A MULTIFUNCTIONAL COATING FOR AUTONOMOUS CORROSION CONTROL

Luz M. Calle and Paul E. Hintze
NASA
Kennedy Space Center, FL 32899

Wenyan Li, Jerry W. Buhrow, and Scott T. Jolley
ASRC Aerospace
Kennedy Space Center, FL 32899

ABSTRACT

[Corrosion is a destructive process that often causes failure in metallic components and structures. Protective coatings are the most commonly used method of corrosion control. However, progressively stricter environmental regulations have resulted in the ban of many commercially available corrosion protective coatings due to the harmful effects of their solvents or corrosion inhibitors. This work concerns the development of a multifunctional, smart coating for the autonomous control of corrosion. This coating is being developed to have the inherent ability to detect the chemical changes associated with the onset of corrosion and respond autonomously to control it. The multi-functionality of the coating is based on micro-encapsulation technology specifically designed for corrosion control applications. This design has, in addition to all the advantages of other existing microcapsules designs, the corrosion controlled release function that allows the delivery of corrosion indicators and inhibitors on demand only when an where they are needed. Corrosion indicators as well as corrosion inhibitors have been incorporated into the microcapsules, blended into several paint systems, and tested for corrosion detection and protection efficacy.

1. INTRODUCTION

Metals and alloys are present in some shape or form in nearly every facet of our lives. Nearly all metal and metal 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 structure damage or loss of function of the metals and their alloys. Because corrosion is mostly an electrochemical process, pH and other electrochemical changes are often associated with corrosion, so it is expected that materials that are pH or otherwise electrochemical responsive can be used to detect and control corrosion. The authors developed a smart coating with a controlled-release system that uses pH-triggered release microcapsules for early detection of corrosion and for corrosion protection. The following sections will briefly describe the relation between pH and corrosion, the design of pH sensitive microcapsules and their synthesis, as well as selected test results of the smart coating with pH sensitive microcapsules for corrosion indication and inhibition.

1.1 Corrosion and pH

[Corrosion is largely 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:

Cathodic reaction:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	
Anodic reaction:	$Fe \rightarrow Fe^{2+} + 2e^-$	

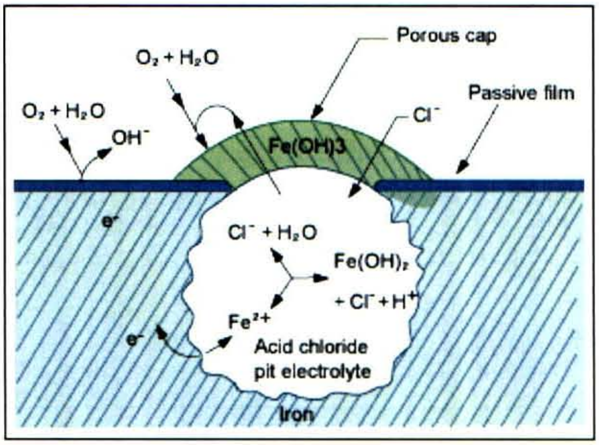


Figure 1. The electrochemical cell set up between anodic and cathodic sites on an iron surface undergoing pitting corrosion.

In the case of localized corrosion, such as pitting corrosion, the anodic reaction happens in a confined area, the metal ions produced are precipitated as solid corrosion products, such as iron(II) oxide, $Fe(OH)_2$, (often further oxidized to iron(III) oxide, $Fe(OH)_3$), which covers the mouth of the pit.

$$2Fe^{2+} + 2H_2O + O_2 + 4e^- \rightarrow 2Fe(OH)_2$$
$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 3Fe(OH)_3$$

This covering traps the solution in the pit and allows the buildup of hydronium ions, H^+, through a hydrolysis reaction:

$$Fe^{2+} + 2H_2O \rightarrow 2Fe(OH)_2 + 2H^+$$

Then, chloride, Cl^-, or other damaging negative ions diffuse into the pit to maintain charge neutrality. Consequently, the solution inside the pit becomes highly acidic. The overall effect is that, while localized corrosion happens, the anode area often has an acidic pH and the cathode has an alkaline pH.[1]

Besides pitting, crevice corrosion and dissimilar metal corrosion result in pH changes as the simple demonstration in Figure 2 shows. A universal pH indicator was used to show the pH changes that occur during corrosion of a metal, such as steel. In this demonstration, most of the 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^-.

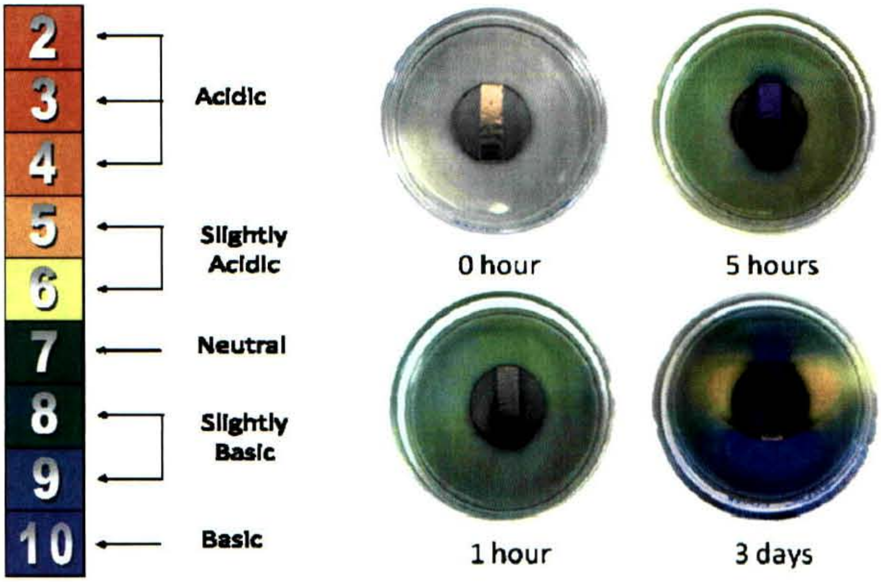


Figure 2. pH Changes associated with corrosion.

pH and other electrochemical changes are often associated with corrosion, so it is expected that materials that are pH or otherwise electrochemical responsive can be used to detect and control corrosion. Various pH and electrochemical responsive materials and their potential applications in smart coatings for corrosion control can be found in our previous review.[2] Self healing coatings is another new development in material design that is important to corrosion control.[3,4,5] Insert text]

1.2 pH sensitive Microcapsules

The authors developed a controlled-release system that combines the advantages of corrosion sensing and corrosion protection by using pH-triggered release microcapsules for early corrosion detection and corrosion protection.[2,6,7] The key component of this technology is a pH sensitive microcapsule with a wall designed to break down and release the encapsulated contents in response to the pH condition of the cathodic site of localized corrosion (as shown the figure below).

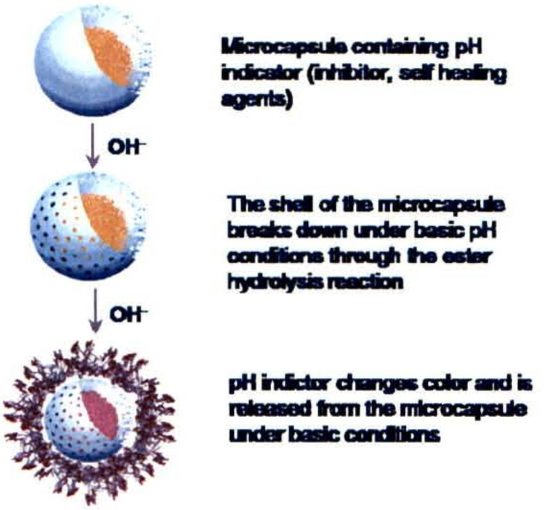


Figure 3. The key component of the smart coating system: pH sensitive microcapsules.

The chemistry of the pH sensitive microcapsules is base-catalyzed ester hydrolysis. The polymeric walls of the microcapsules include a cross-linking agent that has one or more ester and mercapto groups. A typical cross-linker is pentaerythritol tetrakis (3-mercaptopropionate) (PTT), a tetra-functional molecule whose structure is shown below.

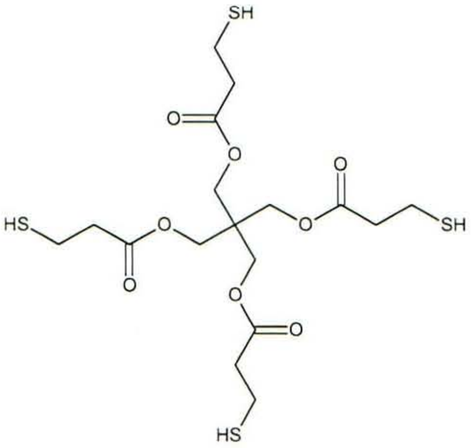


Figure 4. Structure of pentaerythritol tetrakis (3-mercaptopropionate) (PTT).

Since this cross-linker is not a good film former, other prepolymers or monomers are needed to provide the structural integrity of the microcapsule wall. Examples of the film-forming monomers and pre-polymers include urea formaldehyde and melamine formaldehyde monomers and prepolymers. A generalized structure of a urea/formaldehyde/PTT condensation polymer is given in Figure 5.

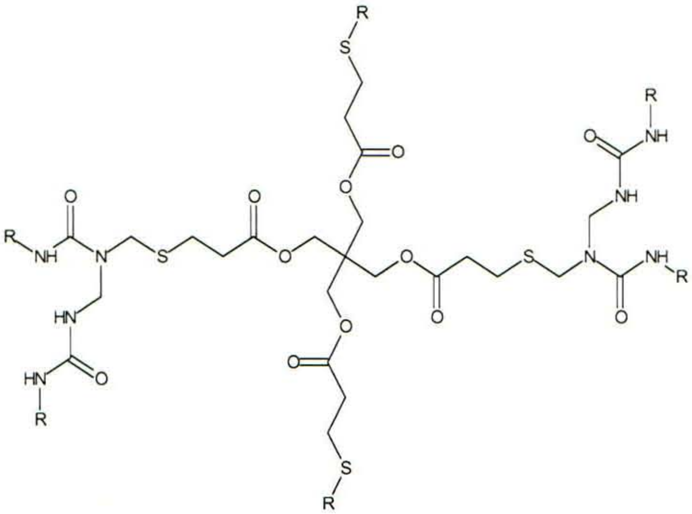


Figure 5. Generalized urea/formaldehyde/PTT structure, where R represents a continuation of the condensation polymer.

