A Multifunctional Smart Coating For Autonomous Corrosion Control

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Introduction

- Nearly all metals and their alloys are subject to corrosion that causes them to lose their structural integrity or other functionality.
- It is essential to detect corrosion when it occurs, and preferably at its early stage, so that action can be taken to avoid structural damage or loss of function of metals and their alloys.
- Because corrosion is mostly an electrochemical process, pH and other electrochemical changes are often associated with it
  - It is expected that materials that are pH, or otherwise electrochemically responsive, can be used to detect and control corrosion.
  - The goal of this research is to develop a corrosion-controlled release delivery system that consists of pH-triggered release microcapsules.
  - These microcapsules can then be incorporated into coatings for early detection of corrosion and for corrosion protection.
  - Additionally, the delivery of healing agents to repair mechanically damaged coatings is being investigated.

What is a “Smart Coating”

- A Smart Coating can be a multifunctional coating formulated by incorporating encapsulated corrosion indicators, corrosion inhibitors, and self-healing systems. The versatility of the microcapsules allows the incorporation of the desired corrosion control functions, singly or combined.
  - 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.
  - The key factor being the relation between pH and corrosion

- The Kennedy Space Center Corrosion Technology laboratory is developing a Smart Coating which uses pH sensitive microcapsules and microparticles that deliver their contents when corrosion starts to:
  - Detect and indicate the corrosion location
  - Deliver environmentally friendly corrosion inhibitors
  - Deliver healing agents to repair mechanical coating damage.

- This research focuses on:
  - The design of pH sensitive microcapsules and their synthesis
  - Testing of coatings with these microcapsules for both corrosion indication and inhibition functions.

Electrochemical Nature of Corrosion

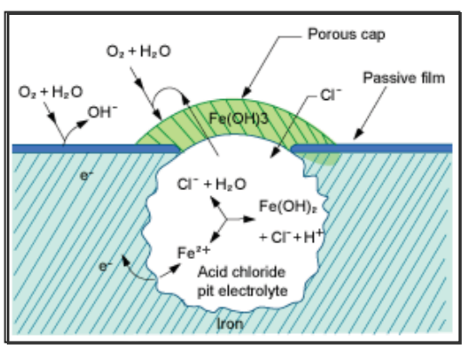
- Corrosion is for the most part an electrochemical phenomenon, because, in most cases, it involves the transfer of electrons between a metal surface and an aqueous electrolyte solution.
- For instance, when iron corrodes in near neutral environments, the typical electrochemical reactions are:

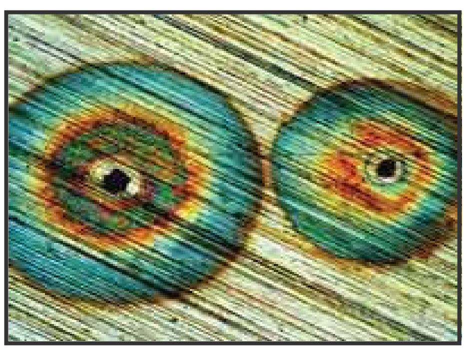
Overall Reaction: $$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

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

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

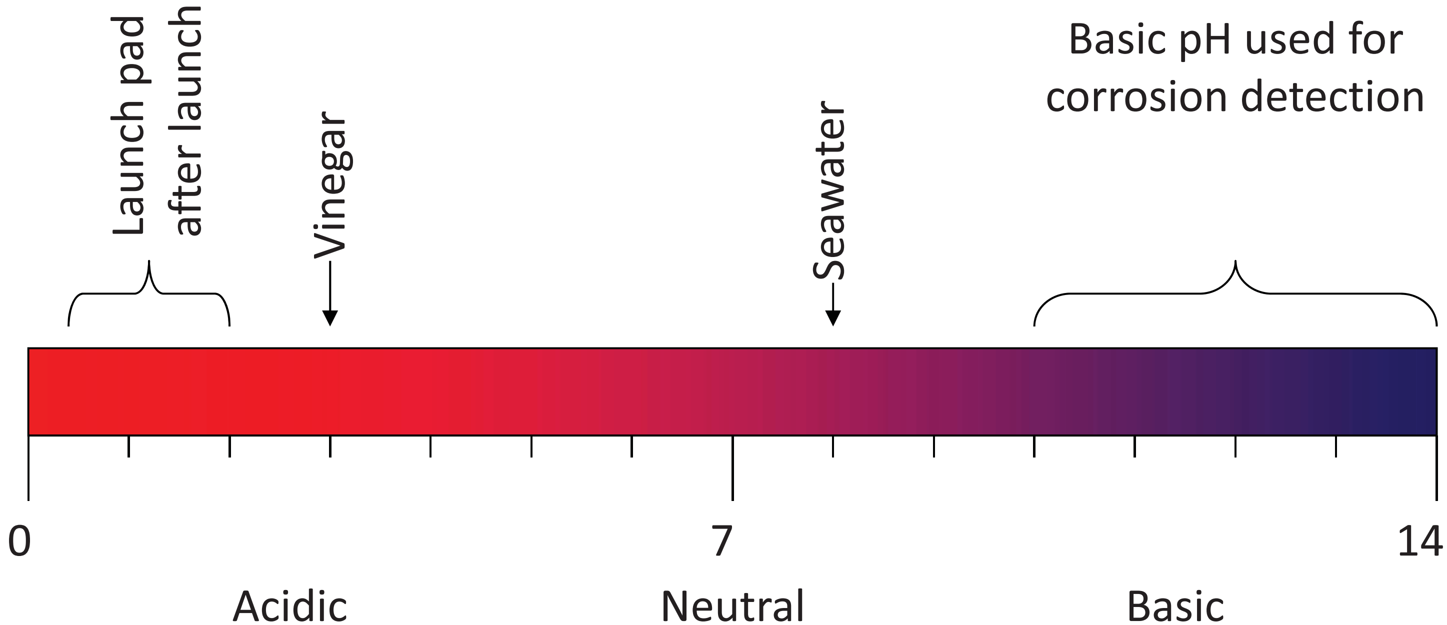
- In the case of localized corrosion, such as pitting corrosion the anodic reaction occurs in a confined area and the metal ions produced are precipitated as solid corrosion products, such as iron oxide, $Fe(OH)_2$, which cover the mouth of the pit. This porous cap covers the solution in the pit and allows the buildup of hydronium ions, H^+ inside the pit.





