

## **MICROENCAPSULATION TECHNOLOGY FOR CORROSION MITIGATION BY SMART COATINGS**

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### **ABSTRACT**

A multifunctional, smart coating for the autonomous control of corrosion is being developed based on micro-encapsulation technology. Corrosion indicators as well as corrosion inhibitors have been incorporated into microcapsules, blended into several paint systems, and tested for corrosion detection and protection effectiveness. This paper summarizes the development, optimization, and testing of microcapsules specifically designed to be incorporated into a smart coating that will deliver corrosion inhibitors to mitigate corrosion autonomously.

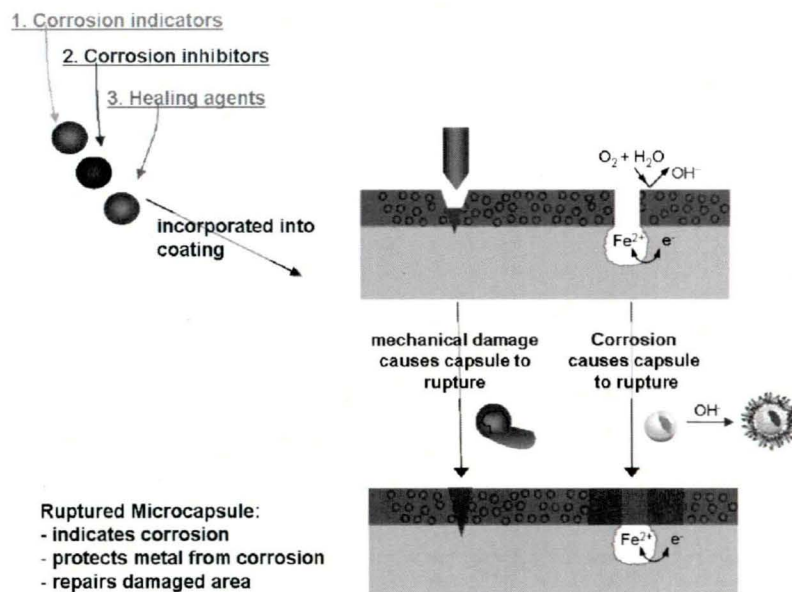
Key words: smart coating, corrosion inhibition, microencapsulation, microcapsule, pH sensitive microcapsule, corrosion inhibitor, corrosion protection paint

### **INTRODUCTION**

Corrosion is a costly problem for a wide range of industries and it affects nearly every facet of our lives. Corrosion can lead to catastrophic metal failure if undetected and untreated. Protective coatings are the most commonly used method of corrosion control.

NASA's Corrosion Technology Laboratory at the Kennedy Space Center (KSC), is developing 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 protection.<sup>1,2,3</sup> Various active compounds, such as corrosion indicators, inhibitors, self-healing agents, and dyes have been encapsulated. These microcapsules can be incorporated into various coating systems for corrosion

detection, protection and self-repair of mechanical coating damage (Figure 1). The pH-controlled release microcapsule design has, in addition to all the advantages of other microcapsule designs, the controlled-release function specifically designed for corrosion detection and control applications. One of the functions of the smart coating is autonomous corrosion mitigation enabled by the controlled release of encapsulated corrosion inhibitors.



**Figure 1. Conceptual illustration of smart coating with pH sensitive microcapsules for corrosion protection applications.**

Recently, the development of environmentally friendly corrosion protective coatings has been one of the most important research and development areas in the field of corrosion protection. This worldwide effort has been driven primarily by progressively stricter environmental regulations that have resulted in removal from the commercial market of the most effective corrosion inhibitors, such as chromates and high volatile organic compounds (VOC) coating systems due to their detrimental environmental impact. Smart coating technologies provide potential solutions to the environmental regulation challenges.

pH-sensitive microcapsules allow “on demand” release of corrosion inhibitors and prevent them from leaching out of the coating prematurely. The incorporation of encapsulated inhibitors that can be protected in a coating until their release is triggered by the onset of corrosion will result in a smart coating that is both environmentally friendly and cost effective. Encapsulation technology can also be used to develop pigment grade inhibitor microcapsules that are more compatible with the typical coating components than inhibitors in their pure or solution form. This can prove very beneficial for coating industries while they are transitioning from solvent-based coating systems to 100% solid or water-based systems while trying to keep the corrosion protection performance of the coating. Another potential benefit of encapsulation is that it will allow the use of highly effective corrosion inhibitors that are not suitable for coating applications due to their high water solubility. Solubility is an important property that can limit the use of a good corrosion inhibitor in a coating. When the solubility of the inhibitor is too high, it will cause blistering and can also lose its long term effect by leaching out of the coating. When the solubility of the inhibitor is too low, the concentration of the active ions can be too low to be effective. These problems can be resolved by encapsulating the inhibitors to produce highly effective corrosion inhibitor pigments.

This paper presents the development of encapsulation methods for corrosion inhibitors and the results obtained by incorporating inhibitor microcapsules into commercially available coatings to test their corrosion mitigation effectiveness.

## **DEVELOPMENT OF CORROSION INHIBITOR MICROCAPSULES FOR CORROSION MITIGATION**

Several microcapsule formulas have been developed to incorporate the corrosion inhibition function into a smart coating: oil-core microcapsules, through the interfacial polymerization process, for organic inhibitors and a few inorganic inhibitors, such as cerium(III) nitrate ( $\text{Ce}(\text{NO}_3)_3$ ) and cerium(III) chloride ( $\text{CeCl}_3$ ); water-core microcapsules, through interfacial polymerization, for various water soluble corrosion inhibitors, as well as, microparticles incorporating various corrosion inhibitors.

The oil-core microcapsules were synthesized and optimized to achieve small microcapsule size and even size distribution, higher pH sensitivity, and by changing surfactants to produce an emulsion with appropriate stability. As a result, the emulsion is stable enough during the microencapsulation process but is too stable for the synthesized microcapsules to be separated and harvested from the mixture. The oil-core microcapsules synthesized using a new formula can be easily separated and prepared in the form of a free flowing powder.

Water-core microcapsules have also been synthesized and optimized by changing the emulsion system and by modifying the capsule wall forming materials. Earlier water-core microcapsule formulations tended to form clusters, involved the use of toxic chemicals in the synthesis process, and had low water/oil ratios, which means that fewer microcapsules can be produced from a certain amount of reactants. A comprehensive test matrix was designed to search for an improved water-in-oil emulsion that would result in a stable and monodispersed water-in-oil emulsion using "green" chemistry. The new formula also features a higher water/oil ratio than previous formulas. Another important improvement of the water-core microcapsule is the modification of the capsule wall materials. Solvent soluble pre-polymer and cross linker were used to form the wall of the earlier microcapsules. As a result, water-core microcapsules were synthesized with wall material in the continuous phase, and the interfacial polymerization was carried out by adding acid catalyst into the dispersed (water) phase. This results in a less controllable procedure, as well as water-core microcapsules with acid in their core, which raises concerns for corrosion protection applications. This problem was resolved by synthesizing a water soluble pH sensitive pre-polymer. This formula change provides an easier way to control the synthesis procedure and yields a capsule wall with better mechanical properties.

The latest water-core microcapsules with different corrosion inhibitors at different concentrations were heat treated at different conditions (for different release rates) and incorporated into epoxy and other coatings. The coatings were exposed in a salt fog chamber for corrosion inhibition testing. Several encapsulated inhibitors provided additional protection to the coatings at low and intermediate concentrations. However, it was found that microcapsules with a high inhibitor concentration caused blisters in coatings during salt fog tests. This result indicated that heat treatment alone is not enough to control the permeability of the capsule wall to avoid the leaching of inhibitor into the coating when its concentration inside the microcapsule is too high. This problem was addressed by developing a method to synthesize pH sensitive microparticles as suitable carriers of inhibitors in high concentrations. Unlike microcapsules, where the inhibitor is incorporated into a core surrounded by a polymer shell, these new microparticles contain the inhibitor distributed in a polymer matrix.

The development and optimization of the corrosion mitigation function for the smart coating are summarized in Figure 2.