The mercapto functionality is an excellent participant in forming the microcapsule walls. The proton on the thiol moiety is quite acidic, allowing it to function as an excellent active hydrogen group. The pKa value of alkyl mercaptans falls generally in the 10-11 range which is significantly lower than water (15.7) and alcohols (16-18).[8] The 3-mercaptopropionate version proved to be more useful than other commercially available mercaptoesters based on mercaptoethyl ester chemistry. Mercaptoethyl versions reacted more quickly[9] and cross- linked to a greater degree than the mercaptopropyl chemistry, which could result in a polymer condensation rate too fast for the optimized encapsulation conditions when *in-situ* polymerization is used. The hydroxyalkyl polyol esters were also considered as possible candidates for use as hydrolysable crosslinkers, but their preparation presents difficulties due to the self condensation side reaction.

Capsule wall breakdown under basic conditions can be observed visually. Figure 6 shows such breakdown occurring in response to exposure to a small amount of water containing sodium hydroxide, NaOH, (pH of 12). Soon after the NaOH solution was added, the solution starts to penetrate the microcapsule wall, as indicated by the color change inside the microcapsules (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 content continues to be released until (as seen on frame i), it dissipates into the solution. The microcapsule wall eventually collapses as shown in frames j through n.

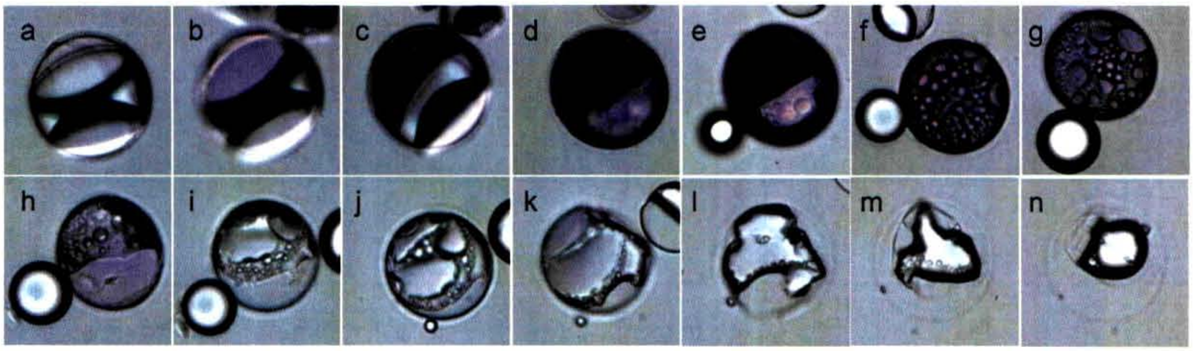


Figure 6. Microcapsule breakdown in basic solution.

1.3 Smart Coating Based on pH Sensitive Microcapsules

Microcapsulation 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 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 (Figure 7). 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. A smart coating that includes encapsulated inhibitors and releases them on demand when corrosion starts, can shorten this long reformulation process for new inhibitors by simply changing the core content of the microcapsules.

The pH-controlled release microcapsule design has, in addition to all the advantages of the regular microcapsule design, the true controlled-release function for corrosion applications. Regular microcapsules release their contents when they are mechanically broken. pH sensitive microcapsules release their contents when corrosion occurs. Mechanical damage in a coating is one of the important causes for corrosion of the base metal. However, it is not the only one. Many forms of defects in coatings, such as air bubbles, uneven thickness, permeation, porosity or edge effects, will 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.

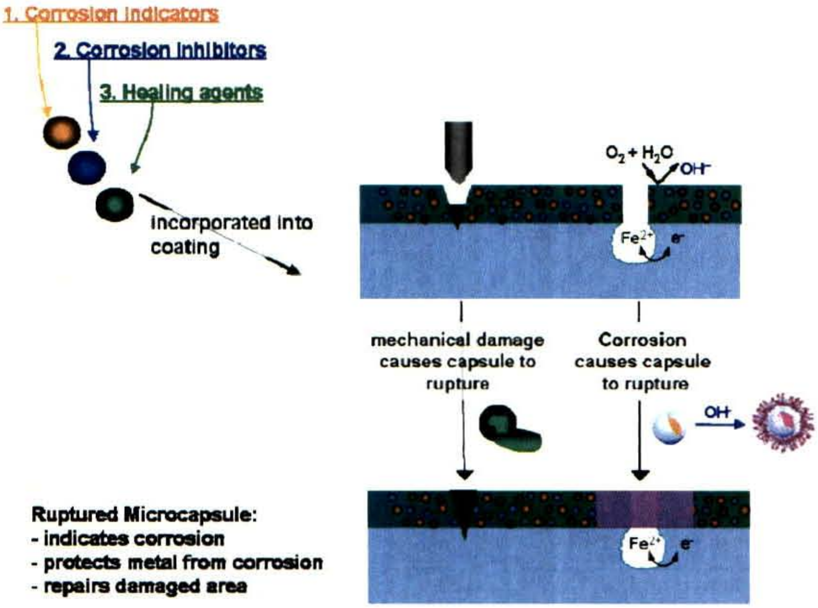


Figure 7. Smart coating with pH sensitive microcapsules for corrosion detection and protection applications.

1.4 Encapsulation Process

1.4.1 Encapsulation Methods

pH sensitive microcapsules are the key component of the smart coatings. Several methods such as spray drying, emulsion polymerization, interfacial polymerization, as well as *in-situ* polymerization have been used to synthesize pH sensitive microcapsules. Interfacial polymerization is illustrated below as an example. There are two main steps involved in the interfacial polymerization process: microemulsion formation and microcapsule wall formation. This technique can be used to form both oil (or hydrophobic) core and water (or hydrophilic) core microcapsules. Figure 8 shows a schematic representation of the steps involved in forming oil core microcapsules: the microemulsion is formed by adding the oil phase (with prepolymer, shown in yellow) to the water phase (with surfactant, shown in blue) and mixing; the last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization. Figure 9 shows a schematic representation of the steps involved in forming water core microcapsules: in this case, the microemulsion is formed by adding water (shown in blue) to the oil (with prepolymer and the surfactant, shown in yellow) followed by mixing; the last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization.

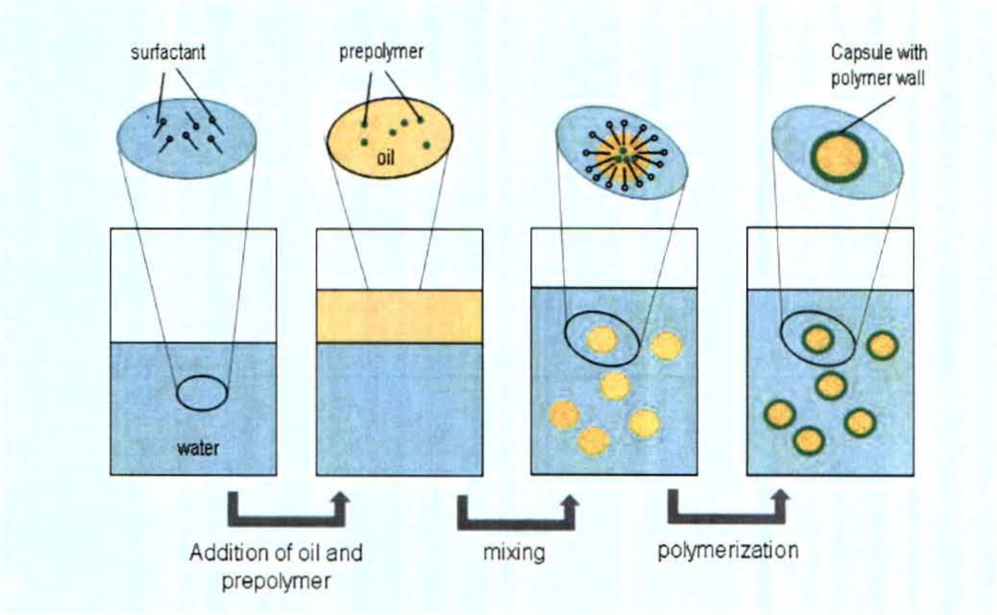


Figure 8. Schematic representation of the steps involved in the interfacial polymerization of an oil-in-water microemulsion for making oil core microcapsules. Oil is shown in yellow and water in blue.

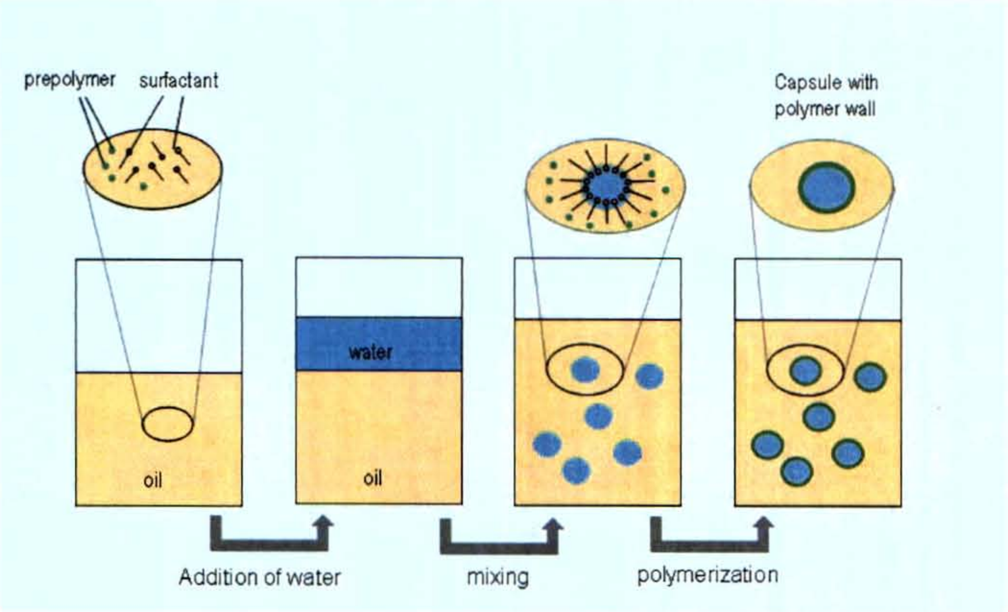


Figure 9. Schematic representation of the steps involved in the interfacial polymerization of a water-in-oil microemulsion to synthesize water core microcapsules. Oil is shown in yellow and water in blue.

The two illustration above involve the use of oil, or hydrophobic solvent soluble wall forming prepolymer. A similar process can be developed to use water soluble wall forming materials by dissolving the wall forming prepolymer in the water phase and the catalyst in the oil phase. The reaction at the interface will form the capsule.

