MICROENCAPSULATION OF CORROSION INDICATORS FOR SMART COATINGS

Wenyan Li, Jerry W. Buhrow, and Scott T. Jolley
ESC-Team QNA
Mail Code: ESC-24
Kennedy Space Center, FL 32899

Luz M. Calle
NASA
Mail Code: NE-L2-C
Kennedy Space Center, FL 32899

Joshua S. Hanna and James W. Rawlins
University of Southern Mississippi
118 College Dr.
Hattiesburg, MS 39402

ABSTRACT

A multifunctional smart coating for the autonomous detection, indication, and control of corrosion is been developed based on microencapsulation technology. This paper summarizes the development, optimization, and testing of microcapsules specifically designed for early detection and indication of corrosion when incorporated into a smart coating. Results from experiments designed to test the ability of the microcapsules to detect and indicate corrosion, when blended into several paint systems, show that these experimental coatings generate a color change, indicative of spot specific corrosion events, that can be observed with the naked eye within hours rather than the hundreds of hours or months typical of the standard accelerated corrosion test protocols..

1

INTRODUCTION

Corrosion is a costly problem for a wide range of industries and it affects nearly every facet of our lives and it can lead to catastrophic metal failure if undetected and untreated. Coatings are frequently used as a corrosion protective barrier to protect the metallic substrates and they are often able to delay the corrosion process, but not completely prevent it.

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. Many different sensors and techniques are being developed to detect corrosion.[1,2,3,,4] Among different technologies, corrosion sensing coatings are highly desired for corrosion control, especially if the signal can be detected through visual inspection by the naked eye, at a stage much earlier than the appearance of the observable corrosion products.[5, 6,7,8,9, 10]

Earlier corrosion detection can be realized by incorporating an indicator that detects the onset of corrosion, the corrosion product, such as the metal or H^+/OH^- ions generated during corrosion. Therefore, both pH indicators and metal ion indicators have been utilized as corrosion indicators. The detection of corrosion can be either through a visible color change[8,11,12,13] or a fluorescence change.[14,15,16,,17] While observation of a visible color change can be convenient for traditional visual corrosion inspection, fluorescent compounds can be more readily detected by optical equipment.

Corrosion detection is one of the functions of the smart coating being developed at NASA's Corrosion Technology Laboratory at the Kennedy Space Center. The goal of this project is to develop a smart coating that uses pH-triggered release microcapsules for early detection of corrosion and for corrosion protection. This project involves several tasks: the selection of microcapsule materials and candidate indicators and inhibitors; development of the microencapsulation process for these active agents; paint system development to incorporate the encapsulated active agents; and accelerated and long-term corrosion testing to evaluate coating performance and provide insight for optimization.

This paper presents the relation between pH and corrosion, the design of pH sensitive microcapsules, a summary of the development and optimization process of the corrosion indicator microcapsules, and a description of the prototype paint formulation for corrosion detection applications.

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: $Fe \rightarrow Fe^{2+} + 2e^-$
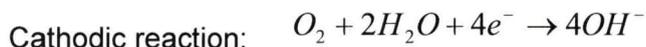
In the case of localized corrosion, such as pitting corrosion, as shown in Figure 1, the anodic reaction happens in a confined area and the metal ions formed are precipitated as solid corrosion products, which cover the mouth of the pit. This covering traps the solution in the pit and allows the buildup of hydrogen ions, H^+. The overall effect is that, while localized corrosion happens, the anode area often has an acidic pH and the cathode has an alkaline pH.[18]
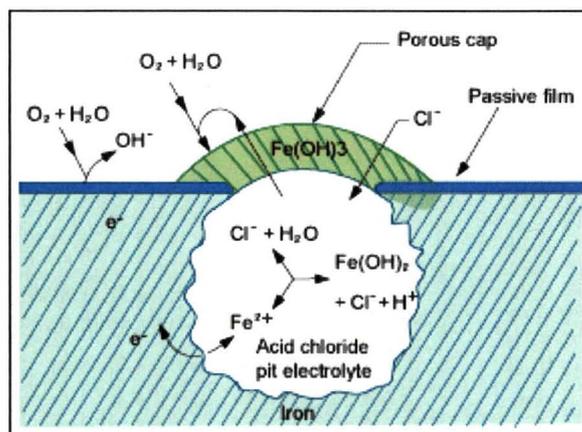
Figure 1. The electrochemical cell set up between anodic and cathodic sites on an iron surface undergoing pitting corrosion.

Besides pitting, crevice corrosion and dissimilar metal corrosion result in pH changes as illustrated by the simple laboratory demonstration shown in Figure 2, where a universal pH indicator was used to show the pH changes that occur during corrosion of a metal, such as carbon 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^-.
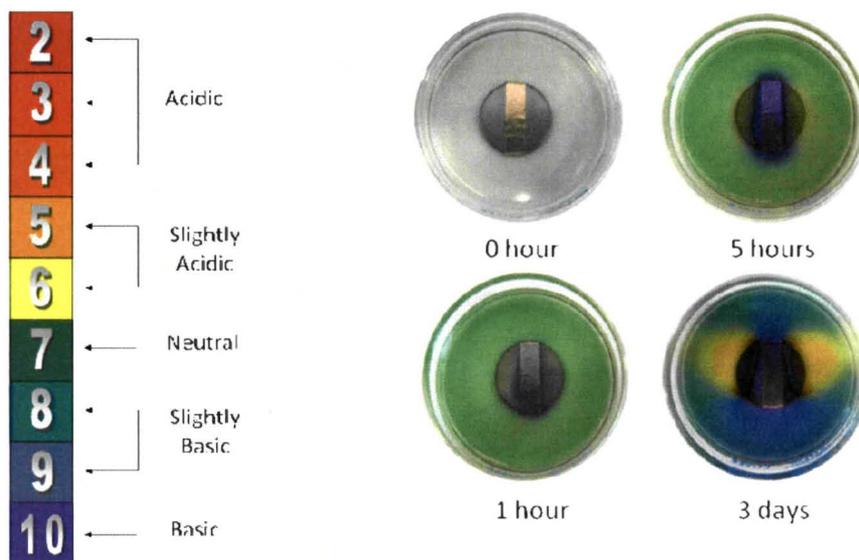
Figure 2. pH changes associated with corrosion.