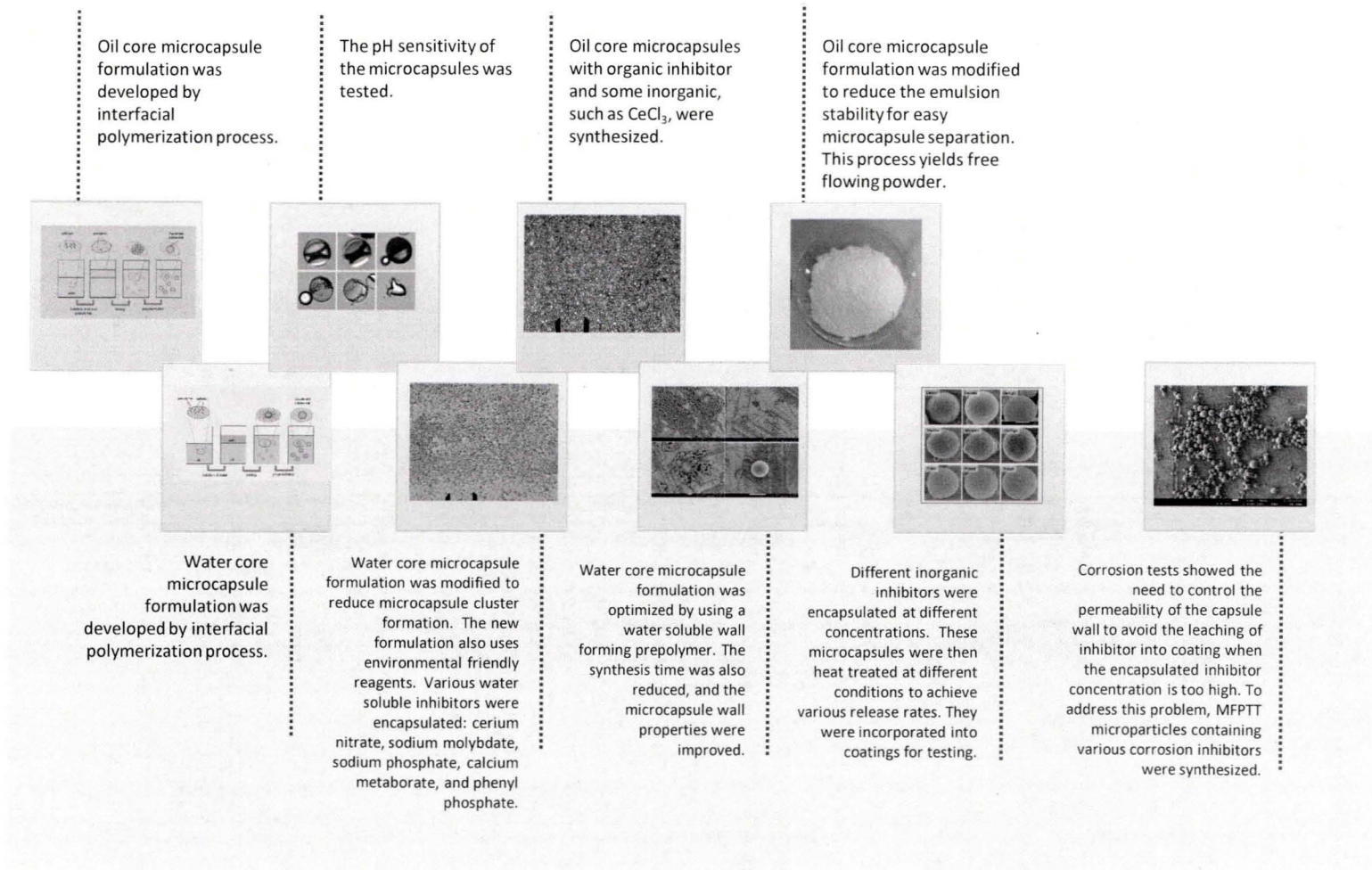
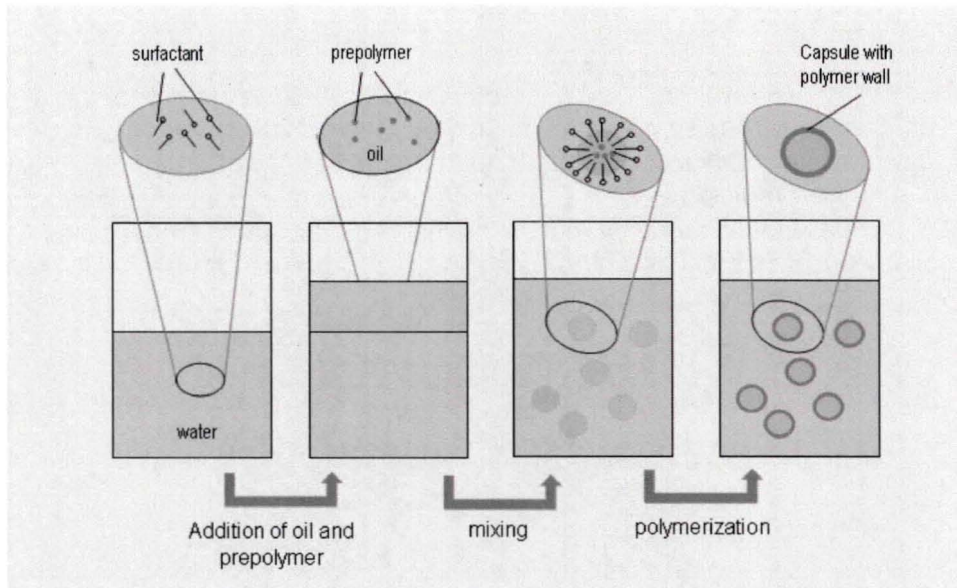


Figure 2. Development and optimization of the corrosion mitigation function.

## Oil-core Microcapsule with Corrosion Inhibitors

Oil-core microcapsules were synthesized through an interfacial polymerization process for organic corrosion inhibitor and a few corrosion inorganic inhibitors (Figure 3). A standard procedure for oil-core capsule formation involves the following:

- (1) Oil Phase Formation: by dissolving pre-polymer and cross linking agent into the selected oil (hydrophobic solvent), such as toluene, to form a clear solution.
- (2) Water Phase Formation: by dissolving surfactant(s) into water.
- (3) Oil-in-Water Emulsion Formation: by dispersing the oil phase in the aqueous phase using any conventional high shear stirrer until desired drop size is achieved.
- (4) Interfacial Polymerization Reaction to form the capsule wall. The reaction is initiated by adding acid as a catalyst to the emulsion and heating the mixture.

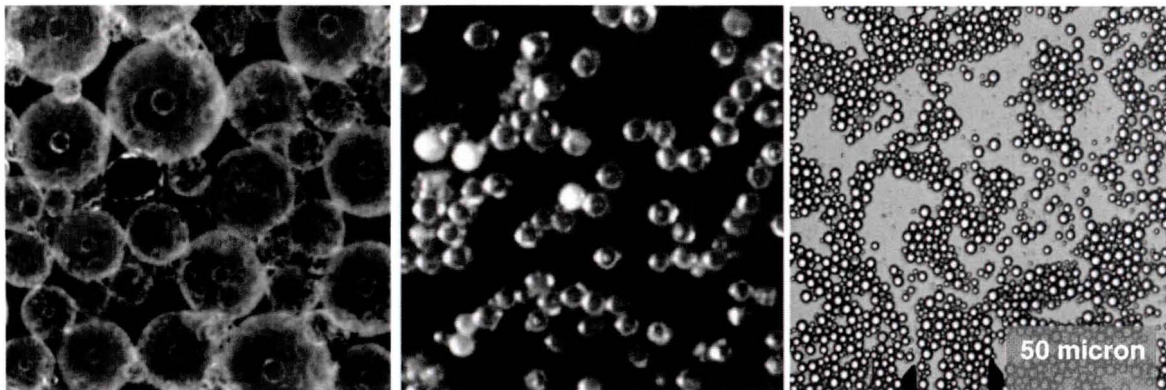


**Figure 3. Interfacial polymerization procedure for oil-core microcapsule synthesis.**

In general, it is relatively simple to form a stable oil-in-water emulsion. For this reason, the initial improvement on the oil-core microcapsule formulation was focused on controlling capsule size, improving the homogeneity of the size distribution, and controlling the pH sensitivity of the capsules.

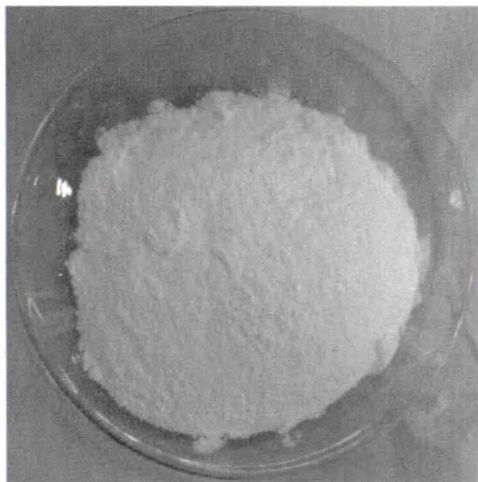
The desired capsule size can be obtained by adjusting the emulsion formula as well as by changing the speed of mixing in the emulsion formation. Microcapsules with sizes from 200 nm to 200  $\mu\text{m}$  (micron) can be obtained, with typical sizes from about 1 to 5  $\mu\text{m}$ . Representative optical microscopy images of oil-core microcapsules of various sizes are shown in Figure 4.

There are two approaches that can be used to increase the pH sensitivity of the microcapsules: increasing the cross-linker content and decreasing the thickness of the capsule wall. The cross-linker provides the ester groups that are responsible for the pH sensitivity of the wall structure. Decreasing the reaction time will result in a thinner capsule shell. It should also be noted that the reduction in the thickness of the microcapsule wall to increase its pH sensitivity is limited because it also lowers the mechanical strength of the capsule wall.



**Figure 4. Optical microscopy images of oil-core microcapsules of different sizes.**

In general, it is desirable to have a stable emulsion. However, an extremely stable emulsion could cause difficulty in the separation of microcapsules after their formation. The oil-core microcapsules were further optimized by changing surfactants to form an emulsion with the appropriate stability. As a result, the emulsion is stable enough during the microencapsulation process but not too stable to hinder the separation and harvesting of the synthesized microcapsules from the synthesis mixture. The oil-core microcapsules made using the new formula can be easily separated and dried into a free flowing powder form (Figure 5).