In situ polymerization is also used to form pH sensitive microcapsules. The distinguishing characteristic between interfacial polymerization and *in situ* polymerization is that the polymerization reaction occurs in the continuous phase and the polymer is formed through the reaction deposits at the interface to form the capsule wall.

Spray drying involves dispersing the wall forming precursor and substance to be encapsulated (the core material) into a continuous phase (water for instance), spraying the mixture into a mist and into a hot gas flow; the liquid droplets are dried into solid particles. In the process, the core material is encapsulated inside the wall materials.

Interfacial polymerization and *in-situ* polymerization are the main approaches used by the authors for microcapsule synthesis. Interfacial polymerization is used to synthesize oil-core and water-core microcapsules with corrosion indicators, corrosion inhibitors, and self healing agents as active core contents. *In situ* polymerization is also used to synthesize microcapsules with corrosion indicators and self healing agents mainly into oil-core microcapsules where water is used as the continuous phase. Spray drying has been used to synthesize solid core microcapsules and as a useful method for drying microcapsules into a free flowing powder form without forming clusters.

1.4.2 Microcapsule Synthesis

Different active core contents have been encapsulated, including corrosion indicators, corrosion inhibitors, dye, and self healing agents. Both water core microcapsules and oil core microcapsules were synthesized using the methods described above.

To tailor these processes for encapsulating corrosion inhibitors and indicators, various indicators and inhibitors were selected and tested for their indicating and inhibiting efficiency respectively. The solubility and dispersibility of the active compounds were surveyed or tested to find a suitable method for their encapsulation.

An active compound that can be dissolved or dispersed in a hydrophobic solvent, such as oil, can be encapsulated into oil core microcapsules. Normally, oil core microcapsules are used for encapsulating oil soluble materials but not water soluble materials, such as salts or polar molecules. However, these materials can still be encapsulated by dissolving them first into a polar co-solvent and adding the resultant solution to the oil phase. Alternatively, a surfactant can be added to the oil phase. This will dissolve or disperse the polar or water soluble reagents into the oil phase. The oil-in-water emulsion can then be formed and the interfacial reaction can be used to encapsulate these reagents into the oil core of the microcapsules (Figure 10).

Similarly, if a compound can be dissolved or dispersed in water, with or without the aid of a co-solvent, or a surfactant, it is possible to encapsulate it into water core microcapsules. For example, phenolphthalein does not dissolve in water, but ethanol can be used as a co-solvent to dissolve moderate amount of the indicator in water making it possible to encapsulate it into water core microcapsules (Figure 11).

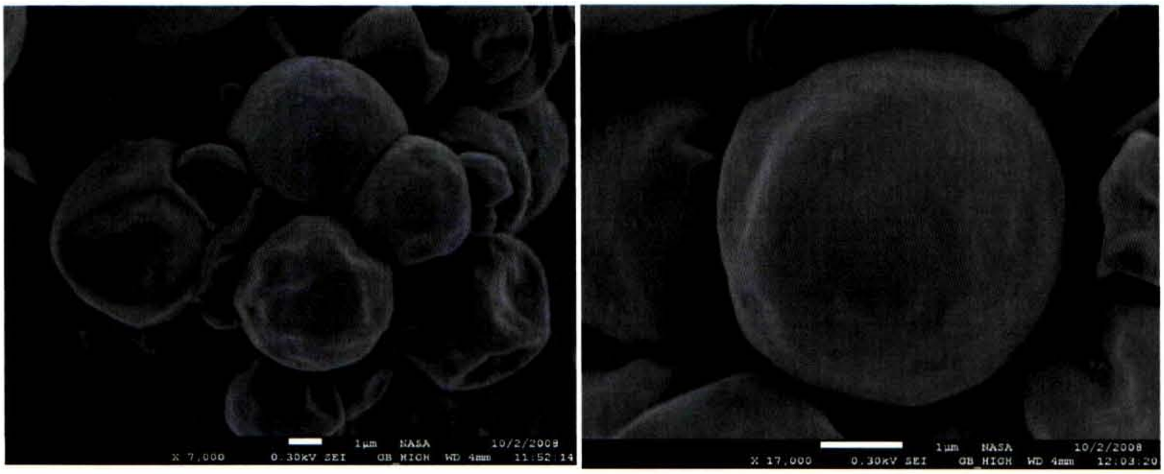


Figure 10. Oil core microcapsules with a pH indicator as core content.

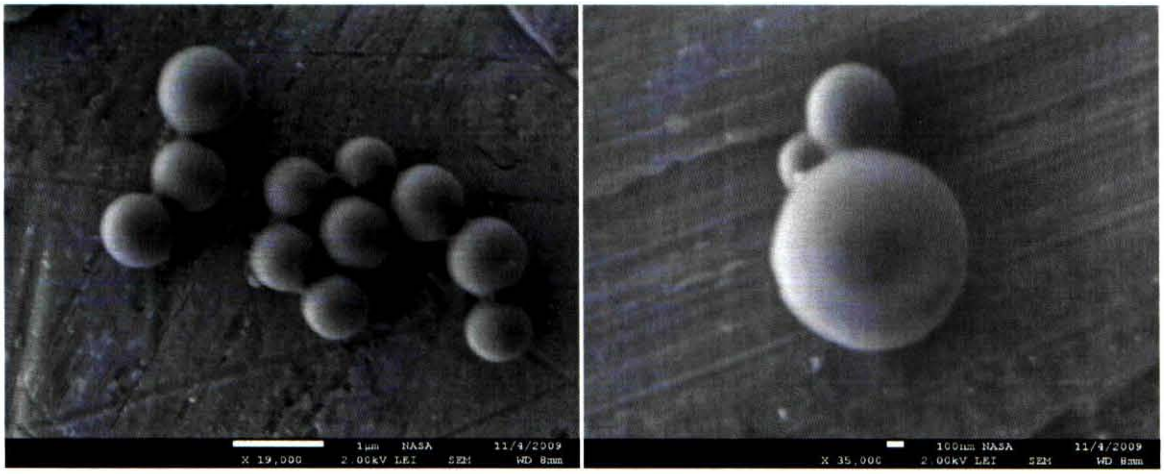


Figure 11. SEM images of the water core microcapsules with phenolphthalein

Various compounds of interest for corrosion control applications have been encapsulated into oil core microcapsules. These compounds include: corrosion indicators such as phenolphthalein, phenol red, and fluorescein; corrosion inhibitors such as cerium(III) chloride, $CeCl_3$; dyes such as Rhodamine B; healing agents such as epoxy and polysiloxane; and various solvents, such as chlorobenzene, which can be used as a healing agent. Some examples of these oil core microcapsules are shown in Figure 12.

Figure 12. Oil Core Microcapsules in free flowing powder form. The core contents of these microcapsules are Rhodamine B (on the left), Phenolphthalein (in the middle), and a universal pH indicator (on the right).

Various corrosion inhibitors and indicators have been encapsulated into water core microcapsules, such as corrosion indicator phenolphthalein, corrosion inhibitor sodium molybdate, Na_2MoO_4, cerium nitrate, $Ce(NO_3)_3$, sodium phosphate, NaH_2PO_4, **calcium metaborate, and phenol phosphoric acid.** Some examples of these oil core microcapsules are shown in Figure 13.

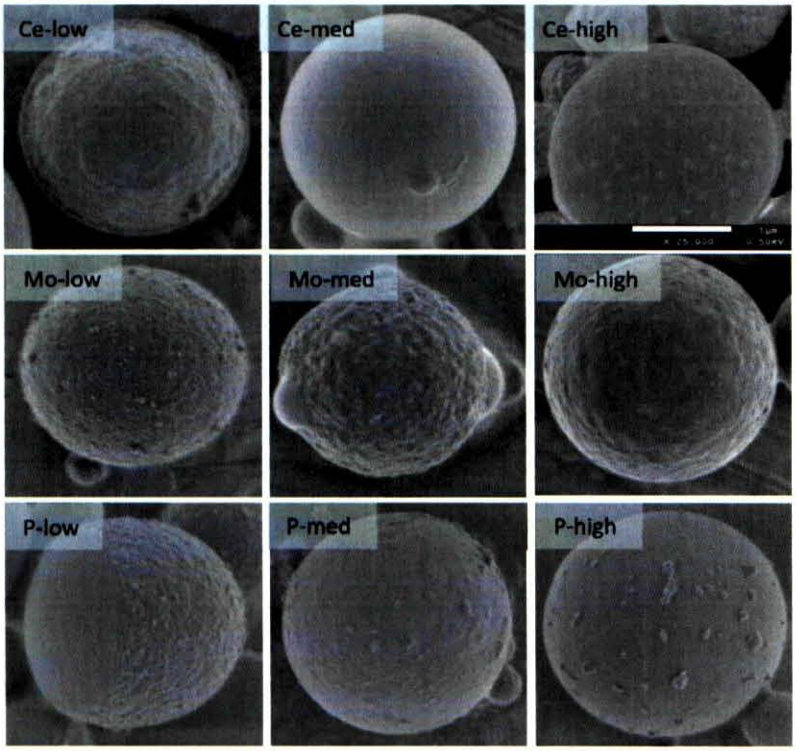


Figure 13. SEM images of microcapsules with different inhibitor core contents at different concentrations. From left to right: low, medium, and high inhibitor concentrations. From top to bottom: $Ce(NO_3)_3$, Na_2MoO_4, and NaH_2PO_4 inhibitors.

After a microcapsule formula is developed, an optimization process usually follows to obtain microcapsules of desired properties, such as a suitable size for its application. The capsule size can be controlled by adjusting the emulsion formula or by varying the mixing speed of the mixer or the homogenizer during the emulsion formation. These methods can be used to obtain microcapsules of a desired size within a narrow range of distribution. Sizes from 200 nm to 200 micron can be obtained, with a typical size from about 1 to 5 microns. Oil core microcapsules of various sizes are shown in Figure 14.

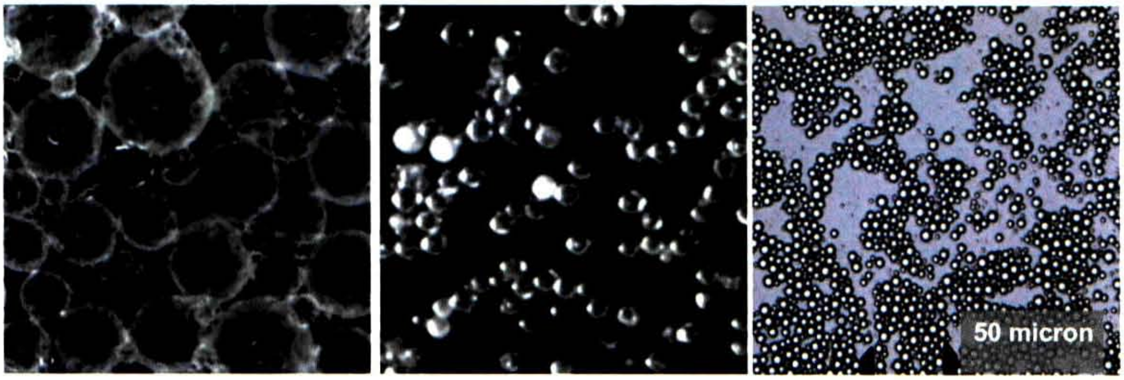


Figure 14. Oil core microcapsules of different sizes.

