NASA KSC Smart Coating for Corrosion Applications

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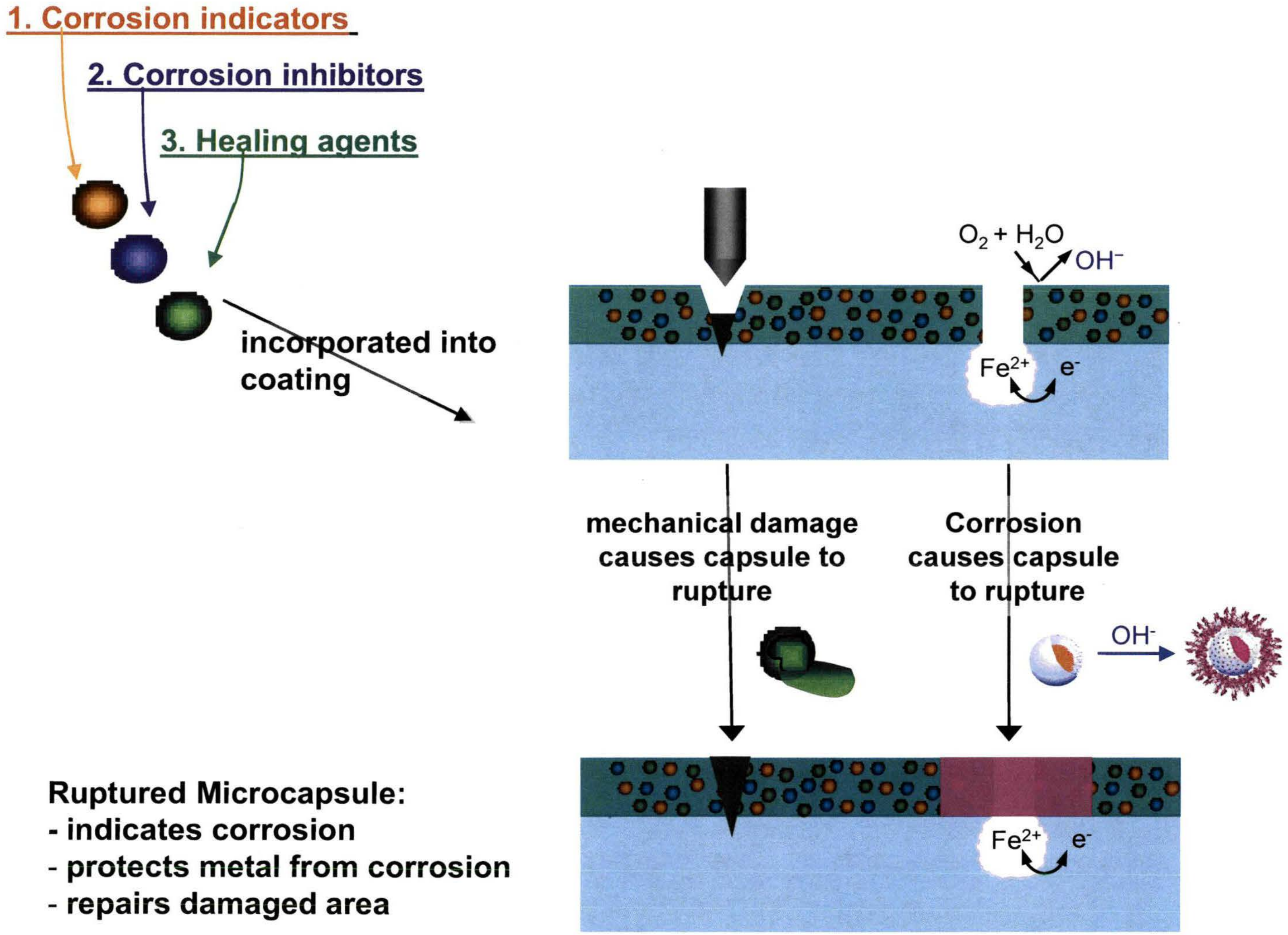
Outline

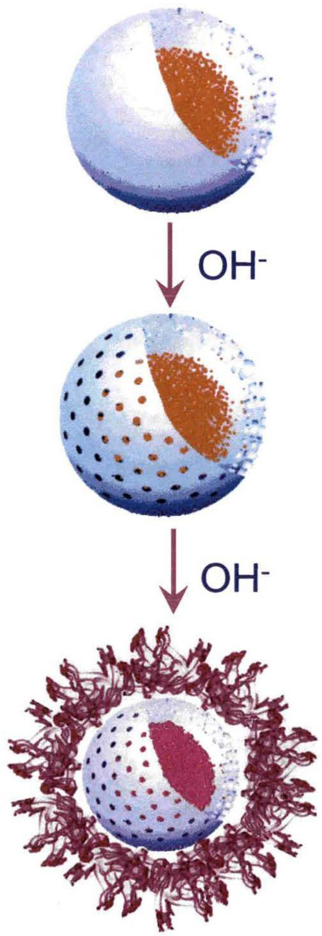
- **Technology Overview**
  - Smart Coatings
  - pH Sensitive Microcapsule
- **Encapsulation Processes**
  - Oil-core Microcapsules
  - Water-core Microcapsules
  - Microparticle formula
  - Development and Optimization
- **Testing Results**
- **FAQ**

Smart Coatings at NASA KSC



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

pH Sensitive Microcapsule



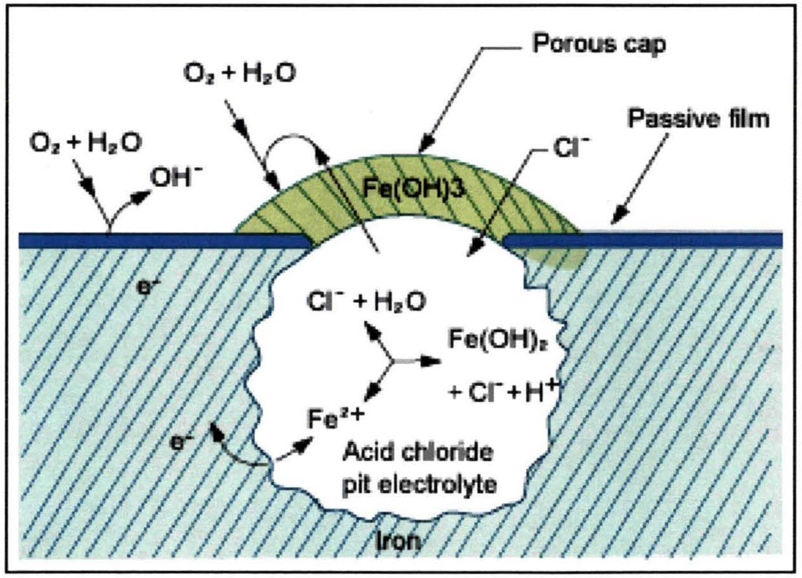
Microcapsule containing pH indicator (inhibitor, self healing agents)

The shell of the microcapsule breaks down under basic pH conditions through the ester hydrolysis reaction

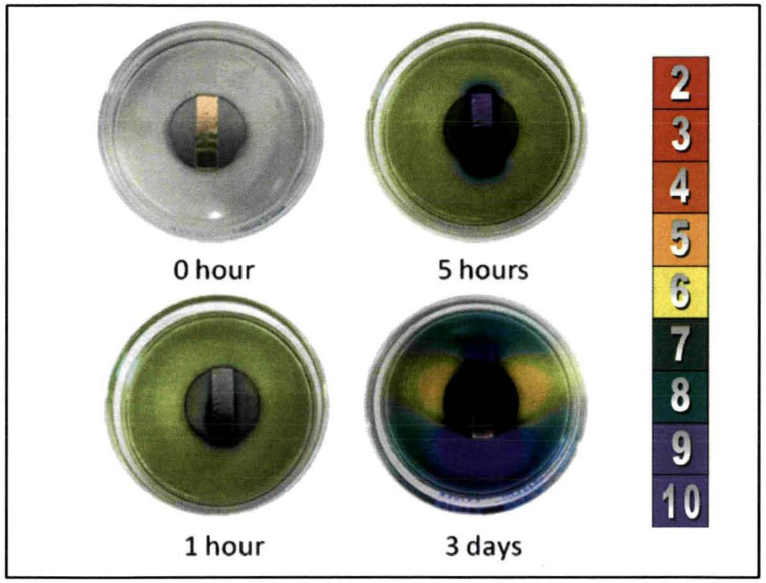
pH indictor changes color and is released from the microcapsule under basic conditions

Why pH Sensitive Microcapsules

Provide a true control release mechanism triggered by the onset of corrosion.

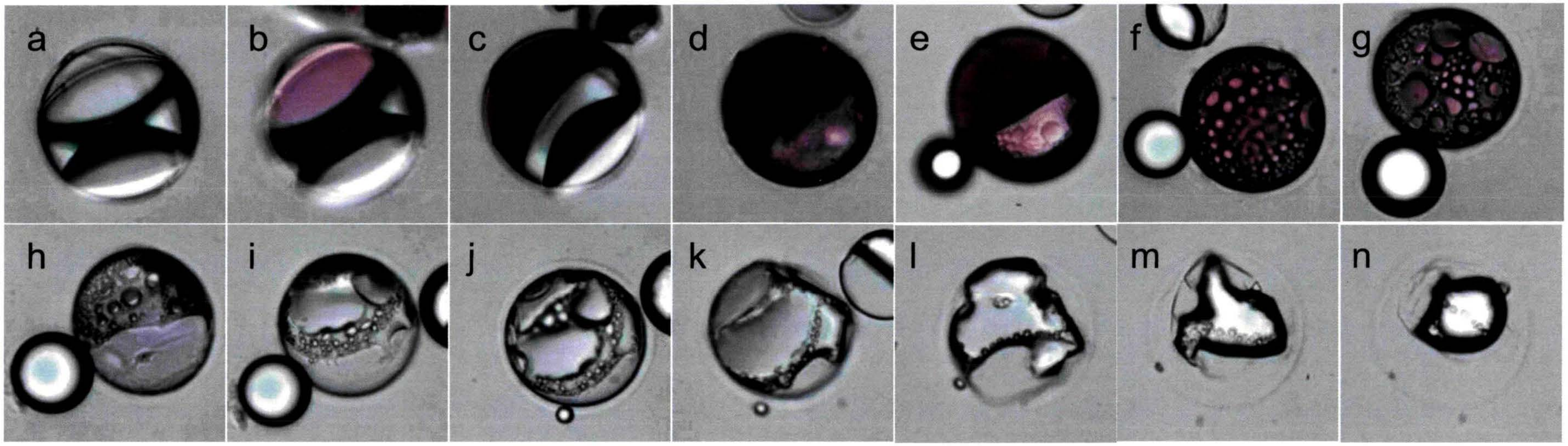


Anodic and cathodic sites on an iron surface undergoing pitting corrosion.



Dissimilar metal corrosion between steel disc and copper tape, universal pH indicator in Agar shows pH changes.

pH Sensitivity



Microcapsule breakdown in basic solution.