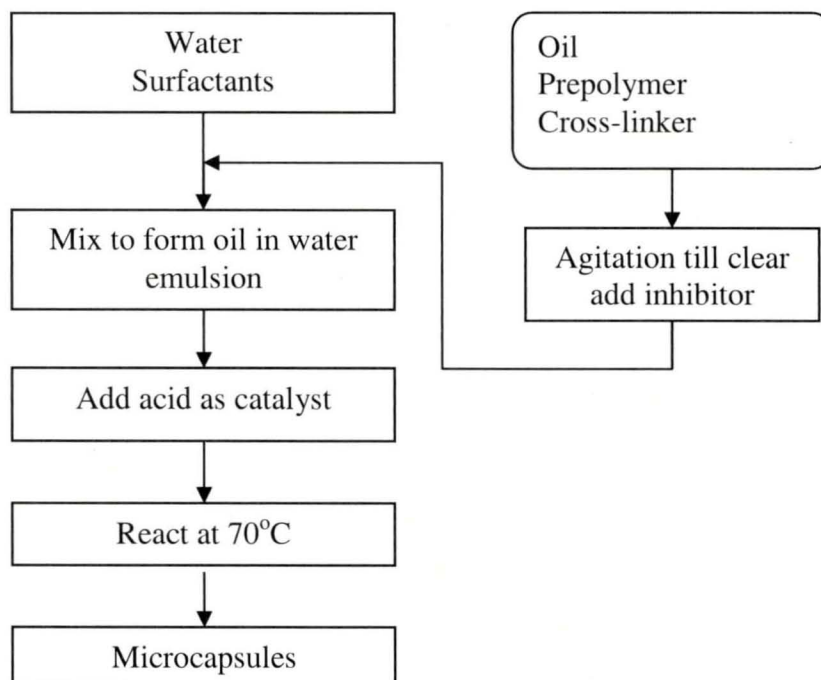


**Figure 5. Oil-core microcapsules in a free flowing powder form.**

After multiple steps of modification, an optimized oil-core microcapsule formulation was developed to encapsulate organic corrosion inhibitors as well as a few inorganic inhibitors. A representative example of an oil-core microcapsule formula is shown in Table 1. A representative procedure to form oil-core microcapsules is shown in Figure 6.

**Table 1. Optimized formula for oil-core microcapsule with inhibitor.**

	Mass (g)	Volume (mL)
<b>Oil Phase</b>		
U-80	16	
penta erythritol tetrakis (3-mercapto propionate)	8	
toluene		80
ethanol		20
inhibitor	0.5	
<b>Water Phase</b>		
Water	300	
PVA (4%)	100	
Igepal CO-520	0.4	
Catalyst (pSTA)	2	
heating	70°C for 3 hours	



**Figure 6. Schematic diagram representation of the synthesis process to form oil-core microcapsules.**

The oil-in-water emulsion formed using this process appeared to have good stability, small size (about 1 to 2  $\mu\text{m}$ ), and even size distribution, as shown in Figure 7. The microcapsules formed appear to be the desired spherical shape, with an average size of 1 to 2  $\mu\text{m}$ , as shown in the scanning electron microscopy (SEM) images in Figure 8.

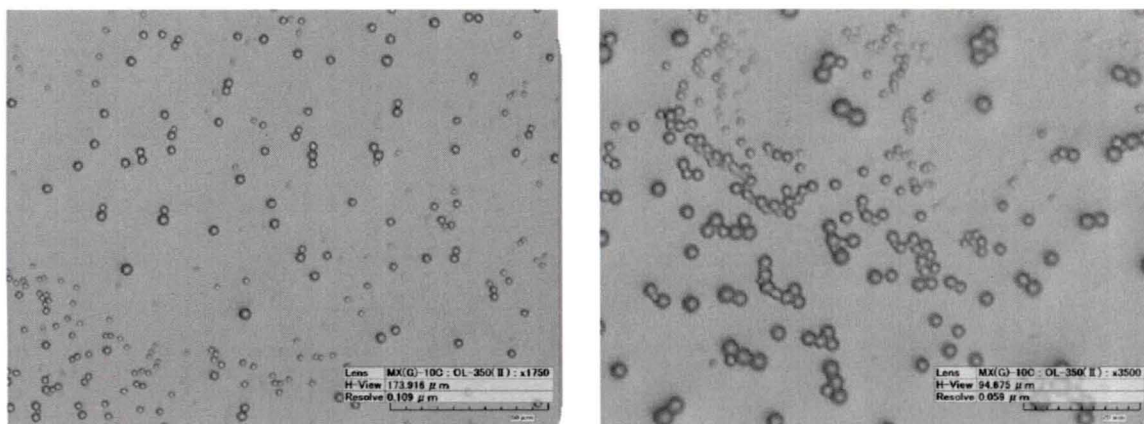


Figure 7. Oil-in-water emulsion under high magnification optical microscope.

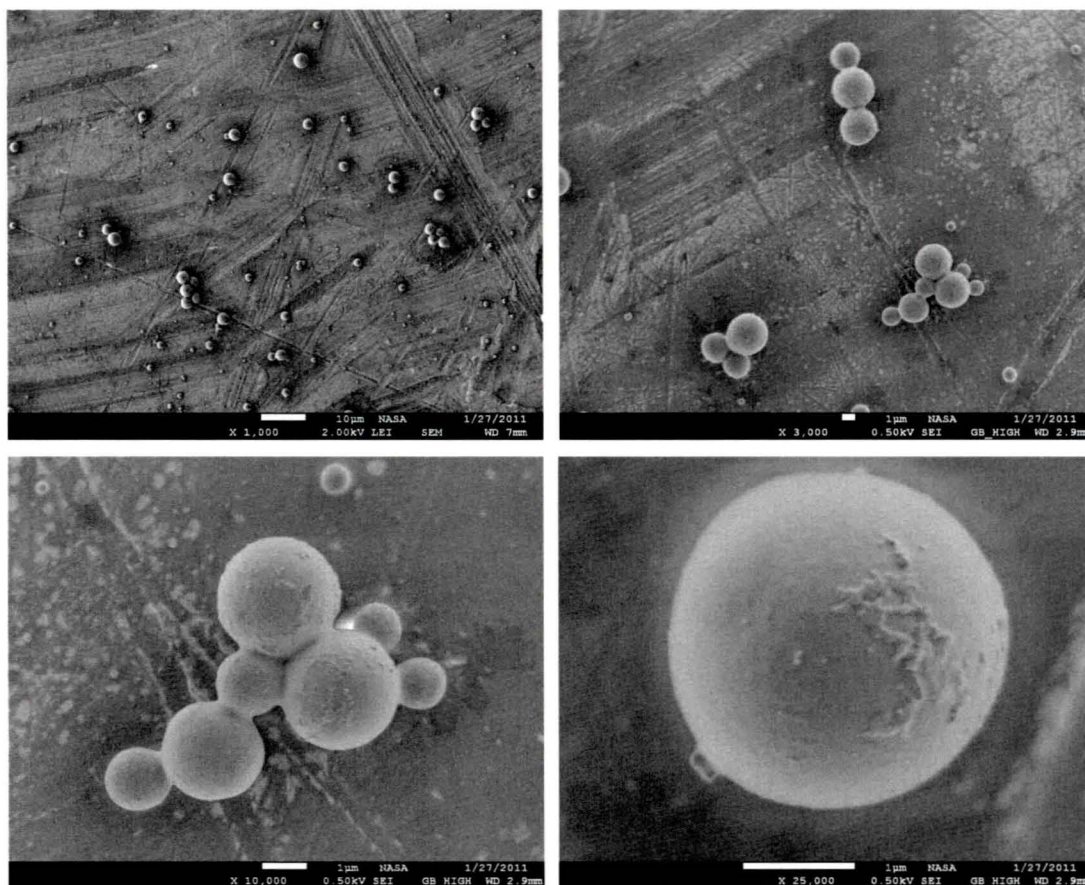


Figure 8. SEM images of oil-core microcapsules containing corrosion inhibitor.

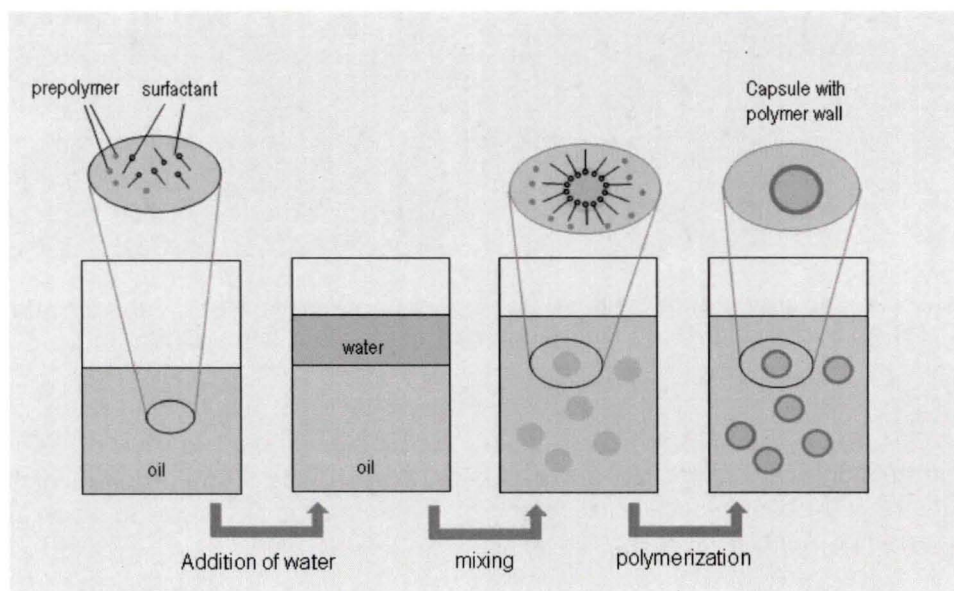


The optimized oil-core microcapsule formulation can be used to encapsulate organic inhibitors, as well as those inorganic inhibitors that can be introduced into the oil phase by using a co-solvent, such as an alcohol. This new formulation yields corrosion inhibitor microcapsules, smaller than a couple of  $\mu\text{m}$ , in a monodispersed, free flowing powder form, which is ideal for incorporation into coatings.

## Water-core Microcapsules with Corrosion Inhibitors

### First Generation Water-core Microcapsules: Synthesis

The first generation water-core microcapsules were synthesized by interfacial polymerization reaction to encapsulate water soluble corrosion inhibitors. The process is shown in Figure 9. The development of the water-core microcapsule synthesis procedure was found to be considerably more difficult than that of the oil-core microcapsule due to their tendency to form clusters. This problem was encountered during the initial attempts of their synthesis and had to be solved to make microcapsules that are suitable to be incorporated into paint formulations.

