Recent Progress in the Development of a Multifunctional Smart Coating for Autonomous Corrosion Detection and Protection

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Introduction

Corrosion Protective Coatings

- Barrier (passive)
- Barrier plus 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)

Electrochemical Nature of Corrosion

Overall Reaction:

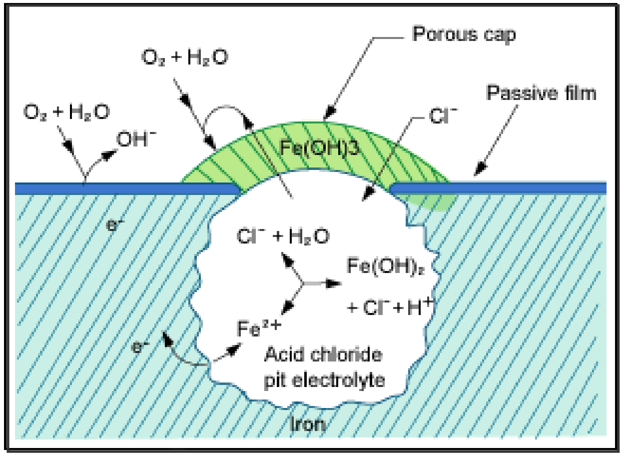
$$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

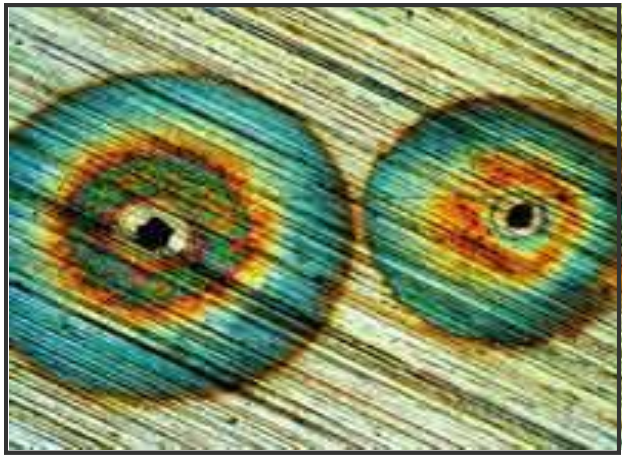
Anodic:

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

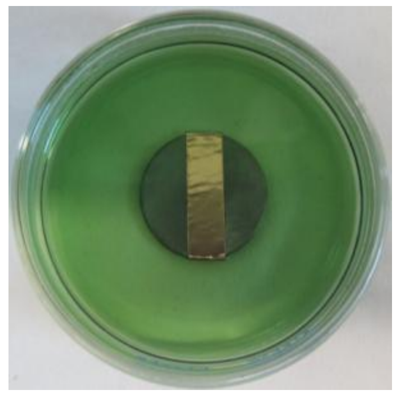
Cathodic:

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

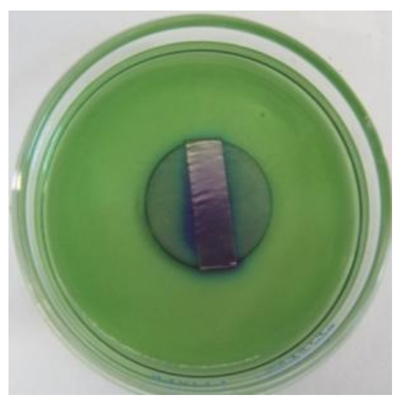




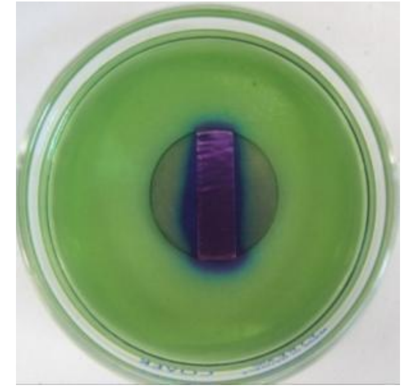
pH change and Corrosion



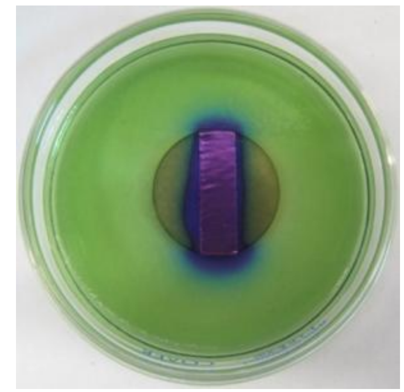
Elapsed Time: 0 hours



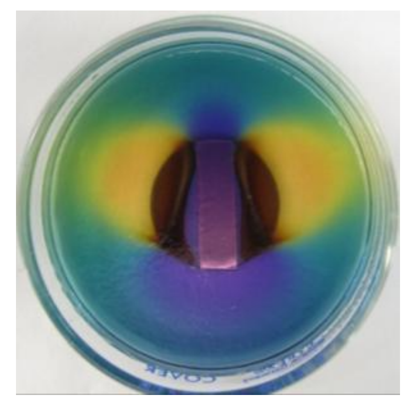
0.5 hours



1.5 hours

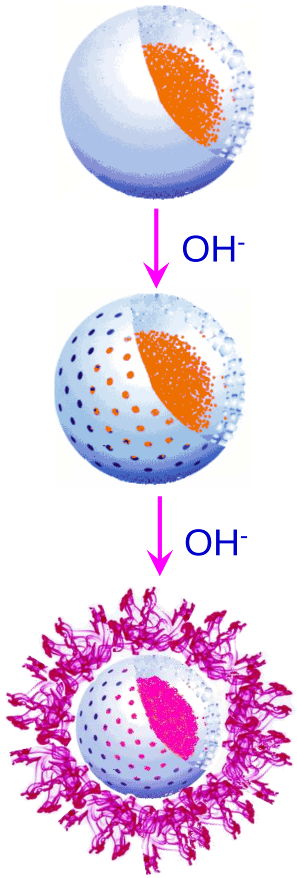


4.5 hours



3 days

pH Sensitive Microcapsule

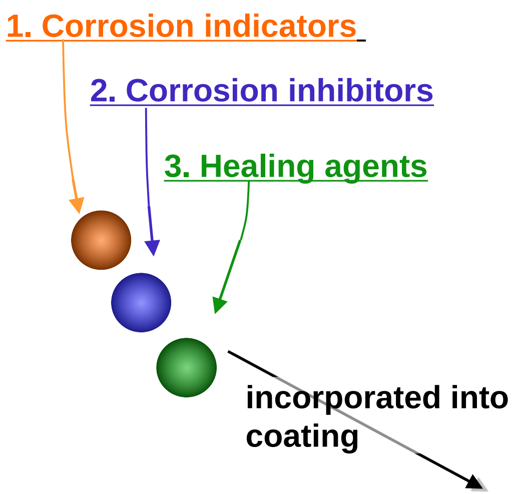


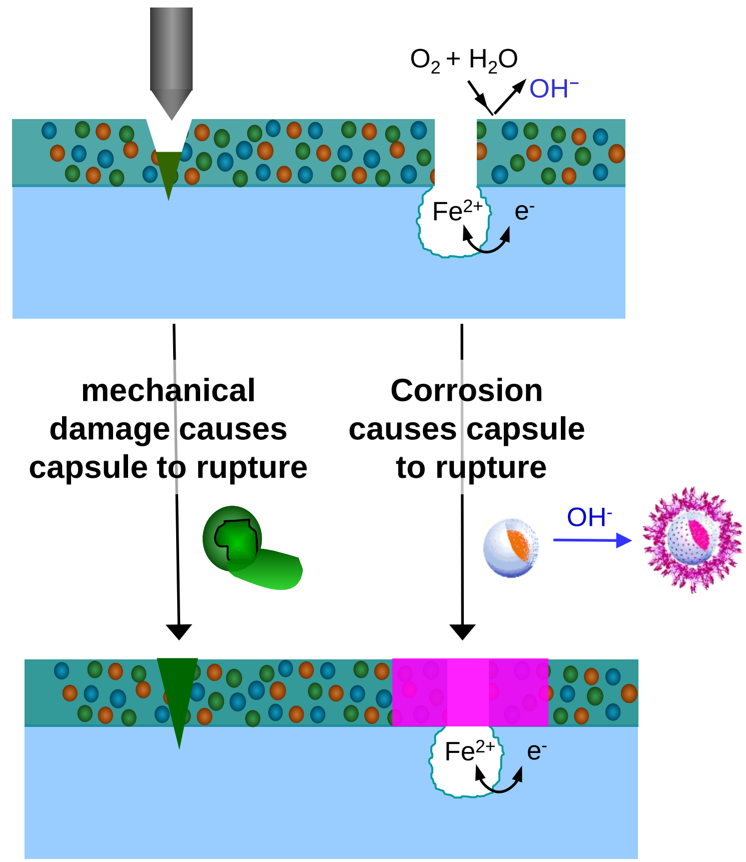
Microcapsule containing pH indicator (inhibitor, self healing agents)

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

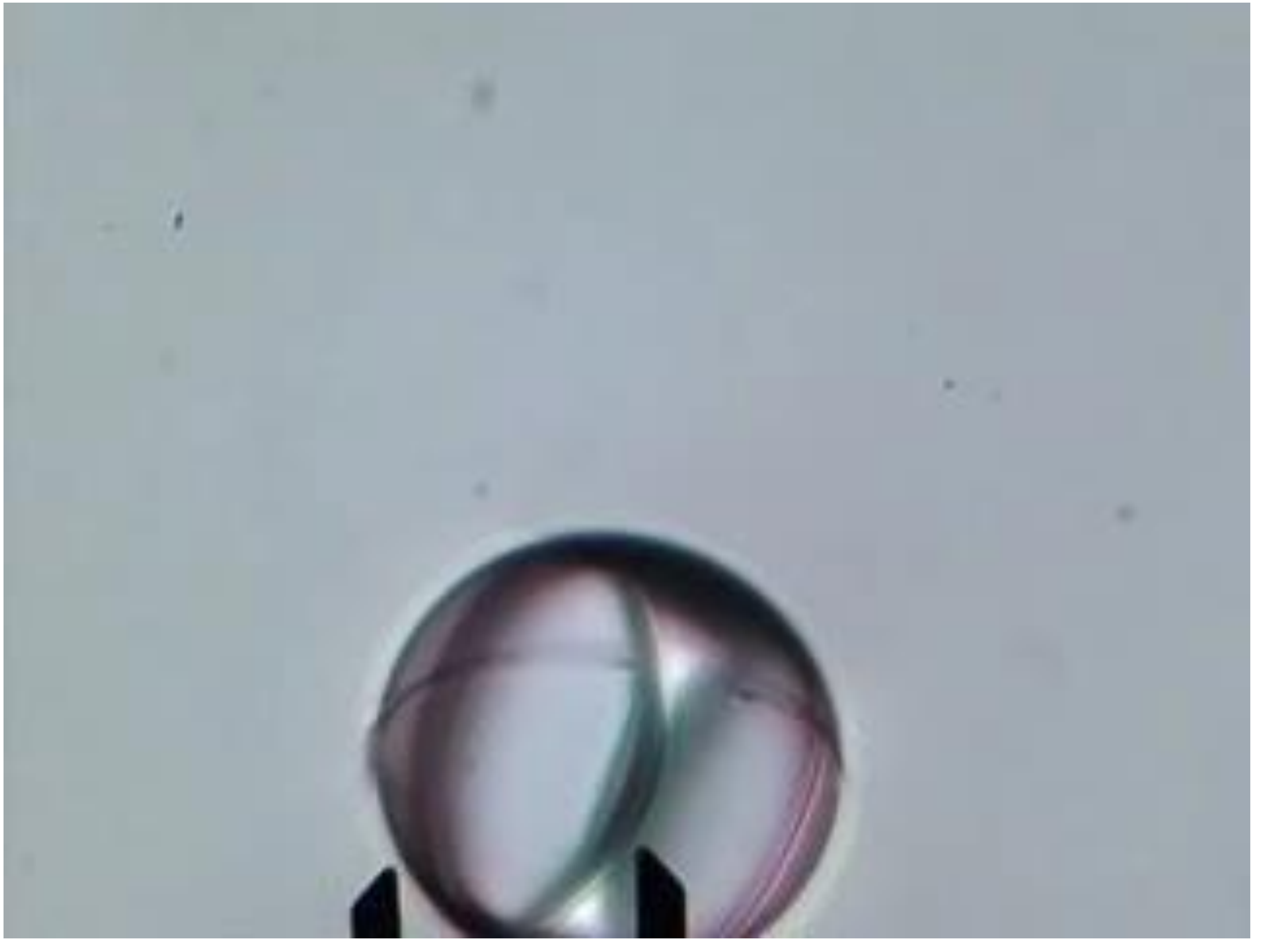




Ruptured Microcapsule:

