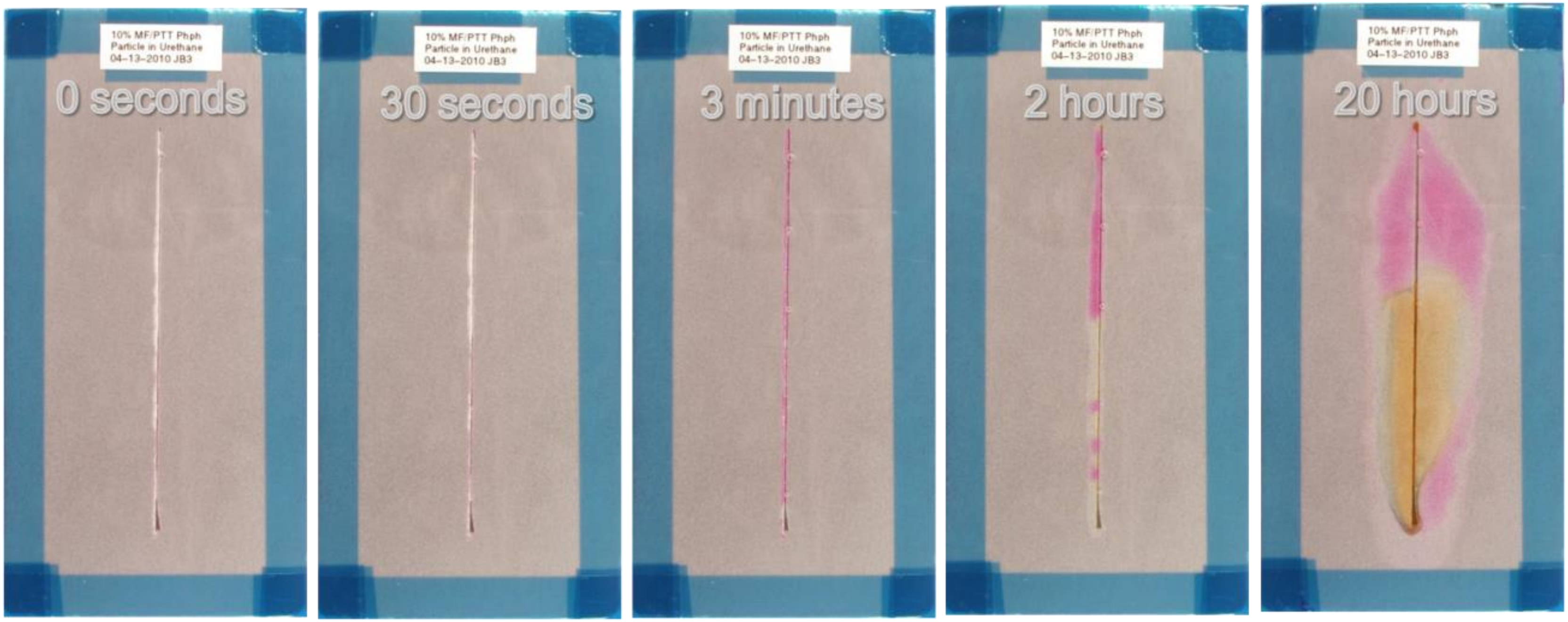
Coating systems used for hidden corrosion indication testing.

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

Early Indication of Corrosion

Early indication of corrosion

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.

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

Early Onset of Corrosion Detection

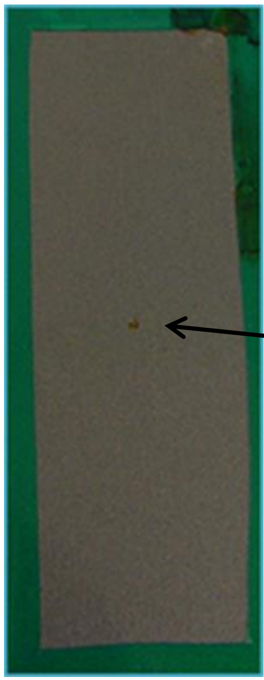
Fluorescent Indicator

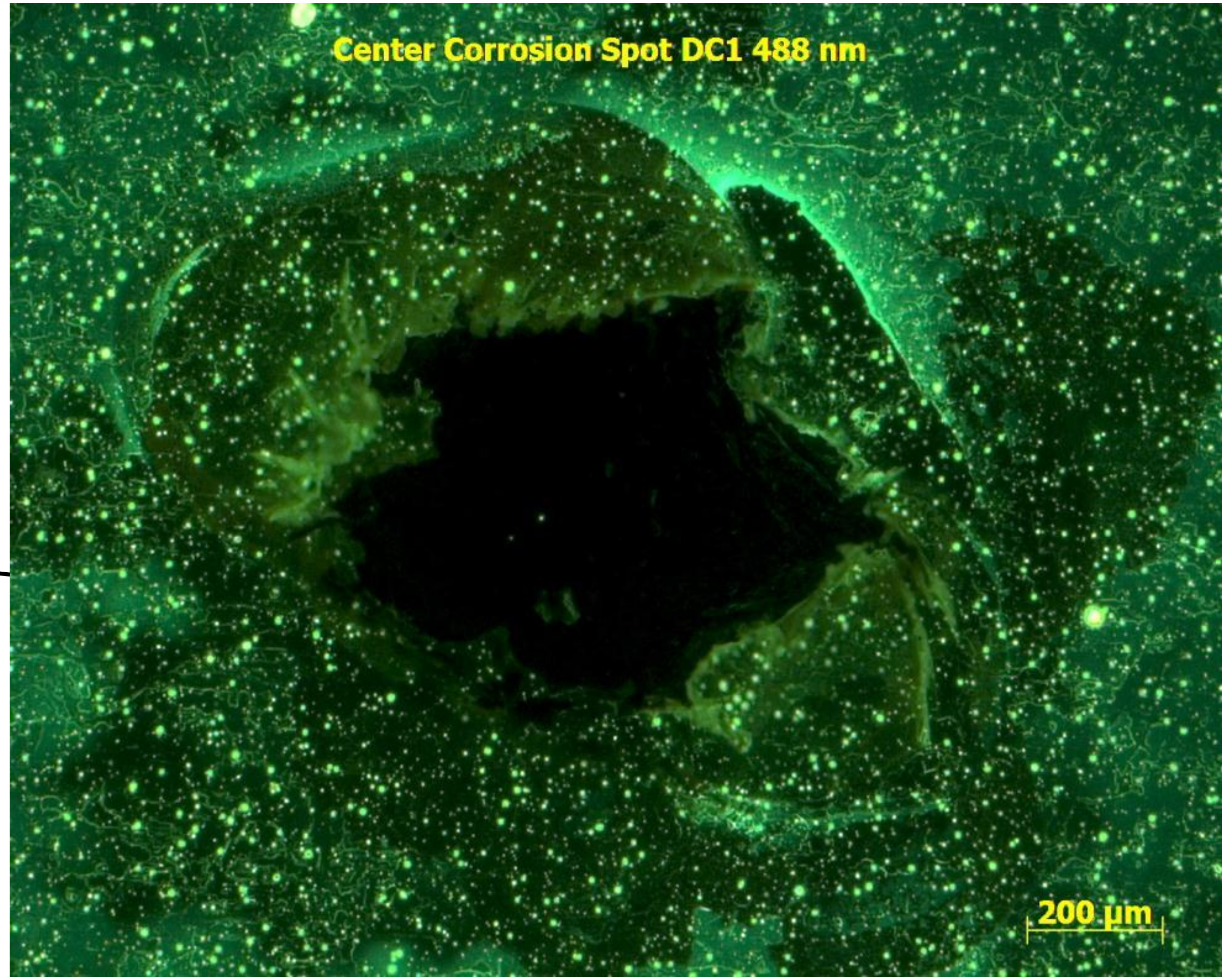
Center scribed 3" x 2" R type Q-Panels coated with Solvent-based 2k acrylic-urethane clear coat with encapsulated fluorescein (0.05 wt%). A scan was taken every 15 minutes for 12 hours examined via digital microscopy with a Keyence VHX-600 digital microscope at 100X magnification to correlate areas of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