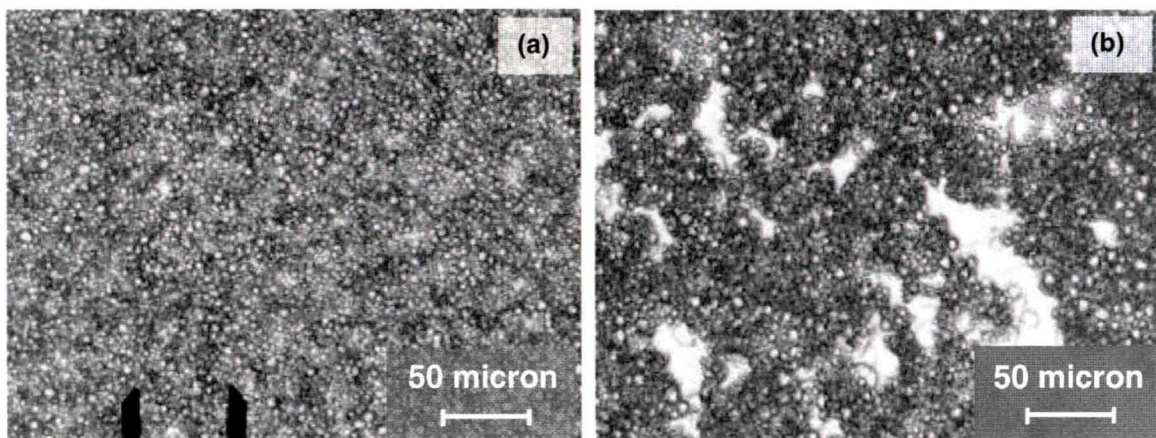


**Figure 9. Schematic representation of the steps involved in the interfacial polymerization of a water-in-oil emulsion process for water-core microcapsules synthesis.**

An analysis of the water-core synthesis procedure indicated that the formation of clusters could be influenced by the following three steps in the procedure: emulsion formation, microcapsule wall formation, and microcapsule drying. In general, it is easier to make stable oil-in-water emulsions (Figure 10) because there are more surfactants available to stabilize oil-in-water emulsions. This is due to the type of intermolecular interactions such as coulombic interactions (in the case of ionic surfactants) or dipole-dipole interactions (for non-ionic surfactants). These interactions are strong and keep the emulsion droplets from coalescing. In the case of water-in-oil emulsions, the major sources of interactions are through London dispersion forces or simple steric effects between the surfactant tails.

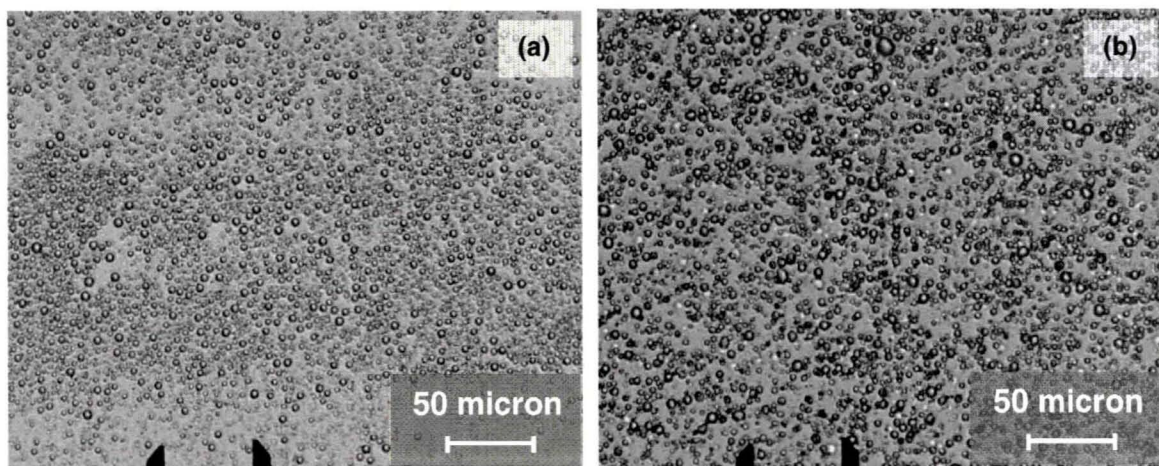
These interactions are weak and are not as effective at keeping the emulsion droplets from clustering (Figure 10b). However, it is possible to obtain water-in-oil emulsions that are kinetically stable.

In order to solve the clustering problem, a matrix study was carried out to find an optimized water/oil/surfactant combination for water-in-oil emulsion formation. This effort was successful in identifying a new water-in-oil emulsion formula, which forms a stable emulsion with monodispersed size distribution of 1 to 5  $\mu\text{m}$  size droplets. The new water-in-oil emulsion formula also features a higher water/oil ratio, which means that more microcapsules can be produced from a certain amount of reactants. A significant advantage associated with the new emulsion system is that it does not involve the use of toxic chemicals, making it a “green” procedure. The continuous phase of the emulsion is made of methyl myristate, a component of vegetable oil, while the older formula used toluene as the continuous phase.



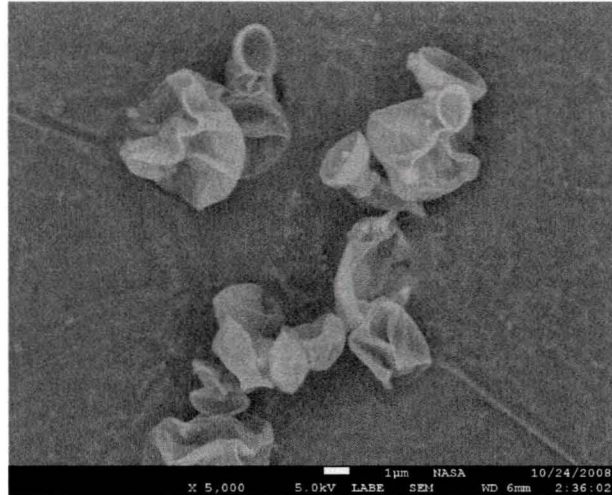
**Figure 10. (a) Oil-in-water emulsion showing a homogenous size distribution and a good dispersion (b) An early water-in-oil emulsion formula showing some clustering.**

This new emulsion formula resolved the clustering (or dispersion) problem of the water-core microcapsules. This new procedure was used to encapsulate various water-soluble corrosion inhibitors, such as  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Na}_2\text{MoO}_4$  (Figure 11).

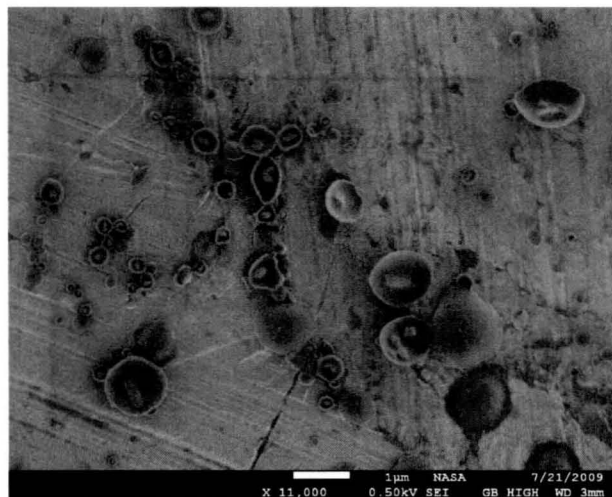


**Figure 11. Water-core microcapsules with: (a)  $\text{Ce}(\text{NO}_3)_3$  and (b)  $\text{Na}_2\text{MoO}_4$  in their core.**

The following SEM images of the inhibitor microcapsules provide evidence that corrosion inhibitors were encapsulated inside the microcapsule walls. Figure 12 shows the SEM image of water-core microcapsules with cerium nitrate ( $\text{Ce}(\text{NO}_3)_3$ ) using a low-angle backscattered electron (LABE) detector. Due to their larger effective diameters for backscattering, the higher-atomic-number elements bounce back a larger number of beam electrons than lower-atomic-number elements. Thus, portions of a backscattered electron image that are bright have a higher atomic number than darker portions of the image. The brighter spots show the presence of the higher-atomic-number element in the inhibitor, cerium. Figure 13 shows the SEM image of water-core microcapsules with and sodium molybdate ( $\text{Na}_2\text{MoO}_4$ ) inhibitor. The inhibitor crystals are evident under the thin shell of the microcapsule.



**Figure 12. SEM image of water-core microcapsules with  $\text{Ce}(\text{NO}_3)_3$  using a LABE (low-angle backscattered electron) detector. The brighter spots show the presence of the higher-atomic-number element, cerium.**



**Figure 13. SEM image of water-core microcapsules with  $\text{Na}_2\text{MoO}_4$  in their core. The inhibitor crystals are evident under the thin shell of the microcapsules.**

Although the SEM images provided evidence of the encapsulation of corrosion inhibitors, they also revealed that the mechanical strength of the microcapsules to be weaker than desired, as they clearly deformed during the synthesis or drying process.

Despite these problems, the first generation water-core microcapsules have been used to encapsulate a range of water soluble inhibitors, including: sodium molybdate, cerium nitrate, sodium phosphate, calcium metaborate, sodium metasilicate, phenyl phosphoric acid, and sodium benzoate. Some of these inhibitor capsules have been incorporated into commercially available coatings to be tested.

### First Generation Water-core Microcapsules: Testing

Test panels, carbon steel Taber abrasion panels with 0.5 mils or less surface profile, coated with Carboline Carbomastic epoxy mastic coating and Devco Cathacoat 304V inorganic zinc primer containing water-core microcapsules have been tested using a salt fog chamber, for approximately 6 months, following the ASTM B117 standard method.<sup>4</sup> Panels were evaluated for both rust grades (ASTM D610)<sup>5</sup> and scribe ratings (ASTM D1654)<sup>6</sup>. Test panels with inhibitor incorporated directly into the coating were also included for comparison. Representative results are shown in Table 2 and Table 3.