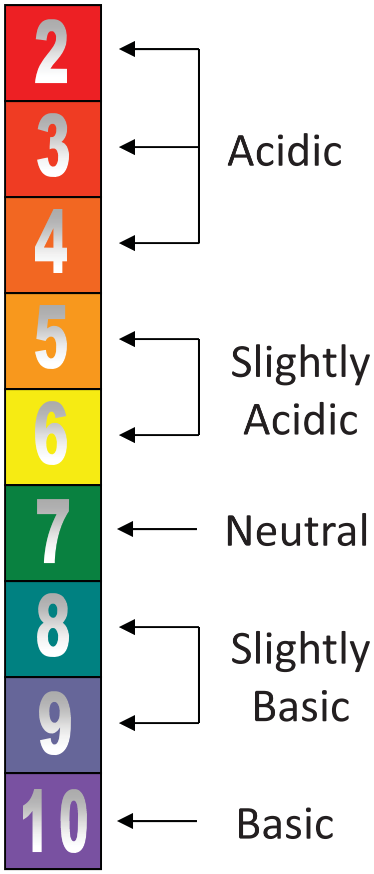
The overall effect is that, while localized corrosion happens, the anode area often has an acidic pH and the cathode has an alkaline pH

Corrosion and pH

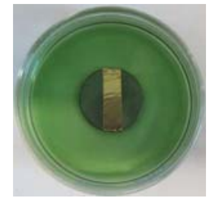


pH Scale

Corrosion Indication



- Basic demonstration that shows how pH changes during a corrosion reaction
- A universal pH indicator was used to show the pH changes that occur during corrosion of a metal, such as steel.
- Here steel was exposed to water while a strip in the middle was wrapped in copper tape.
- The color change of the pH indicator shows that the exposed steel tends to be acidic (yellow color) while the strip wrapped in the copper tape tends to be basic (purple color) due to the oxygen reduction reaction and the release of the hydroxide ion, OH^-.
- Since pH and other electrochemical changes are often associated with corrosion, it is expected that materials that are pH or otherwise electrochemically responsive can be used to detect and control corrosion.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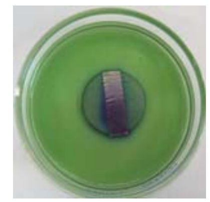
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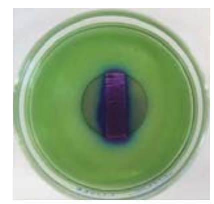
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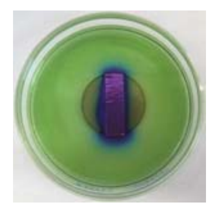
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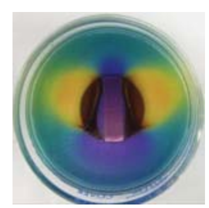

3 days

Smart Coating "Brain"