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. Various pH and electrochemically responsive materials, as well as their potential applications in smart coatings for corrosion control, can be found in our previous review.[19]

PH SENSITIVE MICROCAPSULES FOR SMART COATINGS

NASA's Corrosion Technology Laboratory at KSC developed pH-triggered release microcapsules for early corrosion detection and corrosion protection.[20,21,22] The microcapsule wall is designed to break down and release the encapsulated contents in response to the pH of the cathodic site of localized corrosion (Figure 3.).
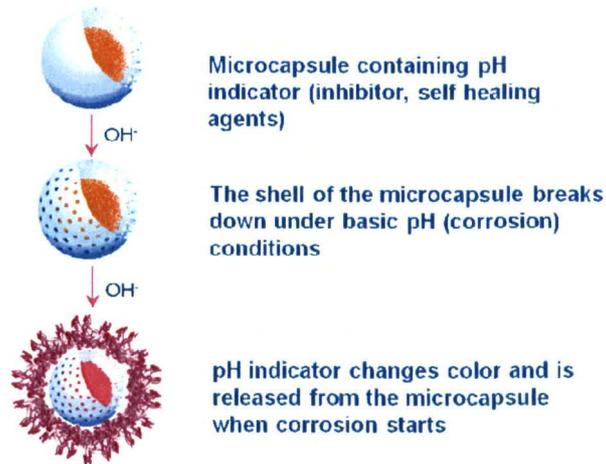

Microcapsule containing pH indicator (inhibitor, self healing agents)

↓ OH⁻

The shell of the microcapsule breaks down under basic pH (corrosion) conditions

↓ OH⁻

pH indicator changes color and is released from the microcapsule when corrosion starts

Figure 3. Conceptual illustration of how pH sensitive microcapsules can be used to indicate corrosion.

Microencapsulation is a versatile approach because it can be used to encapsulate an unlimited number of materials, in both solid and liquid phase. 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 4).
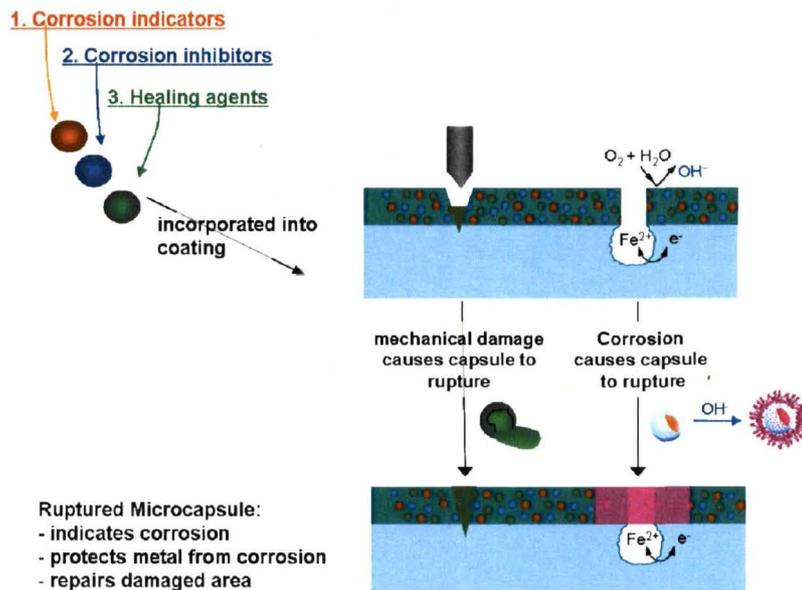

Figure 4. Conceptual illustration of smart coating with pH sensitive microcapsules for corrosion protection applications.

4

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, 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.

MICROENCAPSULATION

The development of corrosion indicator microcapsules for a corrosion sensing coating involves three interactive processes: encapsulation method development, indication function testing, and paint formulation. First, the candidate indicators are tested for corrosion indication. Based on these results and/or other justifications, candidate indicators are selected. Then, an encapsulation path is chosen and a procedure is developed and optimized until the desired properties, such as good corrosion indication and suitable microcapsule size, are obtained. The optimization process is repeated until the microcapsules are ready to be incorporated into a test paint formula. The main objective of the paint formulation effort is to address compatibility issues between the microcapsules and other paint components, as well as application process compatibility. The former concerns the interaction between the microcapsules and other painting components and their effect on each other, while the later mainly concerns the effect of the paint application process on the microcapsules, i.e., how the microcapsules will survive the high speed mixing, spraying, and curing processes. Formulated coatings are tested for corrosion indication and, based on the results, the process can be determined as been a success or needing another round of optimization in the paint formulation and/or microencapsulation process (Figure 5).
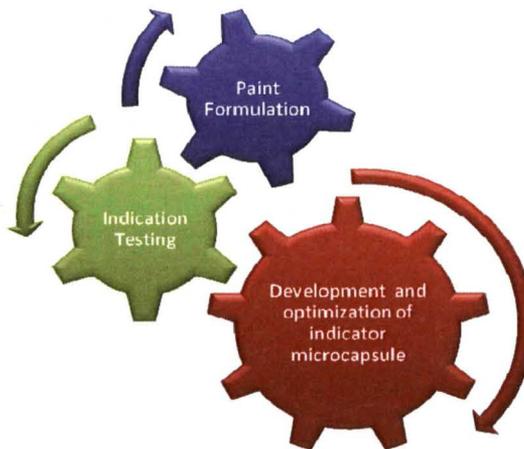
Figure 5. Processes involved in the development of microcapsules for corrosion indicating coating.

Although the initial development process takes a long time, once the development path has been developed and tested for one indicator, it can be easily tailored for other candidate indicators. This is one of the advantages of using encapsulated indicators over free indicators for corrosion sensing coating application.

The following sections describe the process of encapsulating pH indicators as well as ion indicators for corrosion detection applications.
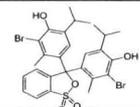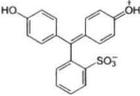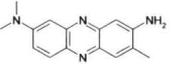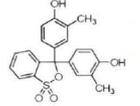
Encapsulation of pH Indicators for corrosion indication

Selection of pH Indicators for Corrosion Indication

While any pH indicator has the potential to indicate corrosion, an ideal corrosion indicator should have a transition pH around 7. Table 1 shows pH indicators with the color transition pH ranges of interest and their structures.[23]

For a cathodic indicator, it is preferable that the color change takes place at a basic pH that is close to neutral so that the indicator would be sensitive to the onset of corrosion while avoiding false positive corrosion indication. A good example would be phenolphthalein (phph) in Table 1.

Table 1. Selected pH indicators that are used for corrosion indication.