**Table 2. Rust grade and Scribe rating of epoxy mastic coatings**

<b>Carbomastic 15 FC Coating Systems</b>	<b>Sample #</b>	<b>Rust Grade</b>	<b>Scribe Rating</b>
Control	1	5	5
	2	10	5
	3	6	5
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% 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

Five different systems were tested using the epoxy mastic coating. Based on the rust grades, the corrosion performance of the test panels of the 5 systems can be ranked, starting with the best in the following order: encapsulated inhibitor phenylphosphonic acid; encapsulated inhibitors cerium nitrate and sodium molybdate; phenylphosphonic acid; control; cerium nitrate and sodium molybdate. Based on the scribe rating, the system containing the non-encapsulated cerium nitrate and sodium molybdate performed worse than the control system while the systems containing microcapsules performed about the same as the control. Test panels were scrapped to reveal corrosion under paint. Pictures of representative systems before and after scrapping are shown in Figure 14.

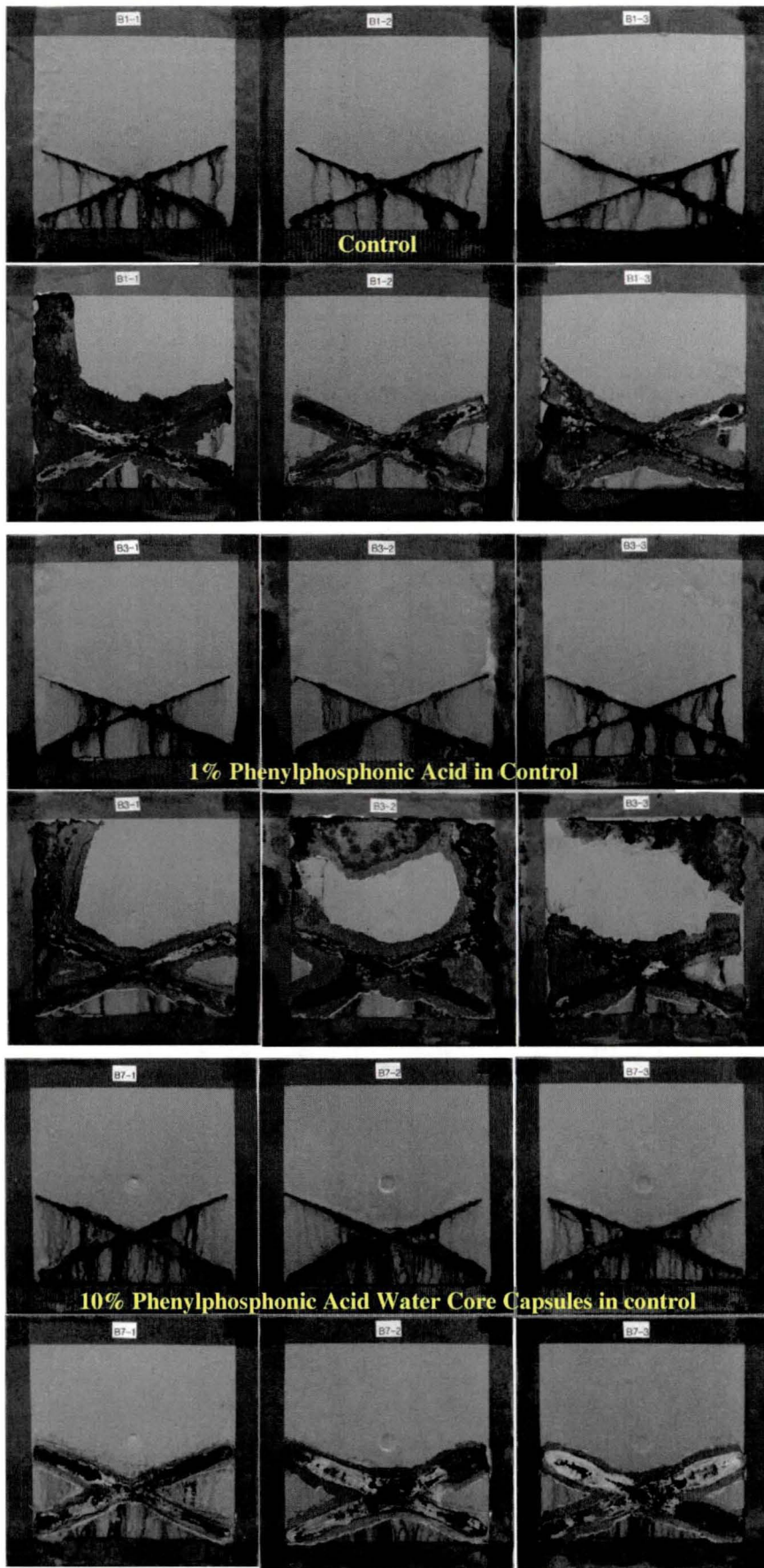
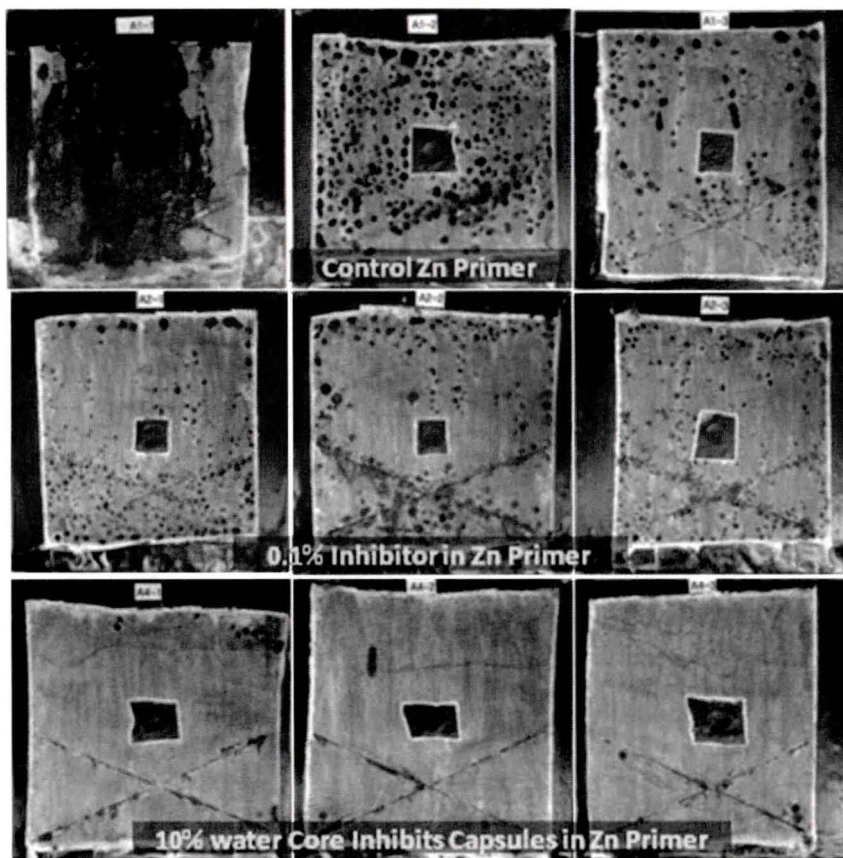


Figure 14. Test panels of epoxy mastic system after 6 month salt fog testing.

Three different systems were tested using the inorganic zinc primer. Test panels were again scrapped to reveal corrosion under paint. The following corrosion performance ranking, starting with the best, was obtained by comparing the rust grades for the test panels of the 3 systems: encapsulated inhibitors cerium nitrate and sodium molybdate; encapsulated indicator phenolphthalein; phenolphthalein; phenylphosphonic acid; cerium nitrate and sodium molybdate; control. Representative pictures of these testing panels were shown in Figure 15.

**Table 3. Rust rating of inorganic zinc primer for salt fog samples**

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



**Figure 15. Test panels of inorganic zinc system after 6 month salt fog testing.**

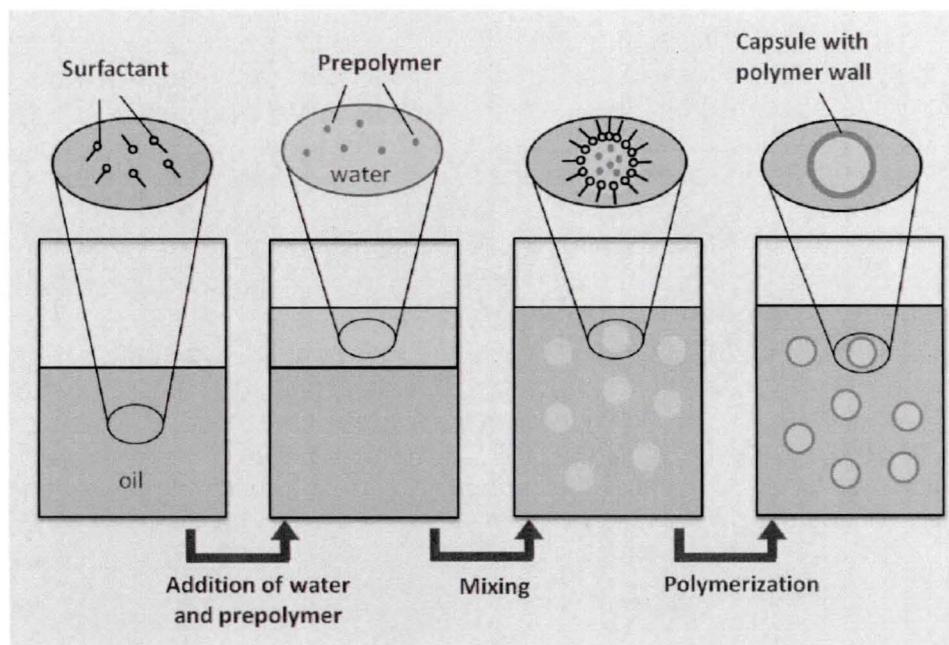
These coatings were tested in a salt fog chamber for over 4000 hours. As the results show, the phenylphosphonic acid microcapsules did better than the controls and better than the cerium nitrate and the sodium molybdate microcapsule combination. It was also observed, when scraping the coating off the panel to view the corrosion, that the phenylphosphonic acid microcapsules improved the adhesion of the coatings to the substrate leading to the conclusion that phenylphosphonic acid may also be an adhesion promoter in addition to being a corrosion inhibitor.