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

Fluorescence Spectroscopy Instrument Parameters

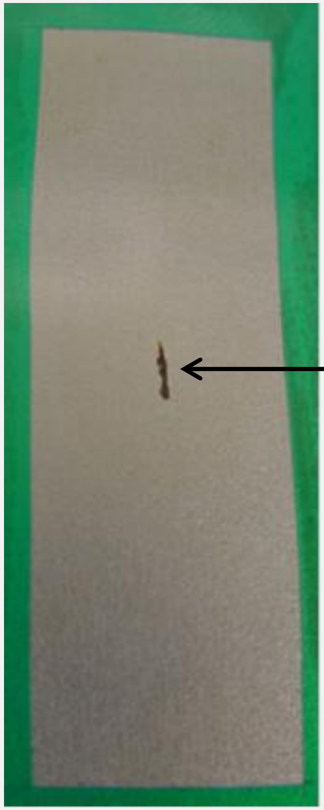
Diamond Clad with Fluorescein

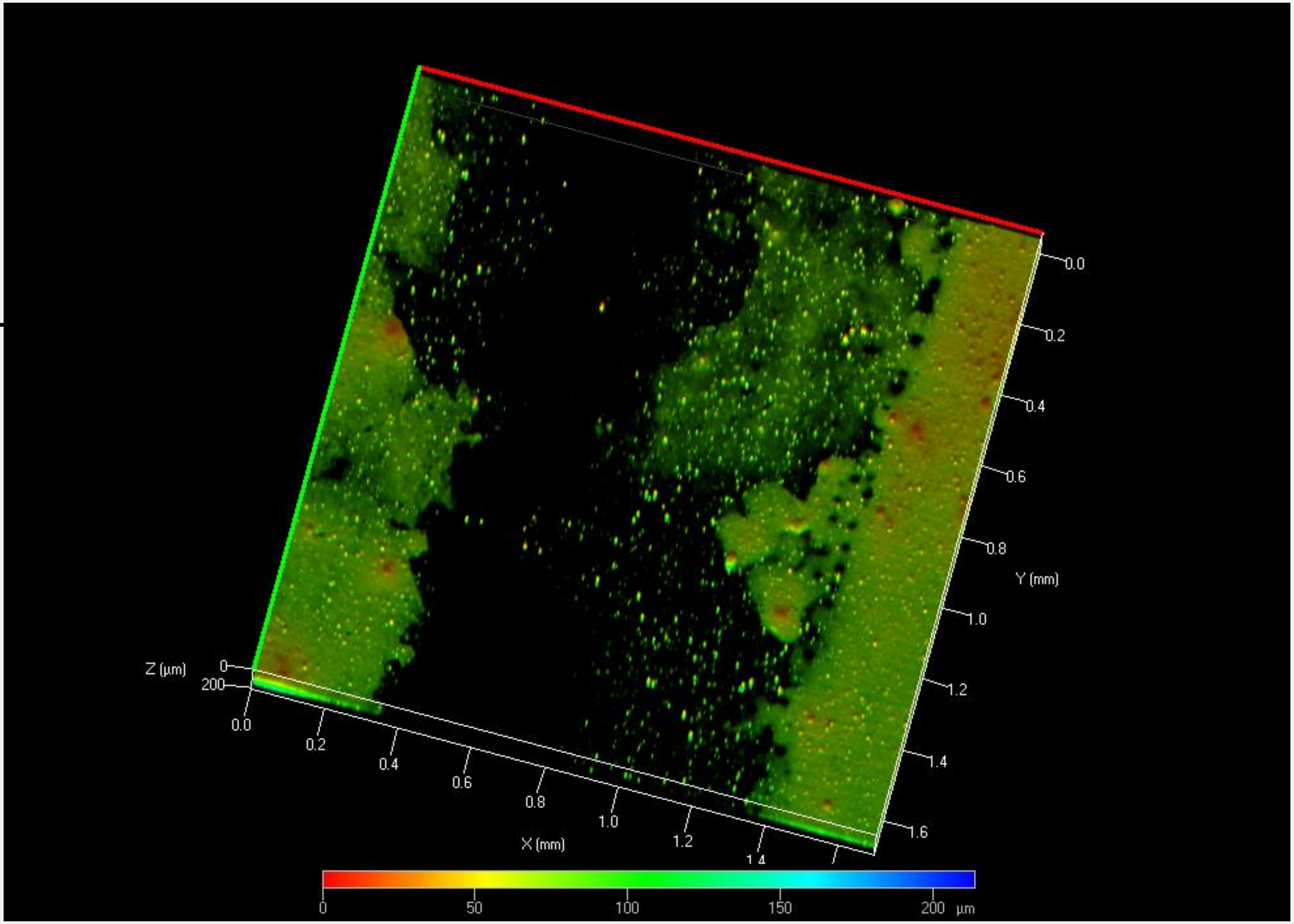




Laser Scanning Microscopy (LSM) confocal fluorescece microscopy image