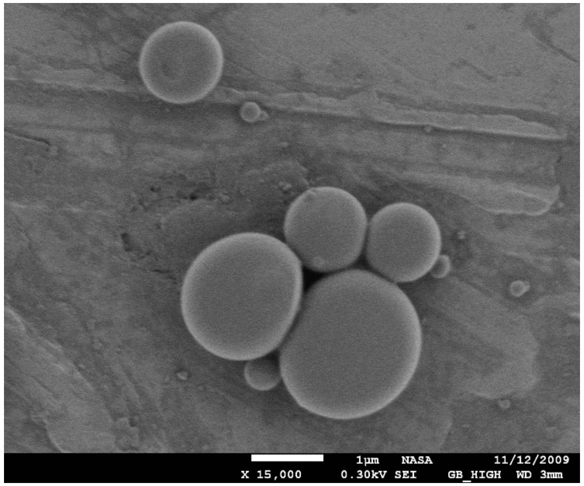
- indicates corrosion
- protects metal from corrosion
- repairs damaged area

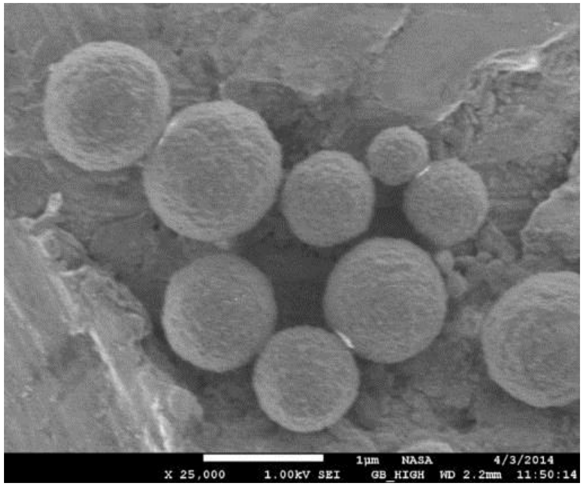
Microcapsule Response to pH Increase

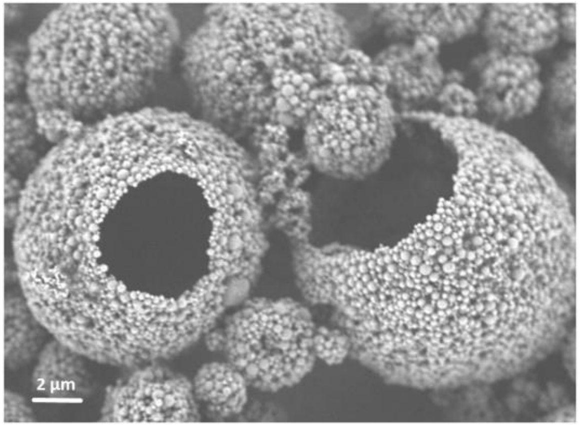


Encapsulation

Concept vs Reality

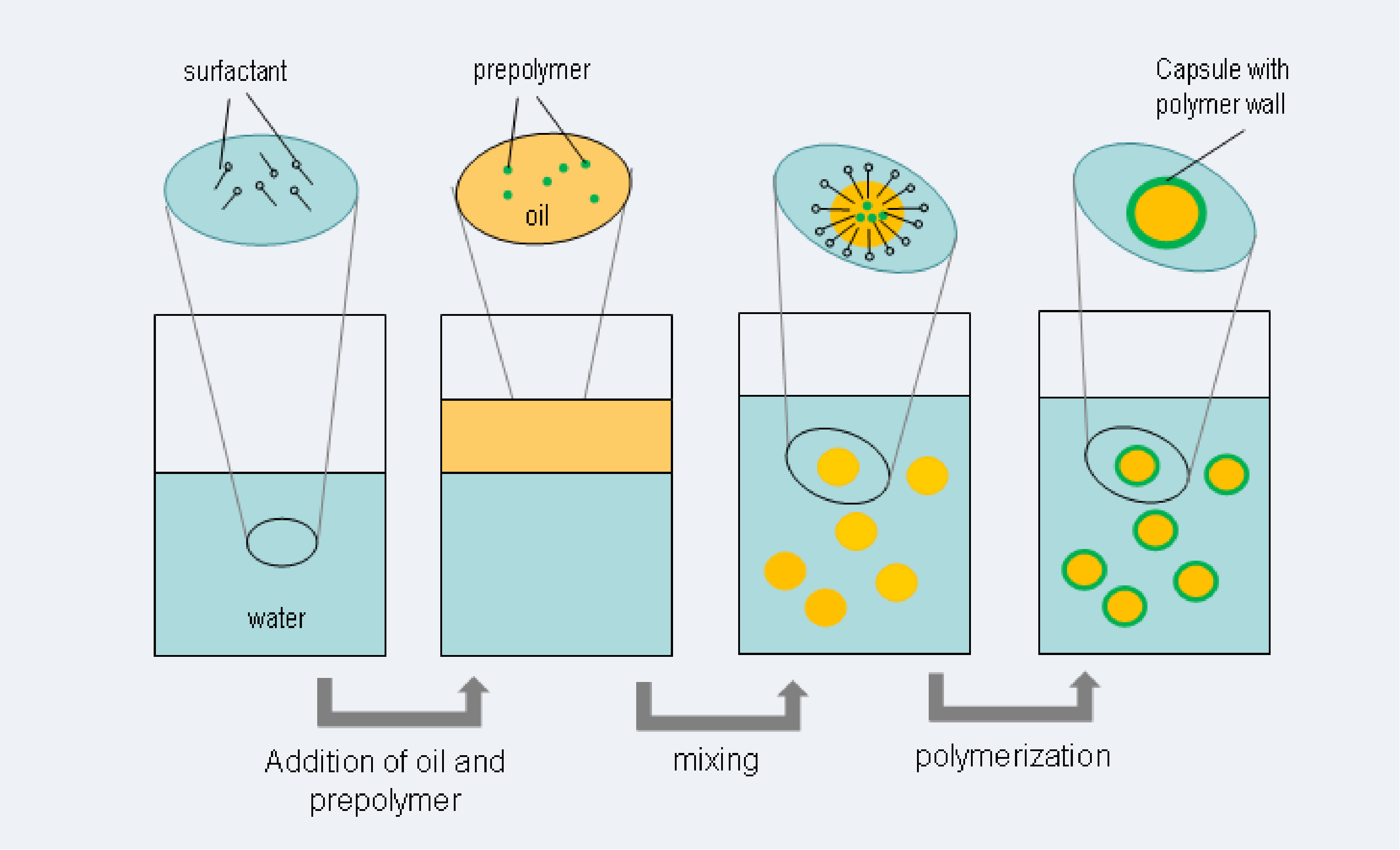






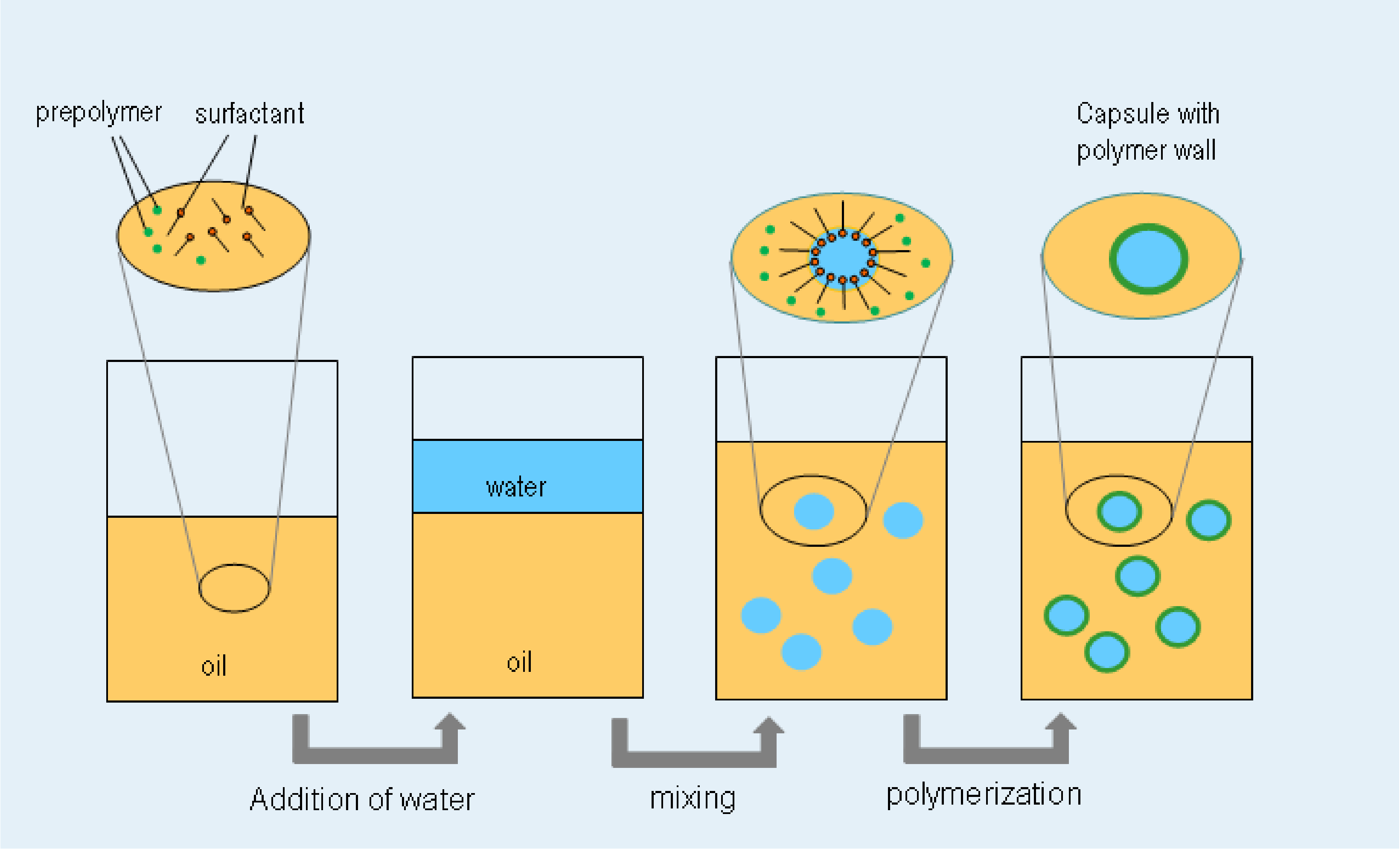
- Initial concept: a simple pH sensitive microcapsule
- Reality: wide range of active ingredients and various coating systems
- Result: a portfolio of different control delivery systems to fit the needs
- pH sensitive microcapsules, pH sensitive microparticles, and inorganic microcontainers.
- pigment-graded materials with good coating compatibility in free flowing powder forms.