Why pH Sensitive Microcapsules

Benefits for corrosion sensing coatings:

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

Why pH Sensitive Microcapsules

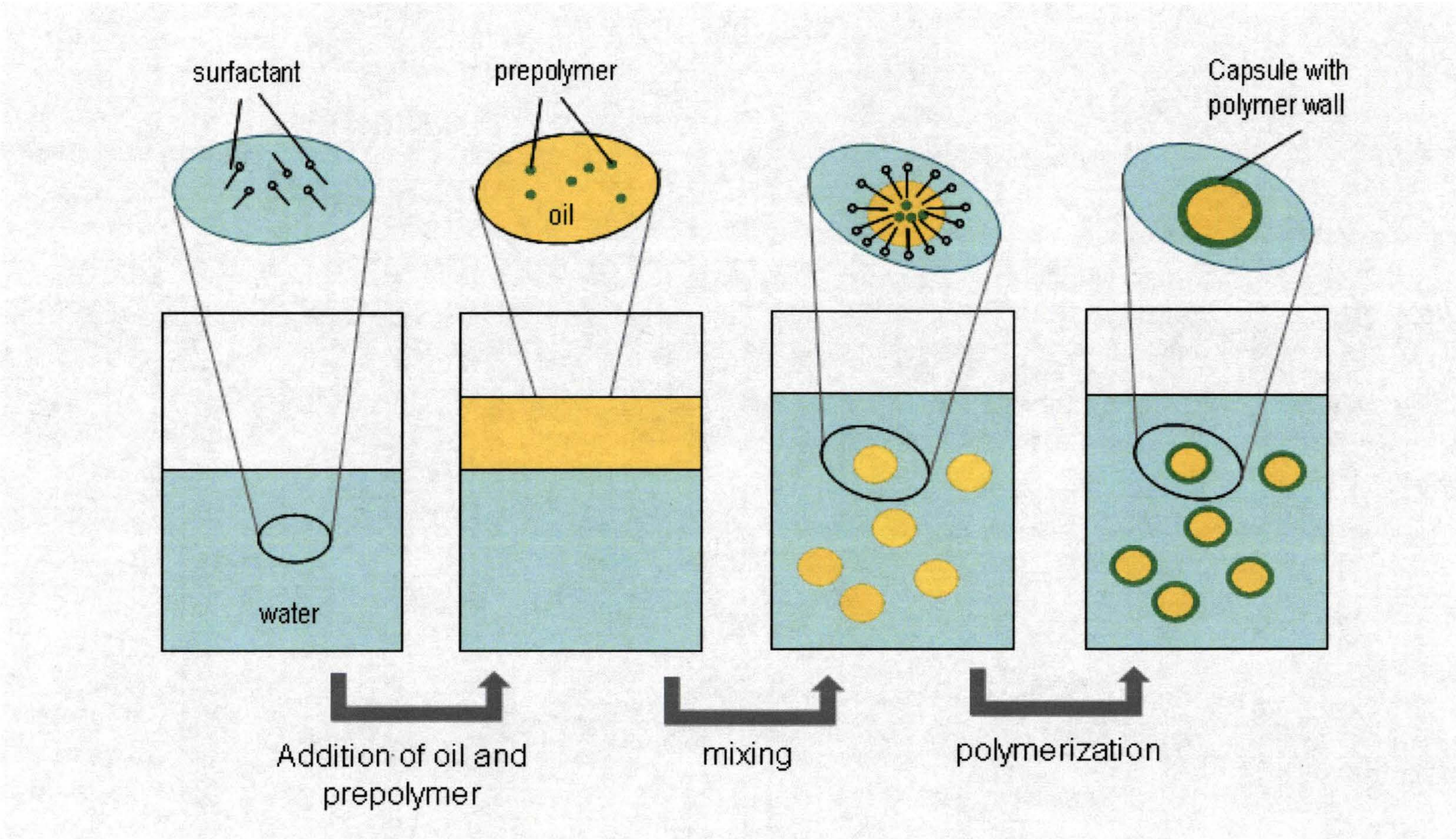
Benefits for inhibitor controlled release:

- **Smart:**
  - provide controlled release, on demand.
  - leach or diffusion can be minimized, if so desired.
  - release can be maximized when corrosion occurs.
  - deliver when and where needed.
- **Green:**
  - it reduces the detrimental impact of inhibitors on the environment.
- **Enabling:**
  - isolate the inhibitor, avoid incompatibility issue with other paint components.
  - allow incorporation of water soluble inhibitor into paint formulation without blistering.

Encapsulation Processes

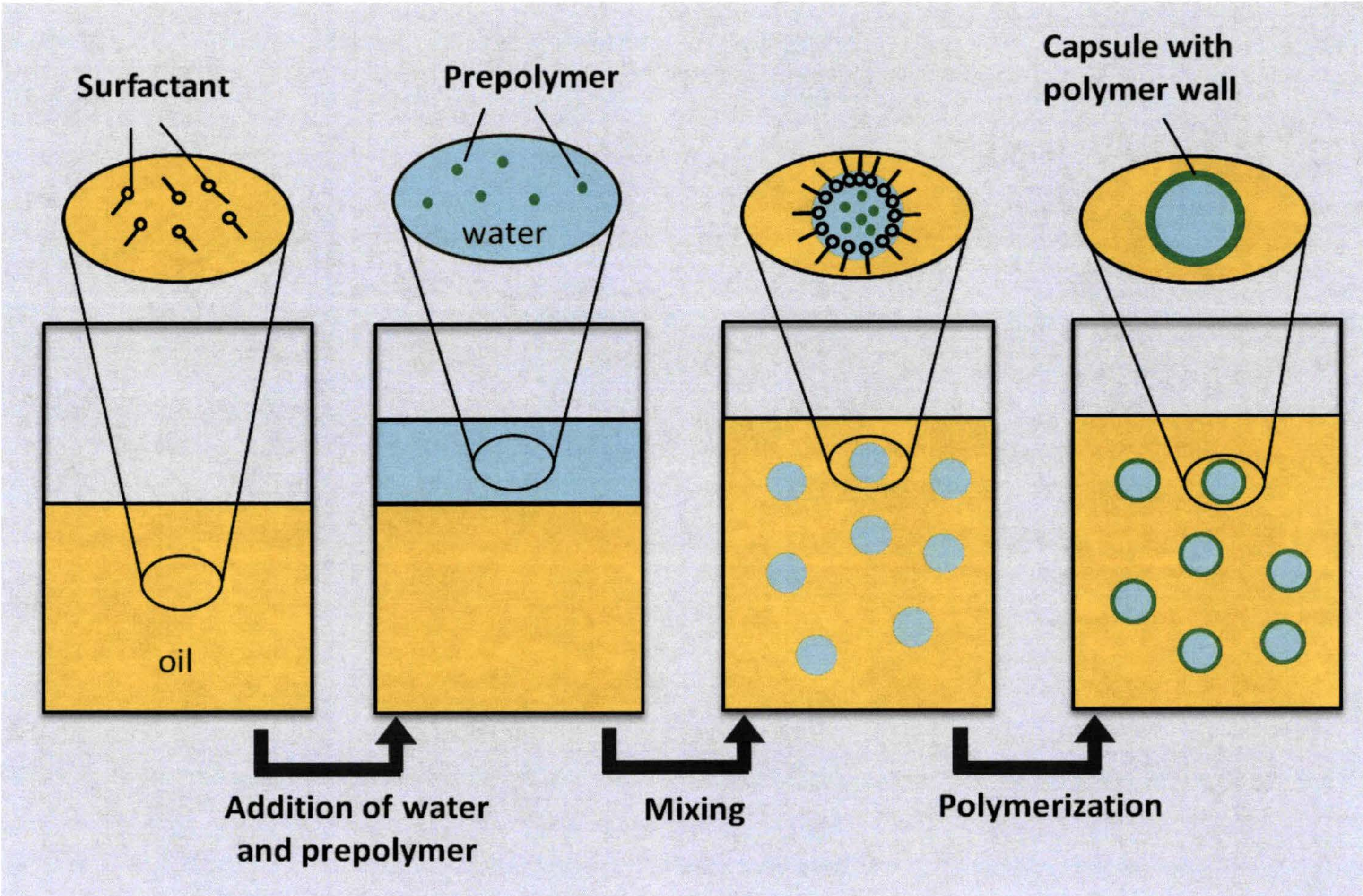
- **Oil Core Microcapsule**
- **Water Core Microcapsule**
- **Microparticle Formula**
- **Development and Optimization**
  - Indication
  - Inhibition

Oil Core Microcapsule



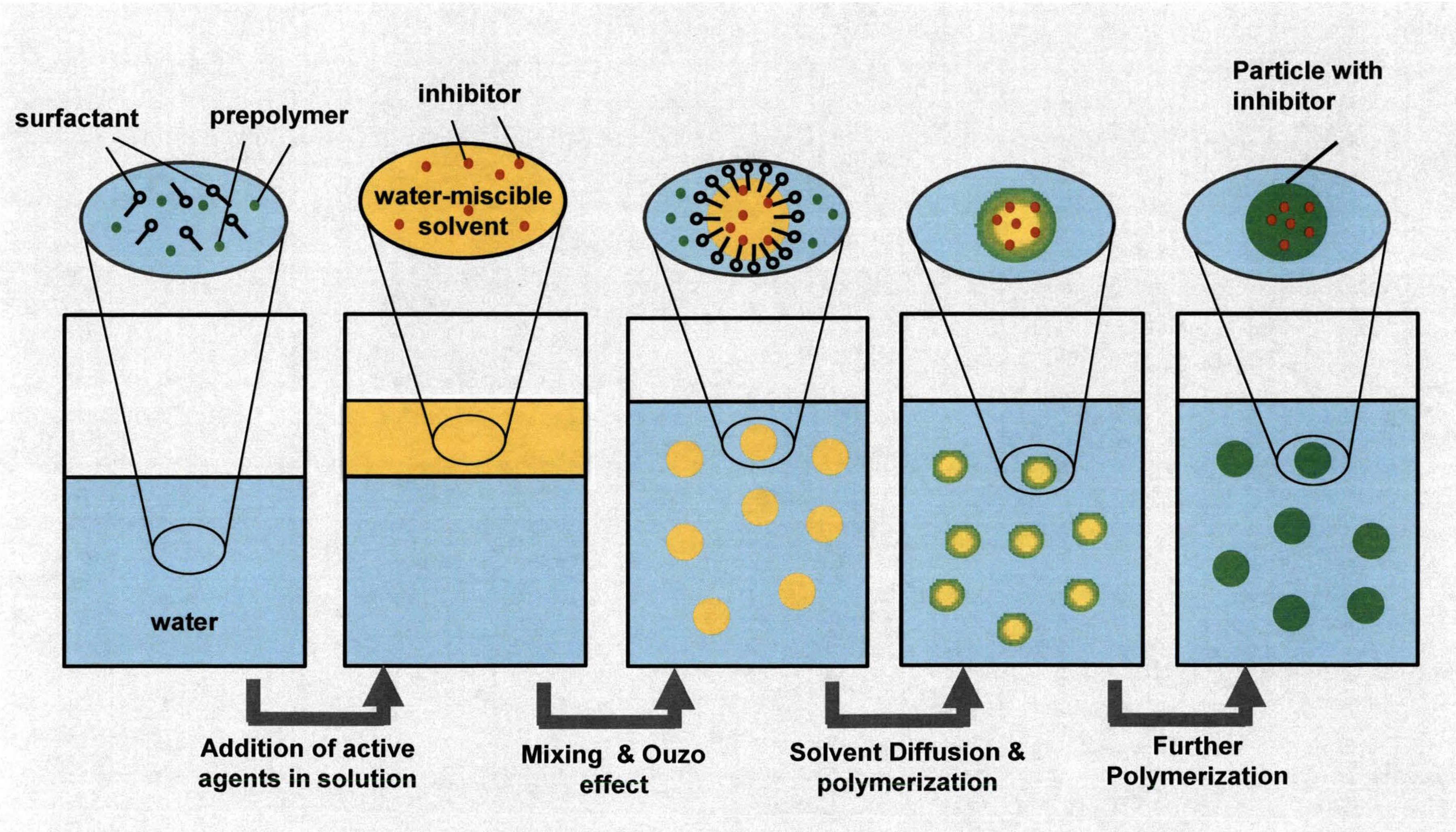
Interfacial polymerization of oil-in-water emulsion process for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.

Water Core Microcapsule



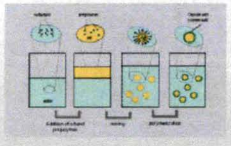
Interfacial polymerization of water core microcapsules, using a water soluble prepolymer as wall material.

Microparticle Formation

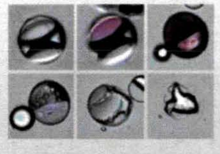


Development and Optimization: Indication

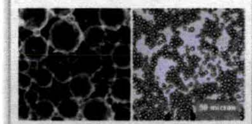
Oil core microcapsule formulation was developed by interfacial polymerization process.