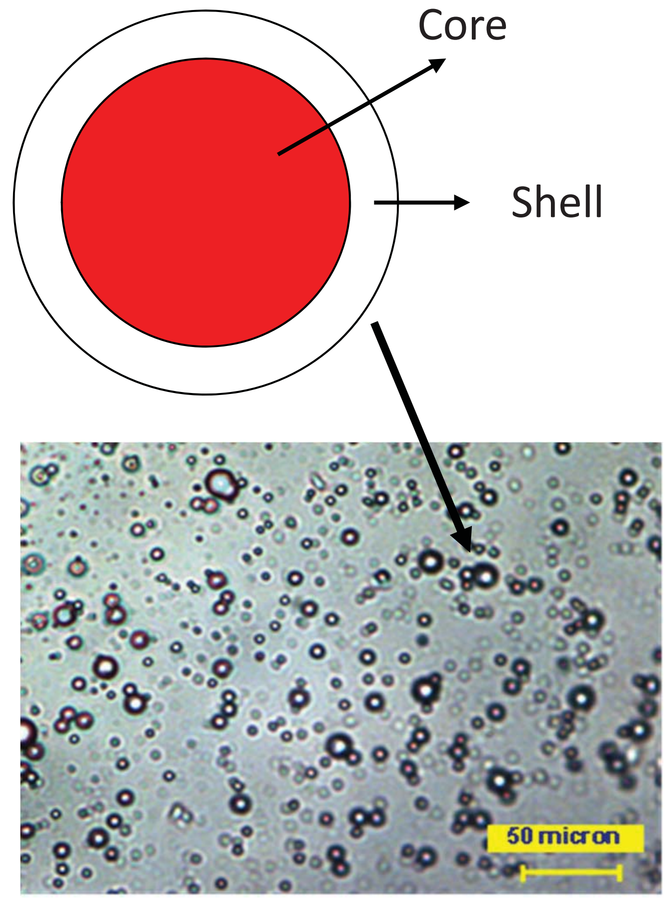
Corrosion indication, detection, and healing of mechanical damage can be achieved using **microencapsulation technology**

What are microcapsules?

Particles or liquid drops coated in polymers. These microcapsules, some as small as the point of a pin, can carry any material that needs protection or controlled release.

Why microencapsulate a material?

- To achieve controlled-release.
- Make active materials easier/safer to handle.
- Compartmentalize multiple component systems.
- Protect sensitive materials from their environment.
- Versatility



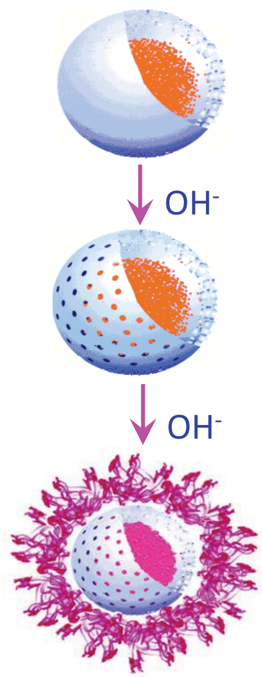
Microcapsules developed at KSC

Technology Development

- The pH sensitive microcapsule has a wall designed to break down and release the core contents in response to the pH of the cathodic site of localized corrosion.

- The microcapsule can release corrosion inhibitors on demand when needed and where they are needed.

- This is advantageous because the encapsulated inhibitors, when incorporated into a coating, will be protected and prevented from interacting with other coating components.

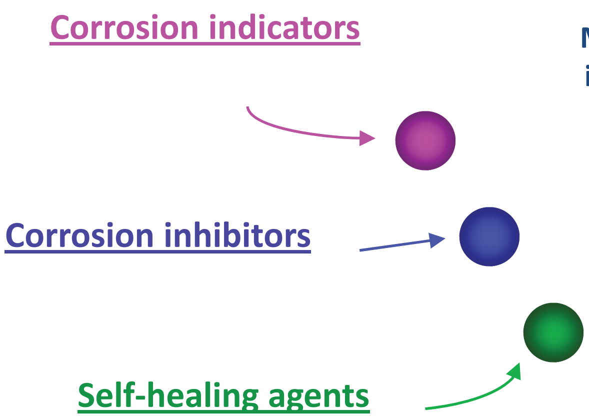


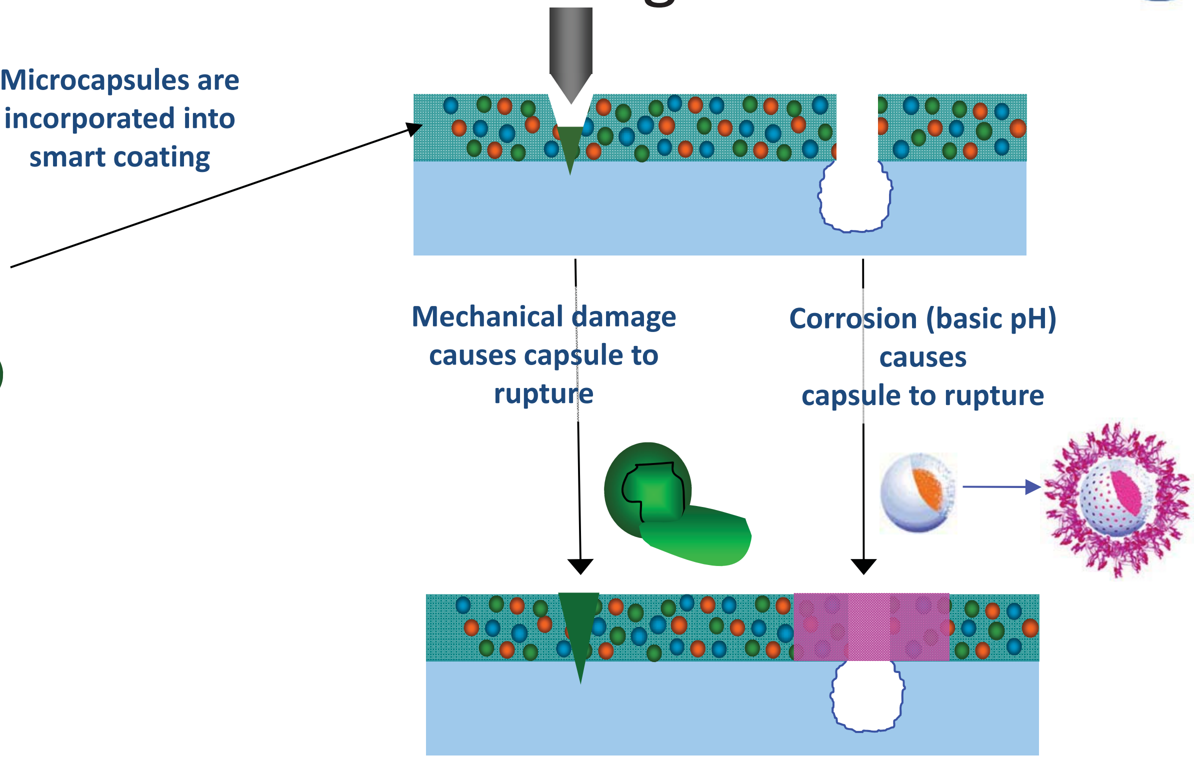
Microcapsule containing pH indicator (inhibitor, self healing agents)