Hydrophobic Core Microcapsules



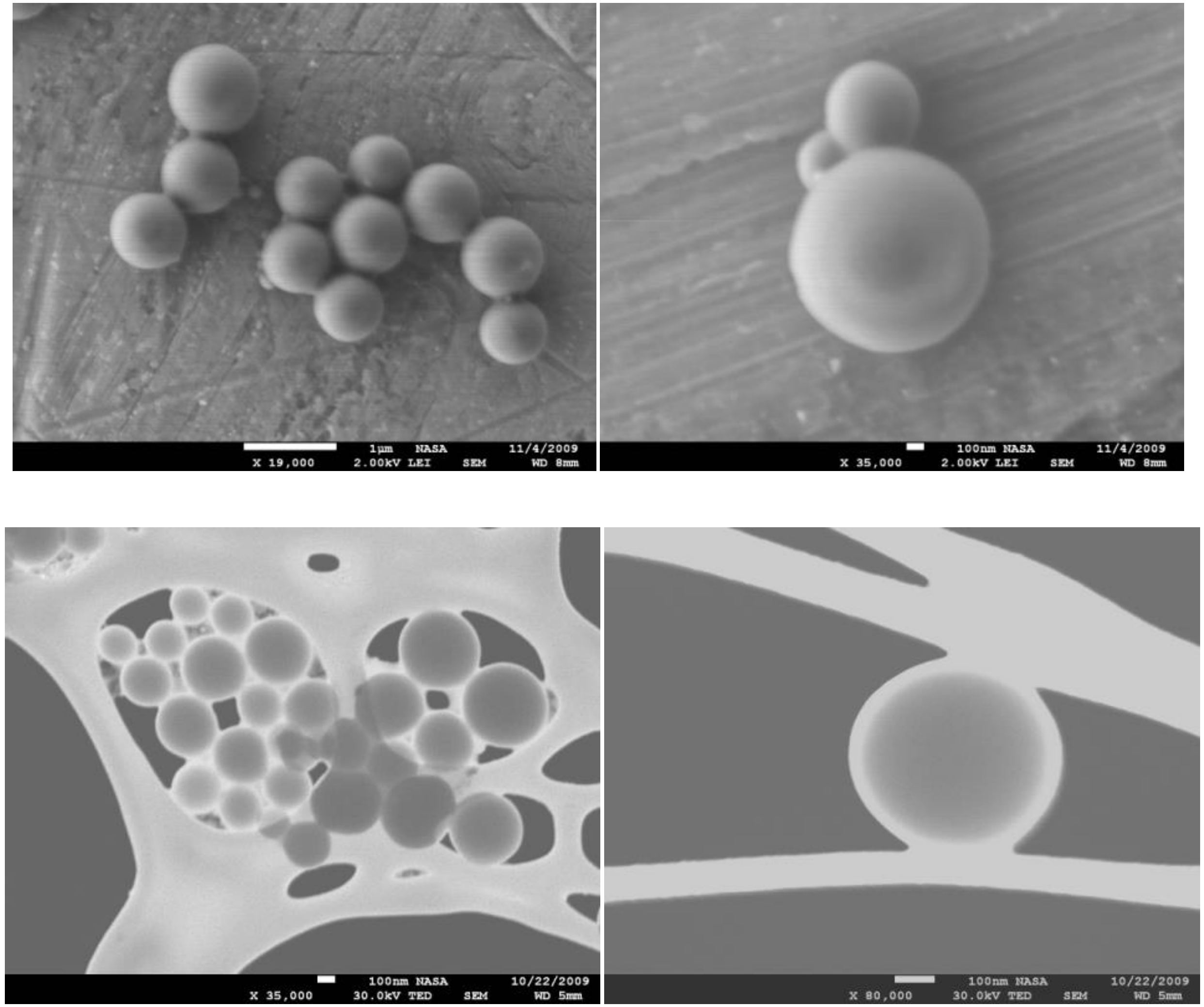
Interfacial polymerization of oil-in-water microemulsion procedure for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.

Hydrophilic Core Microcapsules



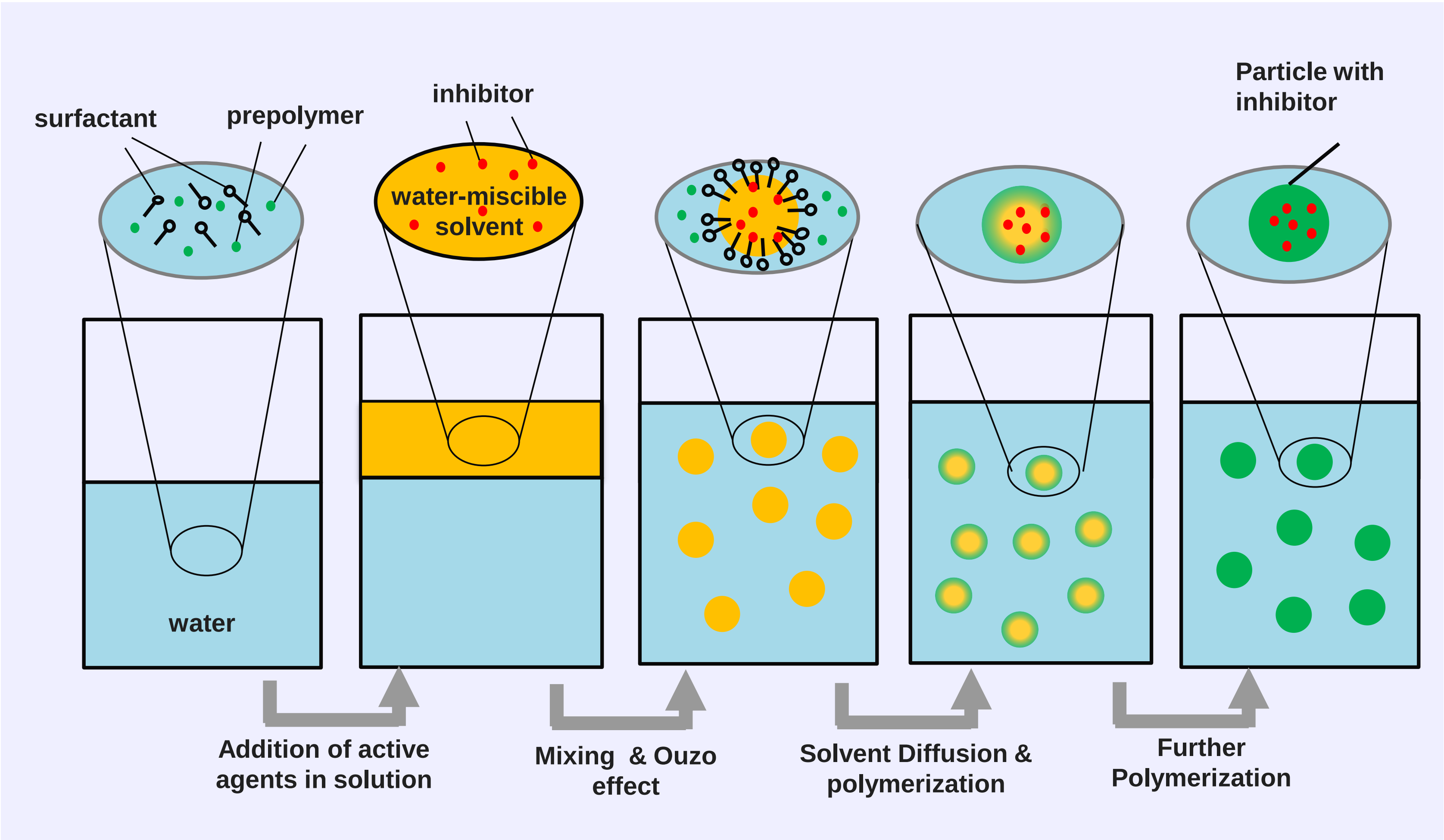
Interfacial polymerization of water in oil microemulsion process for hydrophilic-core microcapsules. Oil is shown in yellow and water in blue.

Hydrophilic-core Microcapsules

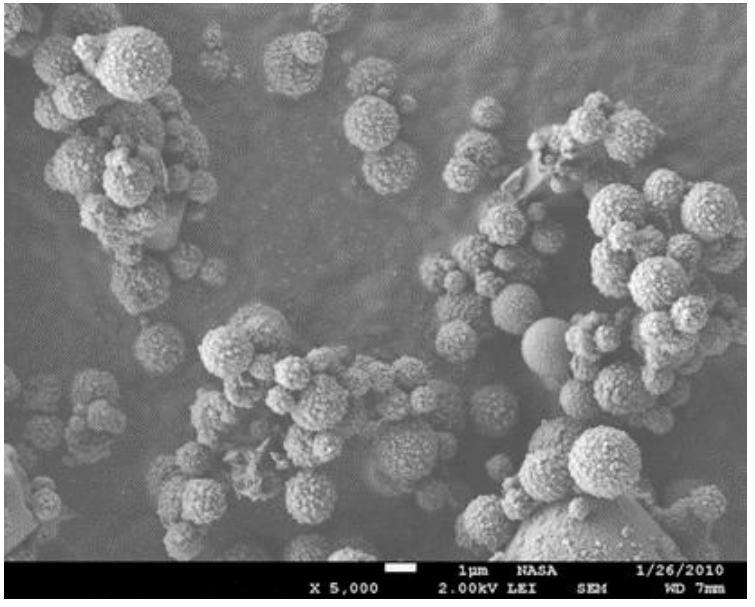


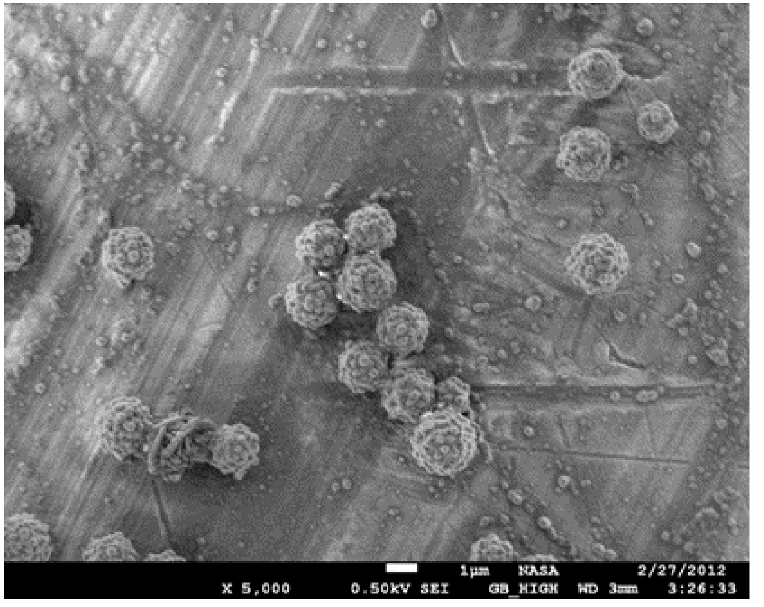
SEM images of hydrophilic-core microcapsules