During coating of the carbon steel panels for testing, a problem with the first generation microcapsules was observed in that, once the coating dried, small bumps could be observed over the surface of the coating. This was attributed to the cluster formation of the microcapsules discussed earlier, which caused some of the larger clusters to protrude through the surface of the coating. The remedy for this was to do a top coat of just coating with no capsules to cover up the protruding clusters. However, this resulted in a thicker coating as well as more time needed to complete the coating process. These coating compatibility issues, the capsule wall weakness revealed earlier by SEM results, and other issues have motivated a continuous search for a better encapsulation formulation. In order to solve these problems, a second generation water-core microcapsule formula was developed.

### Second Generation Water-core Microcapsules: Synthesis

The next important improvement of the water-core microcapsule involved the modification of the capsule wall materials. Previously, solvent soluble prepolymer and cross linker were used as the capsule wall forming materials in both water-core and oil-core microcapsules. As a result, oil-core microcapsules were synthesized with wall materials in the dispersed phase. Wall formation could only occur at the interface where wall materials from the dispersed phase came in contact with the acid catalyst from the continuous phase. Because the polymerization reaction only takes place in the dispersed phase, it is a well controlled process. However, water-core microcapsules were synthesized with the pre-polymer and cross linker in the continuous phase, and the acid catalyst in the dispersed (water) phase. The polymerization reaction occurs in the continuous phase, thus it is a less controllable process. This process also yields water-core microcapsules with acid in the core, which raises concerns for corrosion protection applications.

This problem was resolved when a water soluble pH sensitive pre-polymer was synthesized by the reaction between melamine, formaldehyde, and pentaerythritol tetrakis (3-mercapto propionate). This improvement in the water-core microcapsules synthesis provides an easier way to control the synthesis process. The new process also yields a capsule wall with better mechanical properties, while reducing the reaction time, and avoiding having an acidic capsule core. The introduction of wall formation materials into the dispersed water phase (as shown in Figure 16 ) solved several problems simultaneously.



**Figure 16. Schematic representation of the steps involved in the interfacial polymerization of a water-in-oil emulsion to synthesize water-core microcapsules. Oil is shown in yellow and water in blue.**

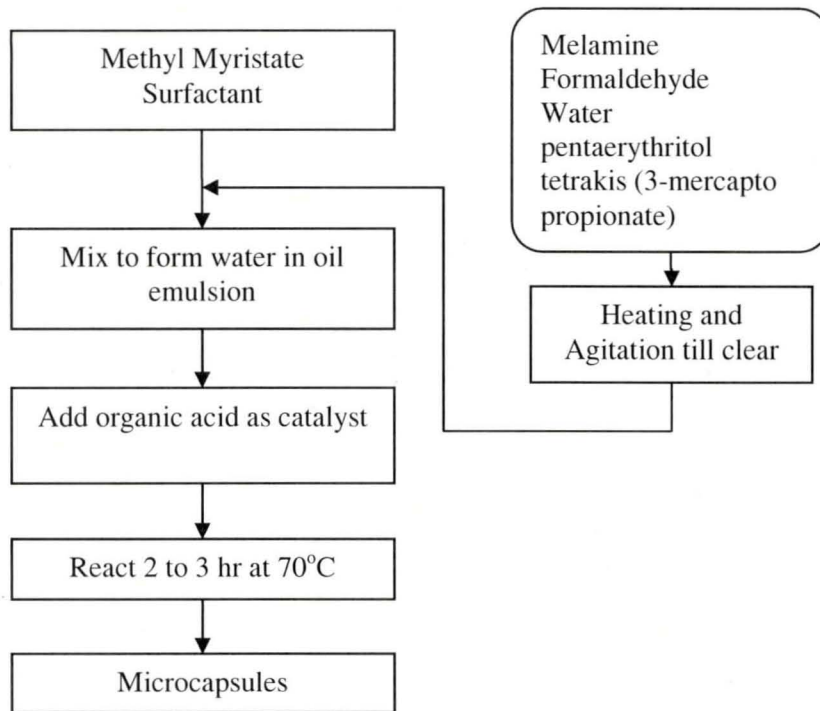
The formulation of water-core microcapsules using water soluble material in their core is shown in Table 4 and their synthesis procedure is described in the schematic diagram shown in Figure 17.

The oil phase is prepared by mixing methyl myristate and amide surfactant using a Powergen500<sup>®</sup> homogenizer. The water, 37% formaldehyde solution, and melamine along with two drops of triethanolamine are mixed and then heated to 70°C. The mixture is stirred until it is clear followed by the addition of pentaerythritol tetrakis (3-mercapto propionate). When the water phase turns clear again, it is added to the oil phase slowly using a pipette to form the emulsion. The emulsion is heated to 70°C and the stearic acid catalyst is added to start the polymerization reaction. Normally, it takes 2 to 3 hours for the wall to form completely.

**Table 4. Formula for water-core microcapsules with water soluble wall material.**

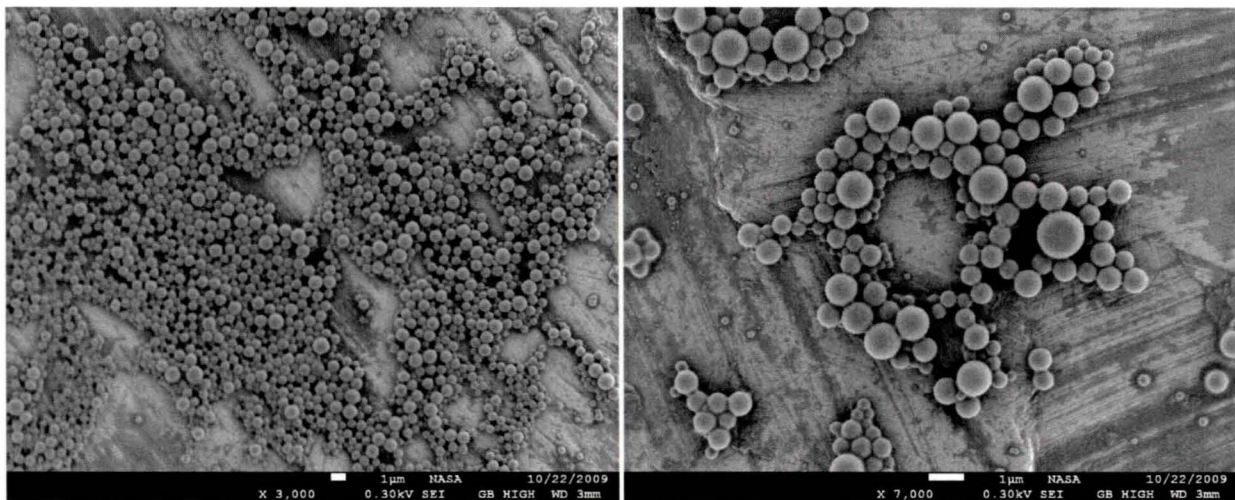
Reagent	Mass (g)
<b>Water Phase</b>	
Water	40
melamine	3.0
Formaldehyde (37%)	6.4
pentaerythritol tetrakis (3-mercapto propionate)	2
<b>Oil Phase (I)</b>	
Methyl Myristate	160
Amide Surfactant	5
<b>Catalyst</b>	
Stearic Acid	0.5



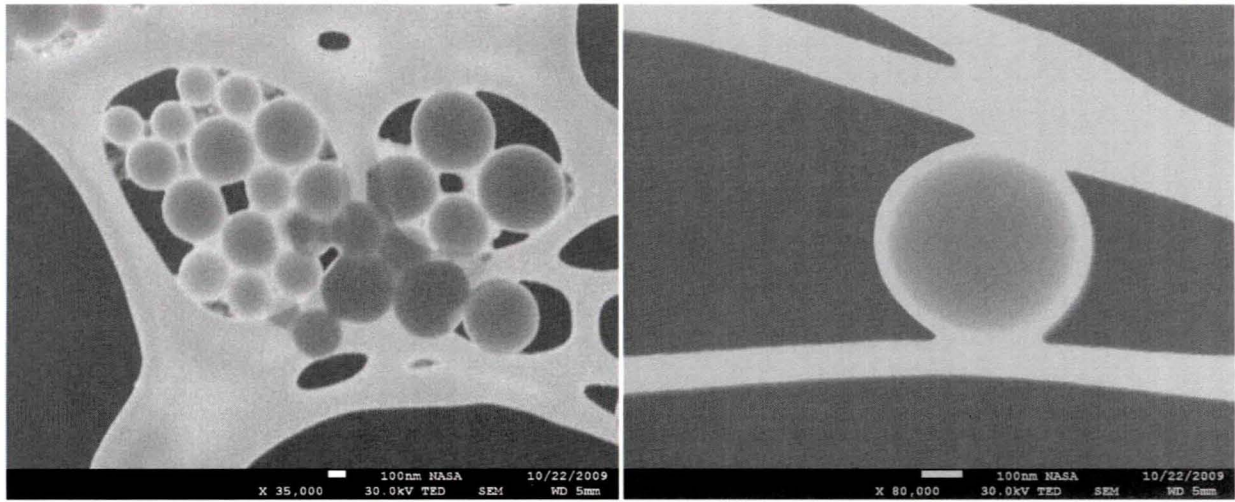


**Figure 17. Synthesis procedure for water-core microcapsules.**

Observations under the optical microscope showed that the emulsion was stable and that the water phase droplet size was homogenous. The following SEM images in Figure 18 show that capsules of a little less than  $1\ \mu\text{m}$  were obtained and that many had the desirable spherical shape. The capsule wall thickness is about  $50\ \text{nm}$ , as shown in SEM images of the microcapsules obtained using a transmission electron detector (Figure 19).