The SEM images in Figure 15 show capsules of spherical shape with less than 1 μm in diameter size. The capsule wall thickness is about 50-100 nm as shown in the SEM images of the microcapsules obtained using a transmission electron detector (Figure 16).

Figure 15. SEM Images of the water core microcapsule.

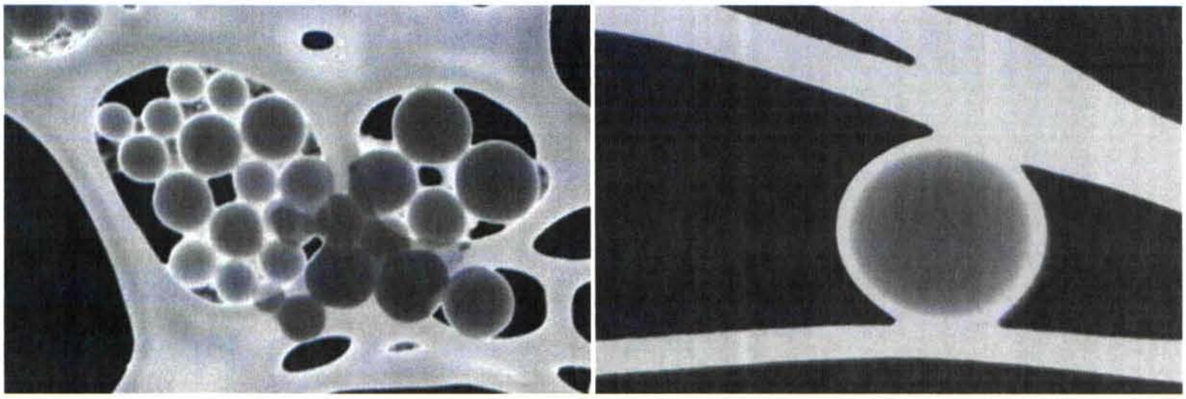


Figure 16. SEM images of a water core microcapsule obtained by using a transmission electron detector.

Figure 17 shows an example of oil core microcapsules with a size range from 10 to 20 microns in which epoxy was encapsulated through the *in situ* polymerization reaction in oil-in-water emulsion for self healing applications. The same figure also shows the relatively smooth wall surface of the microcapsules. The wall thickness of these microcapsules was measured by incorporating the microcapsules into a thin film and observing a cross section of the film by SEM (
Figure 18). This capsule wall appears, on average, to be about 300 nm to 1 micron thick.

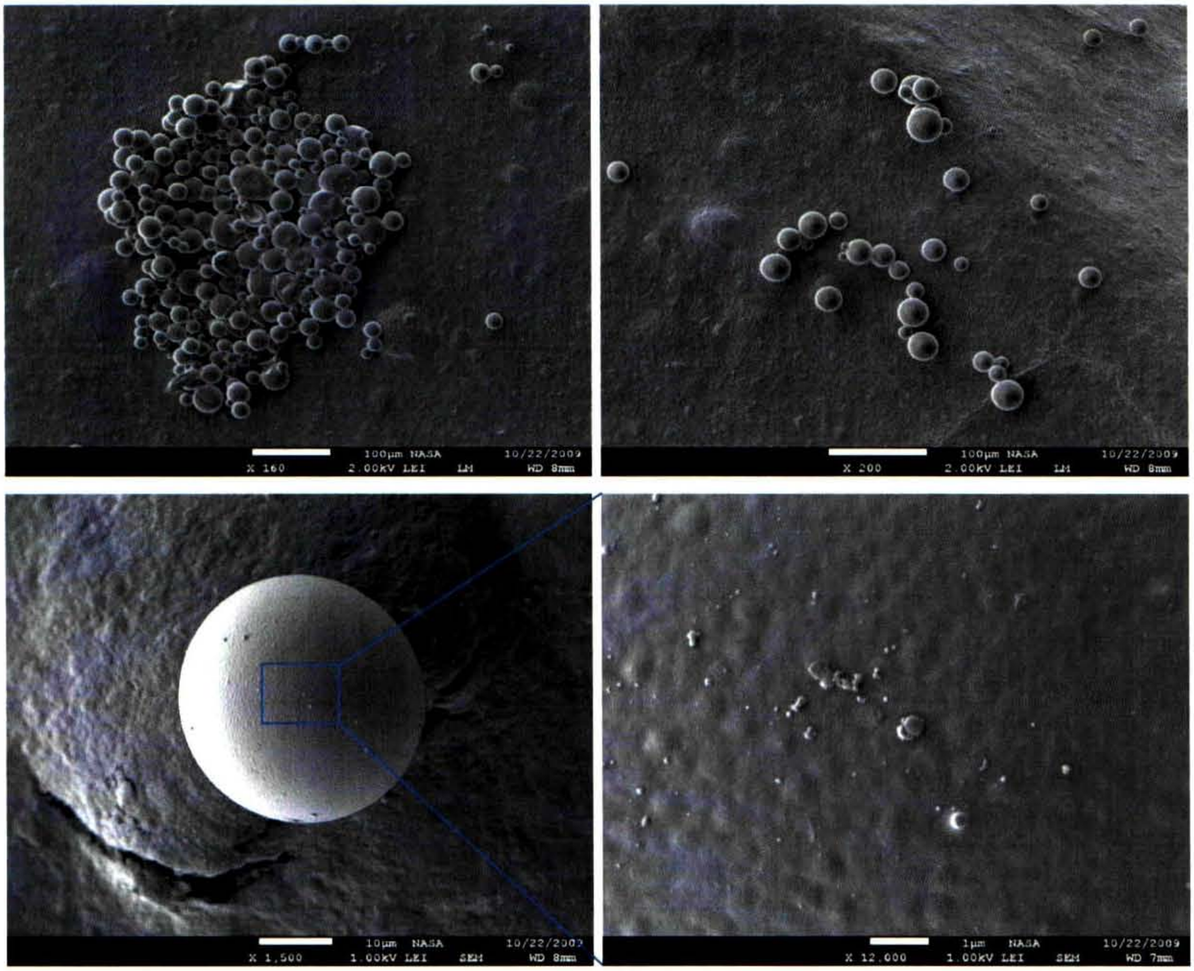


Figure 17. SEM images of oil core microcapsules with epoxy self healing agent.

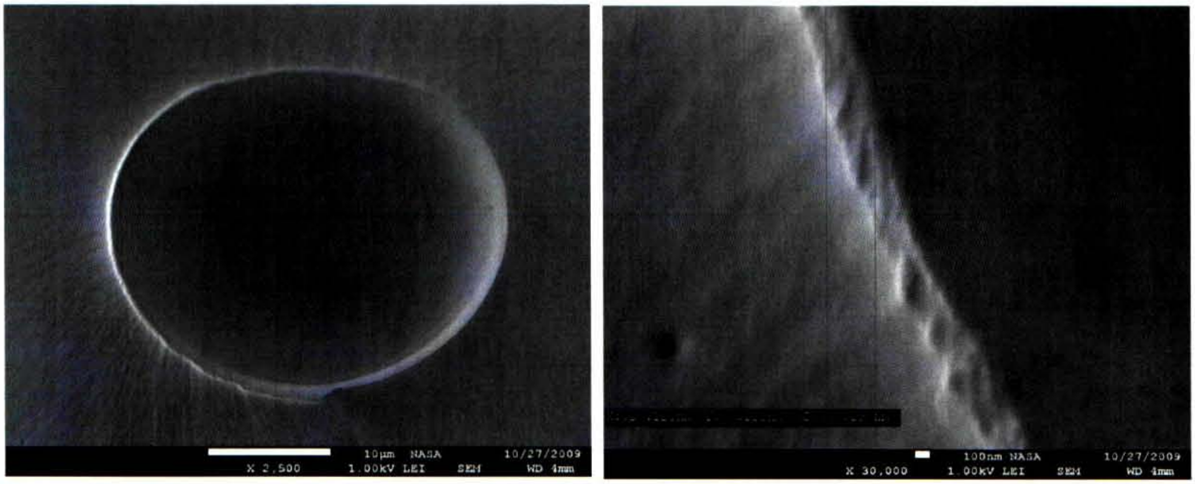


Figure 18. SEM images of the cross section of oil core microcapsules in a polymer film.

1.4.3 Sub sub-heading

2. EXPERIMENTATION AND RESULTS

Microcapsules have been incorporated into different commercially available coatings in order to test their corrosion indication and inhibition functions. Preliminary results of these tests are presented below.

2.1 Corrosion Indication Tests

Corrosion indication is one of the functions of the smart coating for corrosion detection, control, and self healing. This function can be incorporated into the coating by encapsulating a corrosion indicator into pH sensitive microcapsules or particles. Figure 19 shows the results from the salt immersion test of steel panels coated with a clear urethane coating containing 10% of microcapsules with corrosion indicator. The panels were scribed and observed for visual changes over time. It was observed that the indicator signaled the onset of corrosion in the scribe about 1 minute after immersion which is considerably earlier than the 2 hours for the appearance of the typical color of rust.