Microparticle Formation



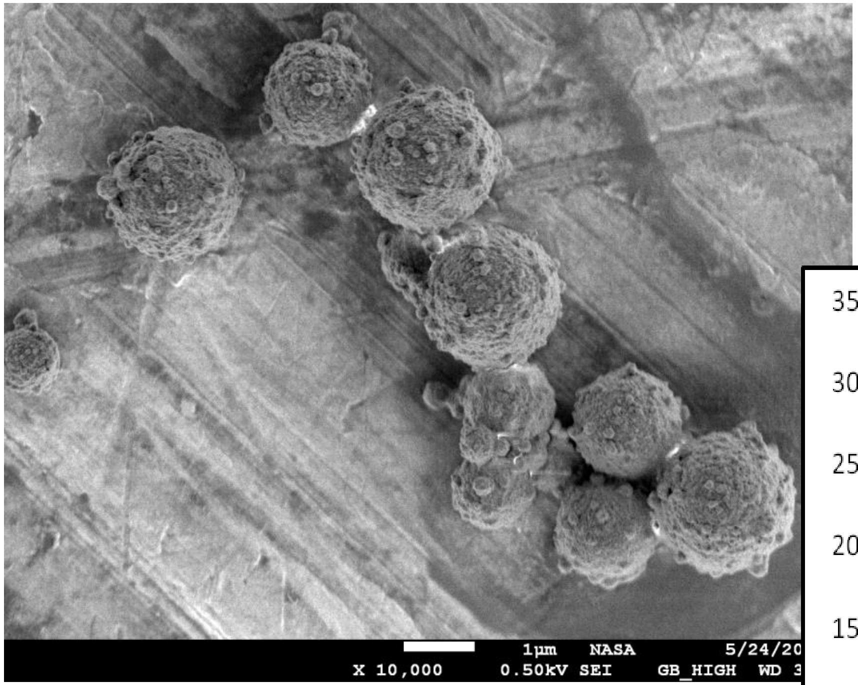
Corrosion Indicating Microparticles

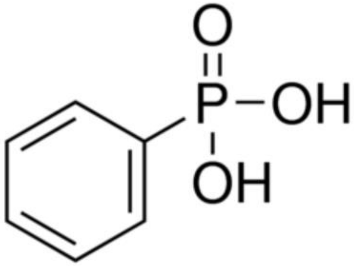


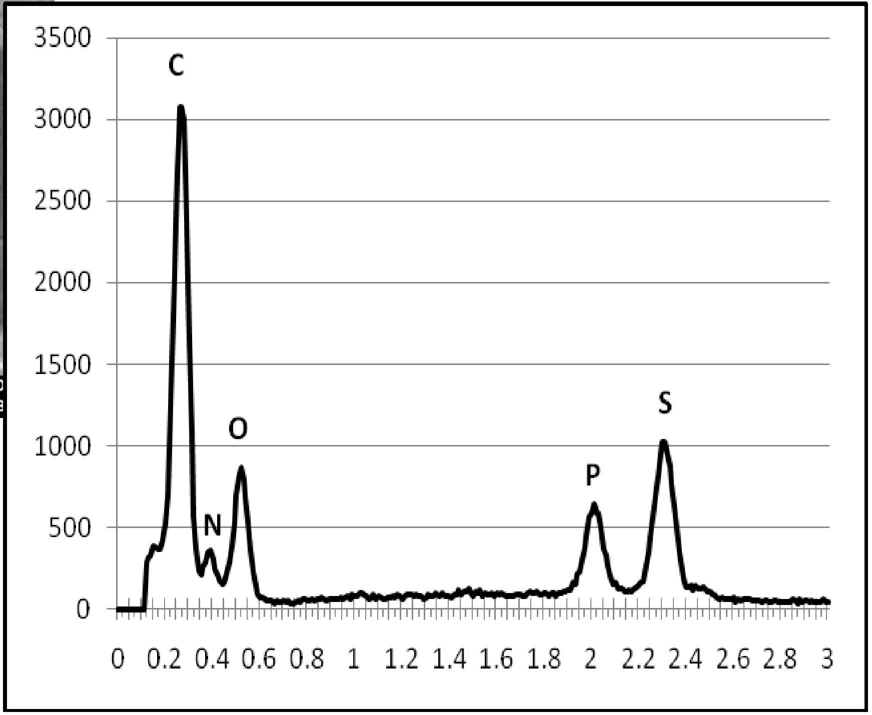


SEM image of microparticles with color changing indicator (left) and with fluorescent indicator (right)

Microparticles with Inhibitors

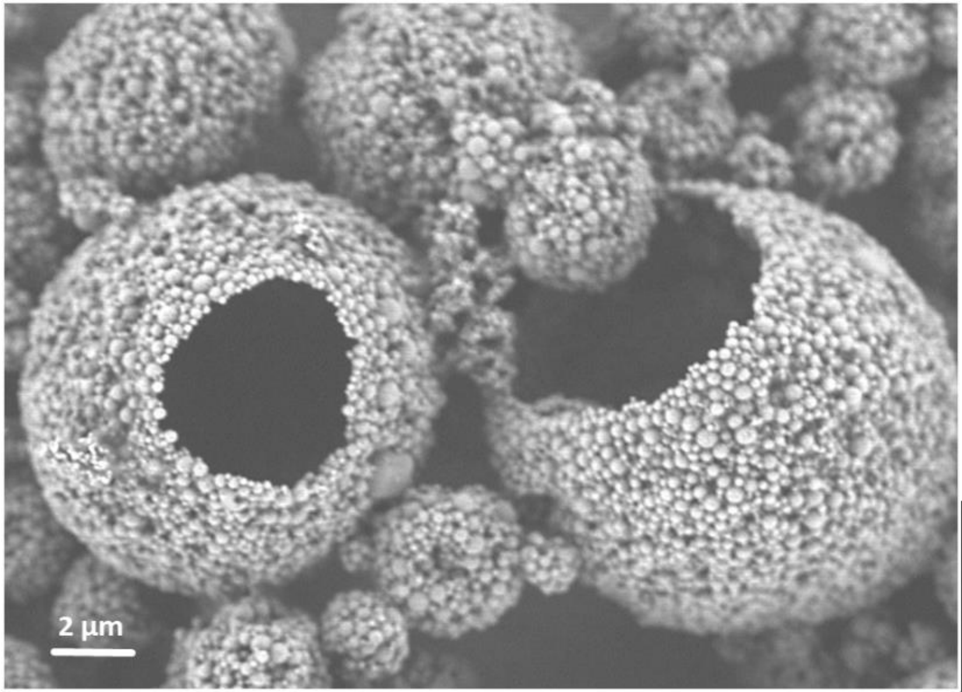


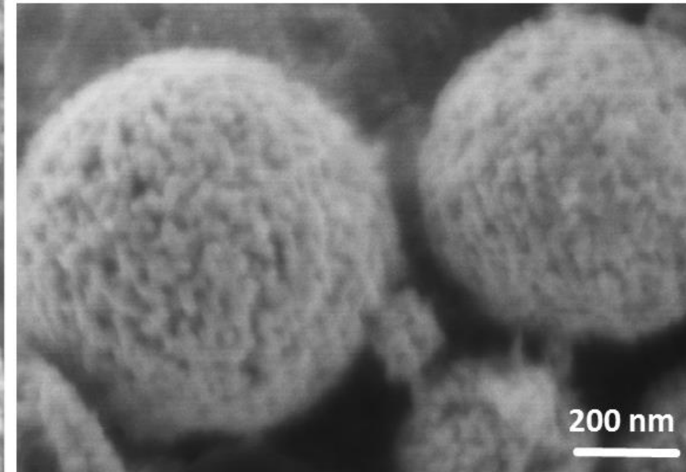


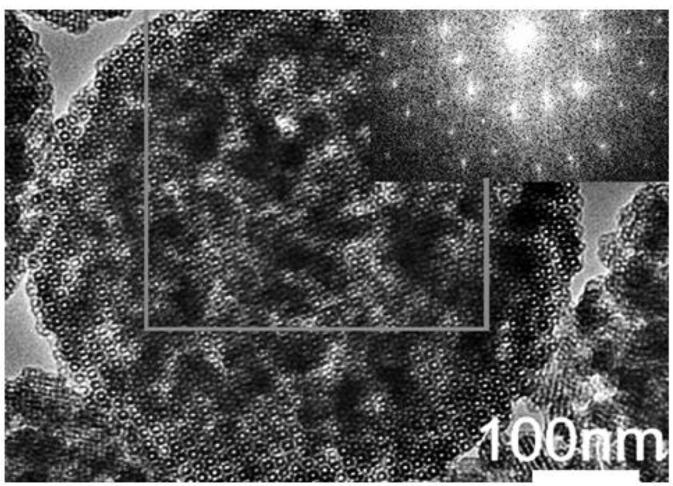


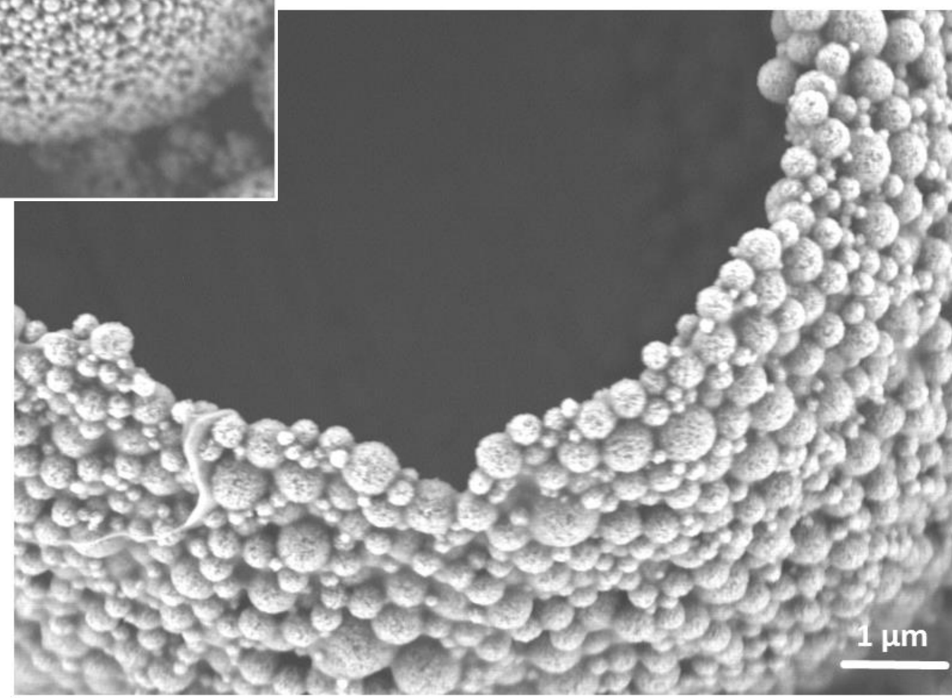
SEM and EDS of microparticles with corrosion inhibitor phenylphosphonic acid (PPA)