Diamond Clad with Fluorescein

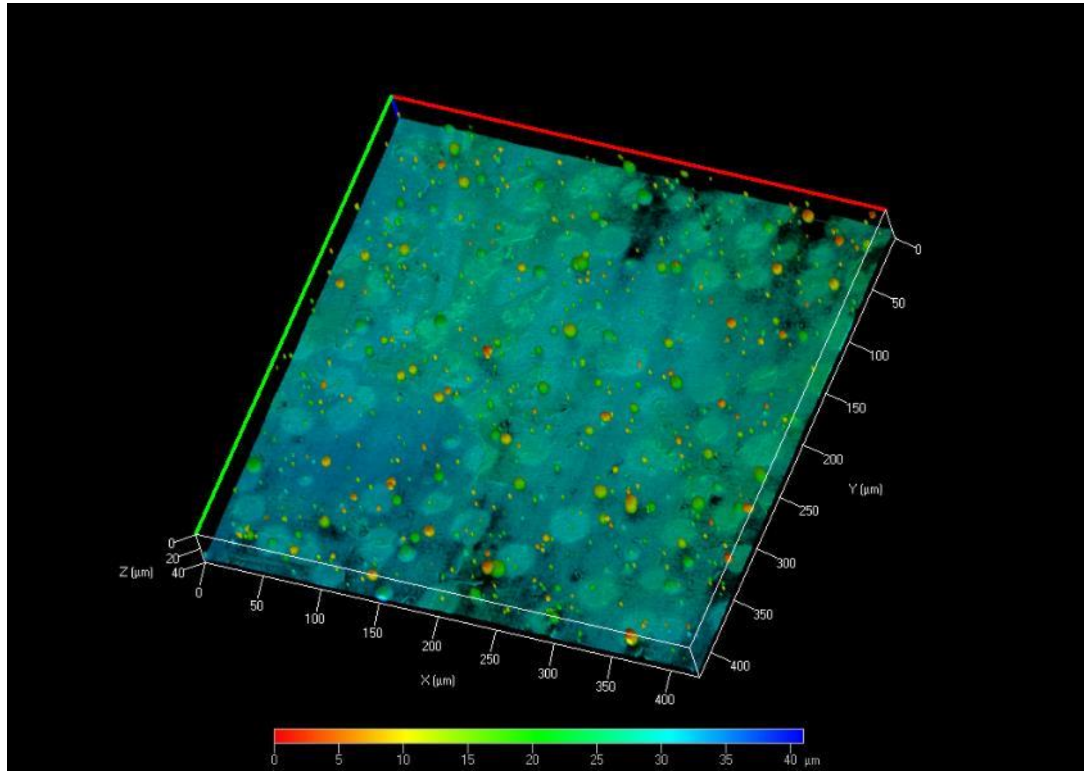


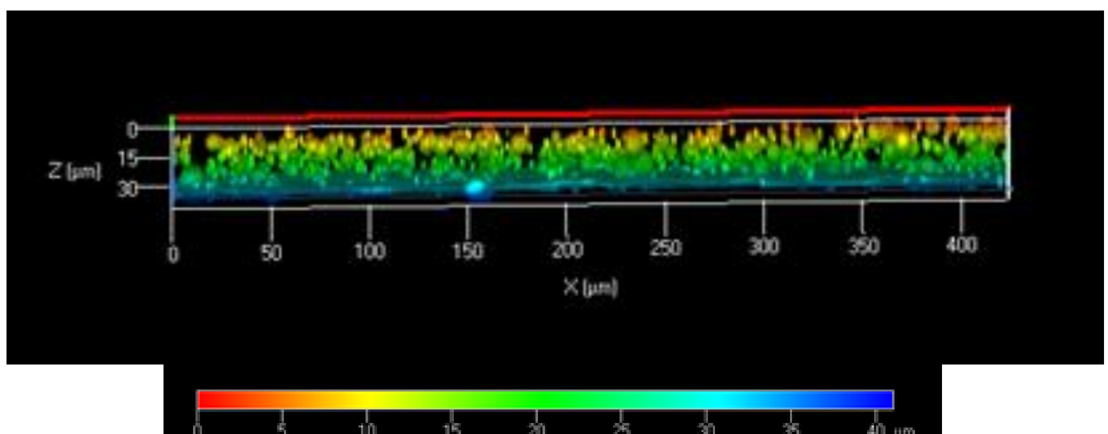


Diamond Clad
2nd Repeat
DC3

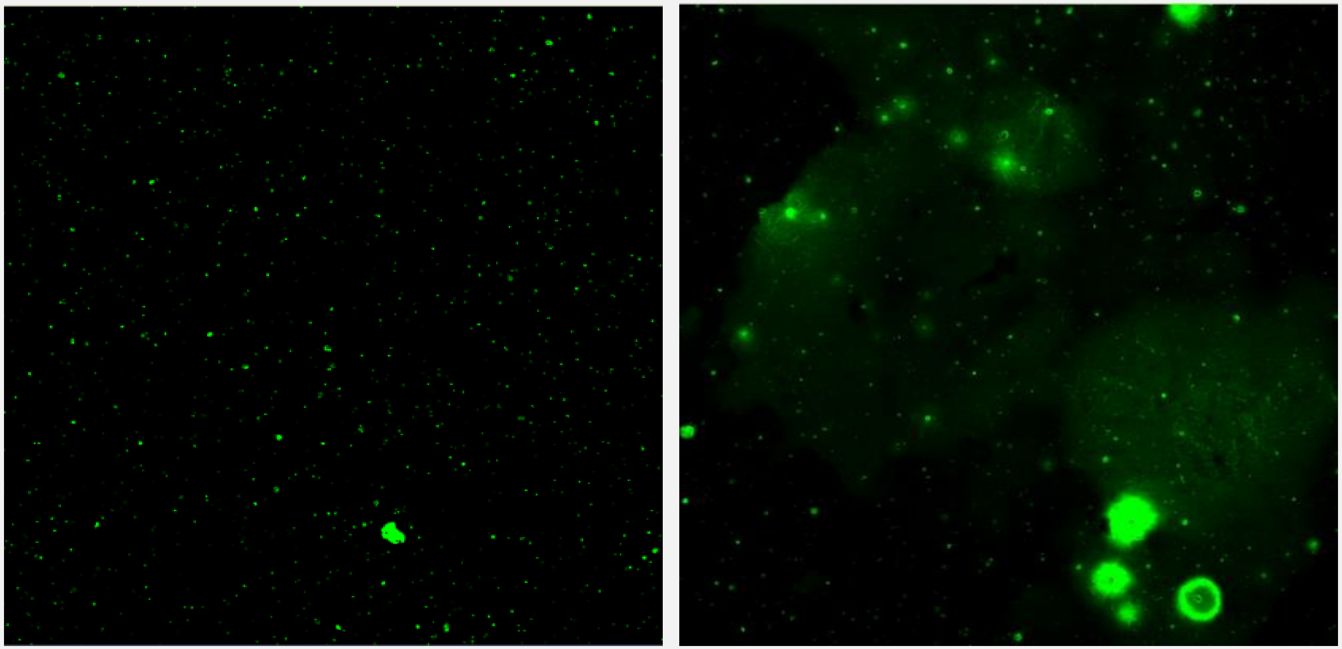
Florescent Corrosion Indicating Coating

- 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.