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 and Mechanical Damage





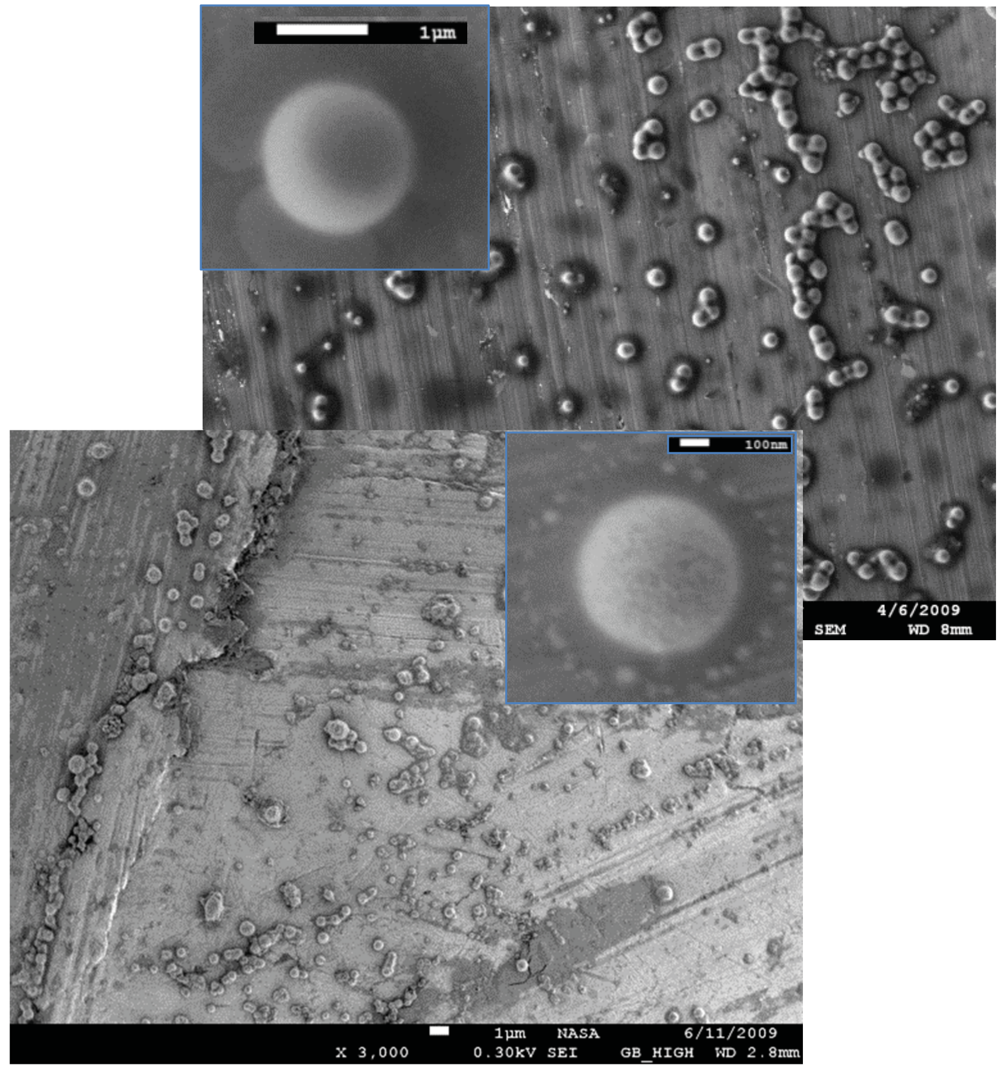
- Microencapsulation is a versatile approach because it can be used to encapsulate an unlimited number of materials, in both solid and liquid phase, and even in the gas phase when entrapped in a material such as aerogel.
- It is possible to incorporate microcapsules into composites or coatings. For corrosion applications, various compounds, such as corrosion indicators, inhibitors, self-healing agents, and dyes can be encapsulated.
- These microcapsules can be incorporated into various coating systems for corrosion detection, protection and self-repair of mechanical coating damage