Inorganic Carriers

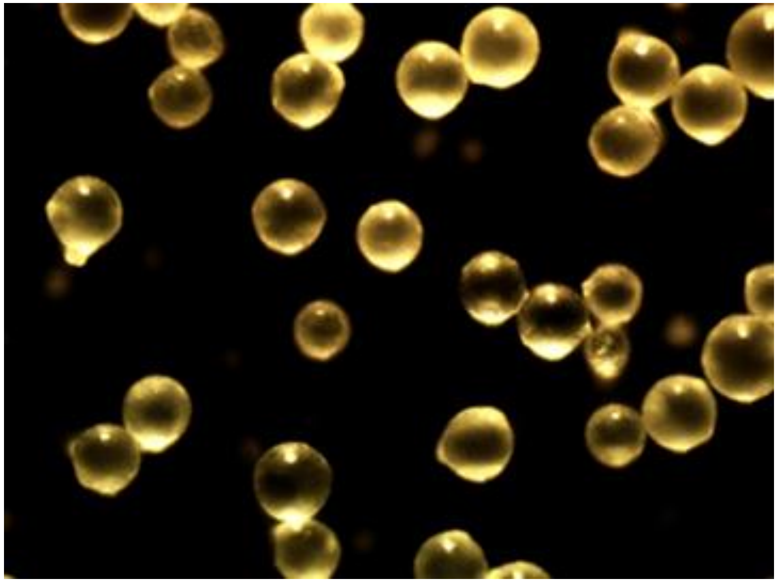


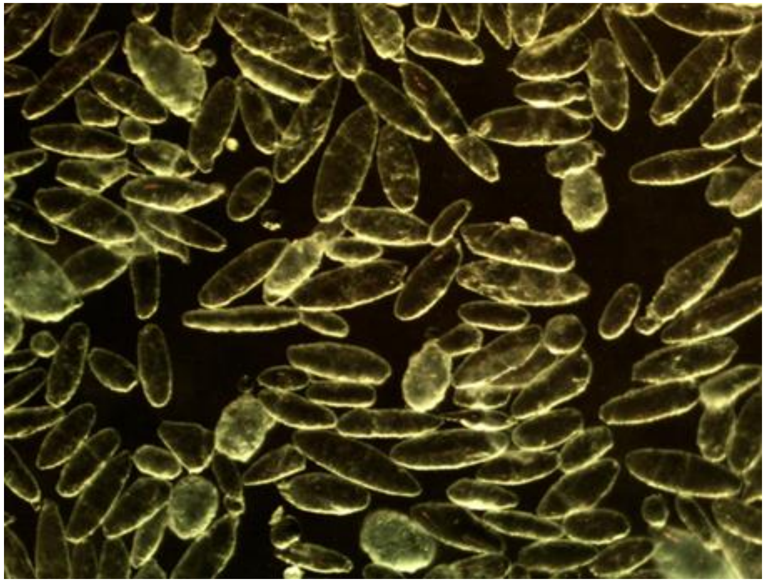






Microcapsules for Self-healing Coatings



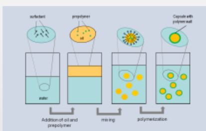


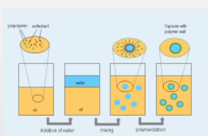
Optical micrographs of spherical and elongated microcapsules for self-healing of mechanical scratches

Corrosion Indication

Development and Optimization: Indication

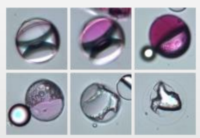
Oil core microcapsule formulation was developed by interfacial polymerization process.

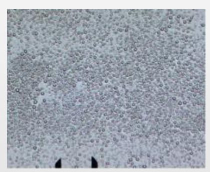




Water core microcapsule formulation was developed by interfacial polymerization process.

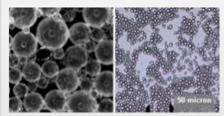
The pH sensitivity of the microcapsules was tested.

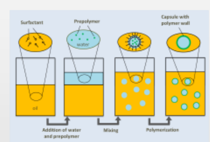




Water core microcapsule formulation was modified to reduce microcapsule cluster formation. The new formulation also uses environmentally friendly reagents.

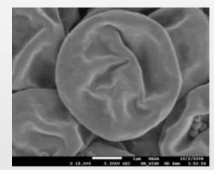
Oil core microcapsule formulation was modified to reduce the capsule size.

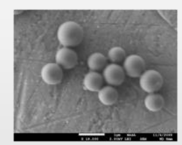




Water core microcapsule formulation was optimized by using a water soluble wall forming prepolymer. The synthesis time was also reduced, and the microcapsule wall properties were improved.

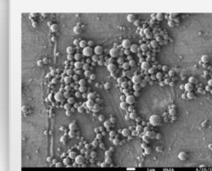
Oil core microcapsule containing corrosion indicator phph (2wt%) was synthesized.





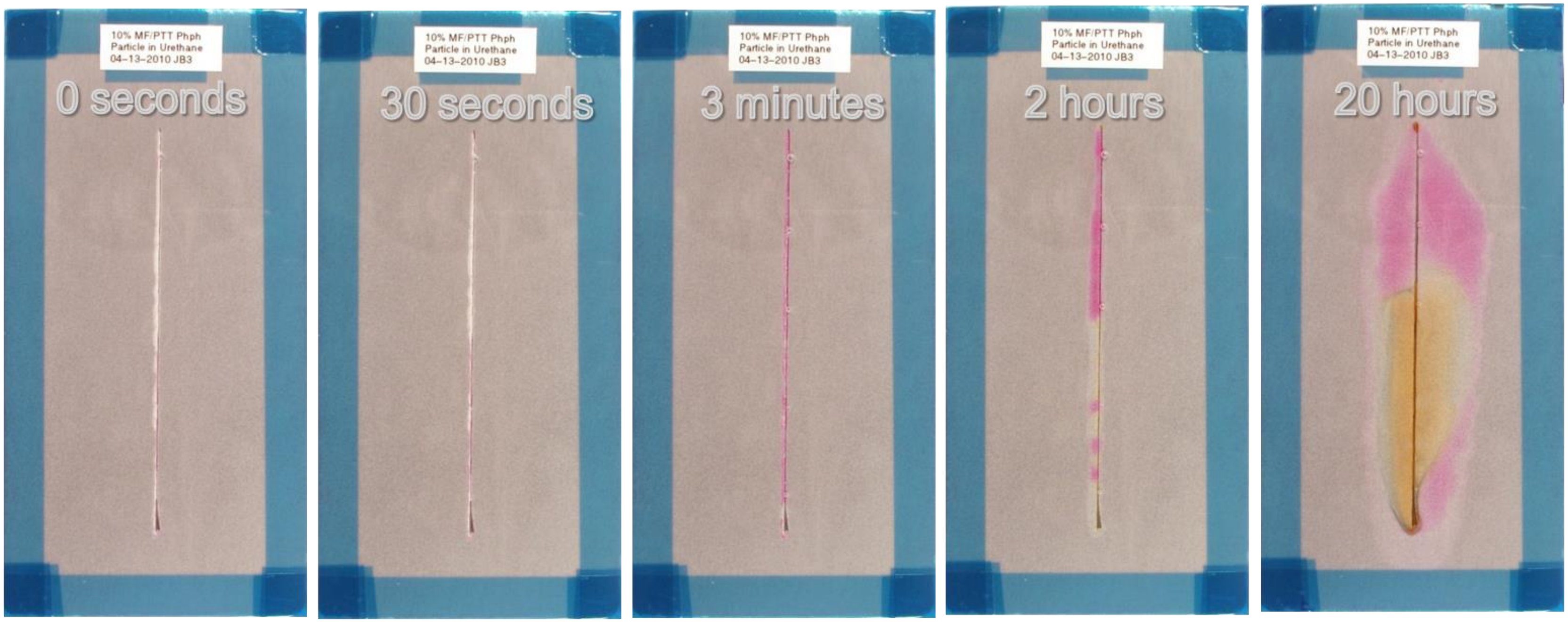
Water core microcapsules containing corrosion indicator phph (5wt%) were synthesized.

Oil core microcapsule formulation was modified to yield free flowing powder. Corrosion indicator microcapsules were prepared as free flowing powder.



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

Early Indication of Corrosion



Salt immersion test results of panels coated with a clear polyurethane coating loaded with 10% indicator microparticles in their core. The coating detects corrosion in the scribed area at a very early stage (30 seconds) before the appearance of rust is visible (2 hours).

Early Indication 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

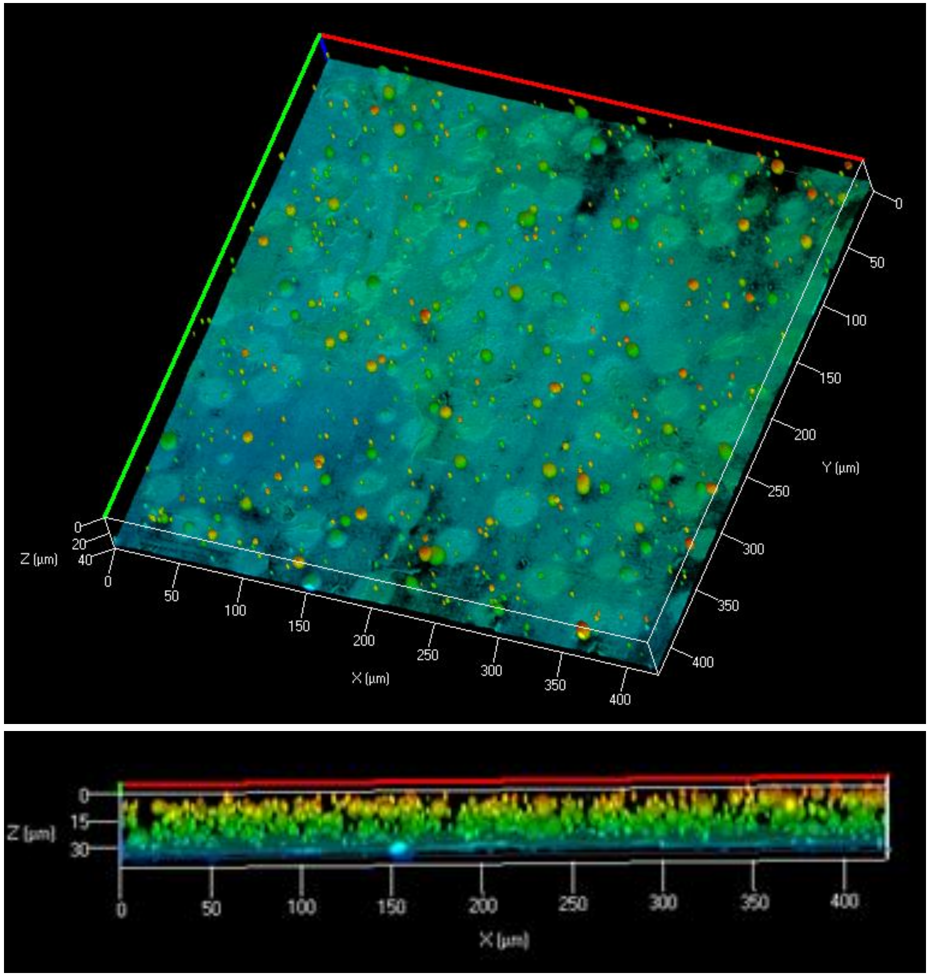
Indication of Hidden Corrosion

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.