Corrosion Sensing through Fluorescence

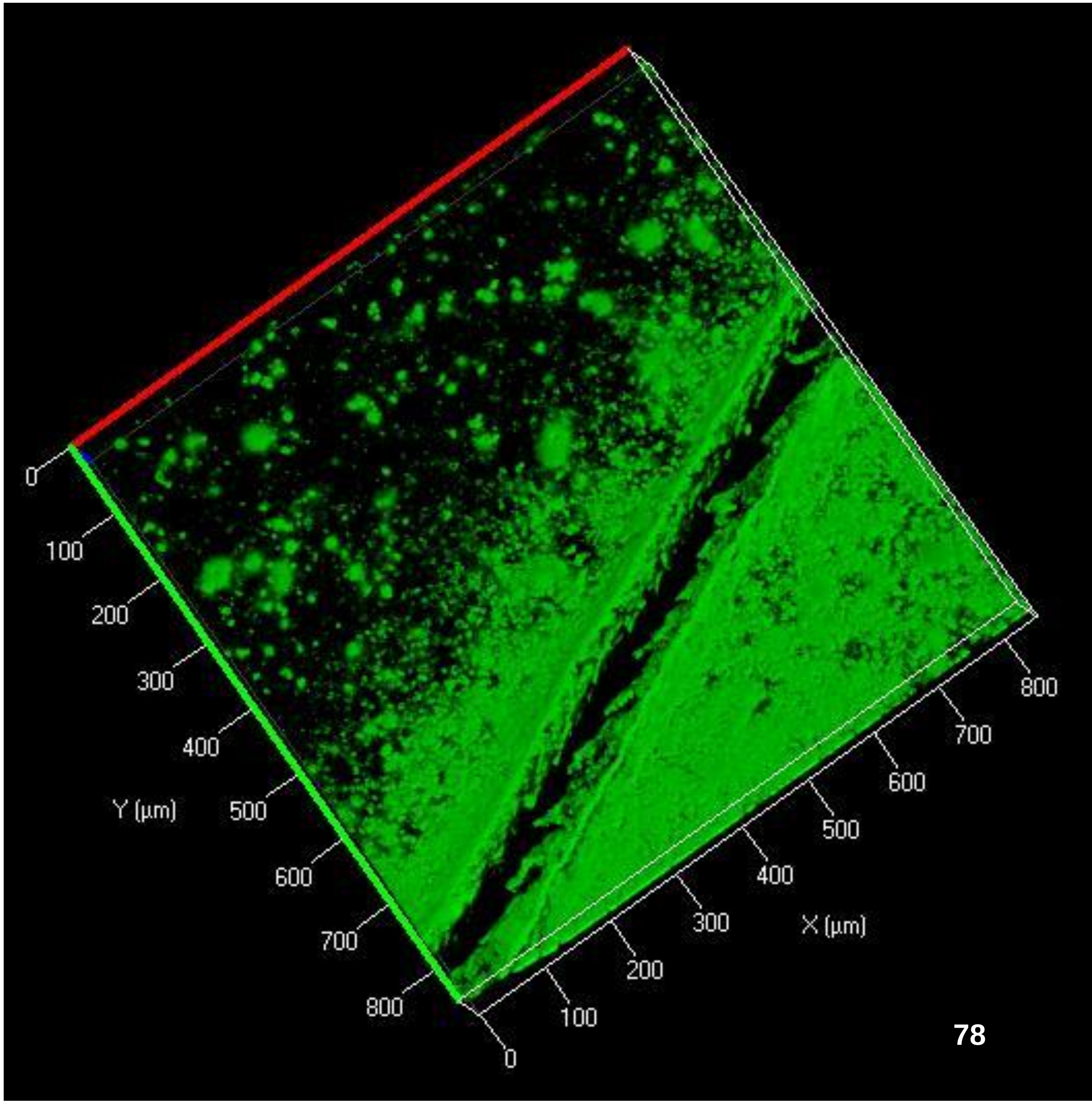


Confocal scanning laser microscopy 2D images of fluorescent corrosion sensing coating on steel. Unexposed panel (left) and near scribe after 15 hours of immersion in 5% NaCl (right).