Benefits of Microcapsules

- The versatility of the design is of special interest in corrosion inhibition applications. Almost all corrosion inhibitors are chemically active reagents. Very often, the reactivity that makes them effective corrosion inhibitors also causes them to be environmentally unfriendly, such as in the case of chromates. Because of this, research for new and environmentally friendly corrosion inhibitors is an on-going effort in the corrosion protection industry.
- After a new inhibitor is developed, it usually takes a long time to incorporate it into a paint formulation.
  - Microencapsulation of the inhibitor can shorten this long reformulation process because it prevents the interference of the inhibitor with other paint components.
- The pH-controlled release microcapsule design has, in addition to all the advantages of the microcapsule design, the true controlled-release function for corrosion applications.
- Most microcapsule applications involve the release of the core contents when the microcapsules are mechanically broken. However, pH sensitive microcapsules are specifically designed to release their contents when corrosion occurs.
- Mechanical damage in a coating is one of the important causes for corrosion of the base metal.
- However, many forms of defects in coatings, such as air bubbles, uneven thickness, permeation, porosity or edge effects, will also result in poor corrosion protection of the coating and allow corrosion to occur.
- pH sensitive microcapsules will release their content for corrosion detection or protection regardless of the corrosion cause.

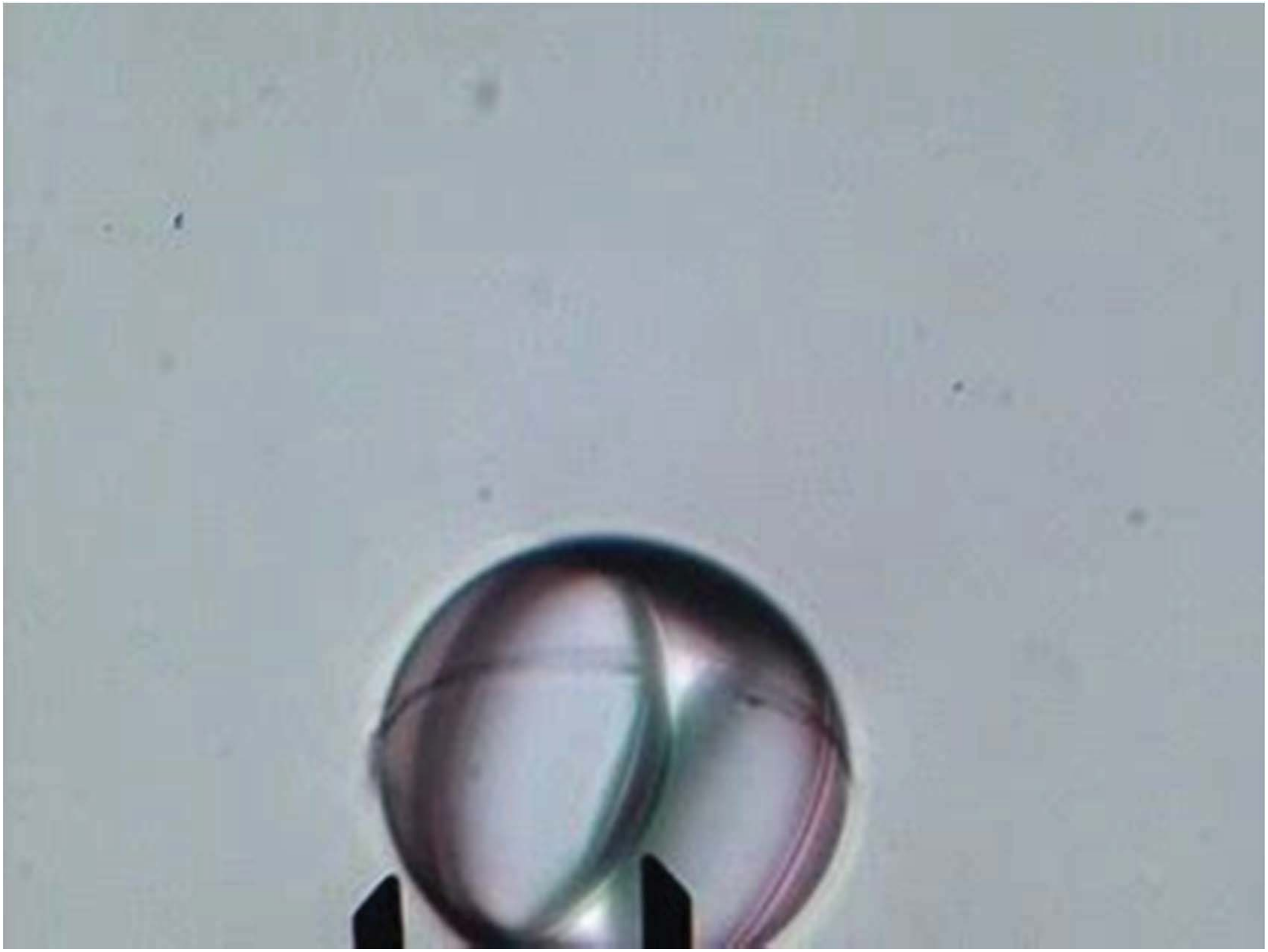
Microcapsules for Corrosion Indication and Inhibition