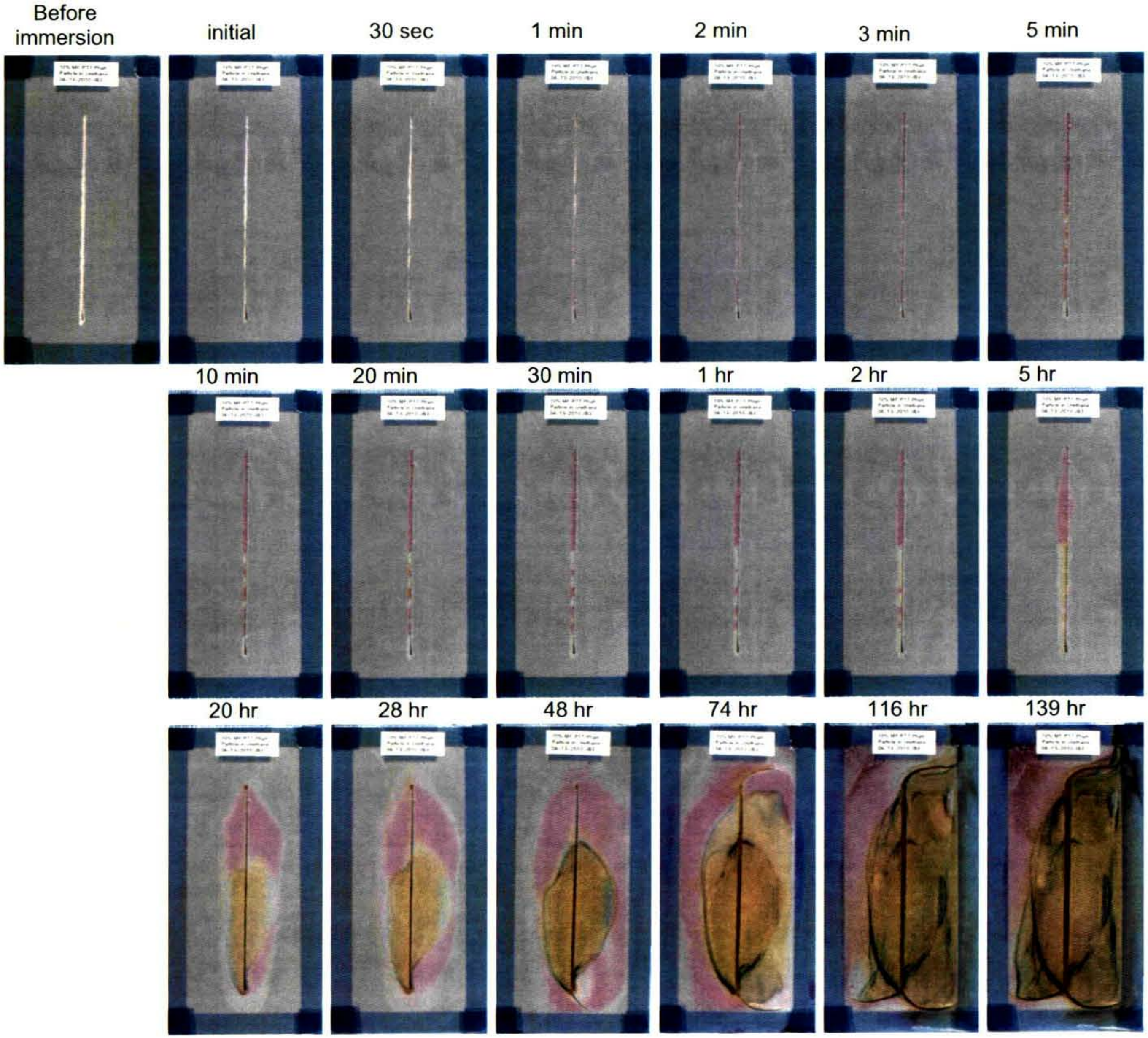

Before immersion
initial
30 sec
1 min
2 min
3 min
5 min
10 min
20 min
30 min
1 hr
2 hr
5 hr
20 hr
28 hr
48 hr
74 hr
116 hr
139 hr

Figure 19. Corrosion indication test reusults.

In addition to early corrosion detection, another potential application of the smart coating is to detect hidden corrosion. A conceptual illustration of how these coatings can be used to detect hidden corrosion is shown in Figure 20.

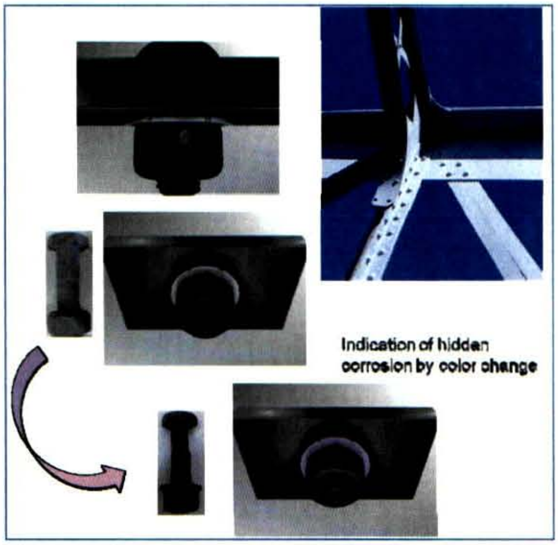


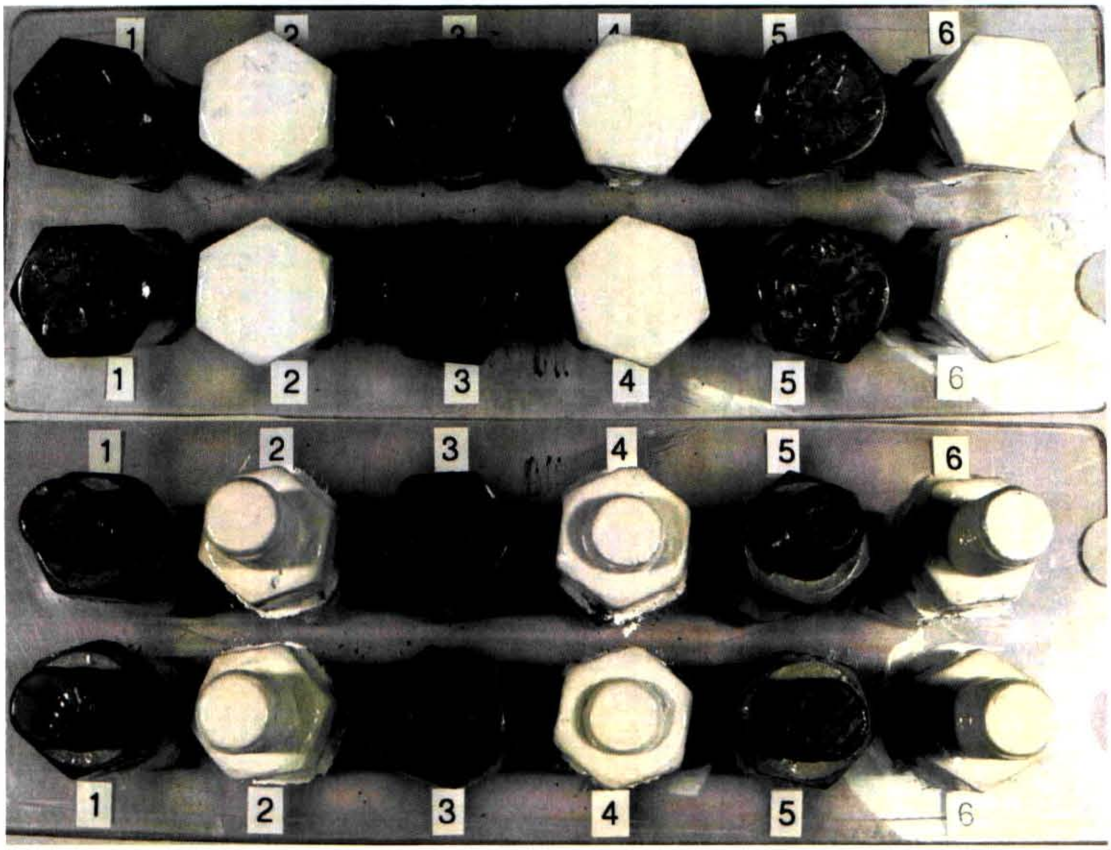
Figure 20. Conceptual illustration of hidden corrosion indication in structural bolts.

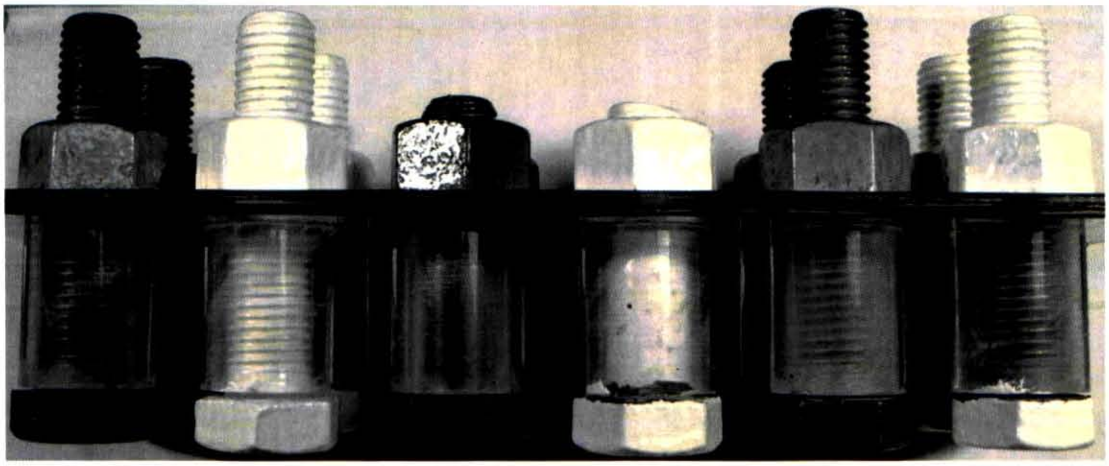
An experiment was designed to test the ability of the encapsulated indicator to detect hidden corrosion when incorporated into a coating system. Several coating systems (Table No) were prepared in order to find a coating system that would indicate crevice corrosion as can be expected to occur in the nut and bolt set up shown in figures No. As it can be seen in Figure No, the epoxy/urethane coating system showed the ability of the coating to indicate hidden corrosion as evidenced by the appearance of the purple color.