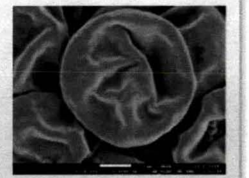
The pH sensitivity of the microcapsules was tested.



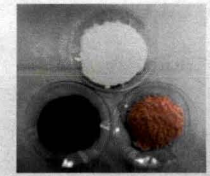
Oil core microcapsule formulation was modified to reduce the capsule size.

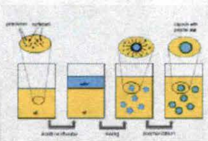


Oil core microcapsule containing corrosion indicator phph (2wt%) was synthesized.

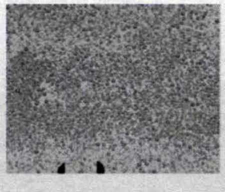


Oil core microcapsule formulation was modified to yield free flowing powder. Corrosion indictor microcapsules were prepared as free flowing powder.

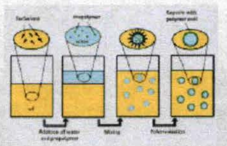




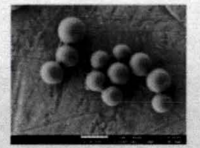
Water core microcapsule formulation was developed by interfacial polymerization process.



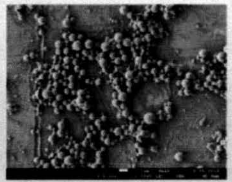
Water core microcapsule formulation was modified to reduce microcapsule cluster formation. The new formulation also use environmental friendly reagents.



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.



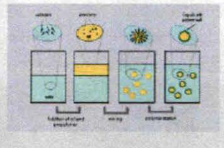
Water core microcapsules containing corrosion indicator phph (5wt%) were synthesized.



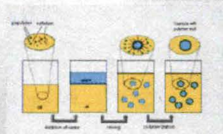
MFPTT microparticles with incorporated phph (30wt%) were synthesized.

Development and Optimization: Inhibition

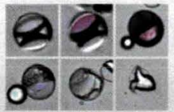
Oil core microcapsule formulation was developed by interfacial polymerization process.



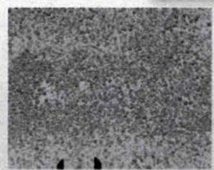
Water core microcapsule formulation was developed by interfacial polymerization process.



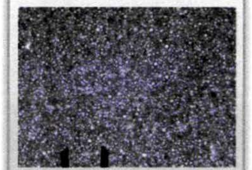
The pH sensitivity of the microcapsules was tested.



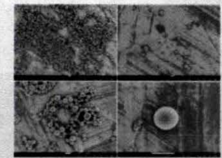
Water core microcapsule formulation was modified to reduce microcapsule cluster formation. The new formulation also uses environmental friendly reagents. Various water soluble inhibitors were encapsulated: cerium nitrate, sodium molybdate, sodium phosphate, calcium metaborate, and phenyl phosphate.



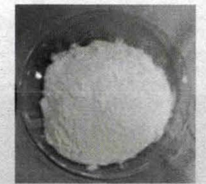
Oil core microcapsules with organic inhibitor and some inorganic, such as $CeCl_3$, were synthesized.



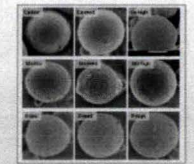
Water core microcapsule formulation was optimized by using a water soluble wall forming prepolymer. The synthesis time was also reduced, and the microcapsule wall properties were improved.



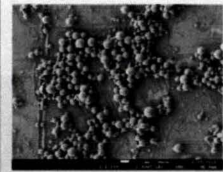
Oil core microcapsule formulation was modified to reduce the emulsion stability for easy microcapsule separation. This process yields free flowing powder.



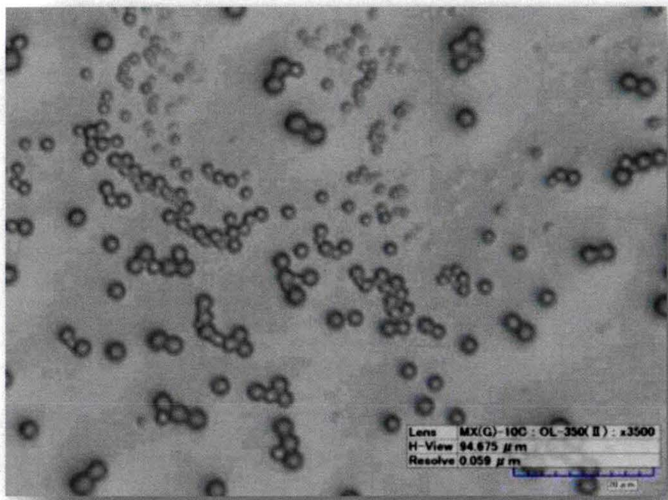
Different inorganic inhibitors were encapsulated at different concentrations. These microcapsules were then heat treated at different conditions to achieve various release rates. They were incorporated into coatings for testing.



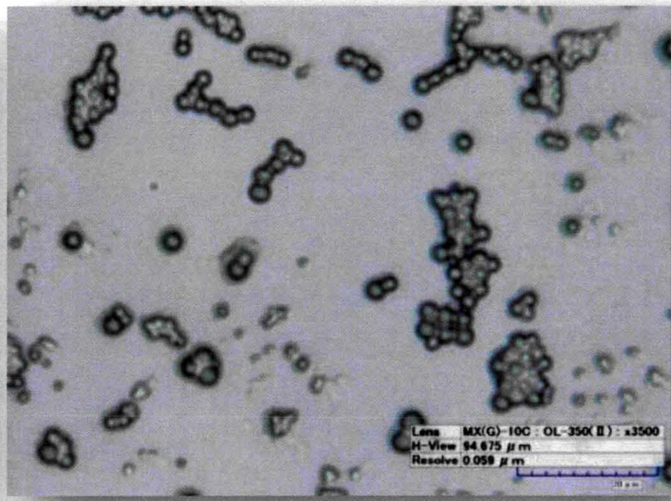
Corrosion tests showed the need to control the permeability of the capsule wall to avoid the leaching of inhibitor into coating when the encapsulated inhibitor concentration is too high. To address this problem, MFPTT microparticles containing various corrosion inhibitors were synthesized.



Oil Core Inhibitor Microcapsules



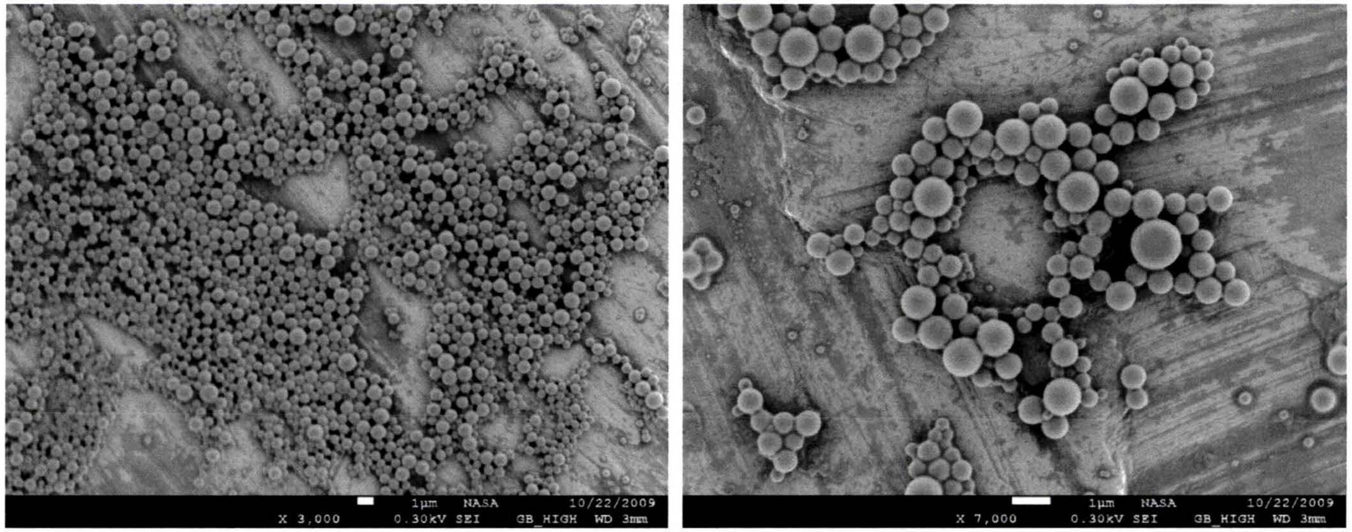
oil-in-water emulsion



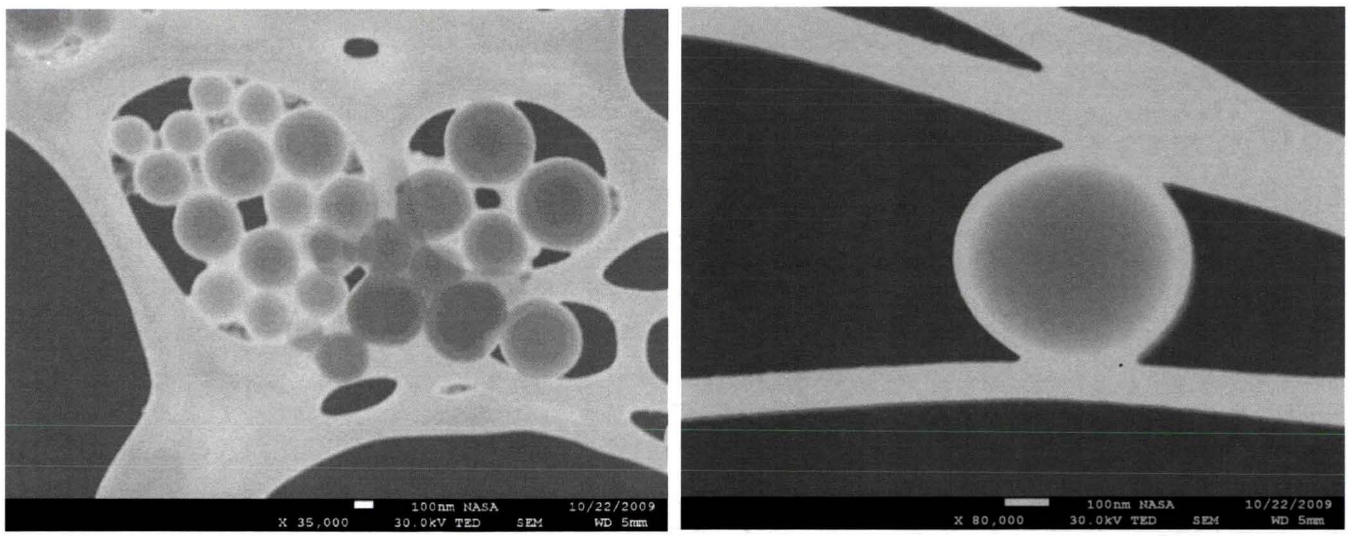
microcapsule formed

SEM of oil core microcapsules containing an organic inhibitor.