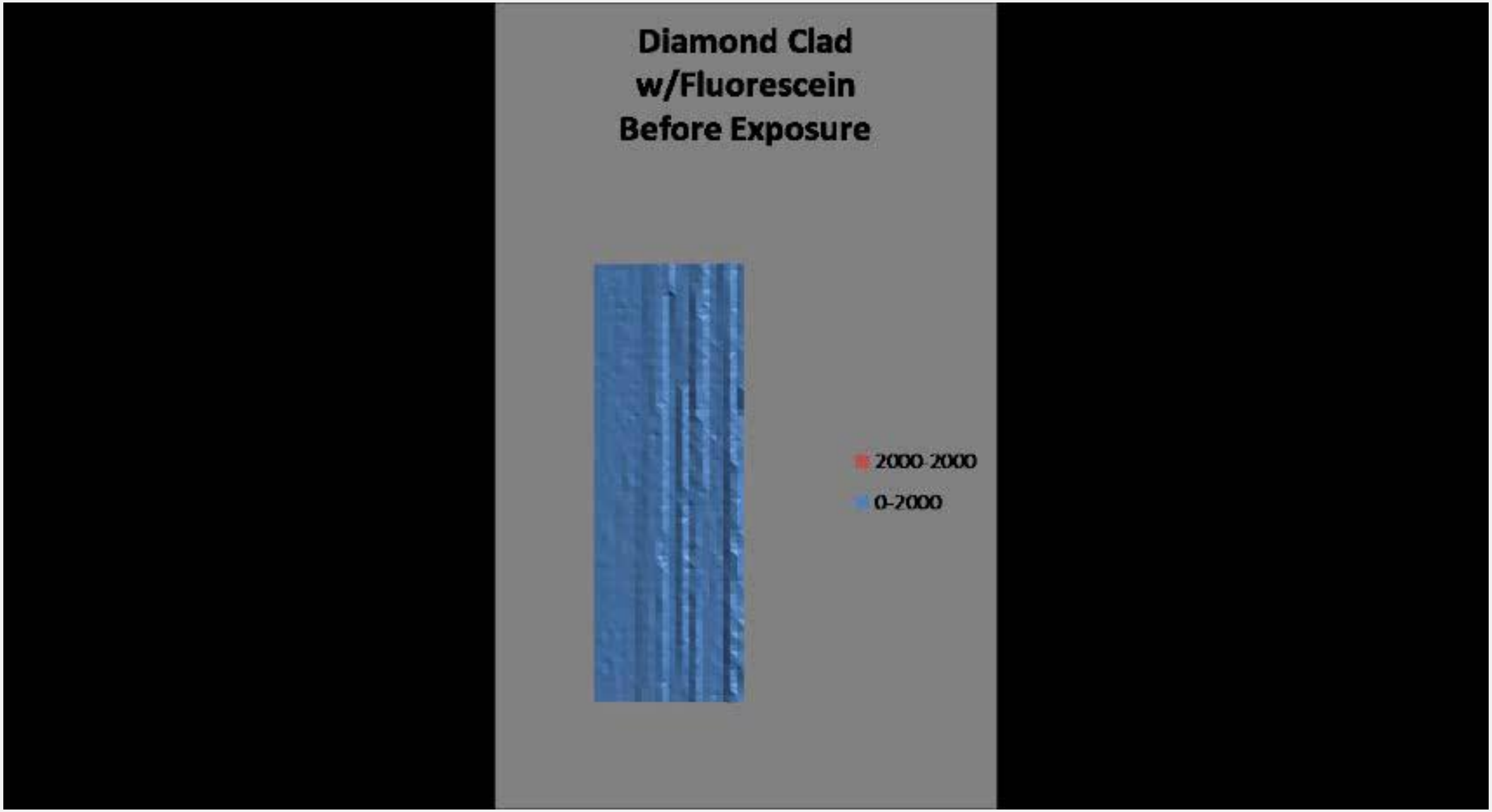
Deft 02GN084 + 0.25% Microparticles on AA2024-T3 at Scribe – 6 hrs. Immersion in 5% NaCl, 488 nm Confocal LSM

Master Gain 446

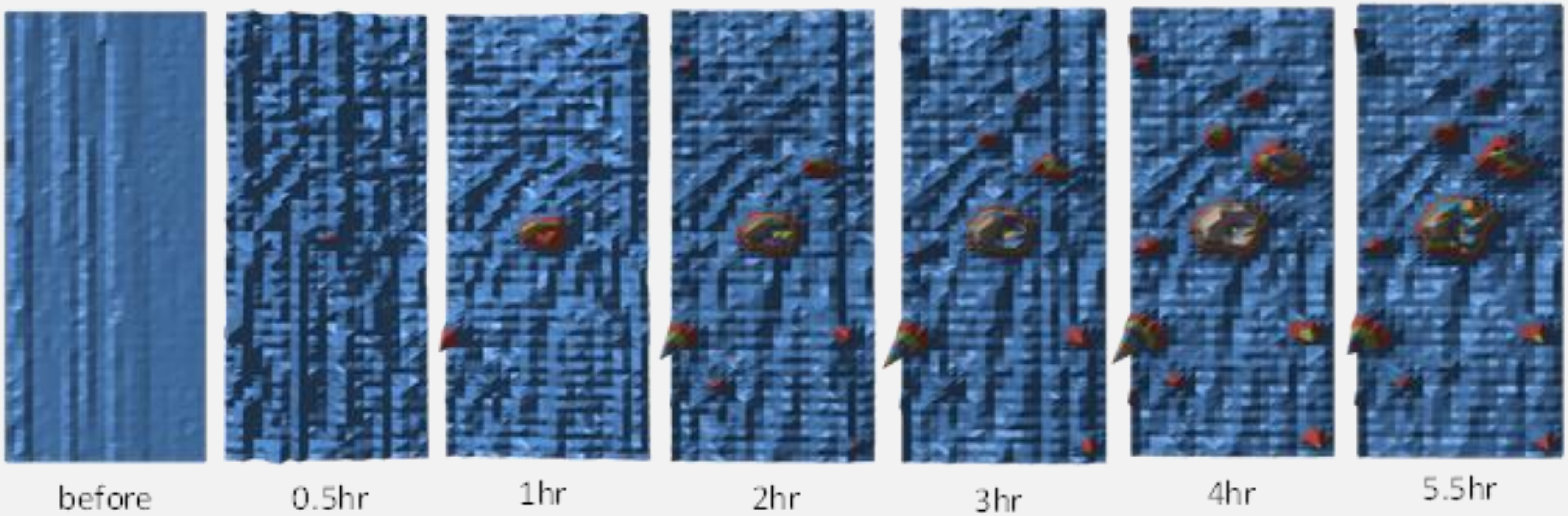
Scaling X	0.791 µm
Scaling Y	0.791 µm
Scaling Z	5.117 µm
Dimensions	x: 512, y: 512, z: 12, 8-bit
Image size	x: 404.06 µm, y: 404.06 µm, z: 56.29 µm
Scan Mode	stack
Zoom	2.1
Objective	EC Epiplan-Apochromat 10x/0.3 HD DIC M27
Pixel dwell	1.58 µs
Average	1
Master gain	446
Digital gain	1.24
Digital offset	0.00
Pinhole	45 µm
Filters	493 - 625
Beam splitters	MBS : MBS 488 MBS_InVis : Plate
Lasers	488 nm : 2.0 %