**Figure 18. SEM Images of the water-core microcapsules.**



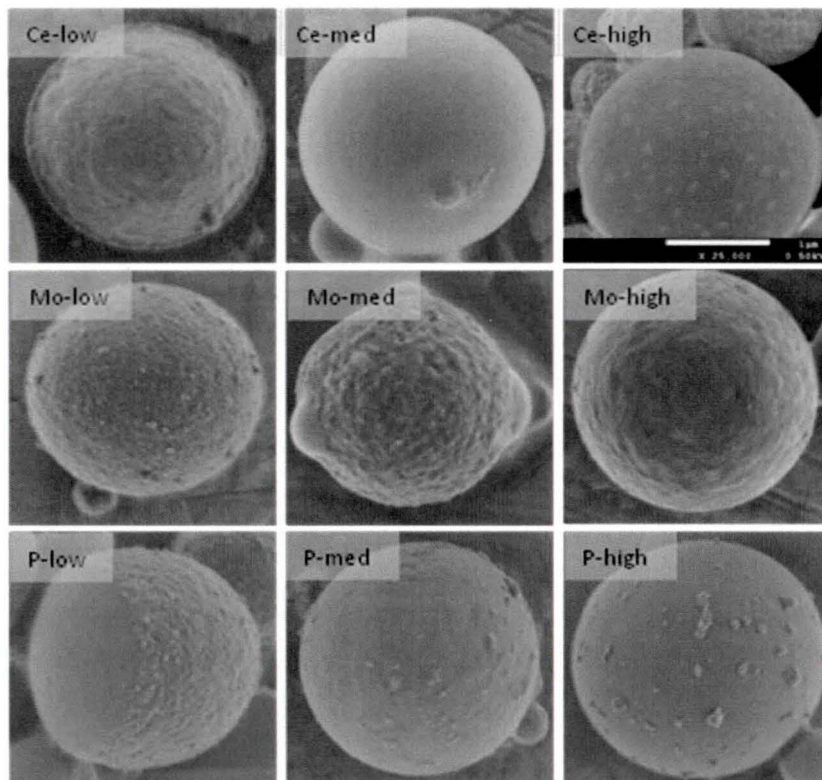
**Figure 19. SEM Images of the water-core microcapsules obtained using a transmission electron detector.**

To date, various compounds, such as the corrosion indicator phenolphthalein, corrosion inhibitors sodium molybdate, cerium nitrate, sodium phosphate, calcium metaborate, and phenyl phosphonic acid, have been encapsulated into water-core microcapsules. Some examples of these water-core microcapsules are shown below:

The latest water-core microcapsules containing different corrosion inhibitors at different concentrations were heat treated at different conditions (for different release rates) and then incorporated into epoxy and other coatings. The coatings were exposed in a salt fog chamber for corrosion inhibition testing. The results obtained indicated that several microcapsules, such as those with the combination of cerium nitrate and sodium molybdate and those with phenyl phosphonic acid provided additional corrosion protection in the coatings at low and intermediate concentration. It was found that microcapsules with high inhibitor concentration caused osmotic blistering in the coatings during the salt fog tests. These results were interpreted to be an indication that heat treatment alone is not enough to improve the impermeability of the capsule wall to avoid migration of the water to the inhibitor (osmotic blistering) when the inhibitor concentration is too high inside the microcapsule.

The latest water-core microcapsules containing different corrosion inhibitors at different concentrations were heat treated at different conditions (for different release rates) and then incorporated into epoxy and other coatings. The coatings were exposed in a salt fog chamber for corrosion inhibition testing. The results obtained indicated that several microcapsules, such as those with the combination of cerium nitrate and sodium molybdate and those with phenyl phosphonic acid provided additional corrosion protection in the coatings at low and intermediate concentration. It was found that microcapsules with high inhibitor concentration caused osmotic blistering in the coatings during the salt fog tests. These results were interpreted to be an indication that heat treatment alone is not enough to improve the impermeability of the capsule wall to avoid migration of the water to the inhibitor (osmotic blistering) when the inhibitor concentration is too high inside the microcapsule.

In order to prevent the formation of osmotic blisters, experiments were conducted to search for another approach to incorporate water soluble corrosion inhibitors into a pH sensitive, but otherwise impermeable carrier. As a result, a microparticle formulation was developed and various corrosion inhibitors were incorporated into the microparticle formulation.



**Figure 20. 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:  $\text{Ce}(\text{NO}_3)_3$ ,  $\text{Na}_2\text{MoO}_4$ , and  $\text{NaH}_2\text{PO}_4$  inhibitors.**

### **pH sensitive microparticle with corrosion inhibitors**

During the microcapsule formulation development process, it became apparent that a microparticle with active components encapsulated throughout the whole matrix of the particle can be advantageous for smart coatings for corrosion applications, especially for the indication and inhibition functions.

The inhibitor microparticle was conceived as a good alternative to microcapsules for delivery and release of an inhibitor for corrosion control in a coating. In the microparticle, the inhibitor could be interspersed throughout the polymer instead of just encased in a polymer wall. This would allow for a more controlled release of the inhibitor over time rather than all at once as with a wall breakdown mechanism. Microparticles also have the potential to use a layering system in which the particle contains different layers that facilitate different inhibitor release speeds and contain different concentrations of inhibitor. This would allow the microparticle to be customized to the requirements of the application.

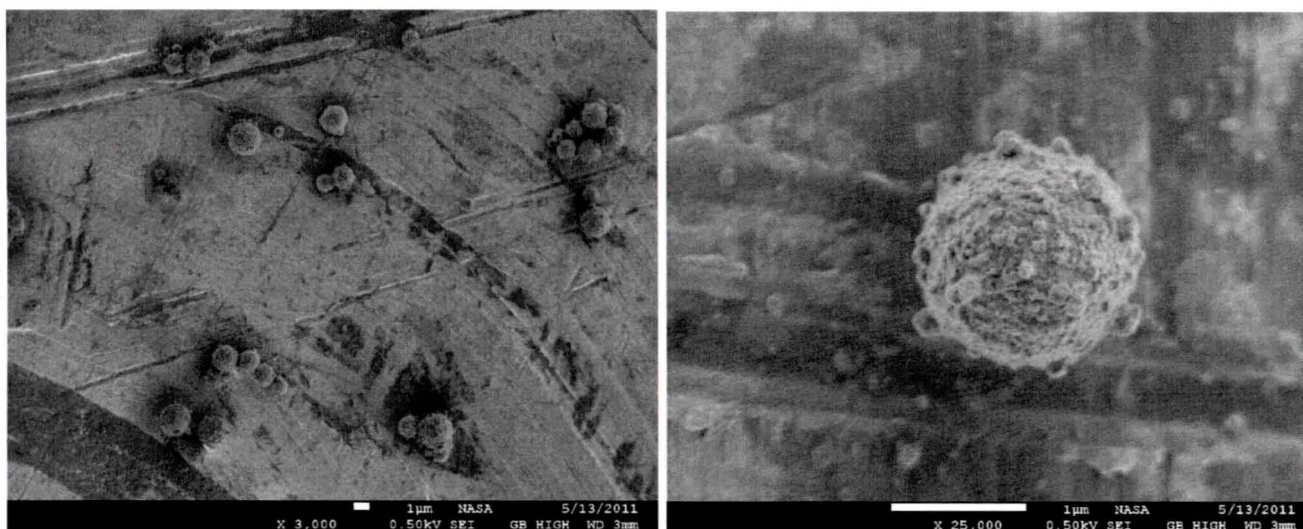
Synthesis of the microparticle uses the water soluble prepolymer developed for the water-core microcapsules but in a more simplified process of formation. The synthesis process includes dissolving the inhibitor into a water miscible solvent first, such as ethanol or isopropanol. The inhibitor solution is then added to a continuous water phase. This process allows the inhibitor to be incorporated into the particle rather than being dissolved into the water. While the process is not completely understood, it is thought that through a somewhat spontaneous microemulsion process, similar to the Ouzo Effect<sup>7</sup> but

less stable, the inhibitor solution is dispersed into droplets. The polymerization reaction then occurs at the interfaces of these droplets which cause the inhibitor to be incorporated into particles before being dissolved into the water. Two surfactants, sodium dodecyl sulfate and arabic gum, and mixing are used to control size and maintain particle distribution. Acid catalyst may or may not be used to speed up the polymerization reaction depending on the pre-polymer and inhibitor used to form the particle.

### Acidic Inhibitor Microparticle

The first inhibitor microparticle successfully synthesized was one using an inhibitor that was acidic in nature. These microparticle formulations are interesting because no additional acid is needed to catalyze the polymerization reaction that forms the particle. The acid inhibitor is what catalyzes the reaction and therefore serves a sort of dual purpose as a catalyst as well as an inhibitor.

Phenylphosphonic acid was chosen as the first acid inhibitor for testing the microparticle process. It was a logical choice, due to the fact that phenylphosphonic acid has been encapsulated into water-core microcapsules and incorporated into a coating for testing. The test results confirmed that it is an effective corrosion inhibitor for a steel substrate. Phenylphosphonic acid is an acid that can be used as an acid catalyst for the polymerization of the prepolymer for particle formation. The SEM images of the final product after spray drying are shown in Figure 21.