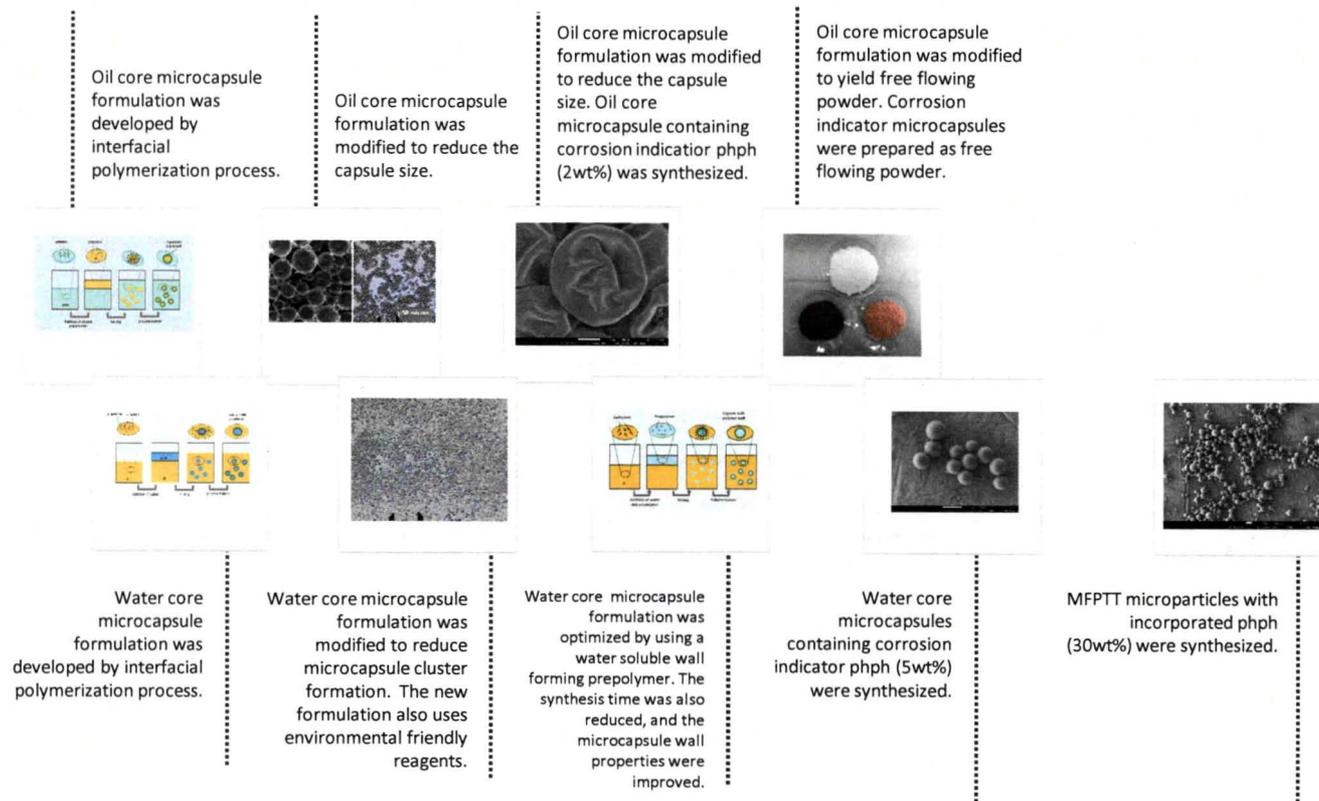| Indicator	Low pH color	Transition pH range	High pH color	Structure
Bromothymol blue	yellow	6.0–7.6	blue	
Phenol red	yellow	6.8–8.4	purple	
Neutral red	red	6.8–8.0	yellow	
Cresol Red	yellow	7.2–8.8	reddish-purple	
Phenolphthalein	colorless	8.3–10.0	fuchsia	
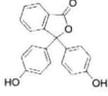
Other desired qualities for corrosion indicators include color intensity and the contrast between the colors before and after transition. Phenolphthalein was chosen as the best candidate corrosion indicator, even though it did not have the highest absorption and reflection coefficients, because its color change, when exposed to basic pH conditions, is more pronounced and easier to detect with the naked eye than that of the other candidate indicators. Phenol red, cresol red and bromothymol blue are colored at neutral conditions where phph is clear. This makes the color change for phph easier to detect visually (from colorless to purple instead of from one color to another color, Figure 6).
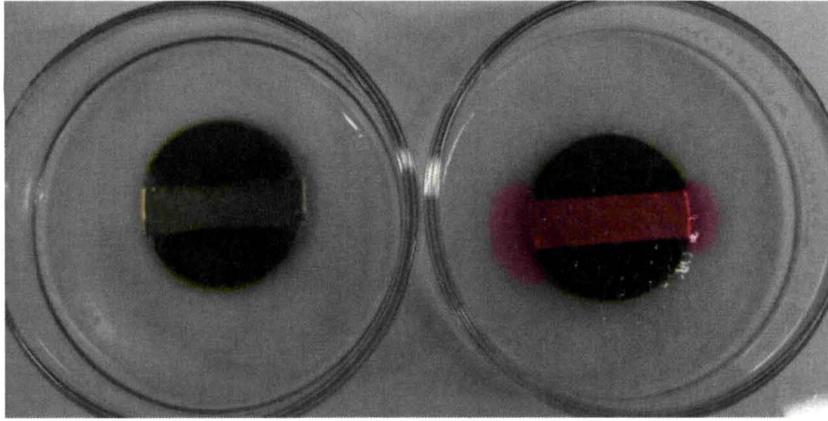
Figure 6. Dissimilar metal corrosion of a steel disc covered partially by a copper tape in Agar gel. The sample on the left is a control, while the one on the right contains phph dissolved in the gel.

Synthesis of pH Sensitive Microcapsules

pH sensitive microcapsules are the key component of the smart coatings. Several methods such as emulsion polymerization, interfacial polymerization, as well as *in-situ* polymerization have been used to synthesize pH sensitive microcapsules. 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 used to synthesize microcapsules with corrosion indicators and self-healing agents, mainly into oil-core microcapsules, where water is used as the continuous phase. *In situ* polymerization is also used to synthesize microparticles with incorporated corrosion indicators and inhibitors throughout their solid matrix. Spray drying has been a useful method for drying microcapsules and microparticles into a free flowing powder form. Figure 7 shows a timeline for the development process and optimization of microcapsules and microparticles for corrosion indication where MFPTT stands for melamine formaldehyde penta erythritol tetrakis (3-mercapto propionate).

Oil core microcapsule formulation was developed by interfacial polymerization process.

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

Oil core microcapsule formulation was modified to reduce the capsule size. Oil core microcapsule containing corrosion indicatior phph (2wt%) was synthesized.

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

Water core microcapsule formulation was developed by interfacial polymerization process.

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

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

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

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

**Figure 7. The development and optimization of corrosion indicator microcapsules and microparticles formulations.**

Synthesis of pH indicator Microcapsules

Several microcapsule formulas have been developed to incorporate the corrosion indication function into the smart coating: oil-core phph and water-core phph microcapsule through the interfacial polymerization process, oil-core phph microcapsules through *in situ* polymerization, as well as phph microparticles. The development and optimization of corrosion indicator microcapsules and microparticles formulations are summarized in Figure 7. All of these microcapsule formulas perform the pH and corrosion indication functions in solution, in gel, and in paint through a color change. The intensity of the color change is largely determined by the amount of phph encapsulated. So far, the microparticle formulas provide the strongest color change because they proved to be more suitable than microcapsules to incorporate a higher amount of phph.