Florescent Corrosion Indicating Coating

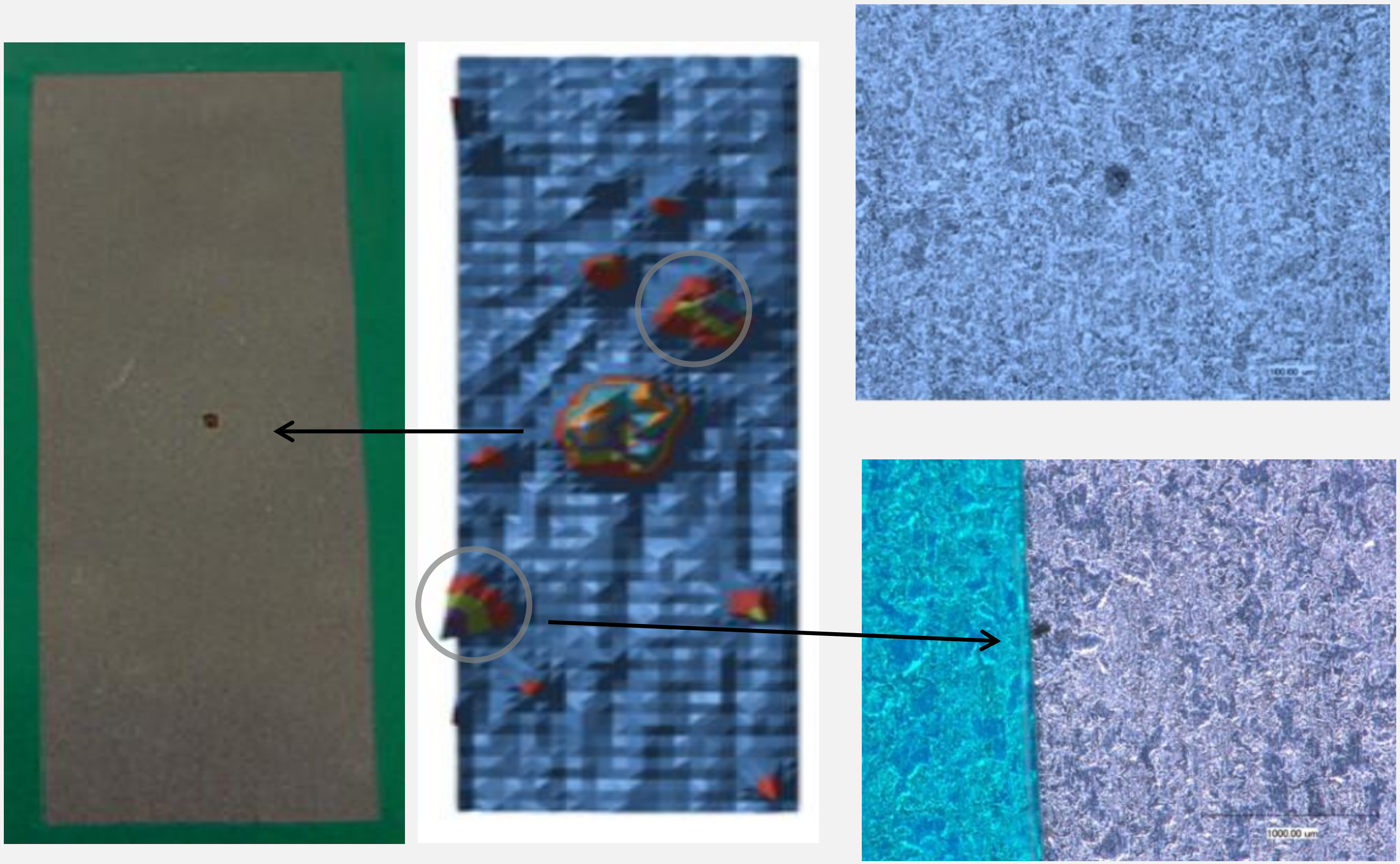


Fluorescent Corrosion Indication



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.

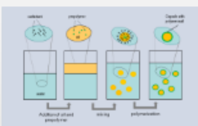
Fluorescence Corrosion Sensing



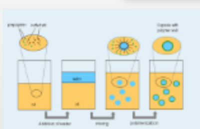
Fluorescent corrosion sensing coating for early corrosion detection. TECAN scan image after 5.5 hours salt water immersion testing is in the middle, while a picture and optical microscopy images (100X) of the panel after 15 hours of salt water immersion testing are shown on the left and right respectively.

Development and Optimization: Inhibition

Oil-core microcapsule developed using interfacial polymerization



Water-core microcapsule developed using interfacial polymerization

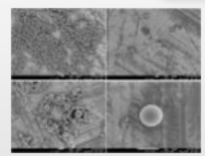


The pH sensitivity of the microcapsules was tested.

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.

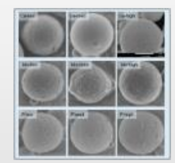
Oil-core microcapsules with organic and some inorganic inhibitors, such as $CeCl_3$, were synthesized.

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.

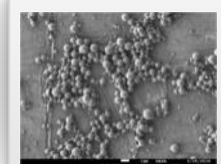


Oil-core microcapsules optimized to reduce the emulsion stability for easy microcapsule separation. This process yields a free -flowing powder.

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.



Corrosion Protection: Steel

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.