Water Core Microcapsules

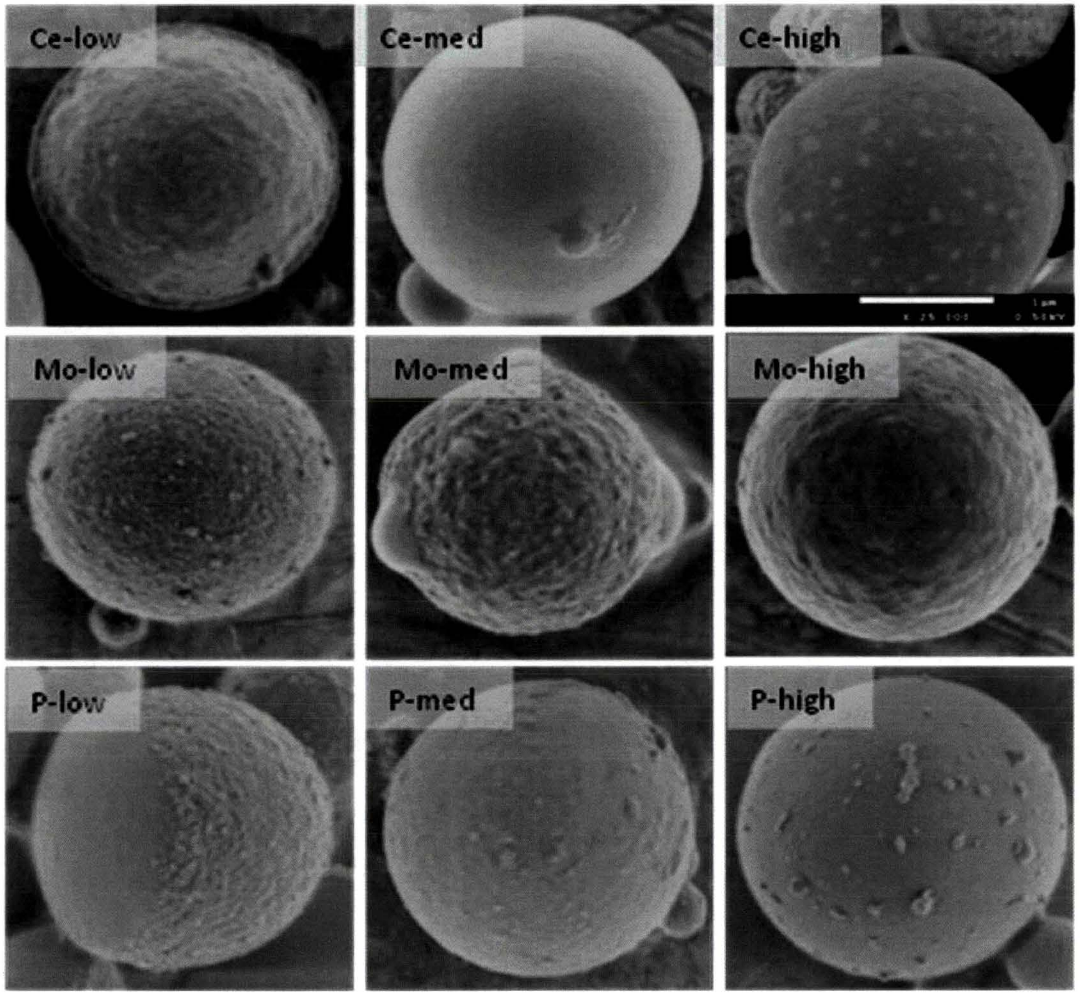


SEM Images of the water core microcapsules: improved wall strength.



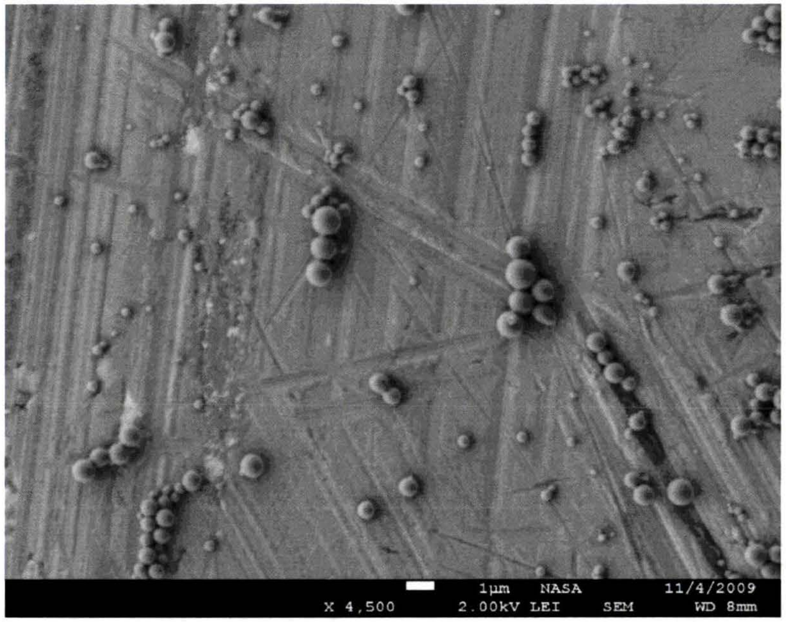
SEM Images of the water core microcapsules using a transmission electron detector.

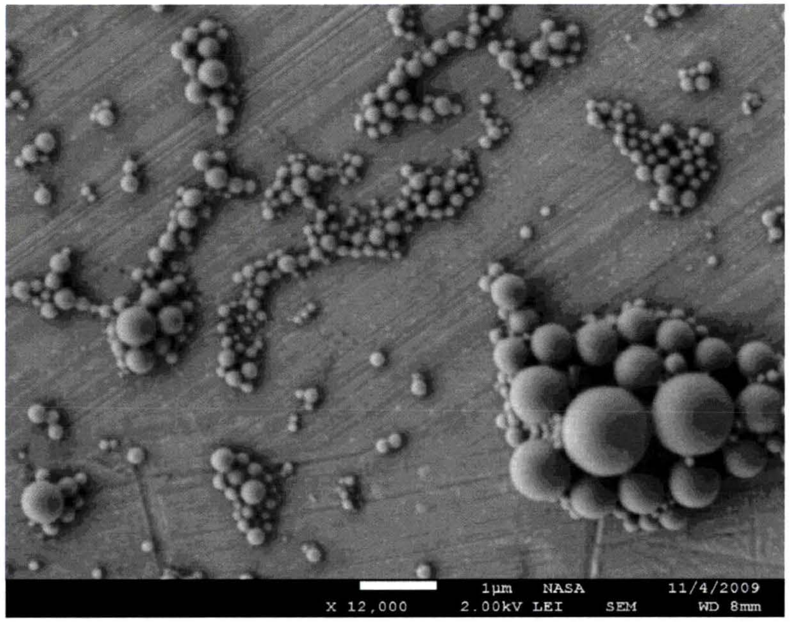
Water Core Inhibitor Microcapsules

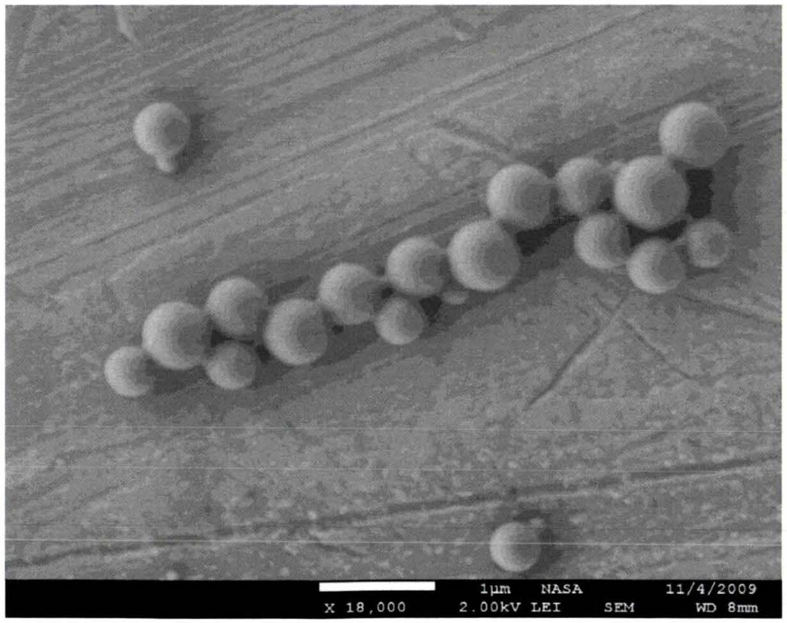


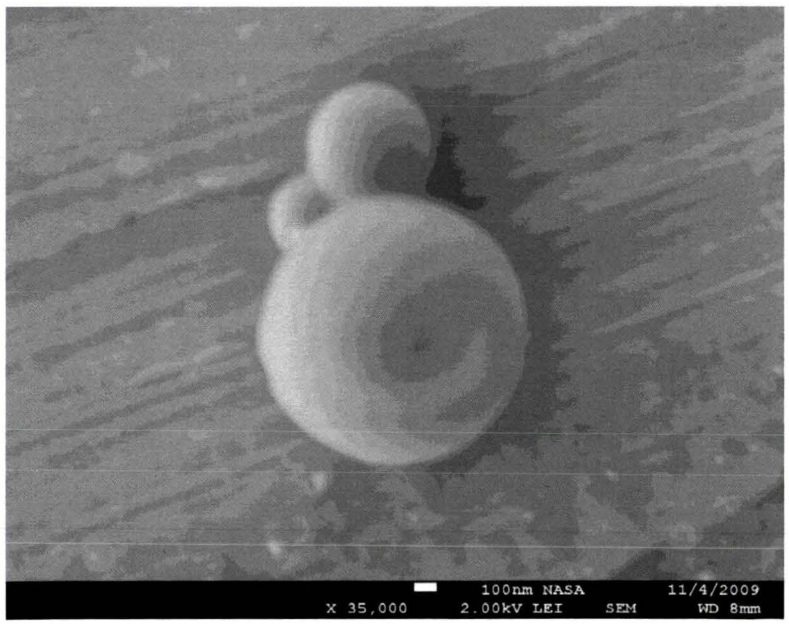
Images of microcapsules with different inhibitor core contents at different concentrations. From left to right: low, medium, and high inhibitor concentrations. From top to bottom: $Ce(NO_3)_3$, Na_2MoO_4, and NaH_2PO_4 inhibitors.