Oil-Core Indicator Microcapsule: Synthesis

An active compound, such as a corrosion indicator, 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 compounds. 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 polymerization reaction can be used to encapsulate these reagents into the oil-core of the microcapsules.

There are two main steps involved in the interfacial polymerization process: emulsion formation and microcapsule wall formation. Figure 8 shows a schematic representation of the steps involved in forming oil-core microcapsules: the emulsion is formed by adding the oil phase (with pre-polymer, 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.
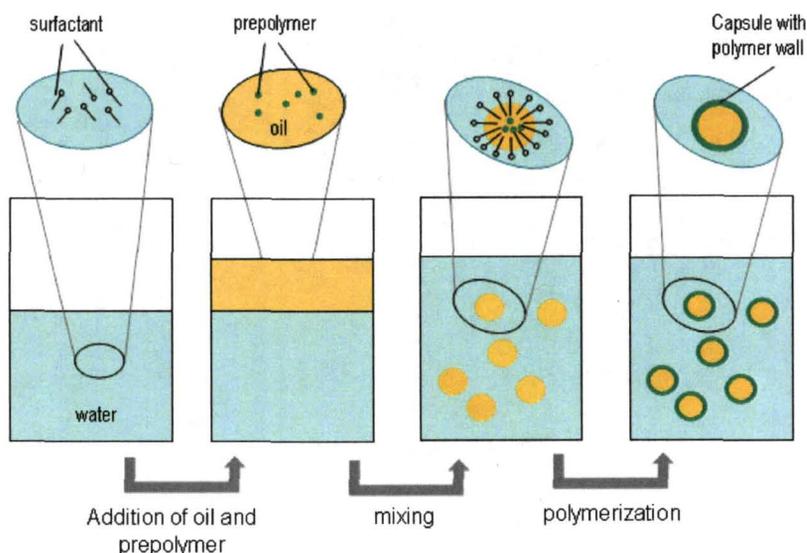

Figure 8. Schematic representation of the steps involved in the interfacial polymerization of an oil-in-water emulsion for making oil-core microcapsules. Oil is shown in yellow and water in blue. The microcapsule wall is shown in green.

9

Corrosion indicators that have high solubility in ethanol or isopropanol are suitable to be encapsulated into oil-core microcapsules using alcohols as co-solvents. The First Generation indicator microcapsules are oil-core microcapsules synthesized using the formula shown in Table 2. Corrosion indicator, phph, was first dissolved in ethanol, and then introduced into the oil phase to be encapsulated into oil-core microcapsules.

Table 2. Formula for First Generation Oil-core Indicator Microcapsules.

| Reagent	Mass (g)
Oil Phase	
Prepolymer	3.85
Crosslinker agent	0.95
Oil	31.4
Cosolvent	5
Indicator	0.5
Water Phase	
surfactants	1.5
water	26
Catalyst	
10% H_2SO_4	pH 2

When the pH sensitivity of these microcapsules was tested, the results showed the breakdown of the microcapsule wall as a result of their exposure to basic pH conditions. Figure 9 shows time lapse images of a single oil-core microcapsule reacting to basic pH conditions. Soon after the addition of a sodium hydroxide, NaOH, solution, the solution started 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 (see small droplet beginning to form on the bottom left quadrant of the frame). The contents 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 thru n.
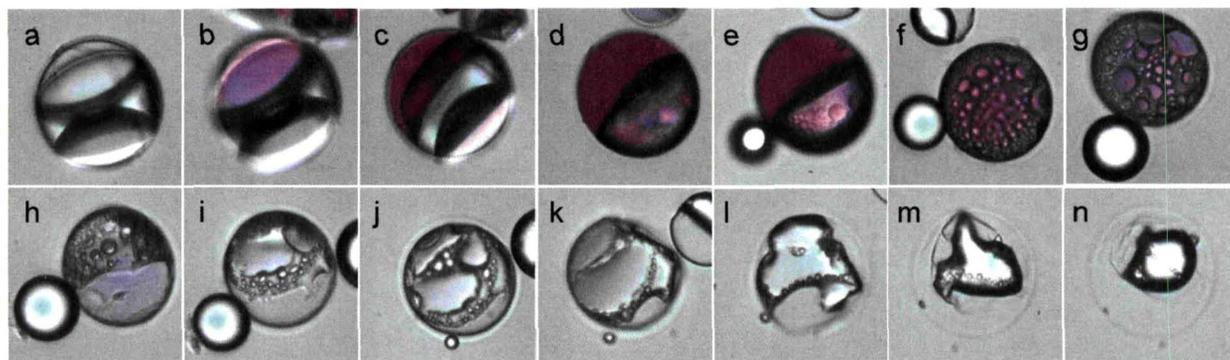
Figure 9. Time lapse pictures of an oil-core microcapsule breaking down under basic pH conditions.

Oil-core Indicator Microcapsule: Optimization

After the initial proof of the concept of the pH sensitive microcapsule, the oil-core indicator microcapsule formula was modified to optimize the capsule size and size distribution. Adjustments in the formula as well as changes in the mixing speed were made to get smaller and even sized microcapsules, as shown in Figure 10.
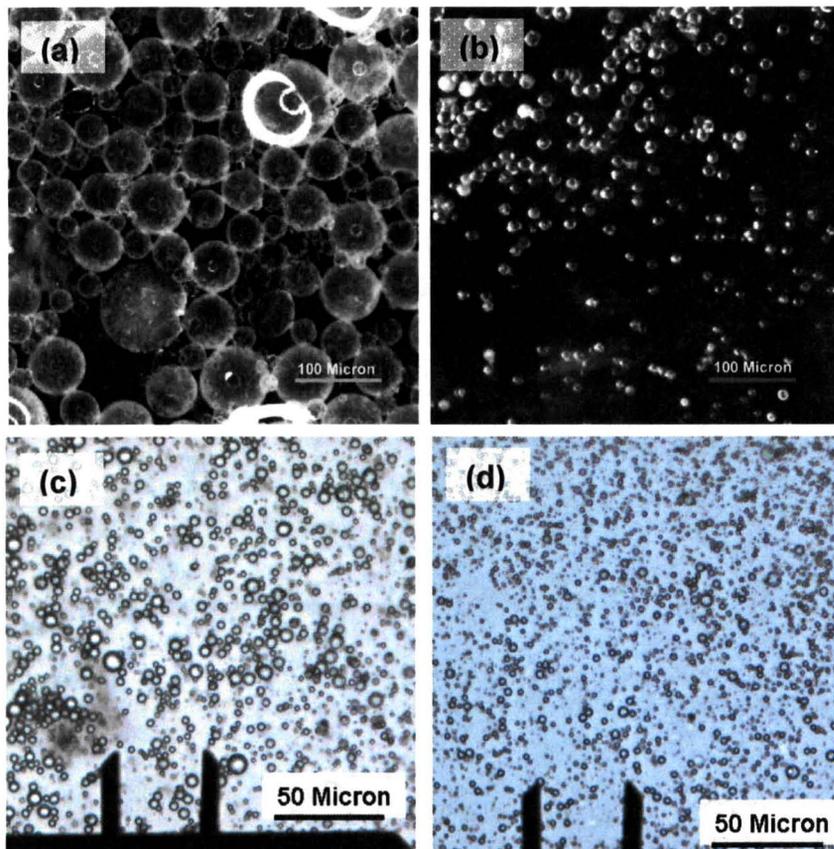
Figure 10. Oil Core microcapsules of different sizes.