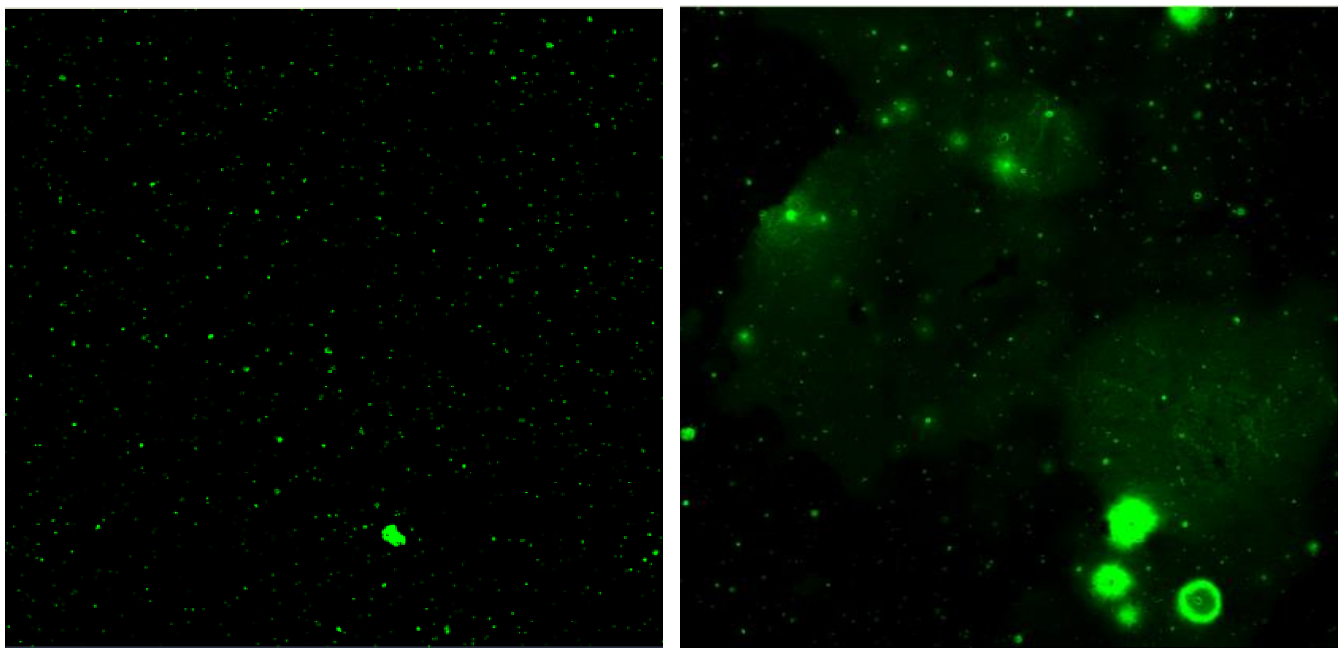
Nut and bolt set up for crevice corrosion testing. The pictures show results after 600 hour of salt fog exposure

Florescent Corrosion Indicating Coating



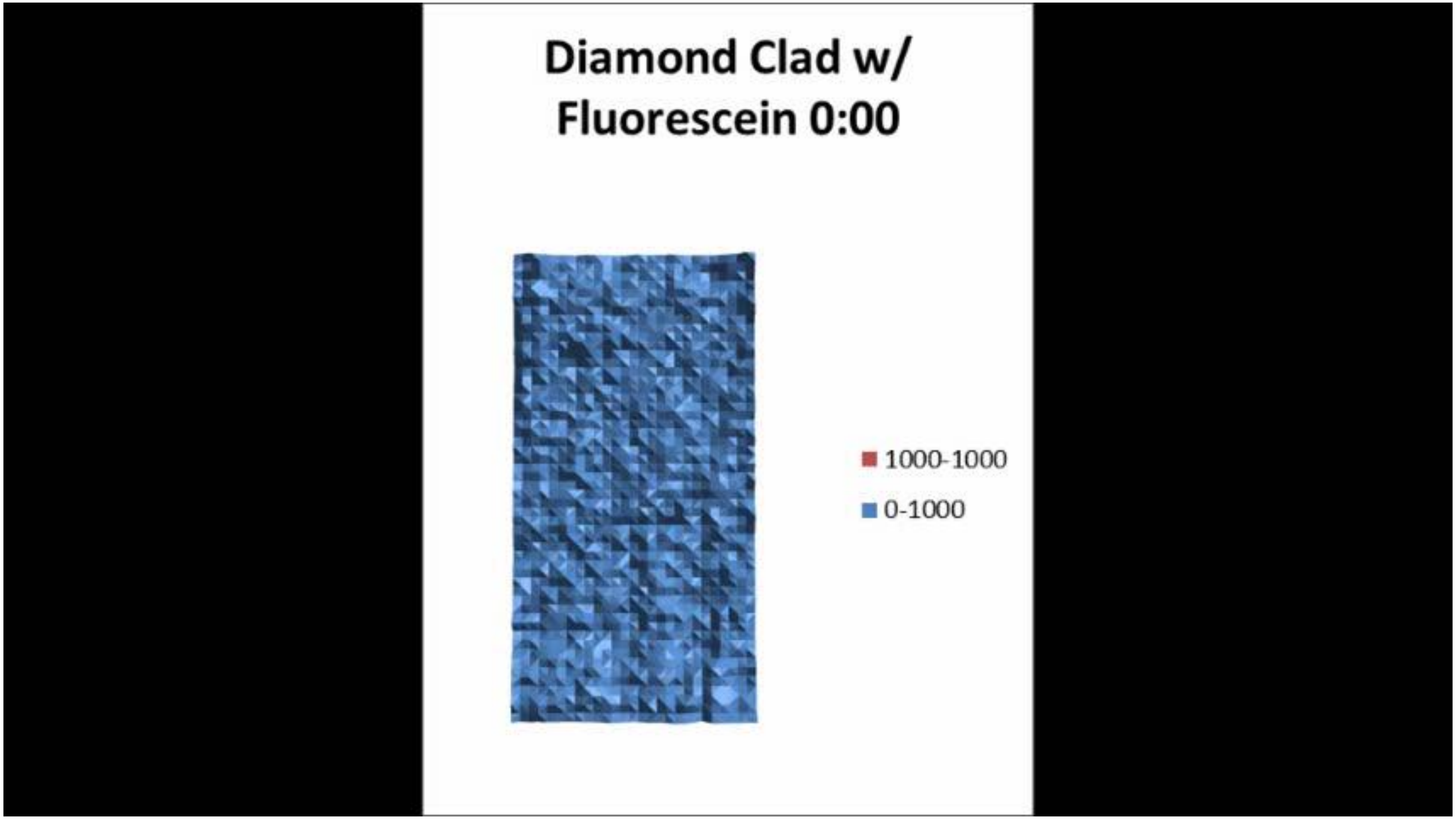
- Color changing corrosion indicators: a simple approach
- Florescent corrosion indicators provide very sensitive detection at very low indictor particle loading (0.05-0.5%) in coatings.

Florescent Corrosion Indicating Coating

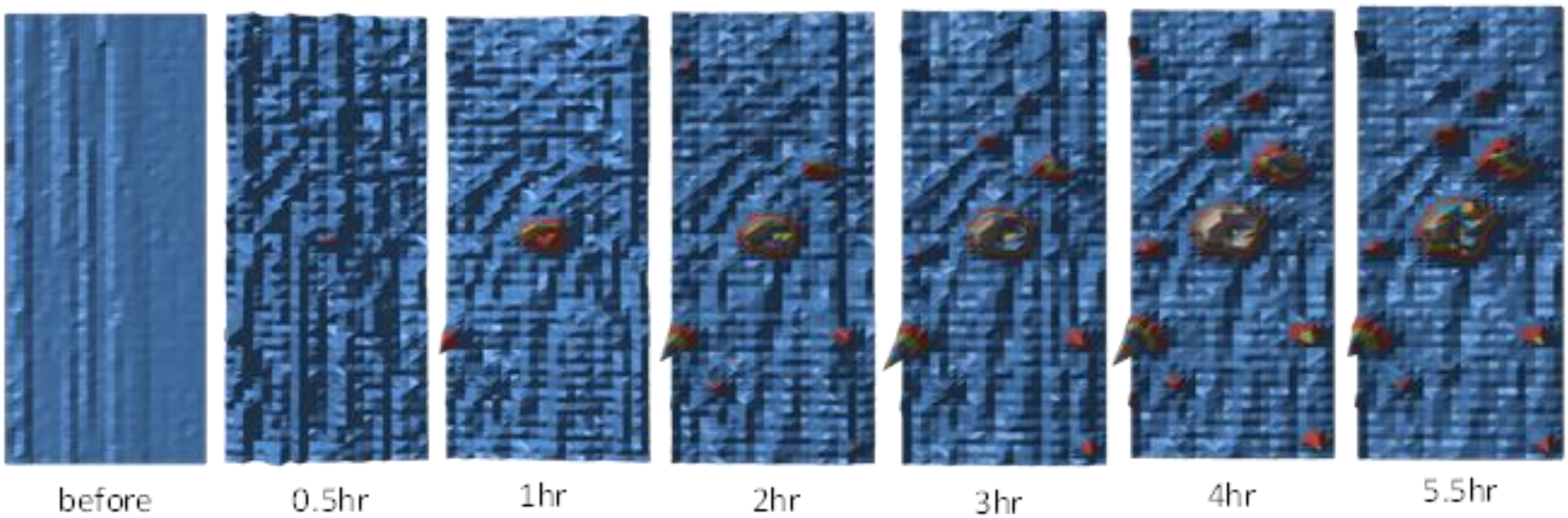


Confocal scanning laser microscopy 2D images of fluorescent corrosion sensing coating on steel. Unexposed panel (left) and near scribe after 15 hours of immersion in 5% NaCl (right).

Florescent Corrosion Indicating Coating

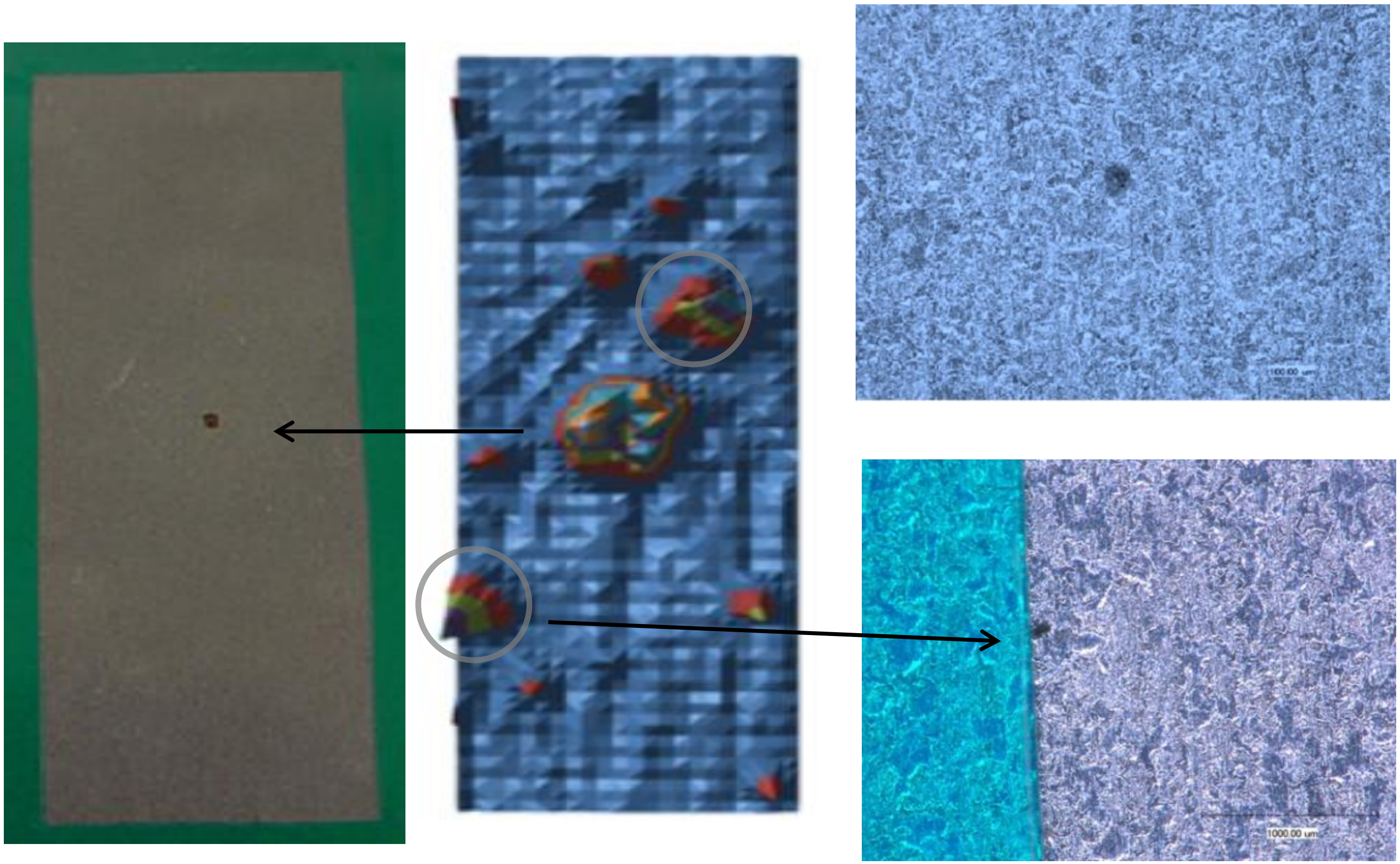


Florescent Corrosion Indicating Coating



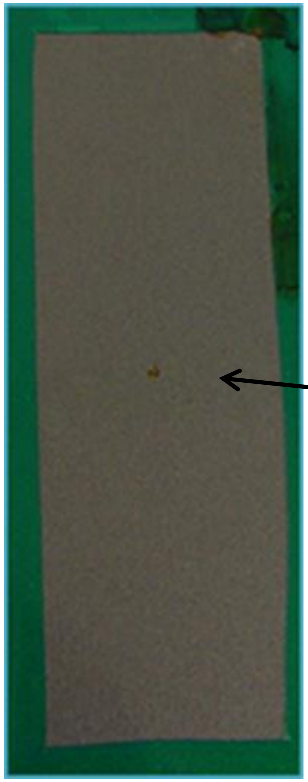
TECAN reflectance fluorescence spectroscopy scanning composite image on the coated cold rolled steel panel during salt immersion exposure up to 5.5 hours, with an artificial defect in the middle. While the main event is at the defect sites, there are many other corrosion events occurring as early as 1 hour.