System #	Description of System
1	Zinc galvanized nut and bolt where coated with Diamond Clad 3-part urethane® containing 10% phenolphthalein particles.
2	Zinc galvanized nut and bolt coated with Macropoxy 2-part epoxy® and top coated with Diamond Clad 3-part urethane containing 10% phenolphthalein particles.
3	Sand blasted nut and bolt to bare carbon steel. The ends of the nut and bolt were coated with Cathacoat 304V® inorganic zinc coating. The entire nut and bolt was coated with Diamond Clad 3-part urethane® containing 10% phenolphthalein particles.
4	Sand blasted nut and bolt to bare carbon steel. The ends of the nut and bolt were coated with Cathacoat 304V® inorganic zinc coating. The entire nut and bolt was coated with Macropoxy 2-part epoxy® and then top coated with Diamond Clad 3-part urethane® containing 10% phenolphthalein particles.
5	Zinc galvanized nut and bolt where the ends of the nut and bolt were coated with Diamond Clad 3-part urethane® containing 10% phenolphthalein particles

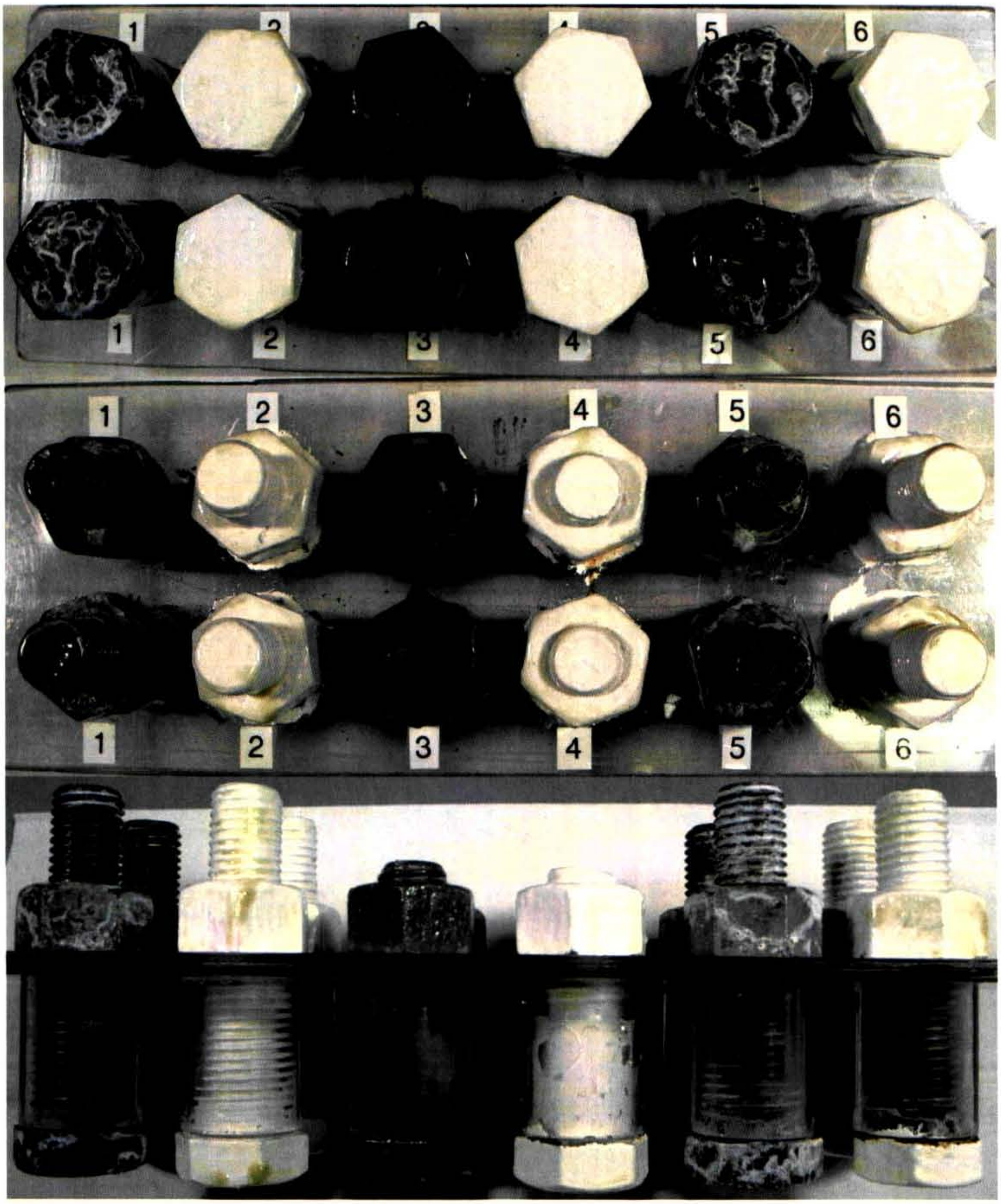
6	Zinc galvanized nut and bolt where the ends of the nut and bolt were coated with Macropoxy 2-part epoxy® and top coated with Diamond Clad 3-part urethane® containing 10% phenolphthalein particles.

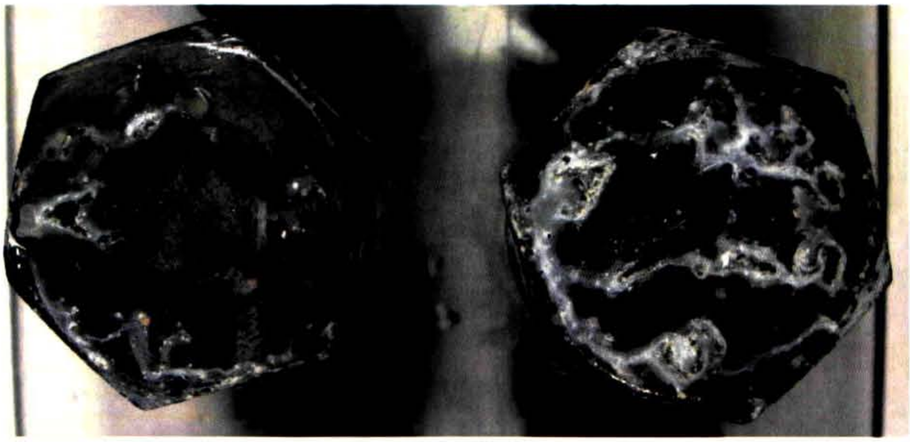
Initial Pictures





237 hours salt fog


1
2
3
4
5
6



605 hours salt fog

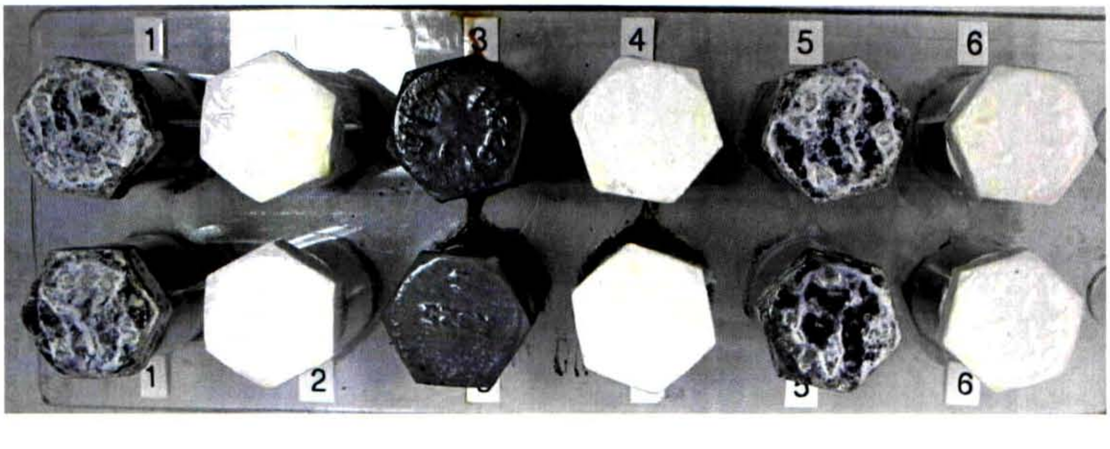


Figure 21. Selected pictures that show hidden corrosion indication.

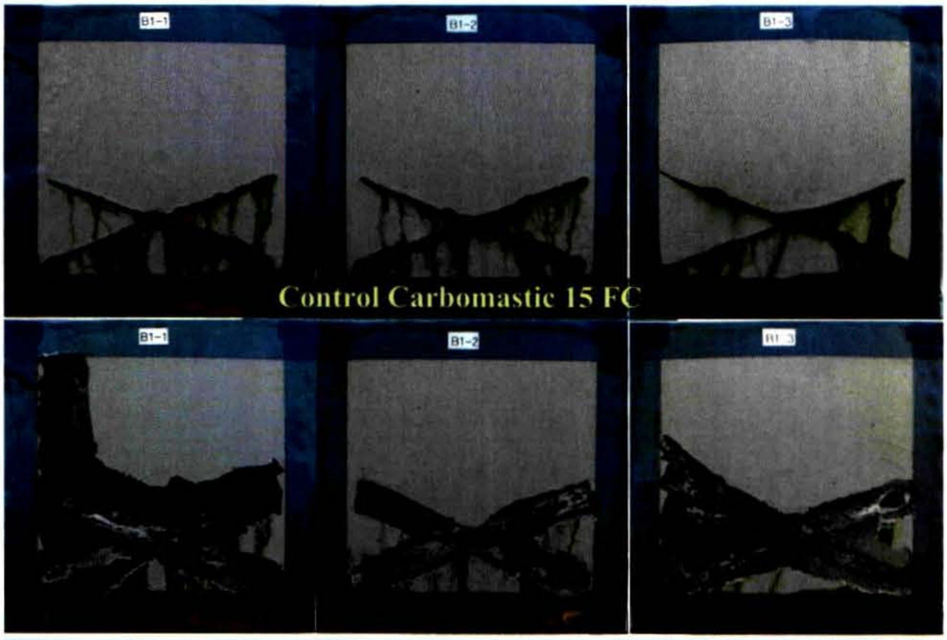
2.2 Corrosion Inhibition Tests

Test panels coated with Carboline Carbomastic 15 FC epoxy mastic and Devoe Cathacoat 304V inorganic zinc primer containing water core microcapsules with either an indicator or an inhibitor have been tested using a salt fog chamber, for approximately 6 months, following the ASTM B117 standard method and evaluated for both rust grades (ASTM D610) and scribe ratings (ASTM D1654). Test panels with inhibitor and indicator incorporated directly into the coating were also included for comparison (Table No.).