Another optimization effort was undertaken to increase the pH sensitivity of the microcapsules, i.e. to achieve a faster breakdown of the microcapsules under the same basic pH conditions. This effort involved increasing the amount of cross-linker and decreasing the thickness of the capsule wall. Increasing the amount of the cross-linker in the reaction yields more ester groups in the wall structure. When pH increases, the wall breaks where the ester groups are located. Decreasing the reaction time will result in a thinner capsule shell that is easier to break. A thinner capsule shell also yields low mechanical strength and this imposes a limitation on by how much the thickness of the capsule wall can be reduced. Figure 11 shows microcapsules in which a pH indicator was used to look at the effect of wall thickness on pH sensitivity.
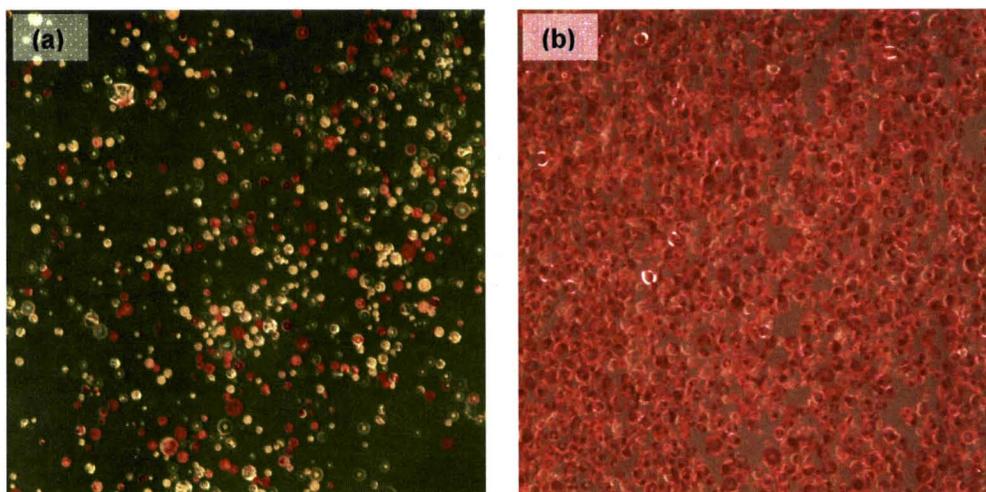
Figure 11. Color change under basic pH conditions for microcapsules with thicker (a) and thinner wall (b).

11

The oil-core encapsulation process has also been optimized to reduce the amount of surfactants used, to facilitate the washing and harvesting process, and to obtain the microcapsules in a free flowing powder form as 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), phph (in the middle), and a universal pH indicator (on the right).

Table 3 shows an example of a formula used to make oil-core microcapsules. The detailed procedure to make these microcapsules is described below.

Table 3: An example of a formula for oil-core microcapsule formation.

	Mass (g)
Oil Phase	
Pre-polymer	4
Cross linker	1
Solvent	20
Co-solvent	4
Indicator	0.2
Water Phase	
Water	100
Surfactant	0.1
Catalyst	0.5

(1) Water phase formation: surfactants are dissolved in water.
(2) Oil phase formation: the indicator is dissolved in the co-solvent (isopropanol) to form a clear solution that is added to the solvent (toluene) with prepolymer and cross linker agent to form the oil phase.
(3) Oil in water emulsion formation: The oil phase is added to the water phase while mixing. Figure 13 shows an optical microscopy image of an oil in water emulsion.

(4) Oil core microcapsule formation: catalyst is added to the emulsion and the mixture is heated at 60°C for 3 hours. Figure 4 shows an optical microscopy image of oil core microcapsules.

(5) The microcapsules are separated from the water phase by centrifugation at high speed (5000 rpm), washed with water, and dried in air. After grinding and sieving, microcapsules in free flowing powder form were obtained. The SEM images of oil-core microcapsules are shown in Figure 15.
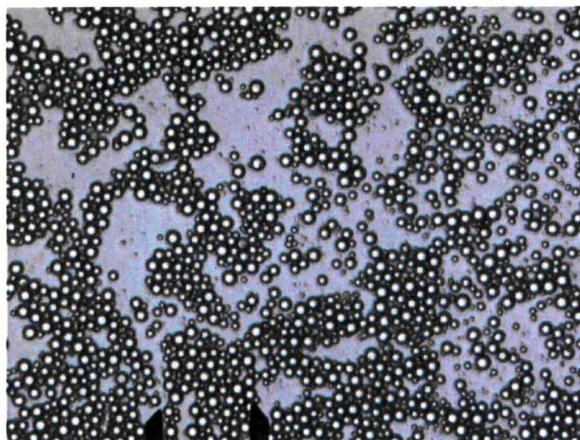