Water Core Indicator Microcapsules

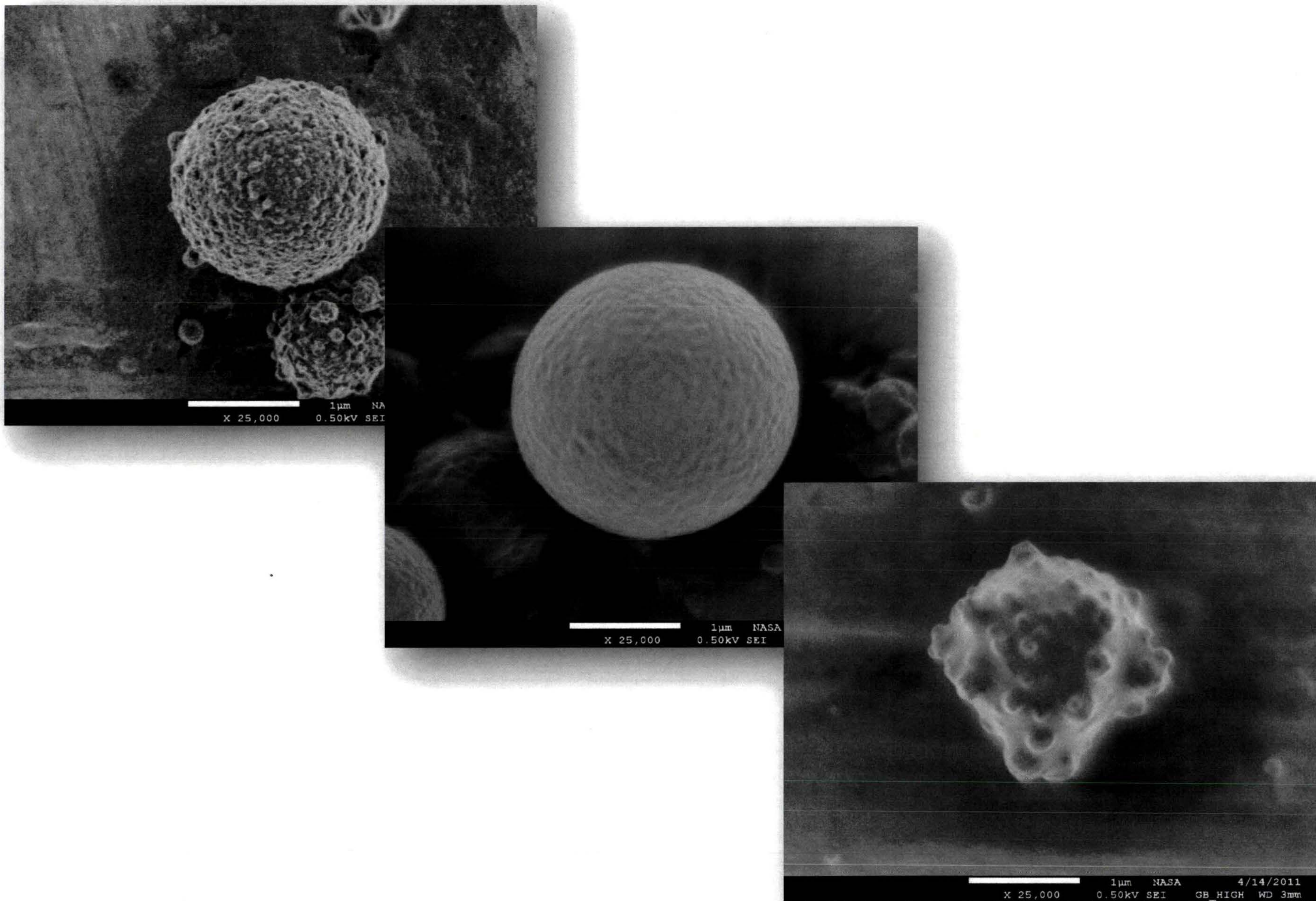




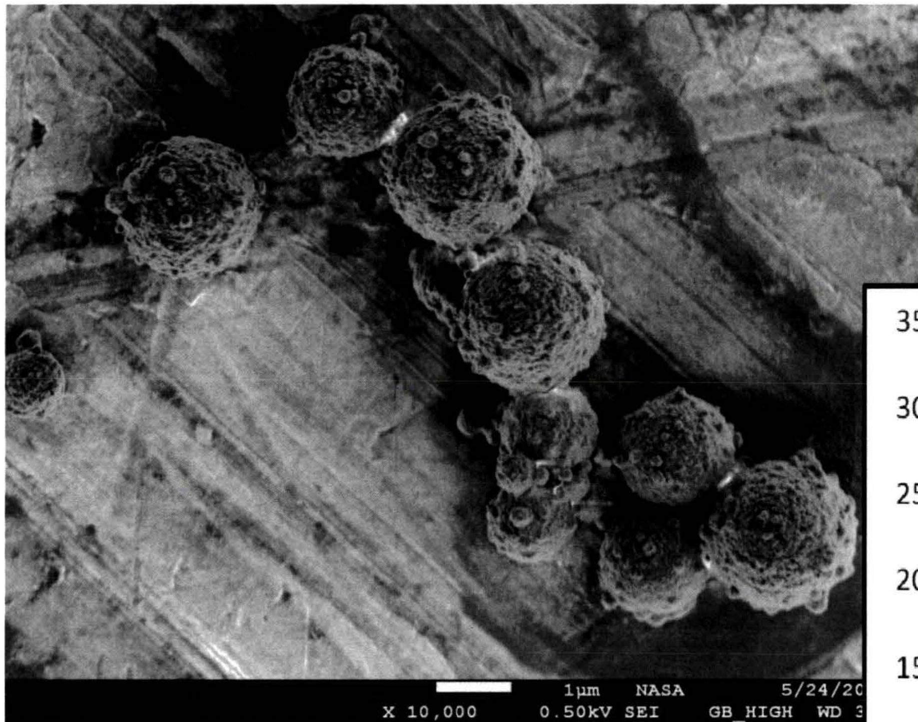


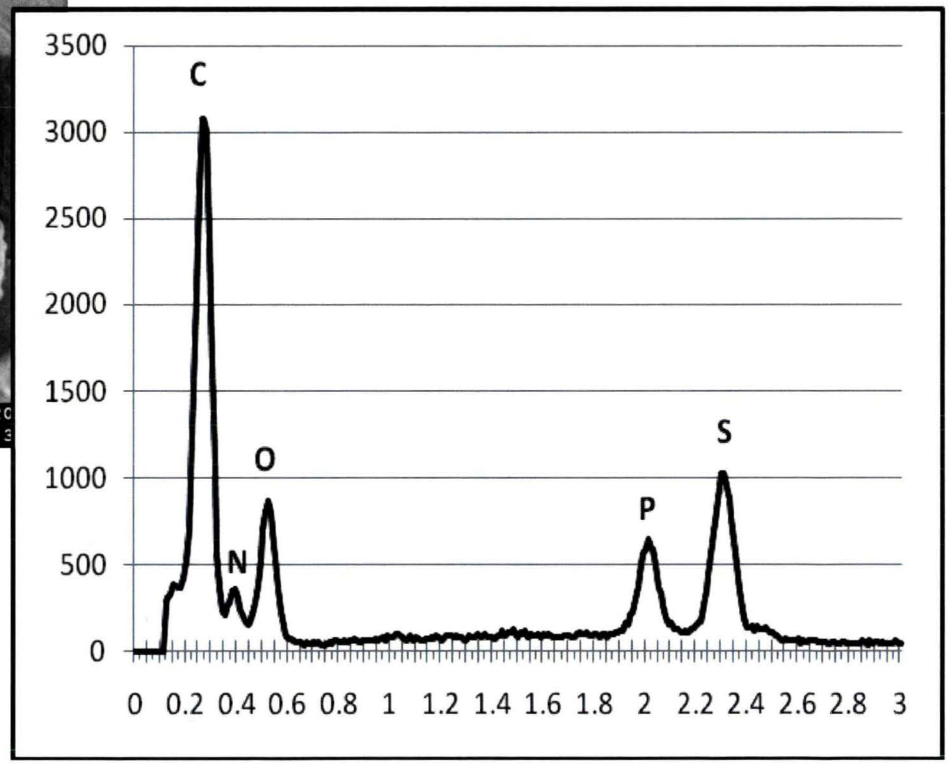


Microparticles with Inhibitors



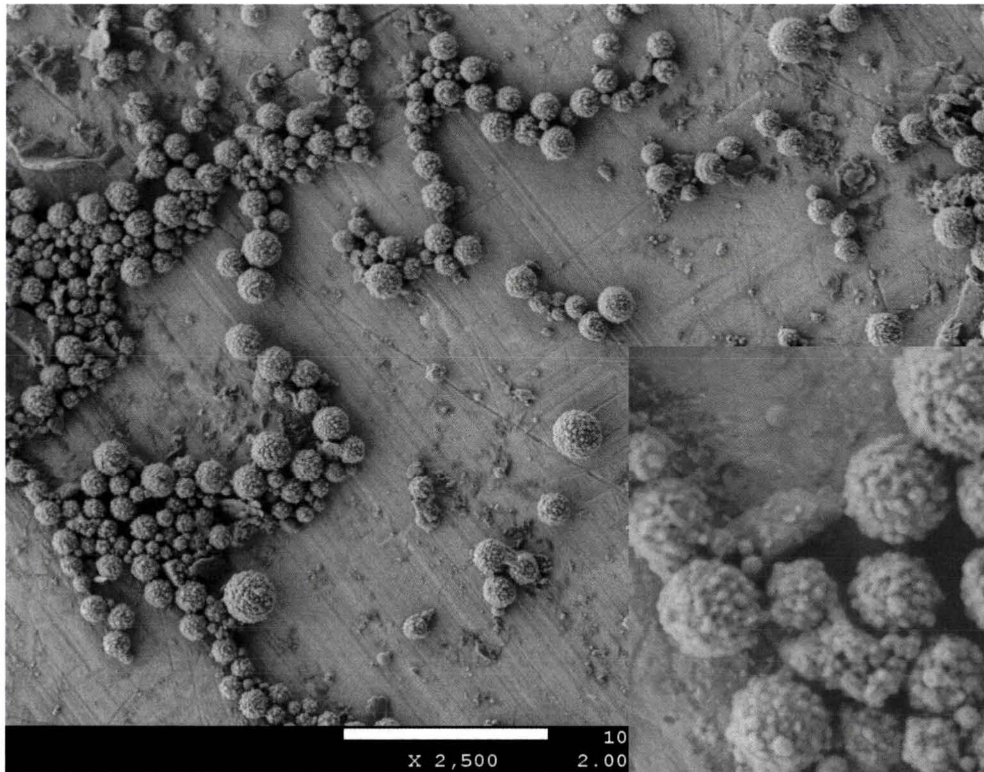
Microparticles with Inhibitors

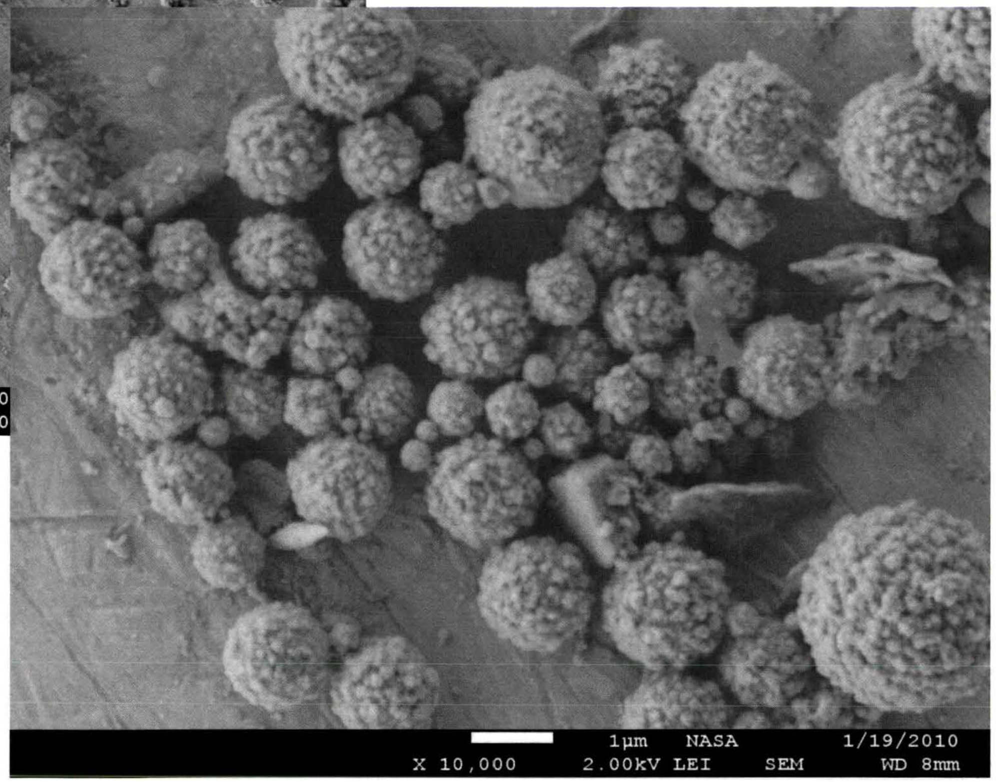




SEM and EDS of PA particles

Microparticle with Indicator





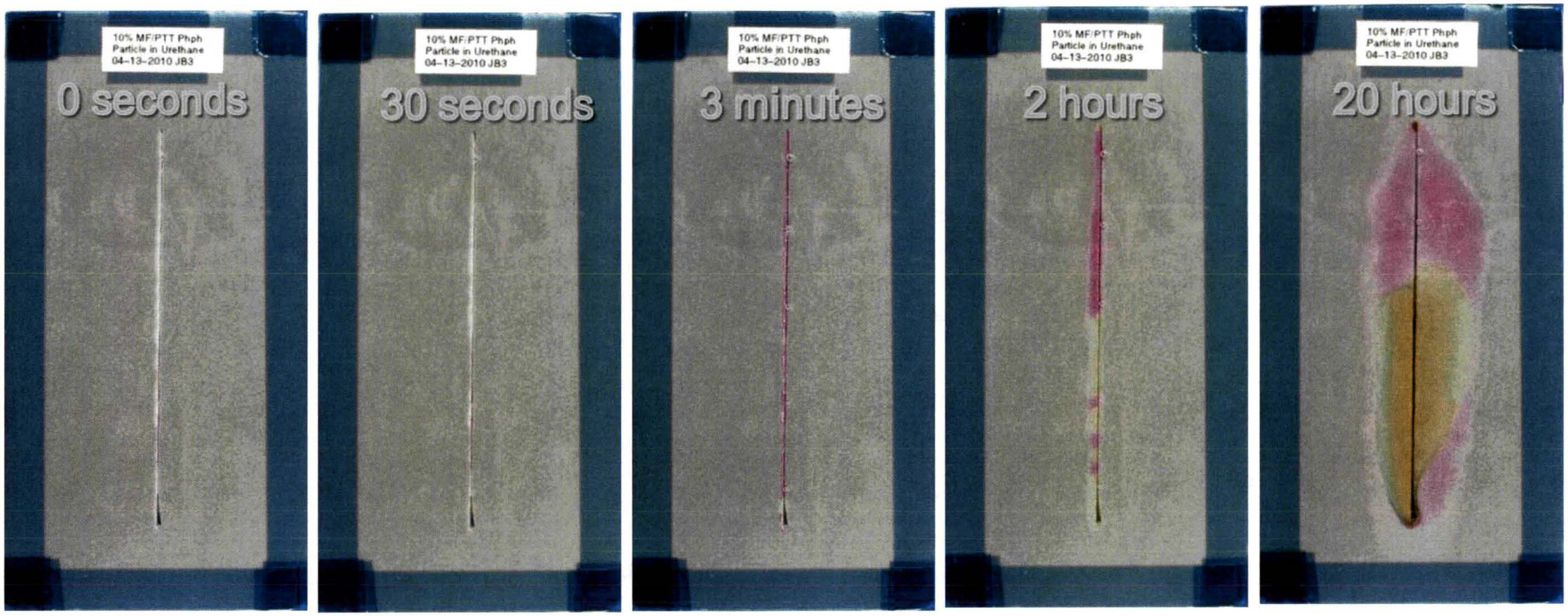
Coating Testing Results

- Indication: Early and Hidden Corrosion
- Inhibition
- Self Healing

Prototype Paint for Corrosion Detection

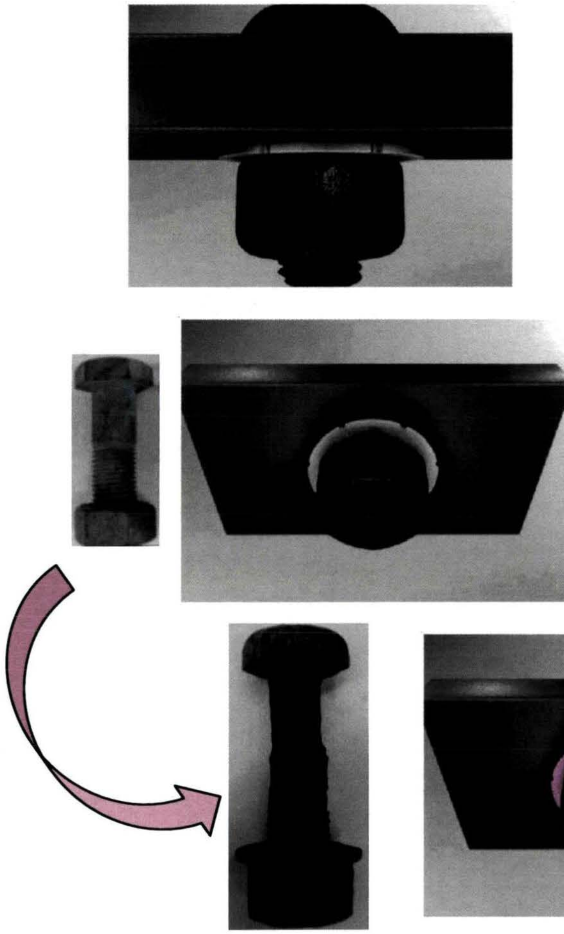
- Indicator: phenolphthalein microparticle (30 wt% phph)
- Microcapsule loading: 10 wt%
- Coating system: clear urethane

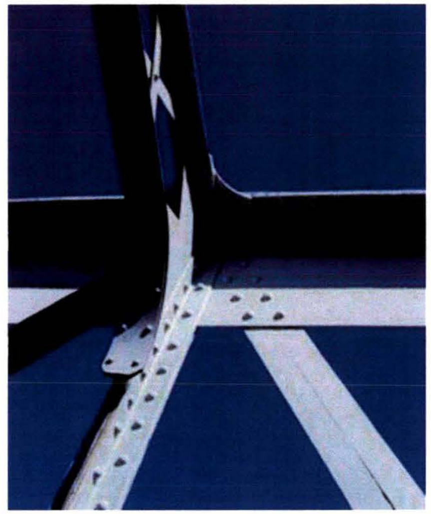