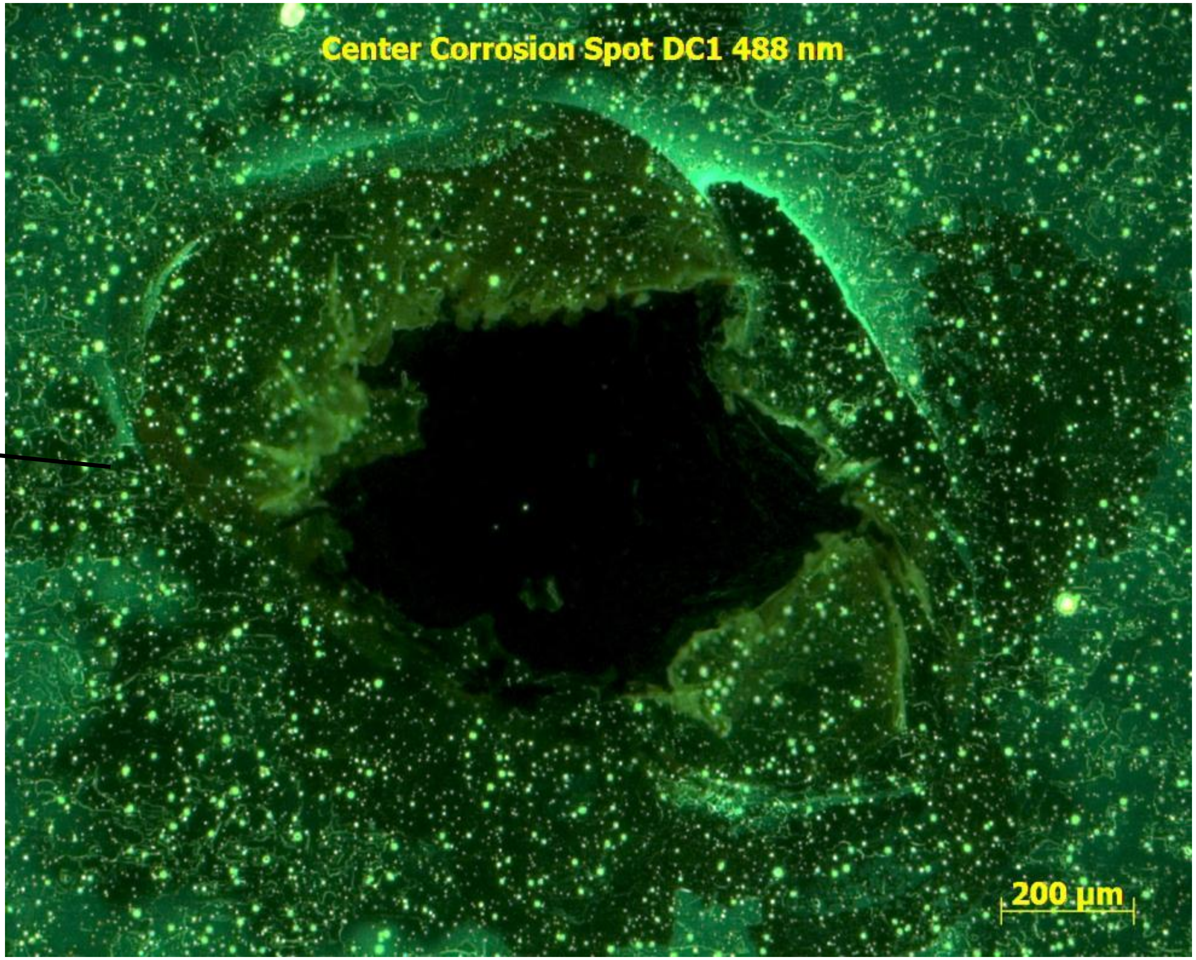
Florescent Corrosion Indicating Coating



Fluorescence 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.

Florescent Corrosion Indicating Coating



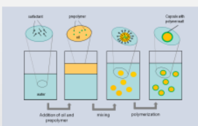


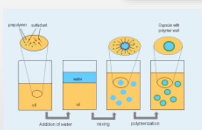
Laser Scannin Microscopy (LSM) confocal fluorescent microscope image

Corrosion Inhibition

Development and Optimization: Inhibition

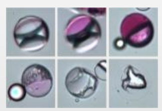
Oil-core microcapsule developed using interfacial polymerization

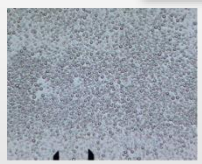




Water-core microcapsule developed using interfacial polymerization

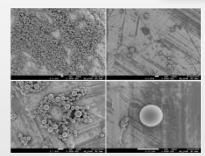
The pH sensitivity of the microcapsules was tested.





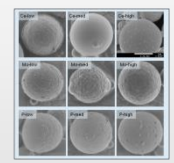
Water core microcapsule modified to reduce microcapsule cluster formation. The new formulation uses environmental friendly reagents. Various water soluble inhibitors were encapsulated: cerium nitrate, sodium molybdate, sodium phosphate, calcium metaborate, and phenyl phosphonic acid.

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

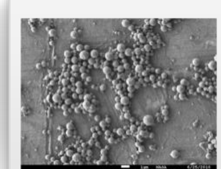


Water core microcapsule synthesis was optimized by using a water soluble wall forming pre-polymer. The synthesis time was also reduced, and the microcapsule wall properties were improved.

Oil-core microcapsule s 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 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 watched for 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.

- Environmental friendly corrosion protective coating through controlled releasing inhibitors.
- Partner with commercial companies for product development.
- Improved protection for steel.

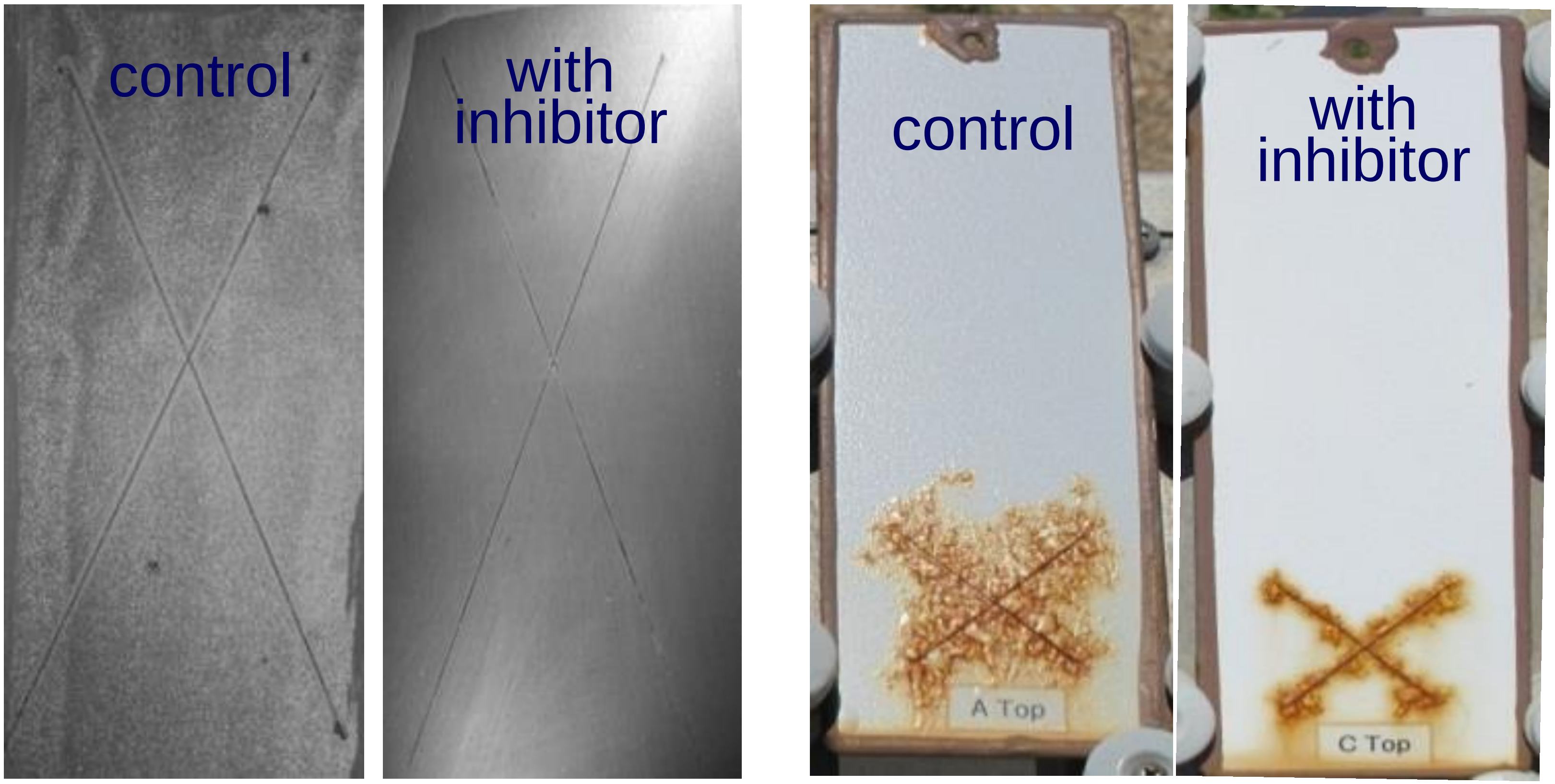
Next Generation: Waterborne

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

Corrosion Protection Function Development

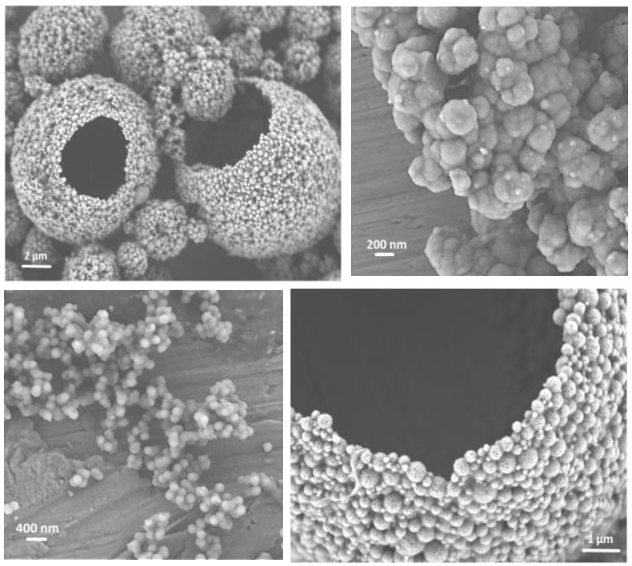
Controlled release inhibitors have been used in three areas of coating development for steel protection: improved inorganic zinc, new Cr free organic coating, and effective solvent-free coatings.