Figure 13. Oil in water emulsion (the distance between the pointers is 50 microns).
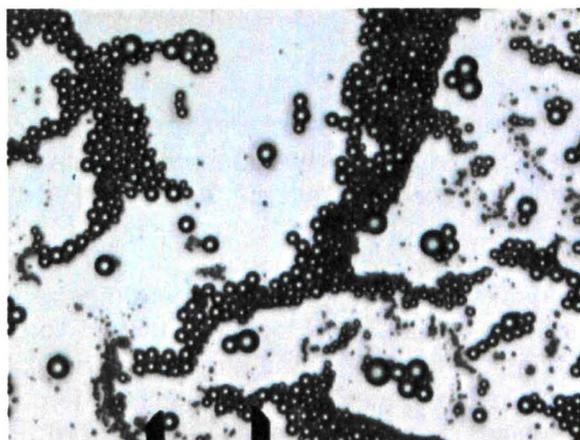
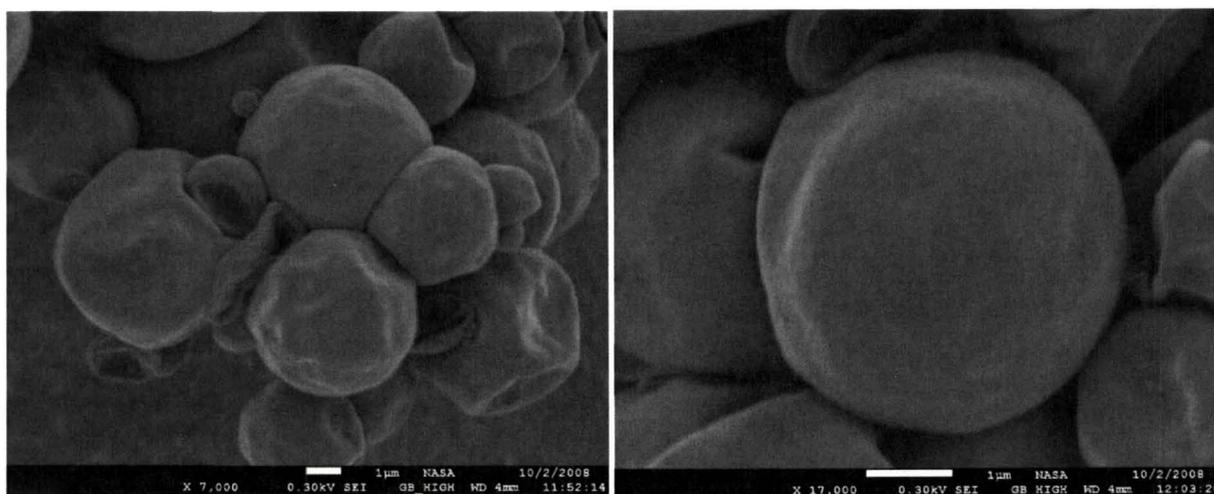Figure 14. Microcapsules formed after 3 hours of heating.

Figure 15. Oil-core microcapsules with a pH indicator as core content.

13

After these microcapsules were synthesized, some of their important properties, such as thermal stability, UV stability, as well as their corrosion indication properties, were tested.

Thermal and UV Stability

The microcapsules must also have thermal and UV stability that is equal to or greater than that of the coating to which they will be added. The microcapsules are determined to be unstable if the wall material is degraded by UV, thus destroying their pH sensitivity and thermal stability, or if UV degradation of the microcapsules leads to premature failure of the coating. Accelerated UV stability tests were performed on the microcapsules to determine if the pH sensitivity and thermal stability of the wall material is degraded by UV light.

Thermogravimetric analysis (TGA) is a method that measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. This allows for determination of material decomposition temperature as well as material composition. A TGA Q 50 instrument was used to obtain the thermal stability of the oil-core microcapsules wall before and after UV exposure. To determine decomposition temperatures and weight changes, the temperature of the samples was increased from $0^{\circ}C$ to $1000^{\circ}C$ at a rate of $10^{\circ}C/min$ in an air atmosphere.

For UV stability analysis, microcapsules were subjected to UV exposure up to 198 hours. Samples were exposed to a light only cycle with an irradiance of 0.35 W/m^2, relative humidity of 50%, and a temperature of $23^{\circ}C$.

Figure 16 and Figure 17 show TGA plots of oil-core microcapsules before and after UV exposure respectively. The plot obtained before UV exposure exhibits one major decomposition around $110^{\circ}C$ with a maximum degradation occurring at $150^{\circ}C$. After 198 hours in the UV chamber, the microcapsule wall undergoes modification in its composition as it is evident from the multiple degradation peaks seen in the derivative weight percent plot in Figure 17. However, this is not a reason for concern since these peaks exist outside the temperatures range for which the microcapsules are being developed. It appears that the thermal stability of these microcapsules was improved by UV exposure, as the percent mass remaining at the same temperature is higher for the systems exposed to UV (Figure 18). A possible explanation is that there were still some unreacted pre-polymer and cross linking agent inside the microcapsules that underwent a UV curing process during the exposure.