Early Corrosion Indication



Salt immersion results of panels coated with a clear polyurethane coating with encapsulated corrosion indicator. The coating detects corrosion at a very early stage (less than a few seconds) before the appearance of rust is visible (about 2 hours).

Indication of Hidden corrosion





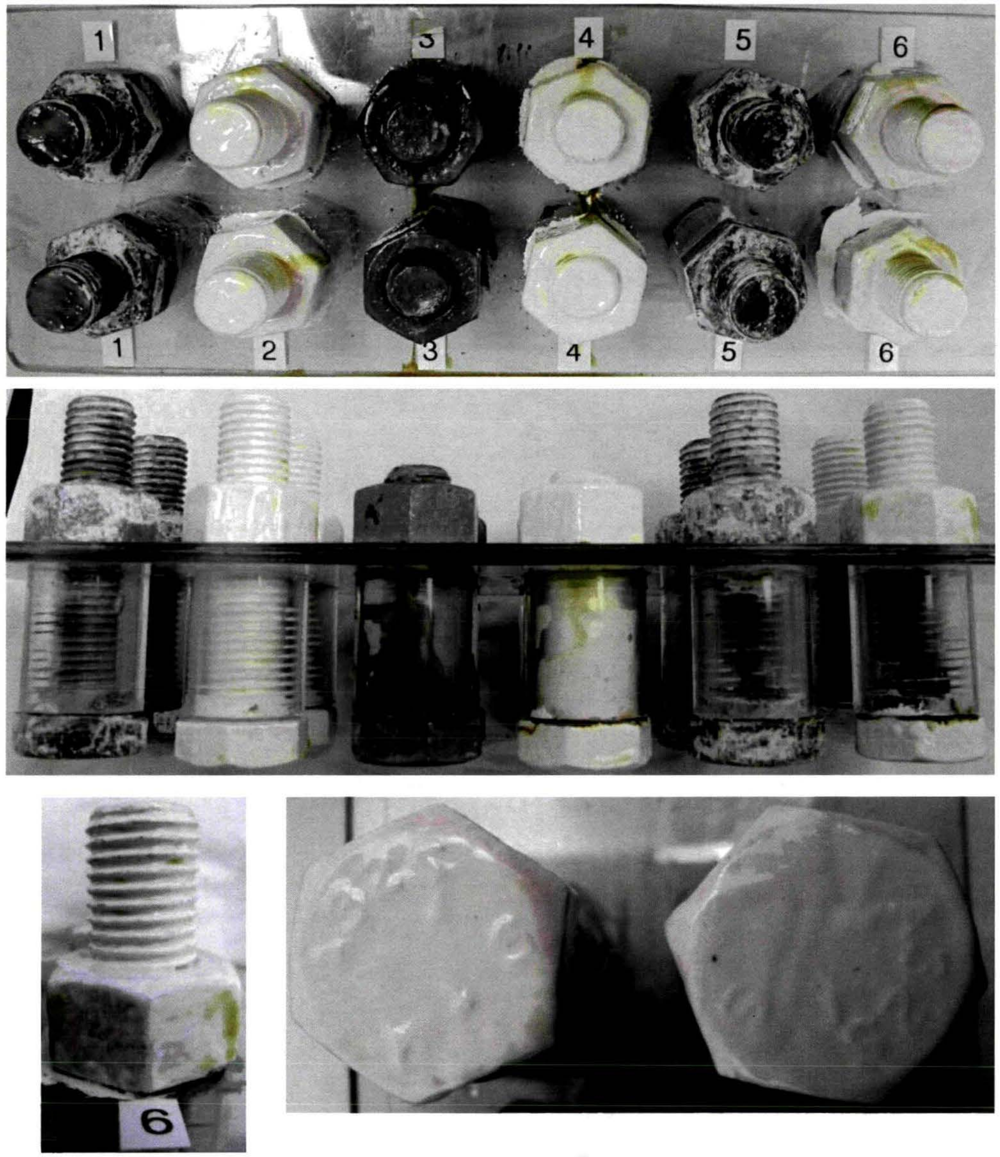
Indication of hidden corrosion by color change

Conceptual illustration of corrosion indication in structural bolts

Indication of Hidden corrosion

Coating systems used for hidden corrosion indication testing.

System label	Metal Substrate	Coating systems
1	Zinc galvanized nut and bolt	Clear urethane coating containing 10% indicator 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.