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



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

Microcapsule Response to pH Increase

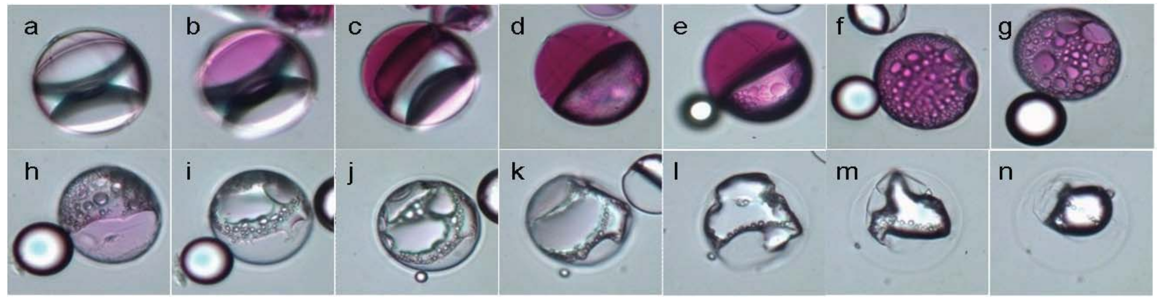


Microcapsules for Corrosion Indication

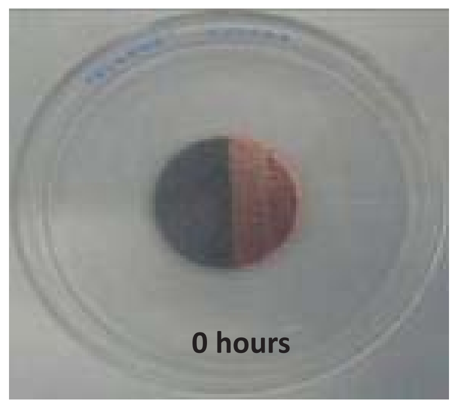
pH sensitive microcapsules with corrosion indicator for corrosion detection

Significance:

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

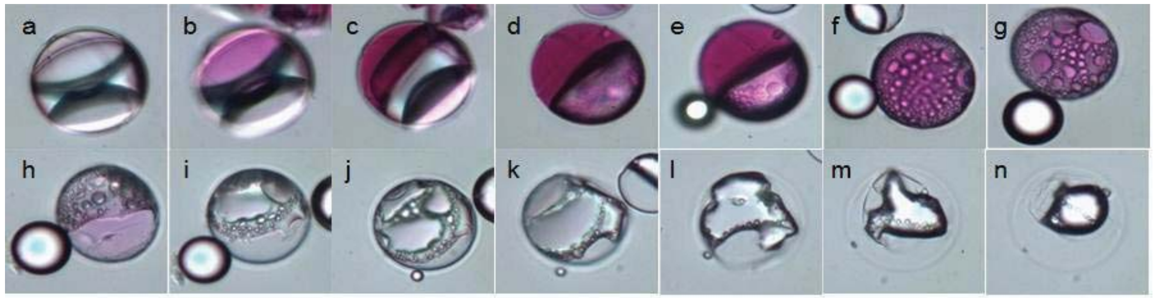


Time lapse pictures of a microcapsule with indicator breaking down under basic pH conditions.