When compared with empty oil-core microcapsules, oil-core microcapsules containing phph show very little change in thermal stability due to UV exposure, as shown in Figure 19. There is a slight improvement in thermal stability after UV exposure in both microcapsules, but it is less noticeable for the phph microcapsules than for the empty oil-core microcapsules. It appears that the indicators have some effects on the microcapsule synthesis process, as well as on the wall properties.
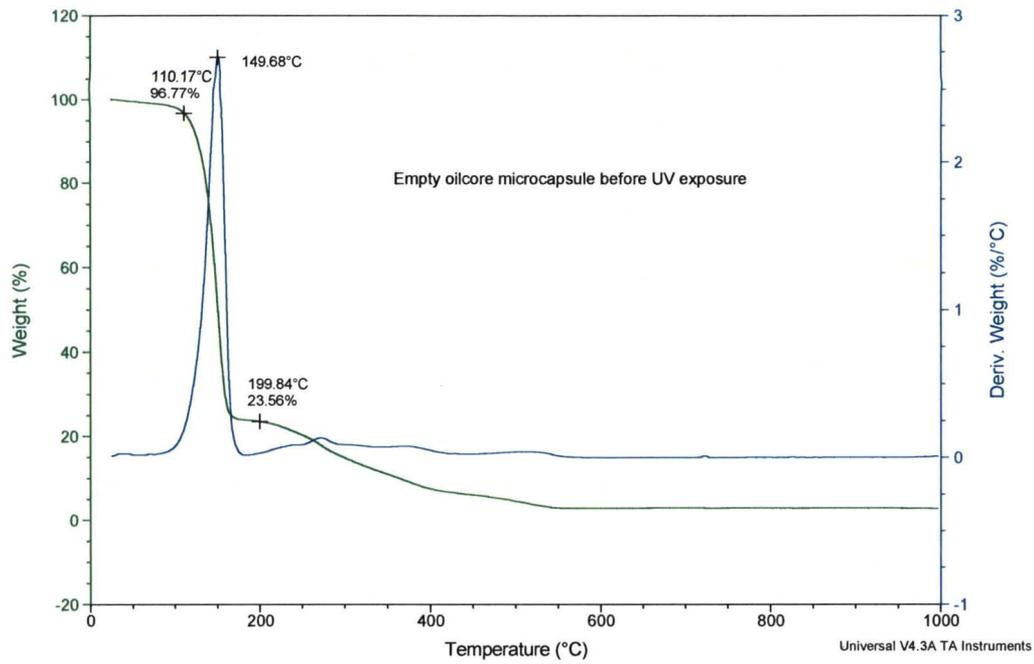
Figure 16. Weight percent vs. temperature (green) and the derivative weight percent vs. temperature (blue) of empty oil-core microcapsules before UV exposure.
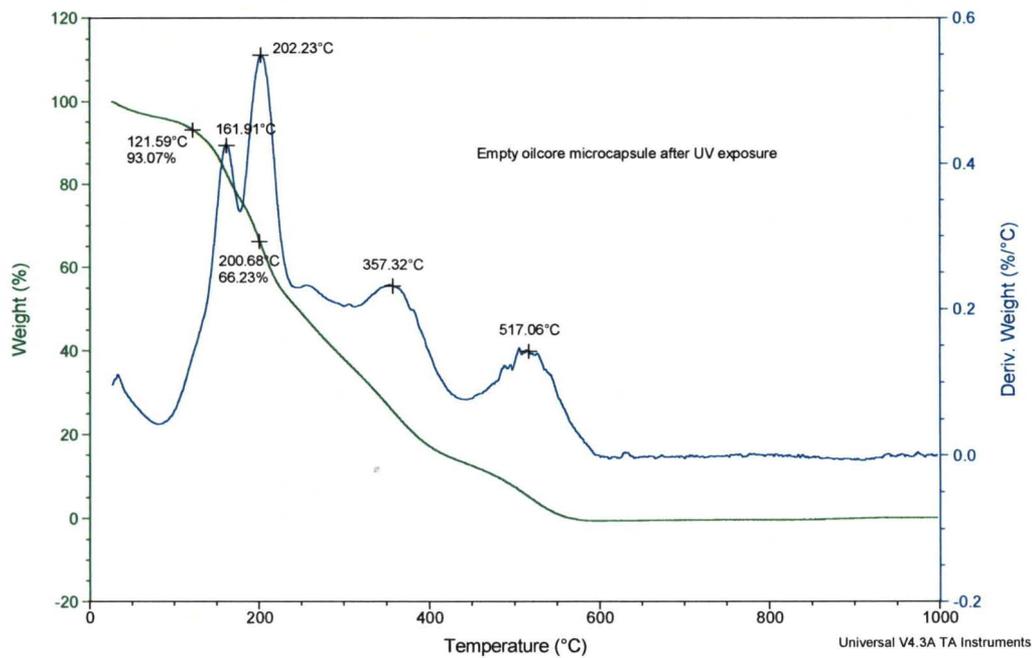
Figure 17. TGA data. Weight percent vs. temperature (green) and the derivative weight percent vs. temperature (blue) of empty oil-core microcapsules after UV exposure.
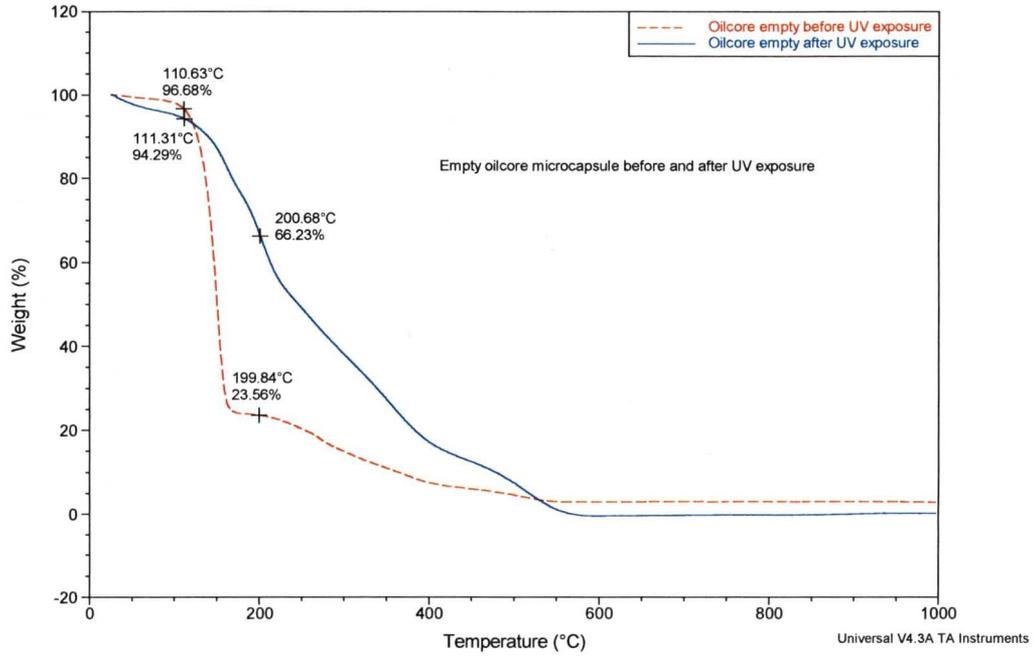
Figure 18. TGA data of oil-core microcapsules before and after UV exposure. Samples were placed in the UV chamber for 198 hours.
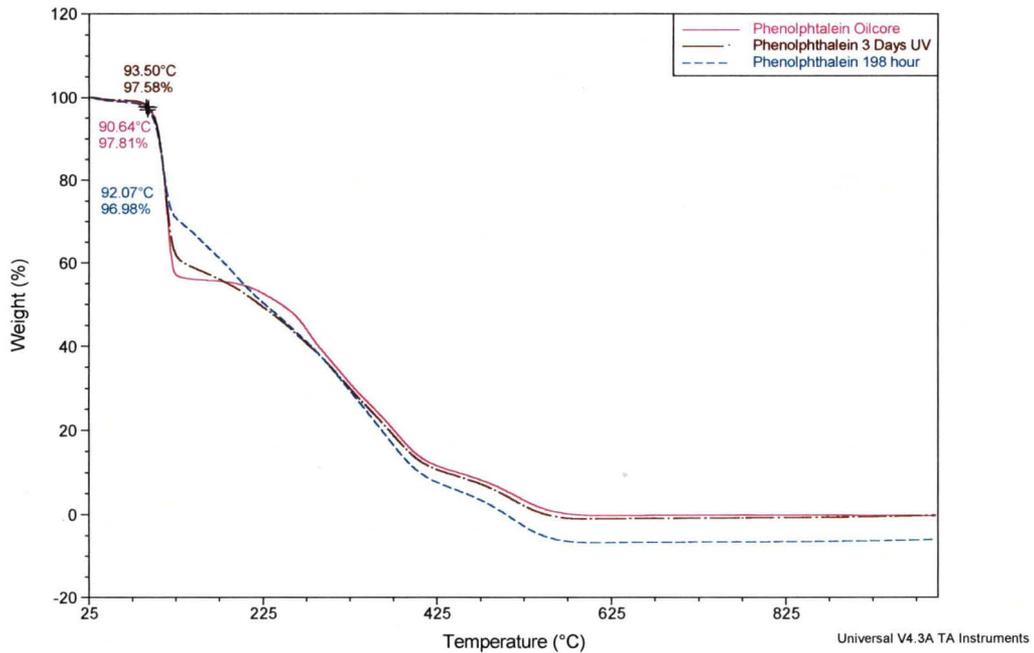

Figure 19. TGA data of phph oil-core microcapsules before and after UV exposures (3 days and 198 hours).