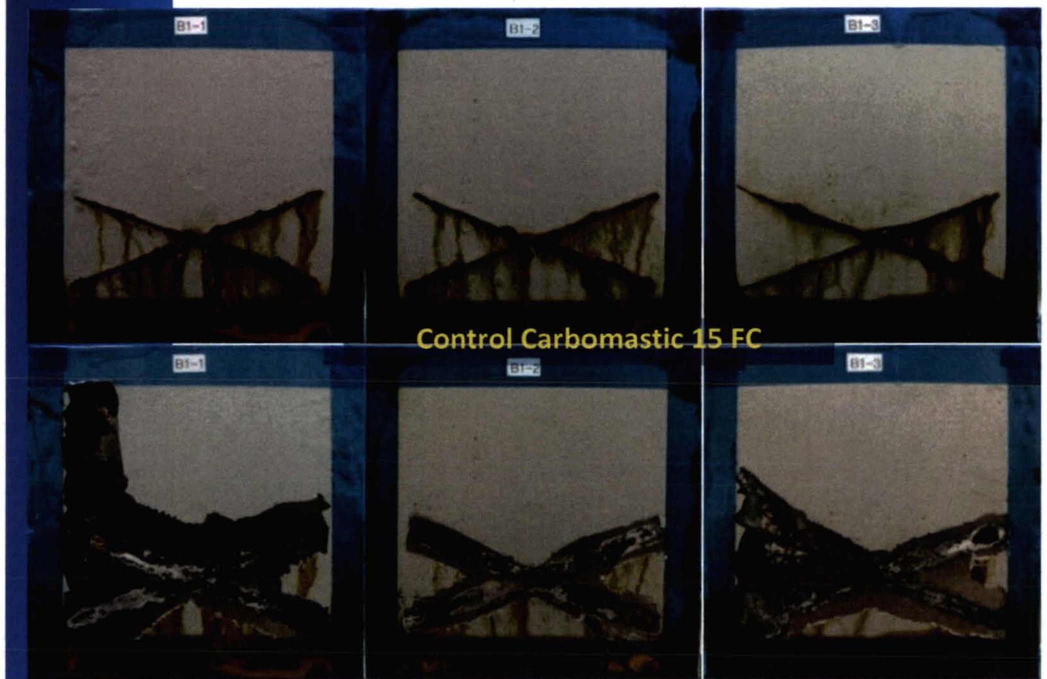


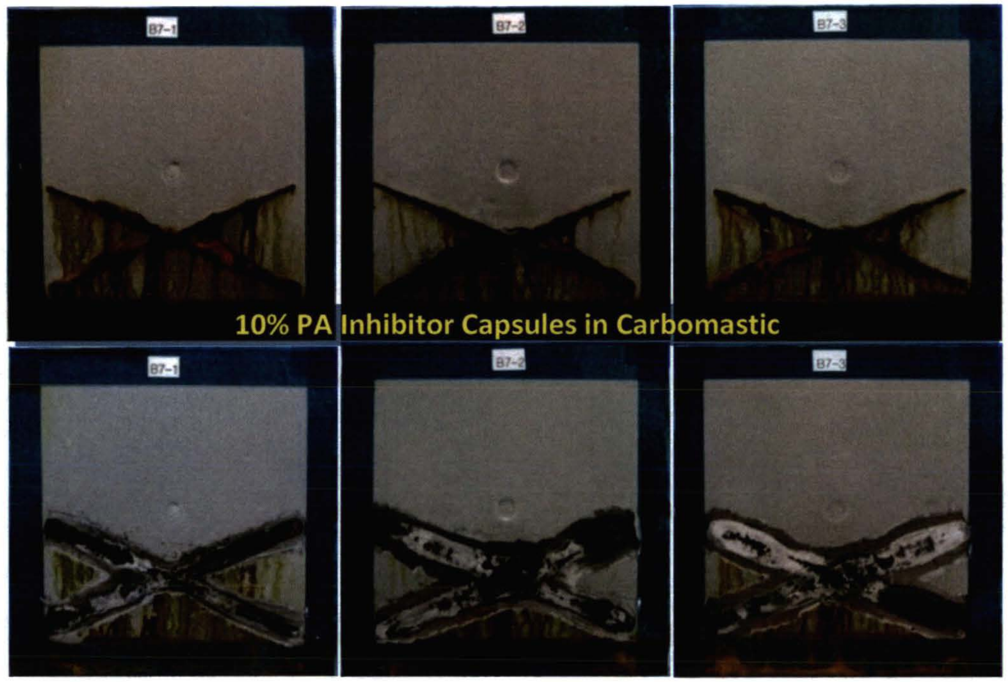
Nut and bolt set up for crevice corrosion testing. The pictures show results after 600 hour of salt fog exposure.

Prototype Paint for Corrosion Protection

- Inhibitors
  - Phenylphosphonic acid (PA) microcapsules
  - $CeNO_3/Na_2MoO_4$ microcapsules
  - PA microparticles
- Microcapsule loading: 10 wt%
- Coating systems
  - Epoxy mastic
  - Inorganic zinc
  - Epoxy

6 Month Salt Fog Testing: Epoxy Mastic

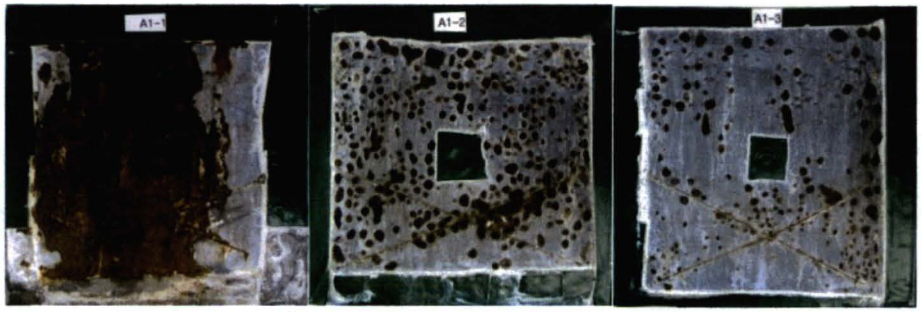




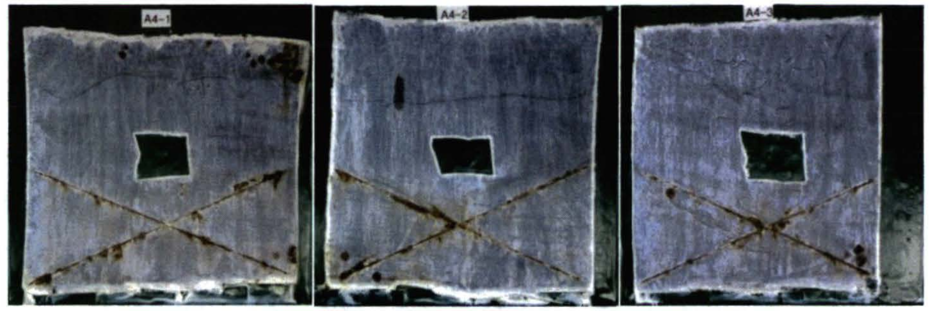
Inhibitor capsules were tested in an epoxy mastic coating. Inhibitor PA (phenylphosphonic acid) capsule containing coatings show improved rust rating than control.

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

6 Month Salt Fog Testing: Inorganic Zinc



Control Zn Primer



10% Inhibitor Microcapsules

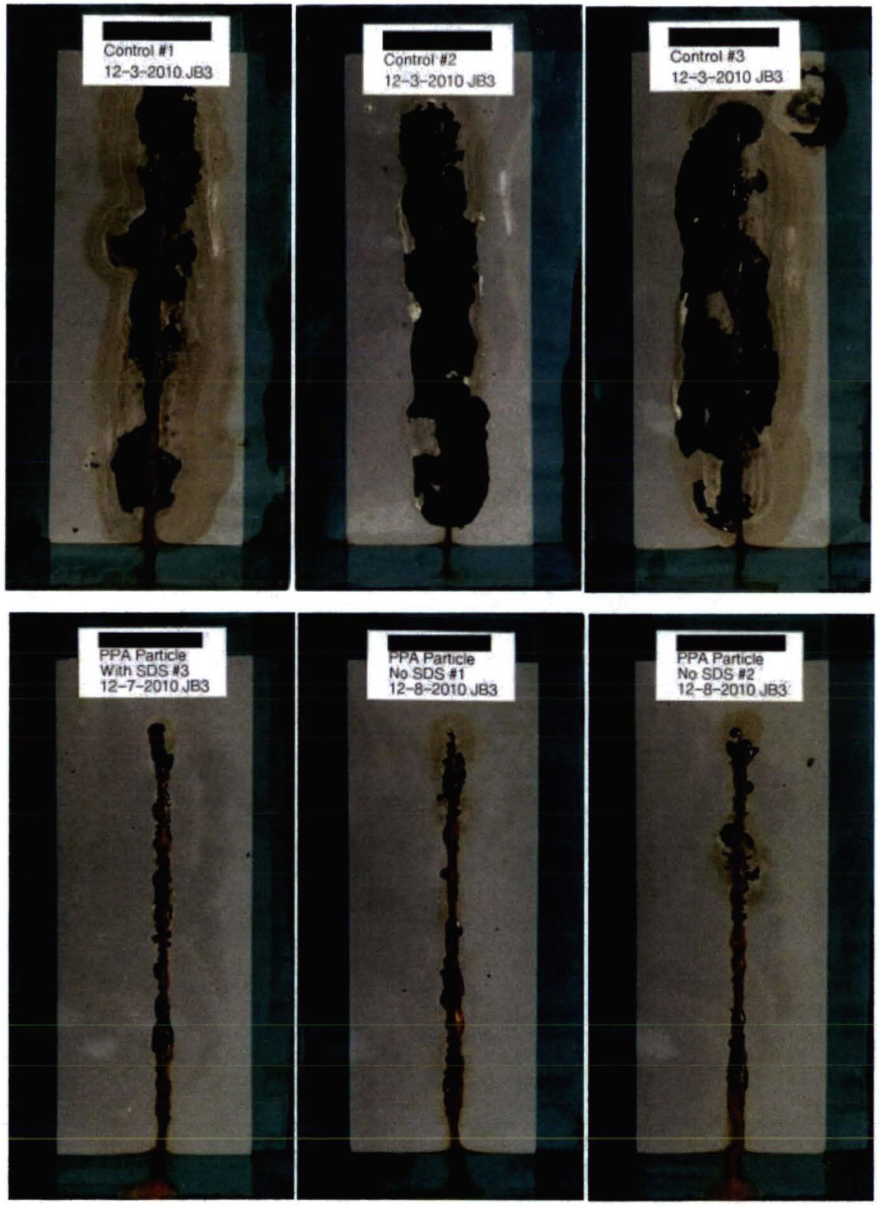
Inhibitor capsules (Ce/Mo) were tested in inorganic zinc coating on steel subtract without surface preparing.

Inorganic zinc provides excellent protection when surface preparation is sufficient to provide good adhesion, this test is done on steel without surface preparation.

The tested encapsulated inhibitor improved the adhesion and protection on steel.

Inorganic Zn	Sample #	Rust Grade
Control	1	1
	2	2
	3	3
10% water-core inhibitor microcapsule slurries	1	6
	2	7
	3	7

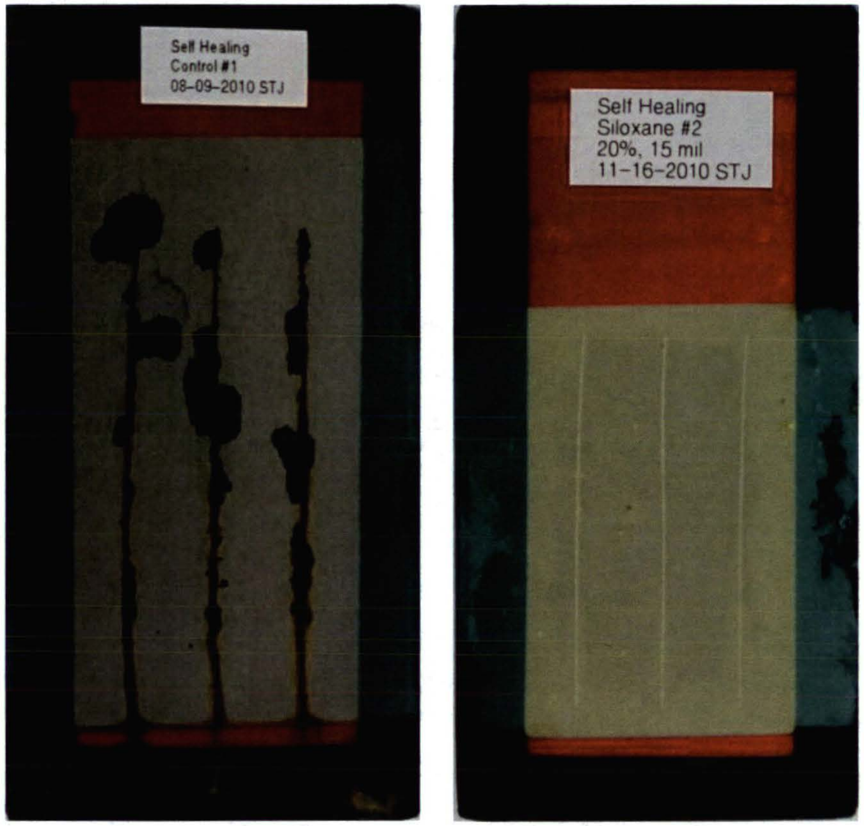
PA Particle in Epoxy: 1000 Hour Salt Fog



Control

With 10% PA Particles

Prototype Paint for Self Healing



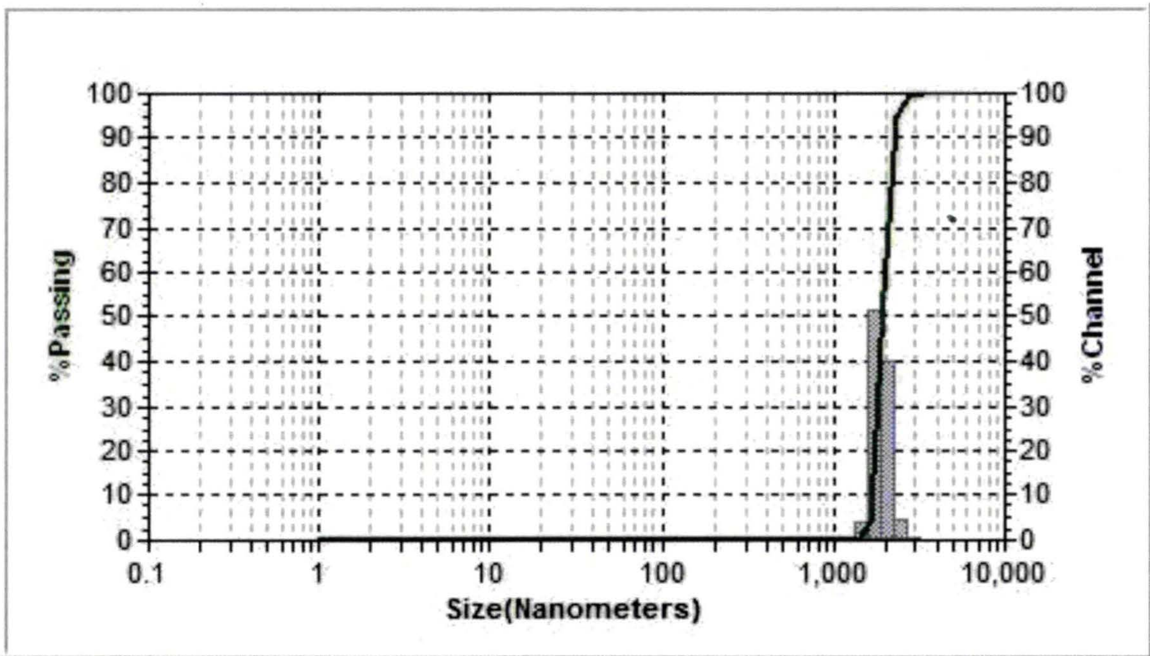
700 hours of salt fog testing results of carbon steel panels coated with a control coating system (left panel) and the same coating with a self healing system (right panel).