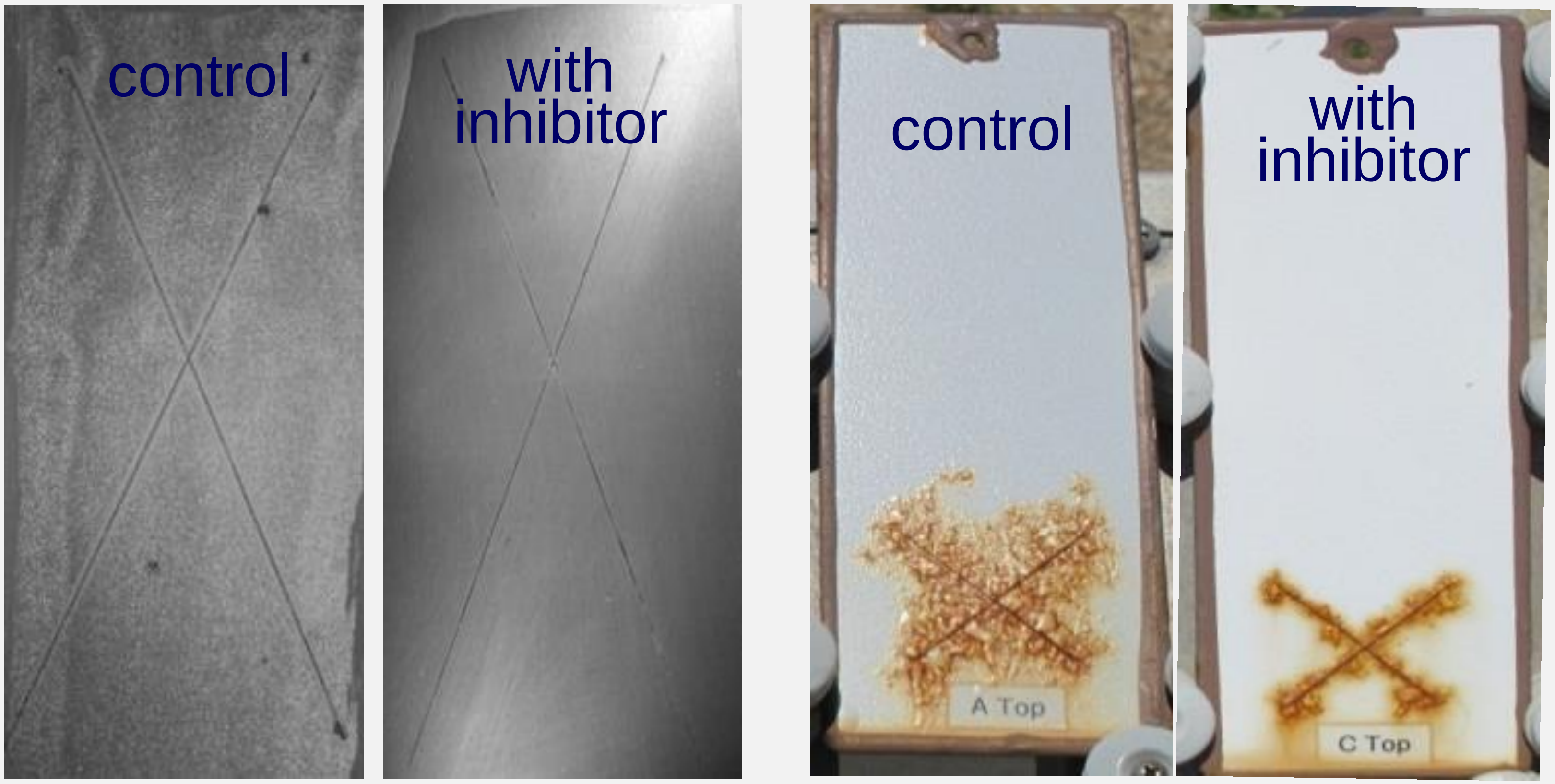
Next Generation: Waterborne

- 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

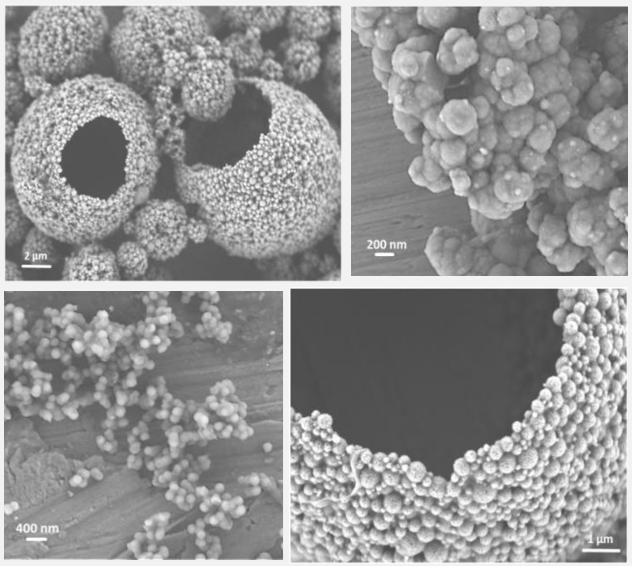
Controlled release inhibitors have been used in three areas of coating development for steel protection: improved inorganic zinc, new Cr(VI) free organic coating, and effective solvent-free coatings.

Corrosion Protection: Steel



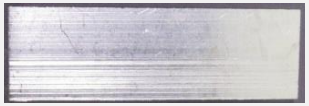
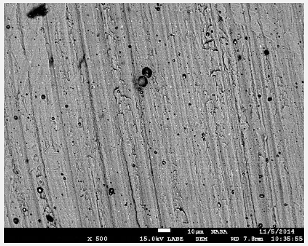
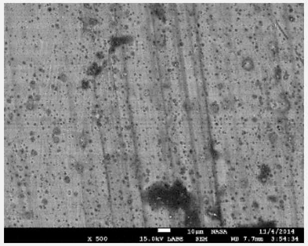
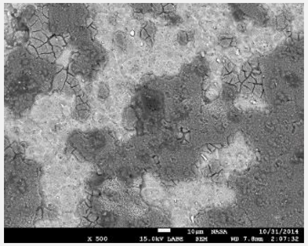
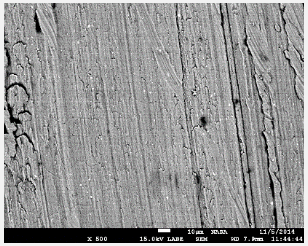
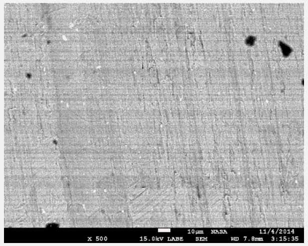
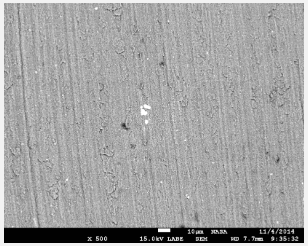
Organic coating formulations being developed with industry partners for steel protection. Steel panels after accelerated cyclic corrosion testing (left), and coated steel panels being tested at beachside atmospheric exposure test site.