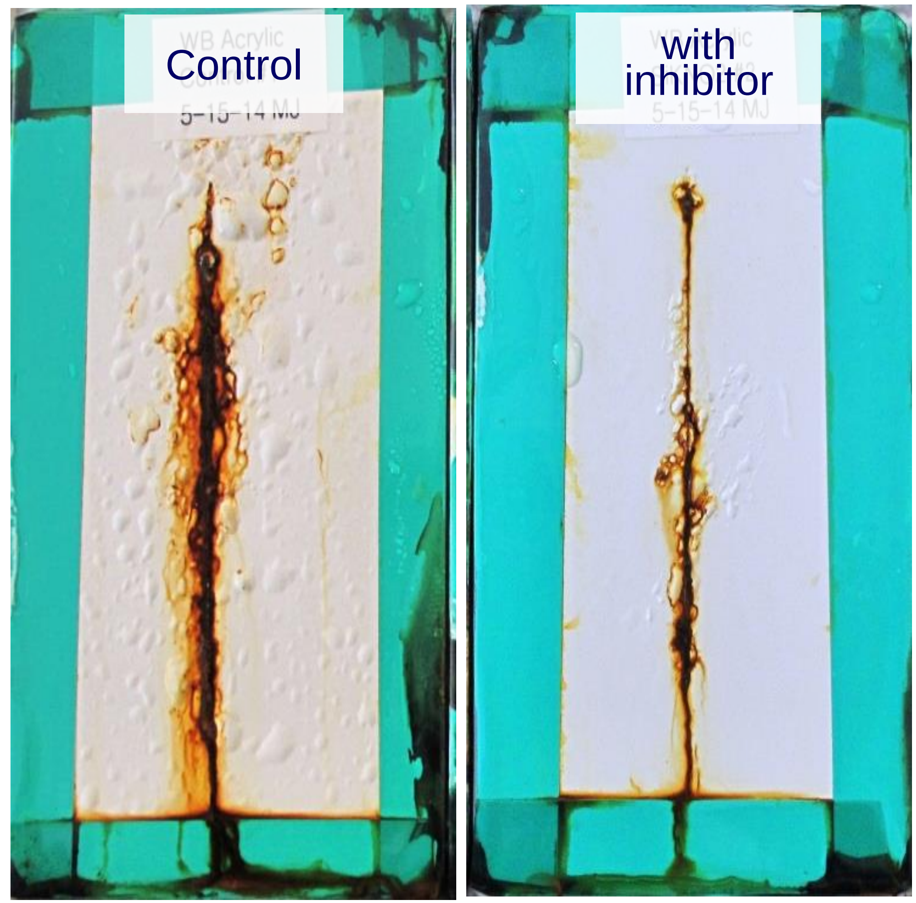
Corrosion Protection: Steel



Organic coating formulations being developed with industrial partners for steel protection. Steel panels after accelerated cyclic corrosion testing (left), and coated steel panels being tested at beach atmospherical testing.

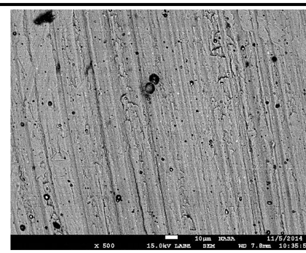
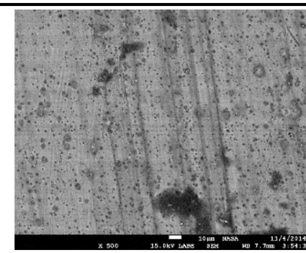
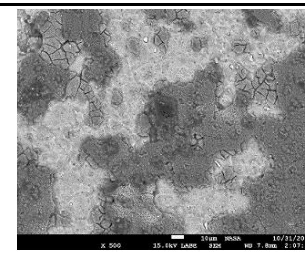
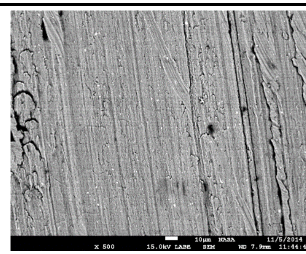
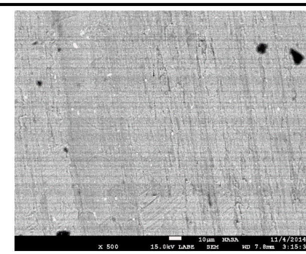
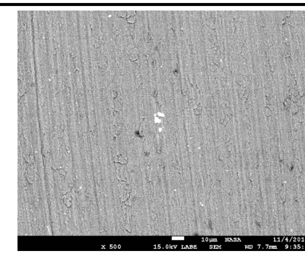
Corrosion Protection: Steel





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

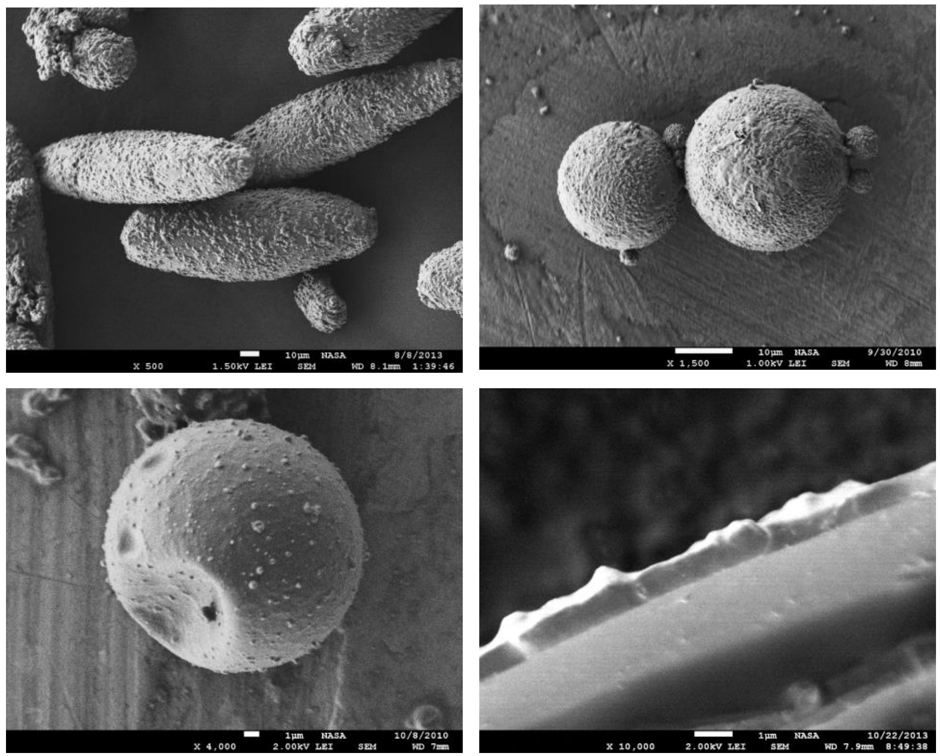
Corrosion Protection: Al Alloys

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 Al alloys.
- Some encapsulated inhibitors proven to be effective for protecting Al alloy substrates as well.
- The inhibitor particles will be used to develop Cr free paint for different Al alloys.

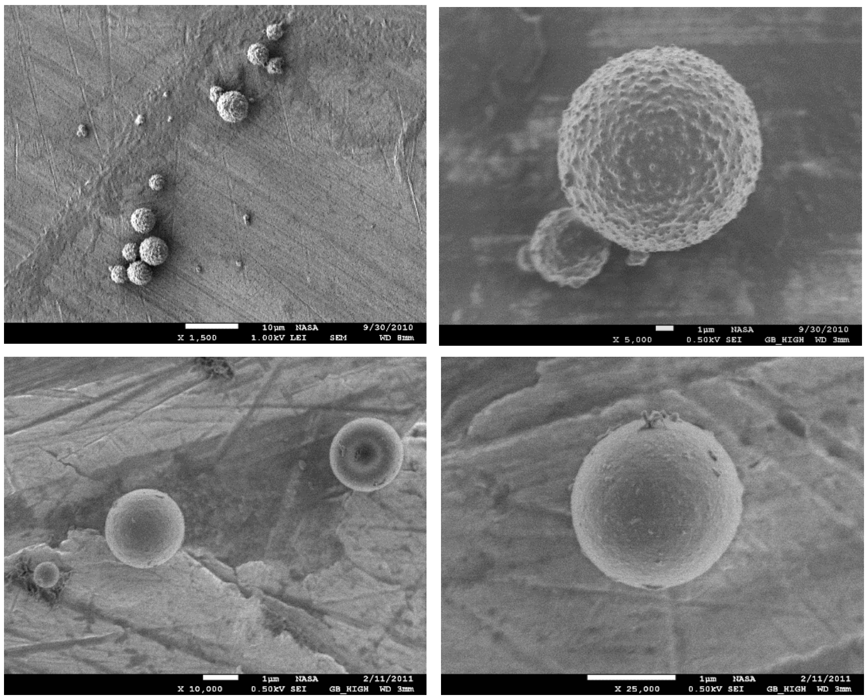
Self Healing

Self- Healing Approaches

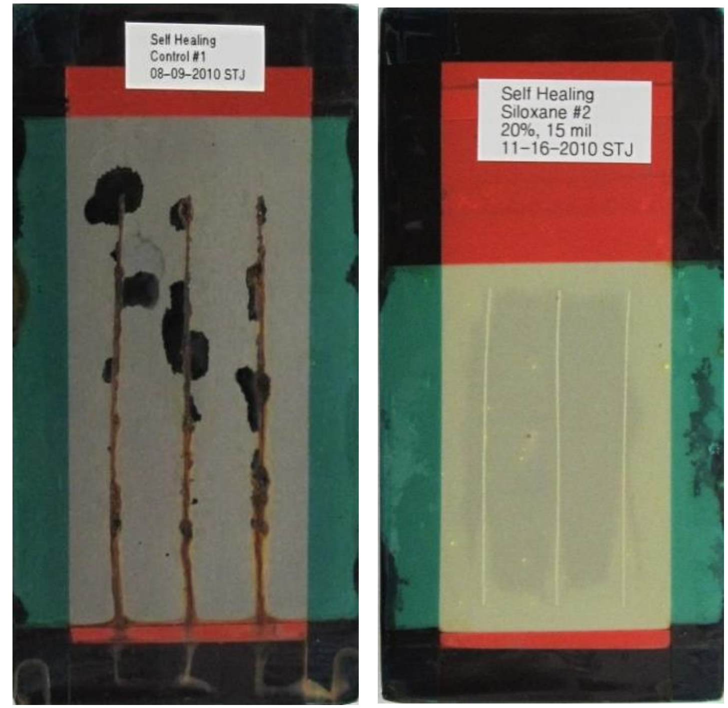


Several self healing coating systems have been developed, including 1 capsule and 2 capsule healing systems, as well as self sealing system using flowable polymers. Elongated microcapsules were also developed for thin film applications. So far, one capsule healing system performs the best and provides significant improvement for epoxy coating on steel substrate.

Self Healing Coating: 2 Capsules



Siloxane (up) and tin catalyst (down) 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%.

Summary

- The authors are developing a smart coating, based on pH-sensitive microcontainers, for early corrosion detection, corrosion inhibition, and self-healing
- The corrosion indicating function has been tested by incorporating encapsulated color changing and fluorescent indicators into coatings of interest. Salt immersion 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.