Frequently Asked Questions

- Particle size
- Types of materials encapsulated
- Mechanical strength or survivability during mixing
- Paint formulation compatibility
- Thermal Stability

Particle Sizes

- The size of indicator and inhibitor microcapsule and microparticles is around 1 micron, with a narrow size distribution (as shown below).



- Microcapsules containing self healing agents need to be larger to provide effective healing.

Encapsulated Materials

- A wide variety of corrosion indicators, inhibitors as well as self healing systems.
- A wide range of materials, both water soluble and solvent soluble.
- Water soluble or dispersible compounds can be encapsulated into water core microcapsules.
- Oil soluble or dispersible compounds can be encapsulated into oil core microcapsules.
- Some materials can also be incorporated into microparticles.

Mechanical Strength

- For corrosion indicator and inhibitor containing microcapsules, the mixing process is not a concern, due to their small sizes.
- The microcapsules are formed under high energy mixing condition (above 5000 rpm), so that the grinding process is not a concern.
- Microparticles are formed under mild mixing condition (500-1000 rpm), but the grinding process is not a concern either, as they do not have a liquid core.

Paint Compatibility

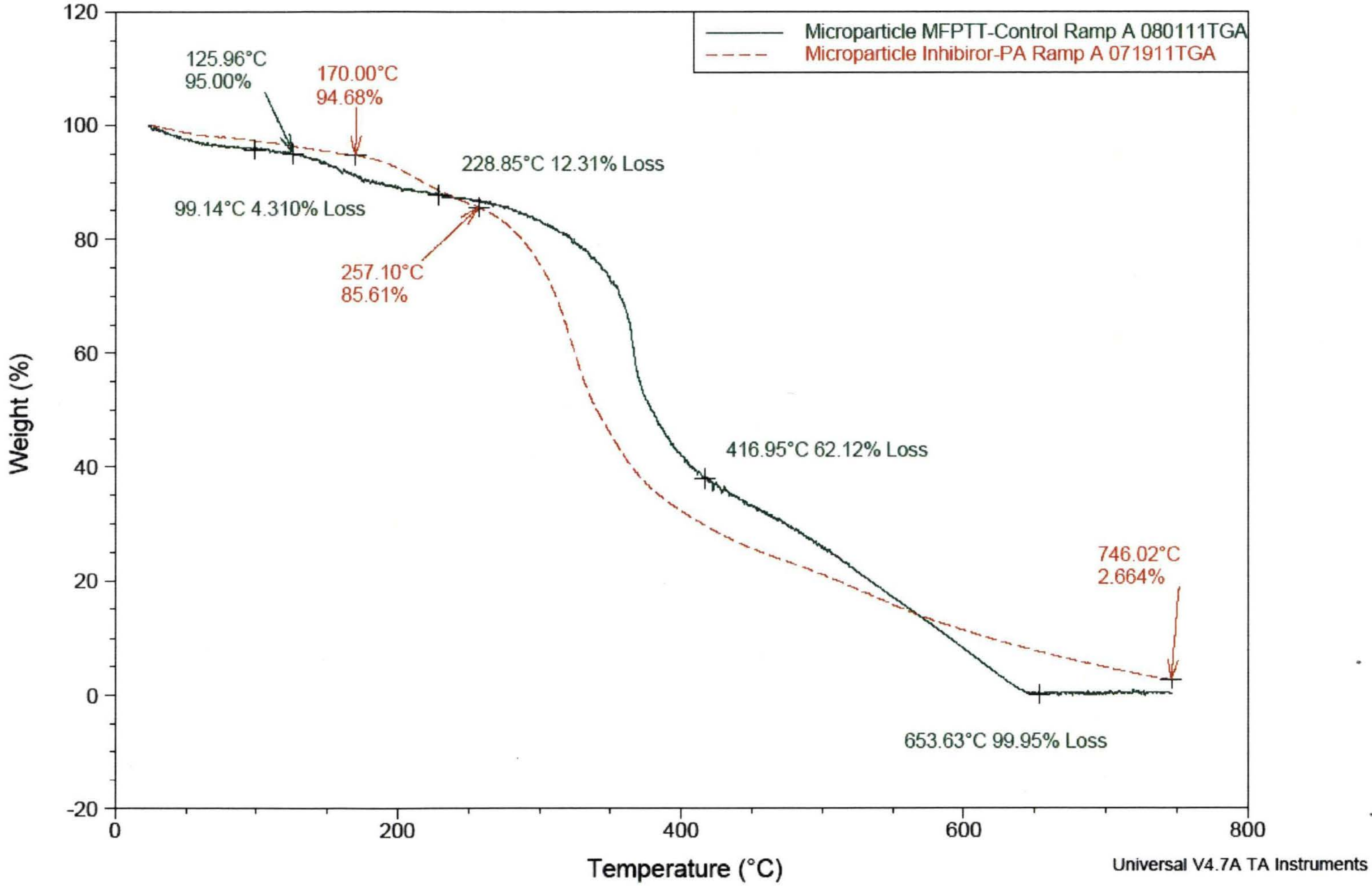
- Paint compatibility involves three factors:
  - Compatible in paint formula: no phase separation or reaction when incorporated into paint
  - Compatible with coating application process: no negative impact on viscosity, pot life, flowability, and other factors that influence the final coating quality.
  - Compatible in dry coating: does not cause coating defect during drying and/or curing process.
- Although paint incompatibility can manifest itself at various coating states, the root cause is normally capsule size or capsule surface chemistry related.
- Large capsules can result in phase separation and many coating defects. At about 1 micron capsule size, this concern is minimal.
- To address the surface chemistry issue, the post-processing and handling of the microcapsules have been optimized. After microparitcles were synthesized, they are separated from he solution, washed with water or solvent to eliminate surface impurities, re-dispersed into water, and finally spray dried into a free flowing powder form. This process has been effective to address coating compatibility problems.

Thermal Stability

- Initial TGA results showed some weight loss between room temperature and 210°C and that major thermal degradation does not begin until 250°C.

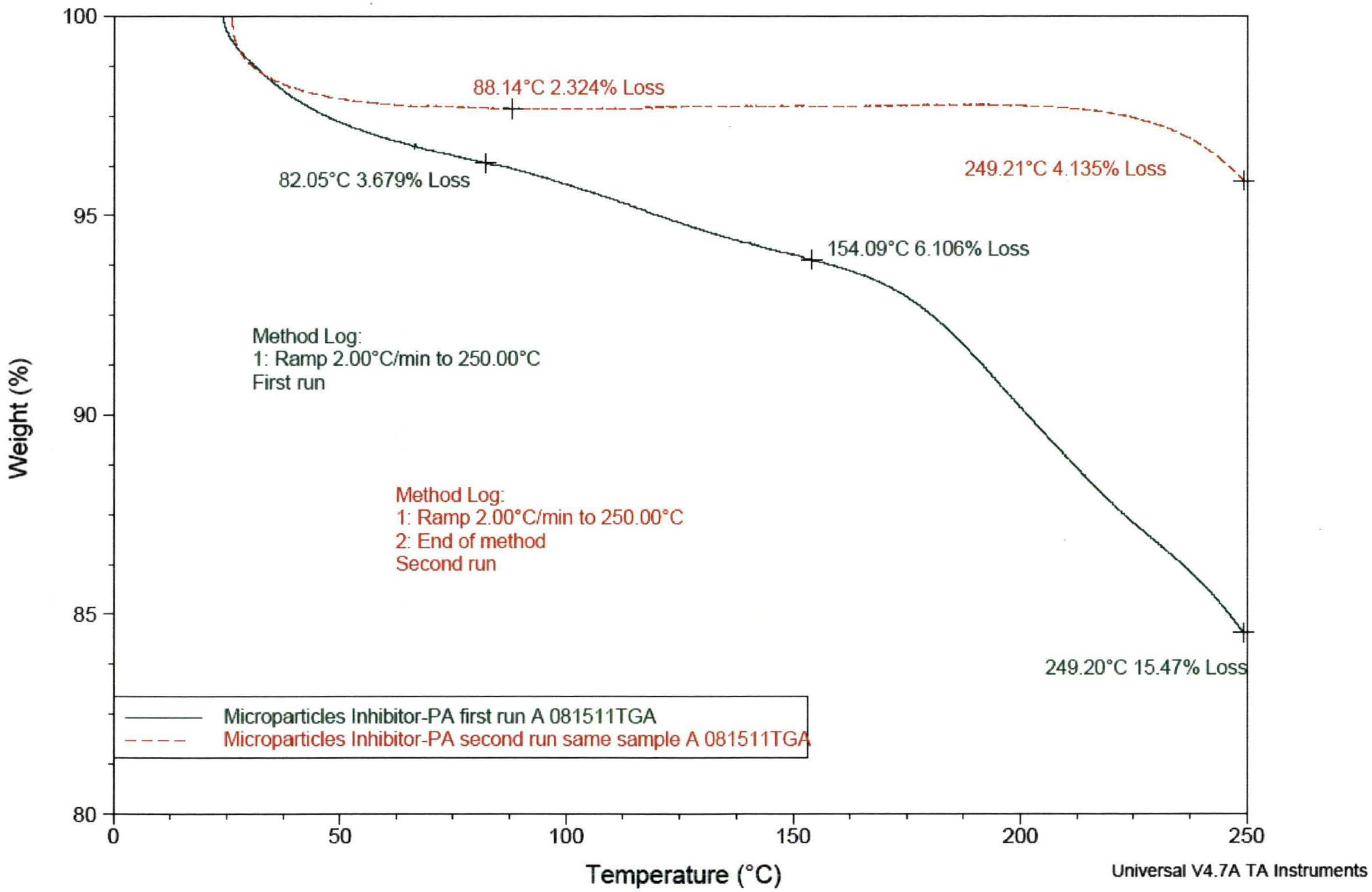
- Further TGA and DSC analysis showed the early weight losses (below 210°C) are likely due to water loss and curing of MFPTT. These weight losses are not observed after the resin is cured (even just partially).

Thermal Stability



Initial TGA results showed some weight loss between room temperature and 210°C and that major thermal degradation does not begin until 250°C.

Thermal Stability



Further TGA analysis showed the early weight losses (below 210°C) are likely due to water loss and curing of MFPTT. These weight losses are not observed when the sample is heated again.