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

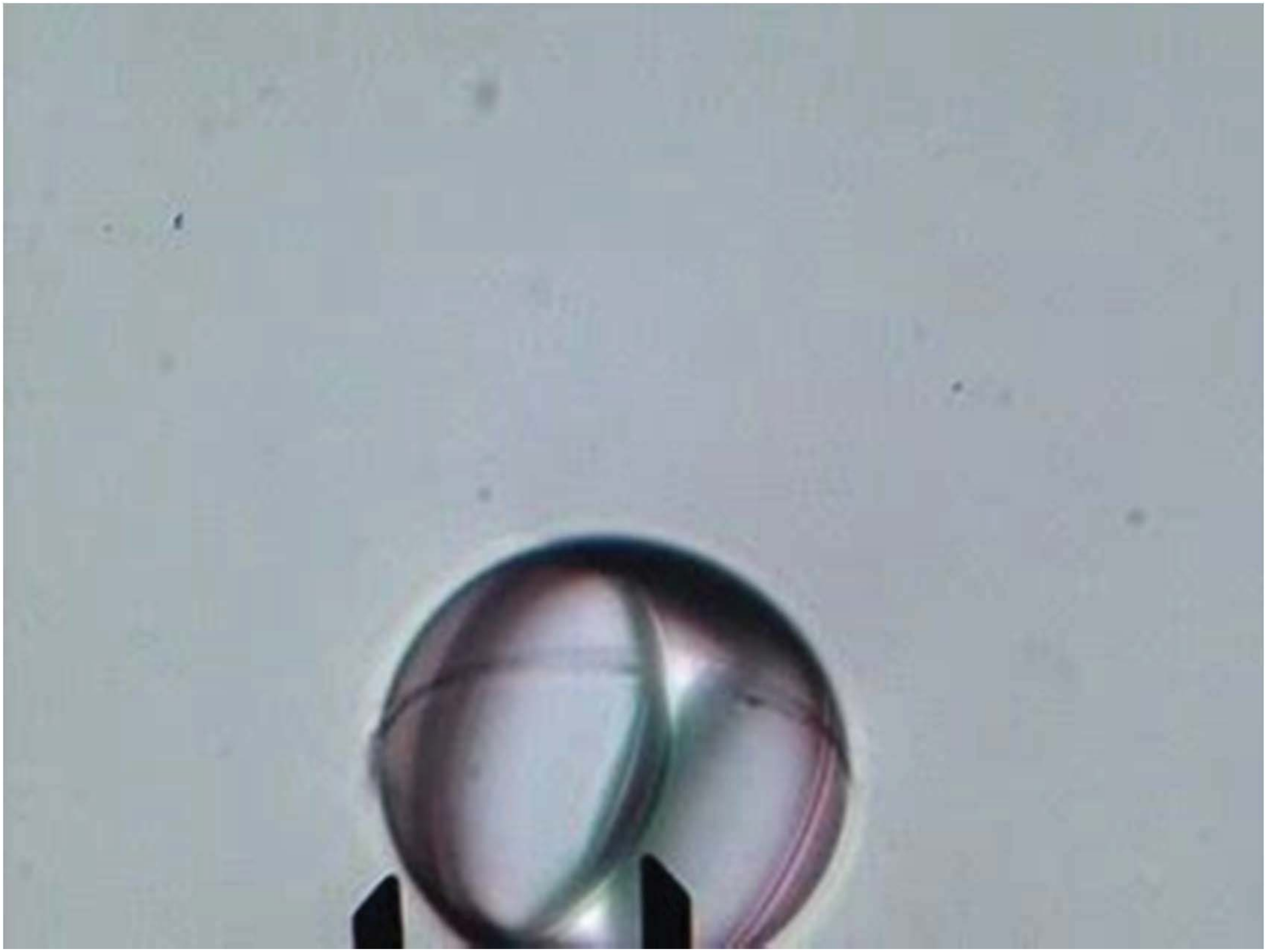
Microcapsules for Corrosion Indication



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

- The figure above shows such a breakdown as it occurs when microcapsules are exposed to a small amount of water containing sodium hydroxide, NaOH, (pH of 12).
- Soon after the microcapsules are exposed to the NaOH solution, the solution starts to penetrate the microcapsule wall, as indicated by the color change of the encapsulated pH indicator (Frames b-d).
- In frame e, the microcapsule begins to slowly release its contents (as evidenced by the small droplet that begins to form on the bottom left quadrant of the frame).
- The presence of droplets observed inside the microcapsules is due to the fact that the core content of the microcapsule is not miscible in water (oil-core microcapsule).
- The content continues to be released until (as seen on frame i) it dissipates into the solution.
- The microcapsule wall eventually disintegrates as shown in frames j through n.