Corrosion Protection: Steel



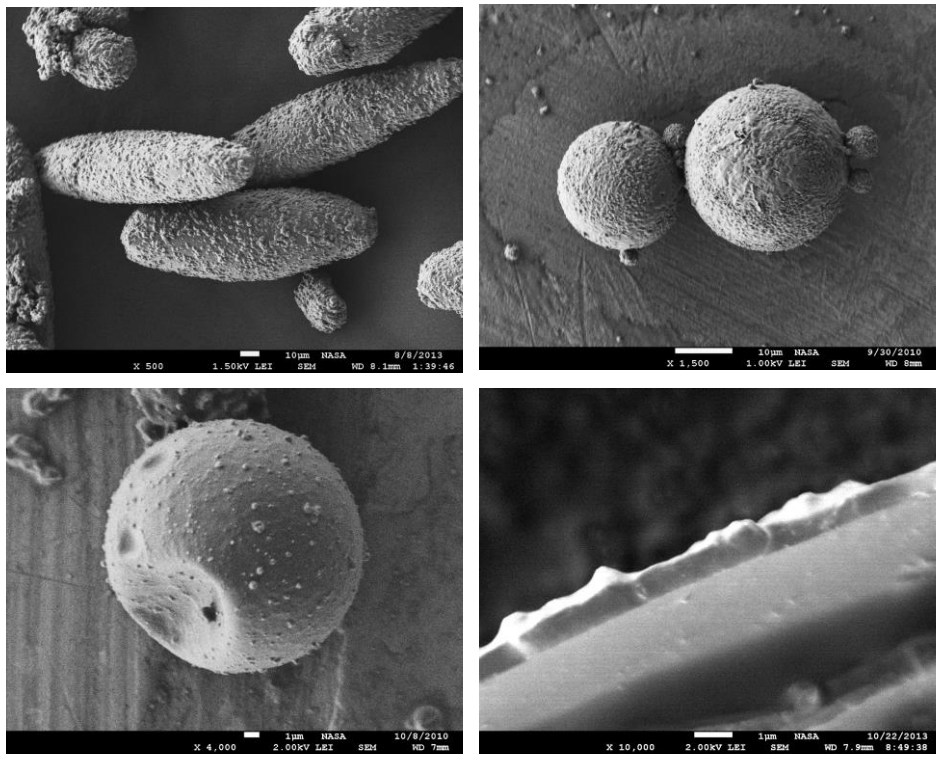
New inorganic delivery systems being developed (left) shows great promise for improving corrosion protection of waterborne system (right).

Corrosion Protection: Aluminum Alloys

Method	System	Al 7XXX (0.3% Cu)	Al7XXX (0.6% Cu)	Al7XXX (0.9% Cu)
Visual	Without Inhibitor			
	With Inhibitor			
SEM (LABE)	without inhibitor			
	With inhibitor			

- 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.

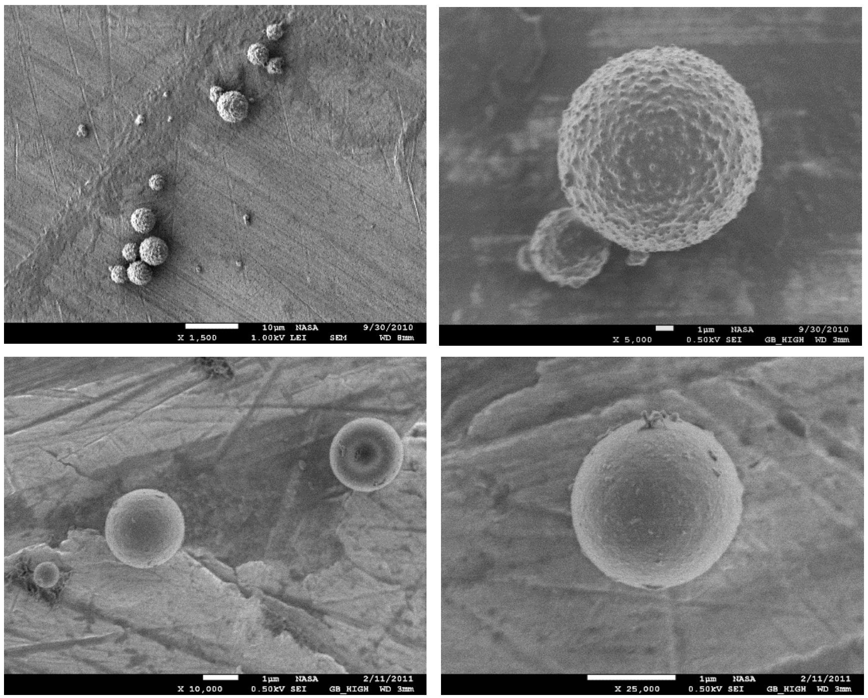
Self-Healing



Several self-healing coating systems have been developed:

- One and two capsule systems
- Self-sealing system using flowable polymers
- Elongated microcapsules

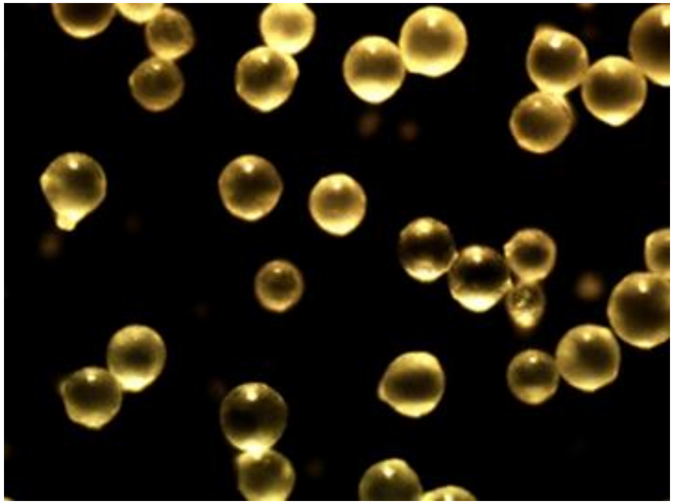
Self-Healing Coatings (2 Capsule System)



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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NASA's Corrosion Technology Laboratory Team

B.P. Pearman, M.R. Kolody, M.N. Johnsey, J.W. Buhrow, L. Fitzpatrick, J. Zhang, L.M. Calle, T.A. Back, S.T. Jolley, E.L. Montgomery, J.P. Curran, and W. Li