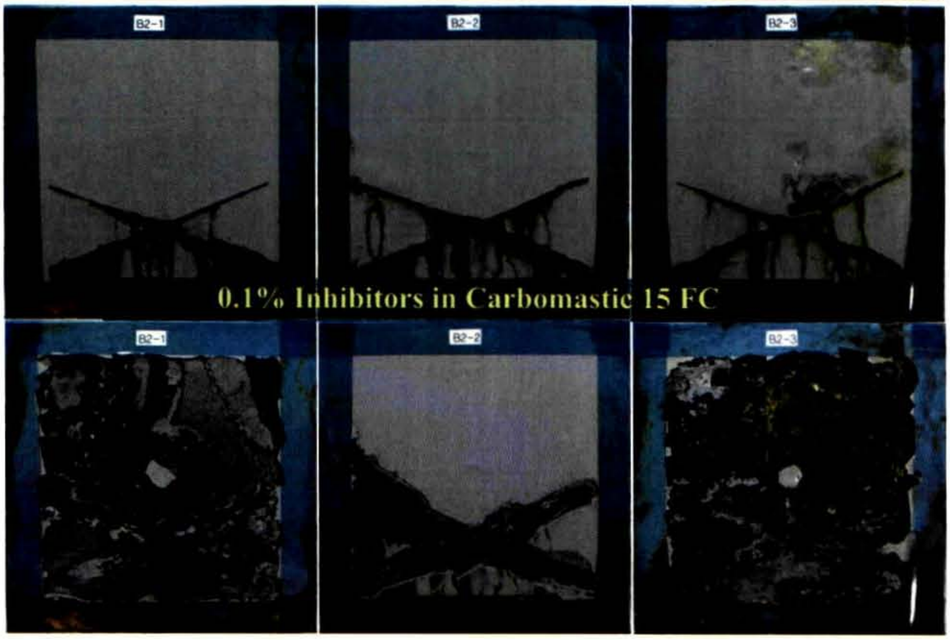
Rust Grade and Scribe Rating of Carbomastic 15 FC experimental coatings

Carbomastic 15 FC Coating Systems	Sample #	Rust Grade	Scribe Rating
Control	1	5	5
	2	10	5
	3	6	5
2.5% (w/v) phenolphthalein	1	0	0
	2	0	0
	3	0	1
0.1% (w/v) cerium nitrate and sodium molybdate	1	1	1
	2	6	5
	3	0	0
1% (w/v) phenylphosphonic acid	1	5	5
	2	3	5
	3	4	5
10% (w/v) water-core phenolphthalein microcapsule slurry	1	7	5
	2	8	5
	3	4	5
10% water-core inhibitor microcapsule slurries	1	9	5
	2	10	5
	3	7	5
10% (w/v) water-core phenylphosphonic acid microcapsule slurry	1	10	5
	2	10	5
	3	10	5

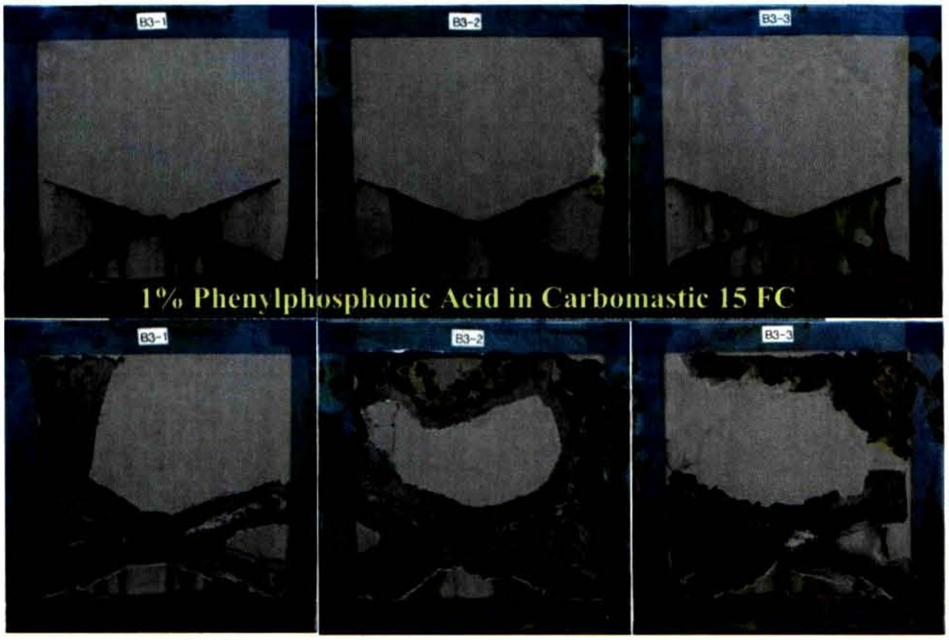
Seven different systems were tested using the Carbomastic 15 FC coating. Based on the rust grades, the corrosion performance of the test panels of the 7 systems can be ranked, starting with the worst in the following order: phenolphthalein, cerium nitrate and sodium molybdate, phenylphosphonic acid, water core indicator phenolphthalein, control, water core inhibitors cerium nitrate and sodium molybdate, and water core inhibitor phenylphosphonic acid. Based on the scribe rating, all the systems containing the non-encapsulated phenolphthalein, cerium nitrate, and sodium molybdate performed worse than the control system while other systems performed about the same.