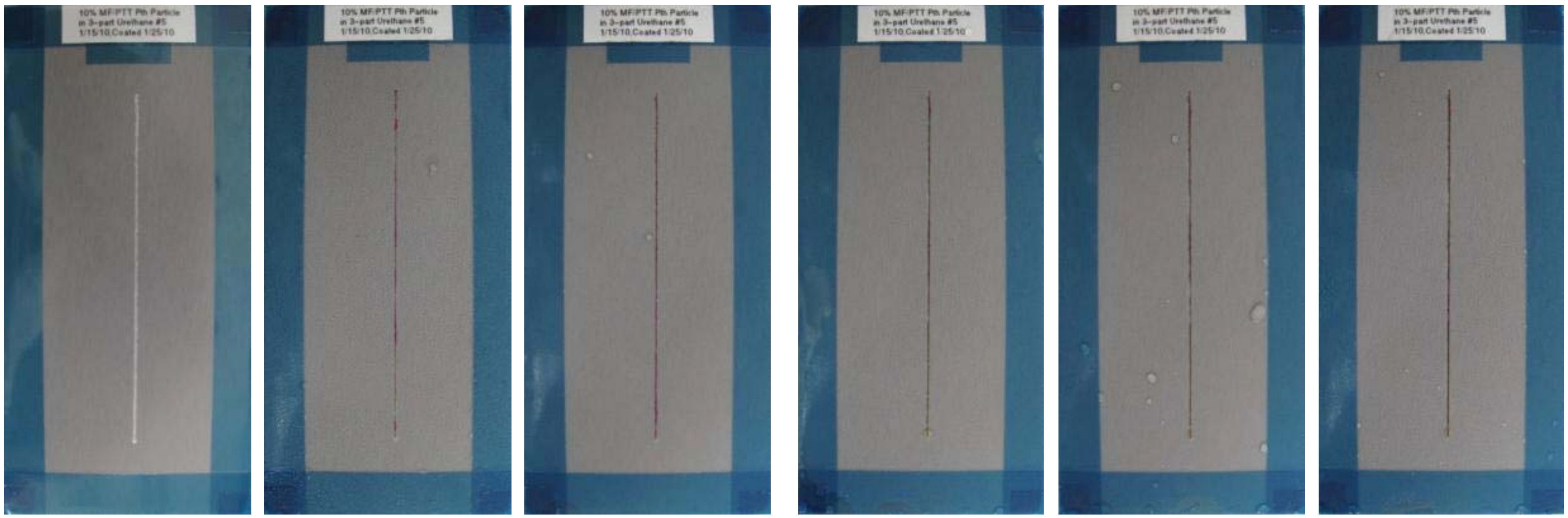
Microcapsule Response to pH Increase



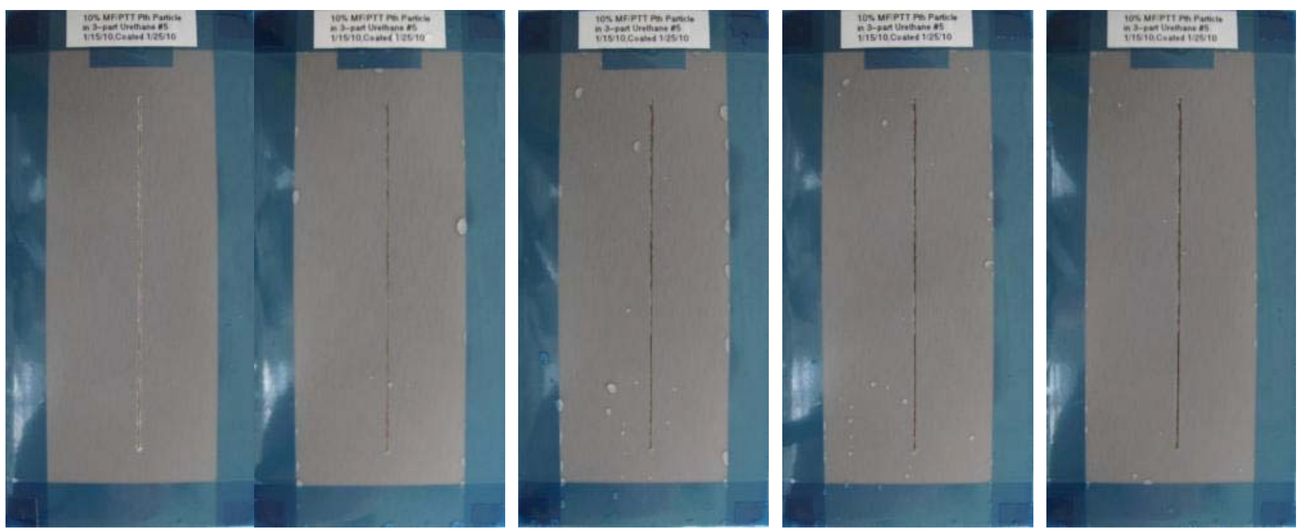
Early Indication of Corrosion

Experimental Corrosion Indicating Coating

Initial 0.5hr 1hr 1.5hr 2hr 2.5hr



0.5hr 1hr 1.5hr 2hr 2.5hr



Corrosion indication test results. Color change observed before rust appears.

Experimental Corrosion Indicating Coating

23.5hr

30.5hr

47.5hr

78.5hr

Testing

Field testing is being proposed on hangar doors at the Corpus Christy Army Depot

Conclusions

- A multifunctional smart coating for the autonomous control of corrosion is being developed using pH-sensitive microcapsules.
  - The microcapsules are designed specifically to detect the pH changes that are associated with the onset of corrosion and respond autonomously to indicate its presence early, to control it by delivering corrosion inhibitors, and to deliver self healing or film forming agents capable of repairing mechanical damage to the coating.
- Various pH-sensitive microcapsules with hydrophobic or hydrophilic cores were synthesized through interfacial polymerization reactions in an emulsion.
  - The microencapsulation process was optimized to obtain monodispersed microcapsules in a size range suitable for incorporation into commercially available coatings. The microcapsules can be harvested in suspension or in free-flowing powder form.
- Preliminary results from salt fog testing of panels coated with commercially available coatings, in which the microcapsules were incorporated, indicate that microcapsules can be used to detect corrosion before visible rust appears and to deliver corrosion inhibitors.
- Current work is being focused on optimizing the concentration of indicator in the microcapsules as well as on optimizing the release properties of the microcapsules when incorporated into coatings of interest.
  - Candidate self healing systems have been encapsulated and tested for self-healing performance. Salt fog test results revealed that the 2-capsule siloxane resin system had the best self-healing performance. Methods designed to accomplish good self-healing corrosion control in thinner films are being evaluated.