**Figure 21. SEM images of phenylphosphonic acid inhibitor particles.**

Figure 22 shows an elemental analysis obtained using energy-dispersive X-ray spectroscopy (EDS). The elements from the polymer: carbon (C), nitrogen (N), oxygen (O), and sulfur (S), as well as the phosphorus (P) from the inhibitor are found within the particle. Its presence in the particles proves that the PA inhibitor was successfully incorporated in the melamine, formaldehyde, penta erythritol tetrakis (3-mercapto propionate) particles.

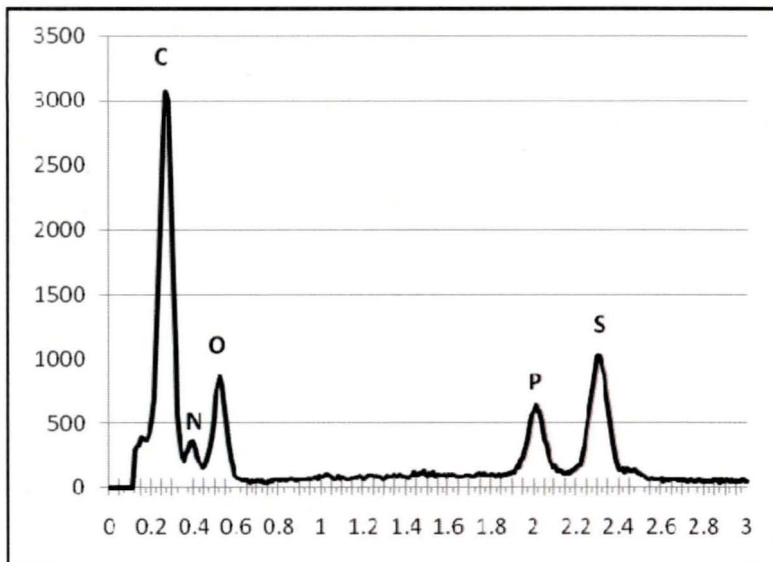


Figure 22. EDS elemental analysis of PA inhibitor particle.

Phenylphosphonic acid particles were incorporated into an epoxy coating for testing. The following pictures show that after 1000 hours of salt fog testing, the phenylphosphonic acid particle provides much better corrosion protection than the control, especially in preventing corrosion under paint around scribes.

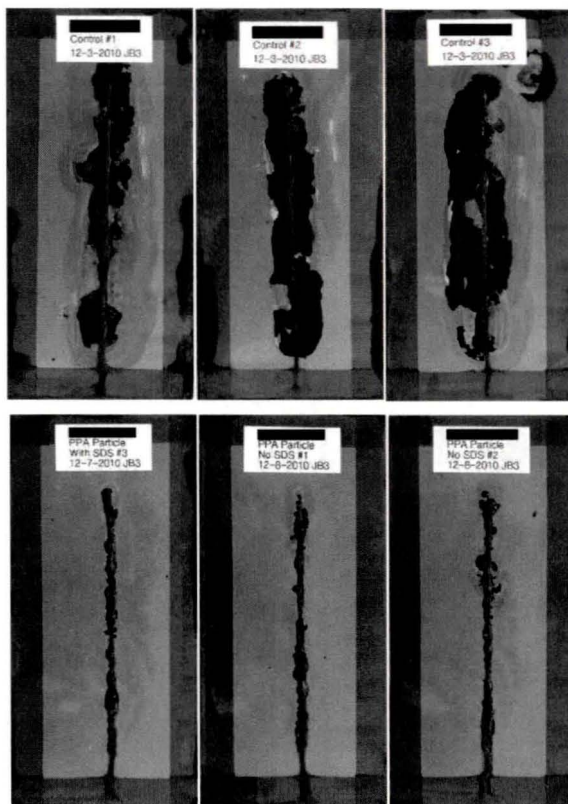
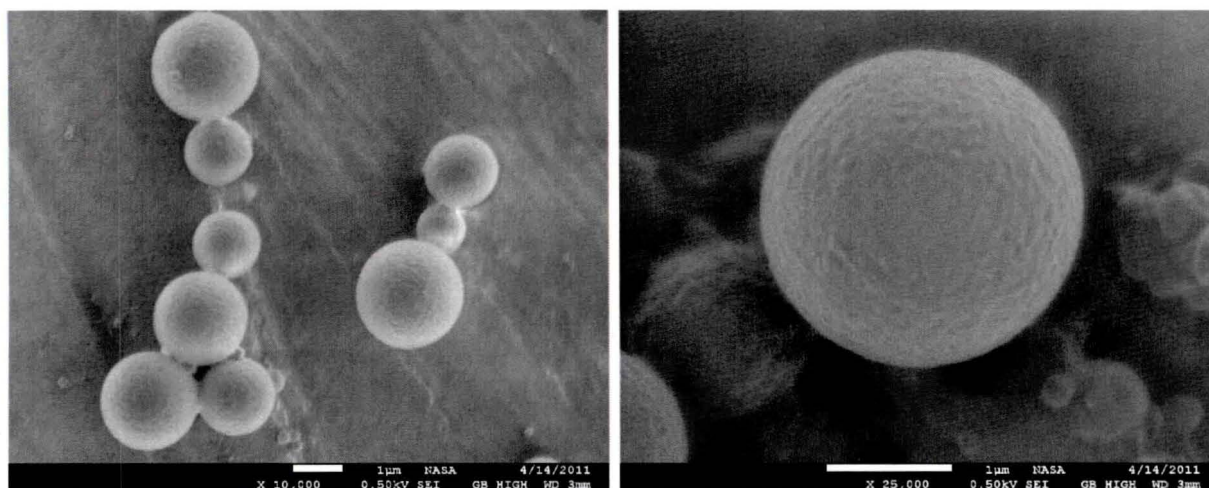


Figure 23. Salt fog testing result (1000 hour) of the phenylphosphonic acid microparticles in epoxy coating (bottom) versus controls (top).

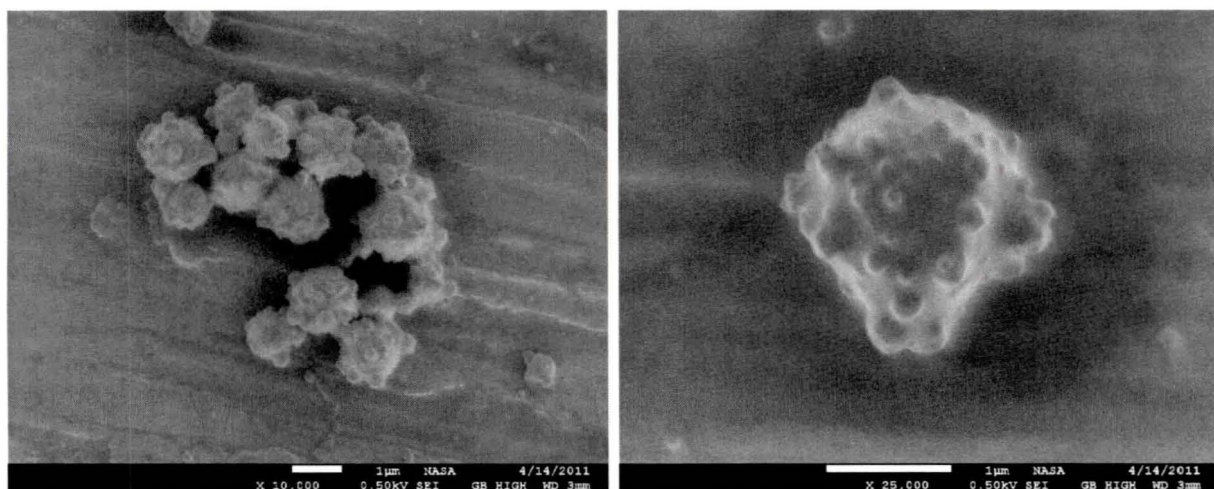
## Non-Acidic Inhibitor Microparticles

Another inhibitor microparticle successfully synthesized was one using an inhibitor that was non-acidic in nature. These microparticle formulations are interesting because they require a certain water miscible solvent, such as N-Methylpyrrolidone (NMP) or Dimethylformamide (DMF), to form the microparticle. Solvents like the ones listed are very interesting in that not only do they dissolve high amounts of the inhibitor, leading to a fairly large concentration of inhibitor in the microparticle, but they also seem to help promote the polymerization reaction as a catalyst would. It can be hypothesized that these solvents actually accelerate the reaction by participating in it. The acid catalyst is still required to fully complete the polymerization reaction but, since the initial microparticle forms fairly quickly, the acid does not have a large negative effect on the system as a whole.

Two different inhibitors were formed into microparticles using this process; one dissolved in NMP the other in DMF. The inhibitors were dissolved into their respective solvents at fairly high concentrations leading to a high concentration of inhibitor, around 30%, incorporated into the microparticle.



**Figure 24. SEM images of inhibitor in NMP solvent microparticles**



**Figure 25. SEM images of inhibitor in DMF solvent microparticles**

## CONCLUSIONS

pH-sensitive microcapsules and microparticles were developed to incorporate the autonomous corrosion inhibition function into a smart coating. The microcapsules and particles 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.

Oil-core and water-core microcapsules were synthesized through interfacial polymerization reactions in an emulsion. The microencapsulation process was optimized to obtain desired size and size distribution, good mechanical strength, and better coating compatibility. Particles with corrosion inhibitor have also been developed using a modified *in situ* polymerization process as well as a spray drying process.

Preliminary results from salt fog testing of panels coated with commercially available coatings in which the microcapsules and particles were incorporated indicate that microcapsules and particles can be used to improve the corrosion protection of the coatings.

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