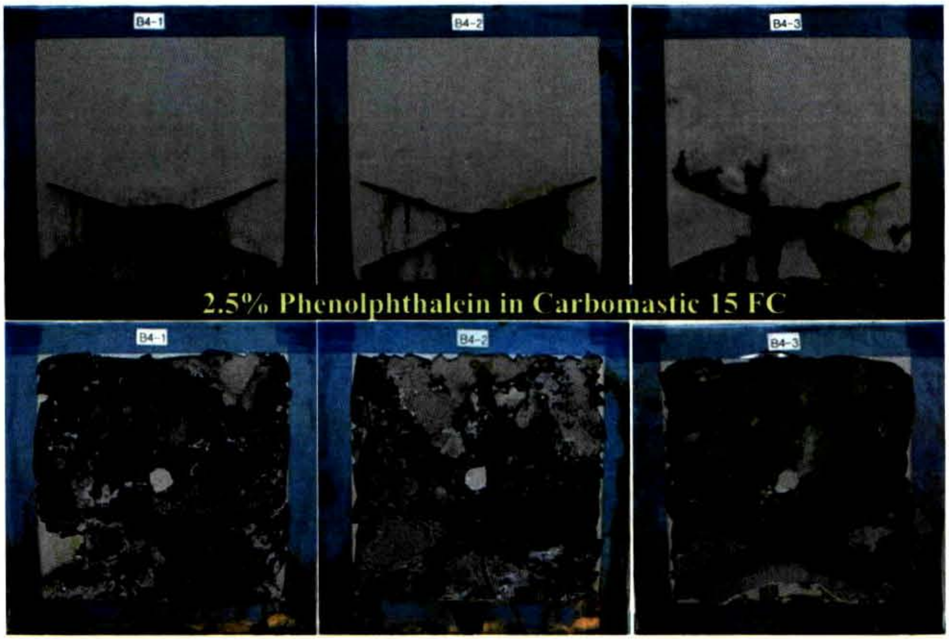


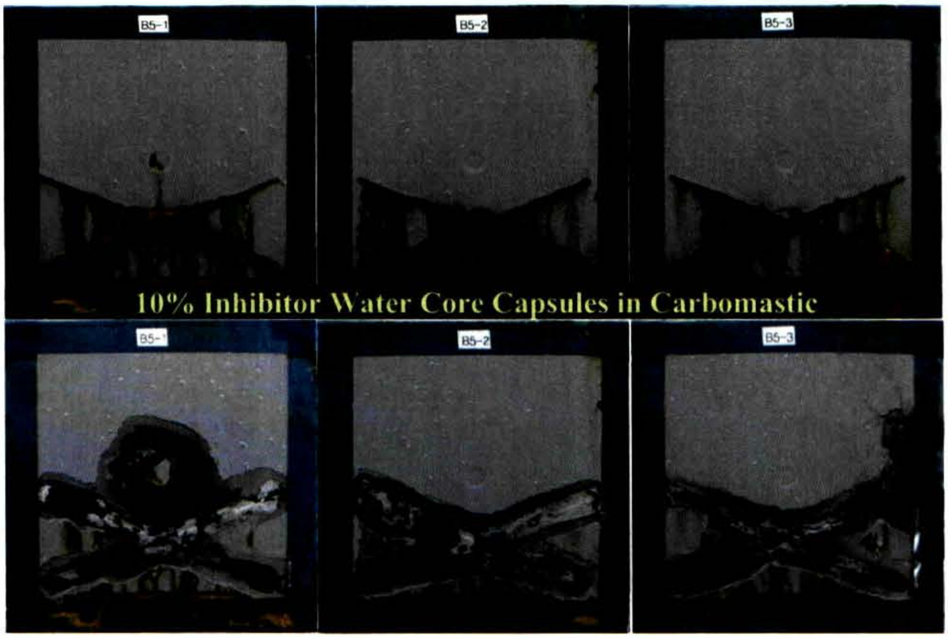
Control Carbomastic 15 FC

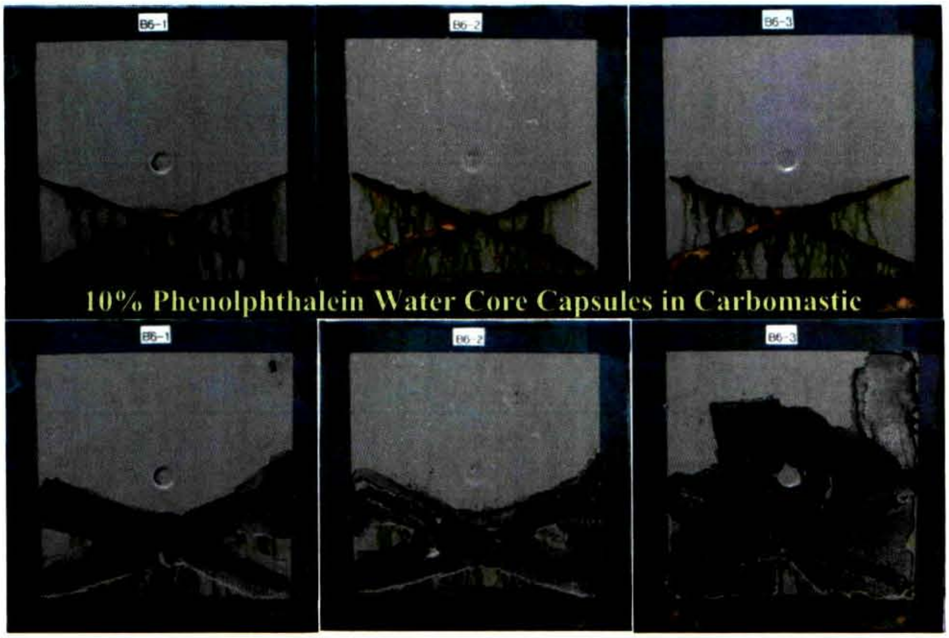


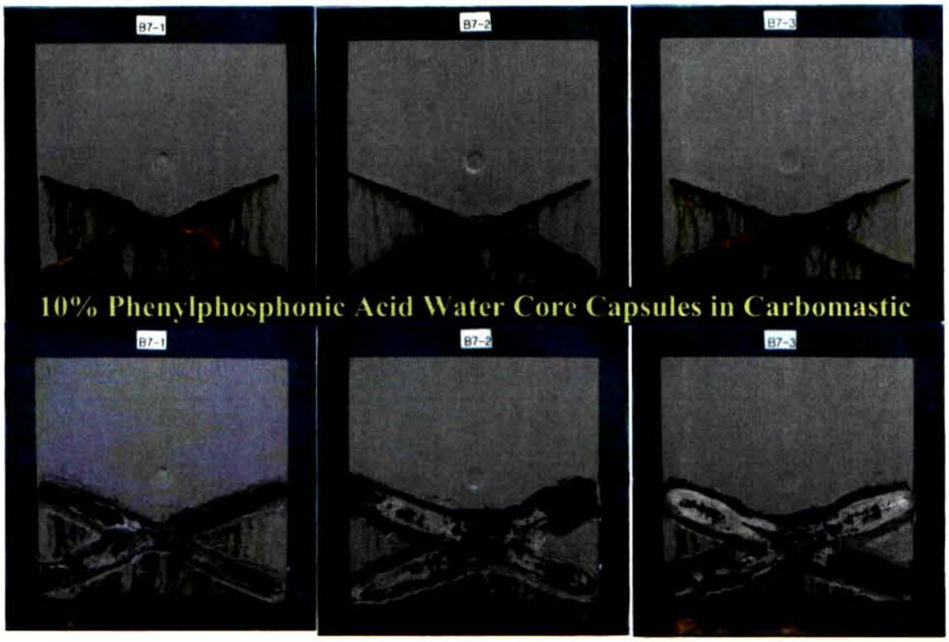
0.1% Inhibitors in Carbomastic 15 FC


B3-1
B3-2
B3-3
1% Phenylphosphonic Acid in Carbomastic 15 FC
B3-1
B3-2
B3-3


B4-1
B4-2
B4-3
2.5% Phenolphthalein in Carbomastic 15 FC
B4-1
B4-2
B4-3


10% Inhibitor Water Core Capsules in Carbomastic

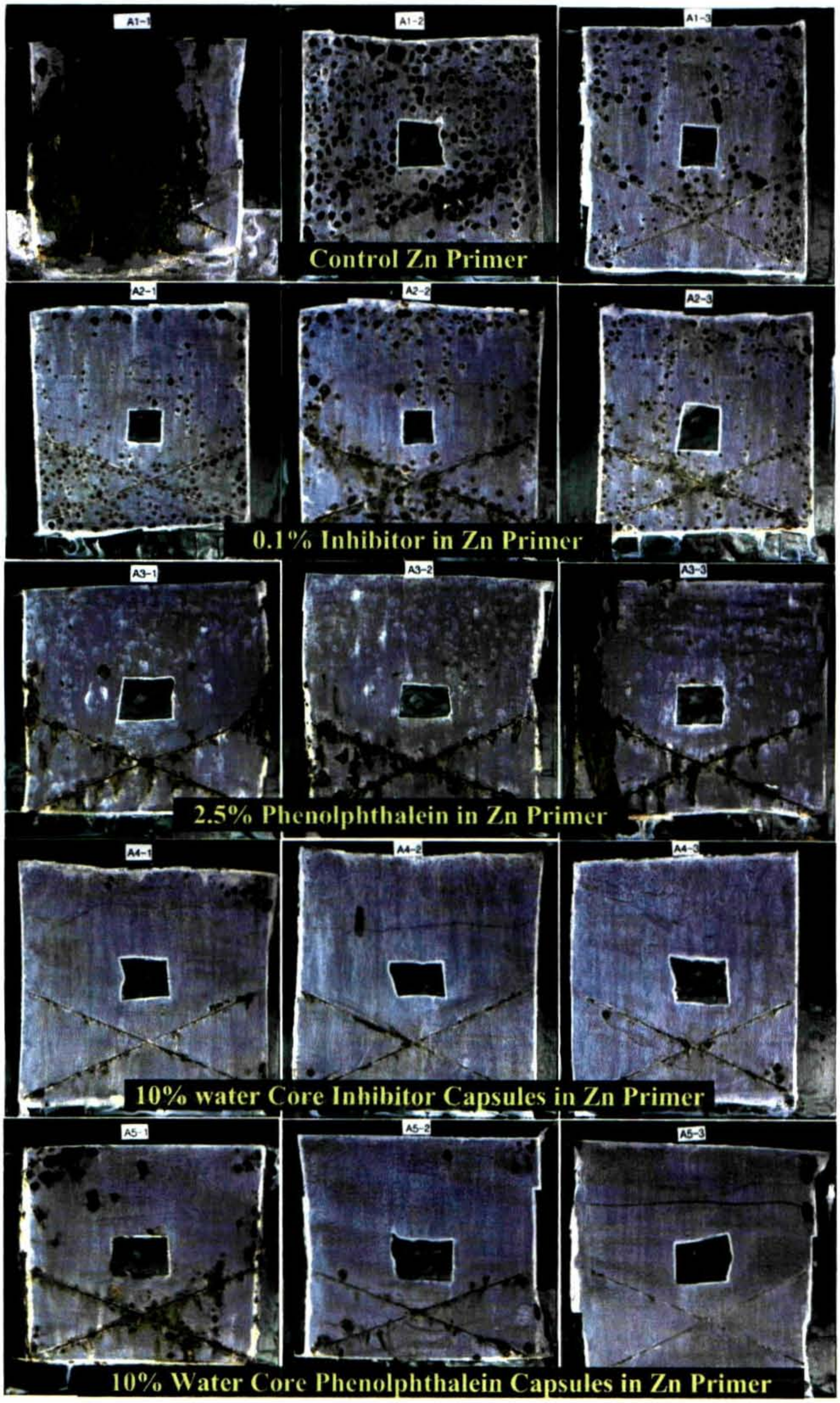

10% Phenolphthalein Water Core Capsules in Carbomastic


10% Phenylphosphonic Acid Water Core Capsules in Carbomastic

Rust Grade for Cathacoat 304V Zn primer for salt fog samples

Cathacoat 304V Coating Systems	Sample #	Rust Grade
Control	1	1
	2	2
	3	3
2.5% (w/v) phenolphthalein	1	5
	2	5
	3	4
0.1% (w/v) cerium nitrate and sodium molybdate	1	3
	2	3
	3	3
10% (w/v) water-core phenolphthalein microcapsule slurry	1	4
	2	6
	3	7
10% water-core inhibitor microcapsule slurries	1	6
	2	7
	3	7

Five different systems were tested using the Cathacoat 304V Zn primer. The follosing corrosion performance ranking, starting with the worst, was obtained by comparing the rust grades for the test panels of the 5 systems: control, cerium nitrate and sodium molybdate, phenylphosphonic acid, phenolphthalein, water core indicator phenolphthalein, water core inhibitors cerium nitrate and sodium molybdate.


Control Zn Primer

0.1% Inhibitor in Zn Primer

2.5% Phenolphthalein in Zn Primer

10% water Core Inhibitor Capsules in Zn Primer

10% Water Core Phenolphthalein Capsules in Zn Primer

Figure 22. Pictures of Devoe 304 Zn primer panels after 15 days in salt fog testing

3. SUMMARY

4. REFERENCES

1. 1. F. J. Maile, T. Schauer, and C. D. Eisenbach, Evaluation of corrosion and protection of coated metals with local ion concentration technique (LICT), Progress in Organic Coatings 38, 111 (2000).
2. 1. W. Li and L. M. Calle, pH and Electrochemical Responsive Materials for Corrosion Control Applications (Invited), NACE Corrosion 2008, New Orleans, LA, March 2008.
3. 1. M. R. Kessler, Self-healing: a new paradigm in material design, Proc. IMechE Vol. 221 Part G: J. Aerospace Engineering, page 479-495 (2007)
4. 1. Magnus Andersson, Gerald O. Wilson, Scott R. White, Evaluation of Self-Healing Polymer Chemistries for Application in Anti-Corrosion Coatings, American Coatings Conference 2008 at Charlotte, NC (June 2-4, 2008).
5. 1. Soo Hyoun Cho, PhD Thesis "Polydimethylsiloxane-Based Self healing Composite and Coating materials", University of Illinois at Urbana-Champaign, Urbana IL (2006).
6. 1. W. Li and L. M. Calle, Controlled Release Microcapsules for Smart Coatings, NACE Corrosion 2007, Paper 07228, Nashville, TN, March 2007
7. 1. W. Li and L. M. Calle, A smart coating for the Early Detection and Inhibition of Corrosion, Proceeding of the Smart Coatings 2007, p.191, Orlando, Florida, February 2007
8. 1. Jerry March, Advanced Organic Chemistry, second edition (1977) (R. H. Summersgill and A. T. Vinnicombe, Eds) McGraw-Hill Book Company.
9. 1. A. E. Rydholm, K. S. Anseth, and C. N. Bowman, Acta Biomater, 3, 449-455 (2007)
10. [Insert reference 1]
11. [Insert reference 2]
12. [Insert reference 3]
13. [Insert reference 4]
14. [Insert reference 5]
15. [Insert reference 6]
16. [Insert reference 7]
17. [Insert reference 8]
18. [Insert reference 9]
19. [Insert reference 10]

---

[1]. F. J. Maile, T. Schauer, and C. D. Eisenbach, Evaluation of corrosion and protection of coated metals with local ion concentration technique (LICT), Progress in Organic Coatings 38, 111 (2000).

2. W. Li and L. M. Calle, pH and Electrochemical Responsive Materials for Corrosion Control Applications (Invited), NACE Corrosion 2008, New Orleans, LA, March 2008.

---

3. M. R. Kessler, Self-healing: a new paradigm in material design, Proc. IMechE Vol. 221 Part G: J. Aerospace Engineering, page 479-495 (2007)

4. Magnus Andersson, Gerald O. Wilson, Scott R. White, Evaluation of Self-Healing Polymer Chemistries for Application in Anti-Corrosion Coatings, American Coatings Conference 2008 at Charlotte, NC (June 2-4, 2008).

5. Soo Hyoun Cho, PhD Thesis "Polydimethylsiloxane-Based Self healing Composite and Coating materials", University of Illinois at Urbana-Champaign, Urbana IL (2006).

6. W. Li and L. M. Calle, Controlled Release Microcapsules for Smart Coatings, NACE Corrosion 2007, Paper 07228, Nashville, TN, March 2007

7. W. Li and L. M. Calle, A smart coating for the Early Detection and Inhibition of Corrosion, Proceeding of the Smart Coatings 2007, p.191, Orlando, Florida, February 2007

8. Jerry March, Advanced Organic Chemistry, second edition (1977) (R. H. Summersgill and A. T. Vinnicombe, Eds) McGraw-Hill Book Company.

9. A. E. Rydholm, K. S. Anseth, and C. N. Bowman, Acta Biomater, 3, 449-455 (2007)