16

Figure 20 and Figure 21 show SEM images of dried microcapsules before and after UV exposure. Noticeable changes of the microcapsules structure after UV exposure is not readily evident.
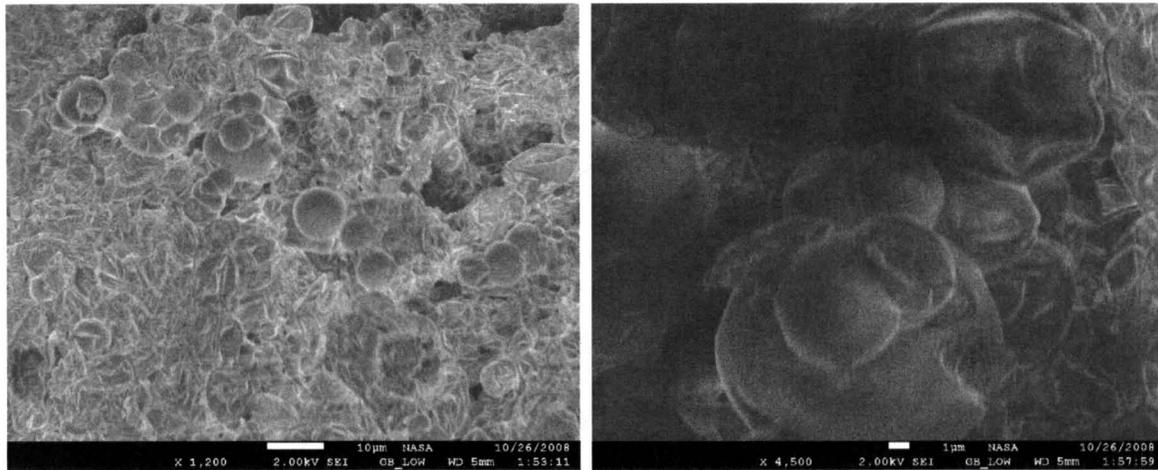

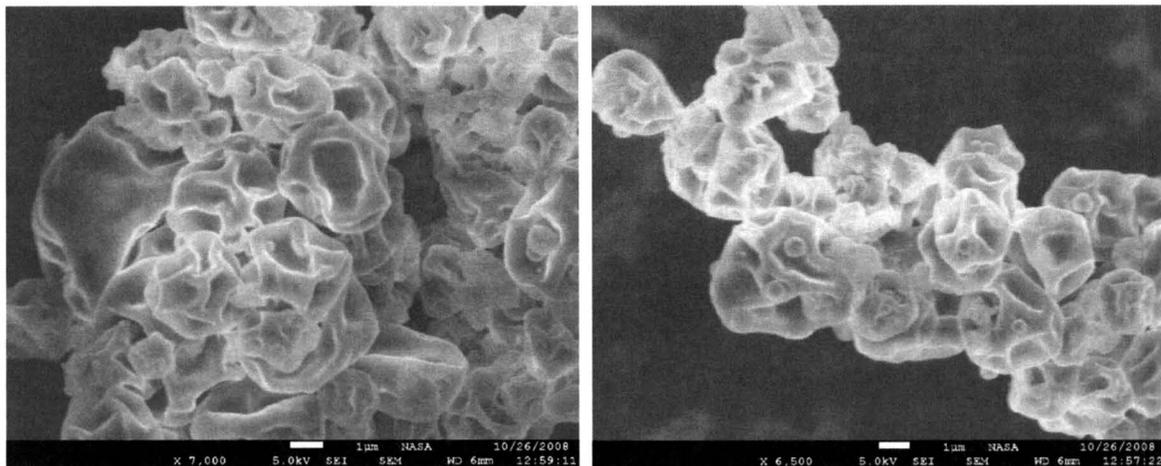**Figure 20. SEM images of empty oil-core microcapsules before (left) and after UV exposure (right).**

Figure 21. SEM images of phph oil-core microcapsules before (left) and after UV exposure (right).

Corrosion Indication Testing

It is clear from the experimental results shown in Figure 9 that the pH sensitive microcapsules will break down and release their content at various basic pH conditions. A galvanic corrosion test cell consisting of a carbon steel disc (anode) in contact with copper tape (cathode) was set up and immersed in gel with microcapsules containing phph as corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released at the cathode where the pH is becoming basic and its color change to purple shows the initiation and progress of corrosion (as shown in the Figure below). This test provided the direct evidence that these microcapsules can release their content "on demand" at the onset of corrosion. It also shows that encapsulated pH indicators can serve as a sensitive corrosion indicator. The color change, indicating cathodic activity, can be observed as early as 0.5 hour after exposure began. Rust was not visually observed until after 4 hours of exposure.
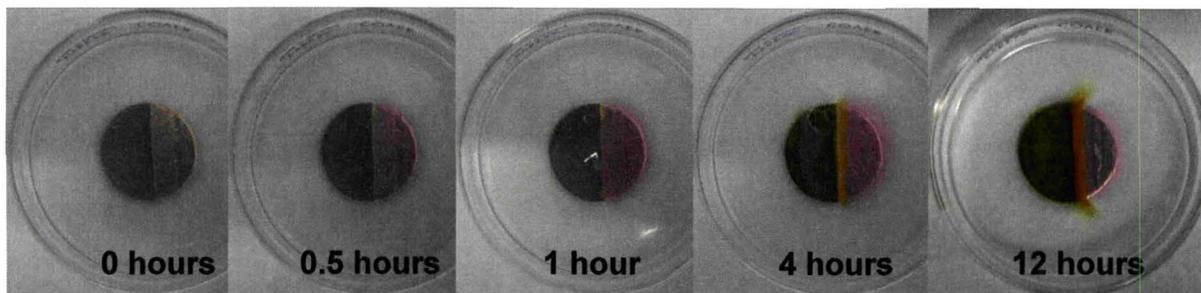
Figure 22. A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was immersed in gel with encapsulated phph.

Oil-core indicator microcapsules have been synthesized, optimized, and their pH controlled release property, as well as their thermal and UV stability, tested. It was proved that encapsulated indicators can be used as corrosion indicators. Although the results obtained with oil-core microcapsules were satisfactory, other microencapsulation approaches, such as water-core microcapsules and solid microparticles, were explored to achieve better corrosion indication: faster response to the onset of corrosion and more intense color changes.

*Water-core Indicator Microcapsule: Synthesis*

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. Figure 23 shows a schematic representation of the steps involved in forming water-core microcapsules: in this case, the emulsion is formed by adding water (shown in blue) to the oil (with pre-polymer 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.
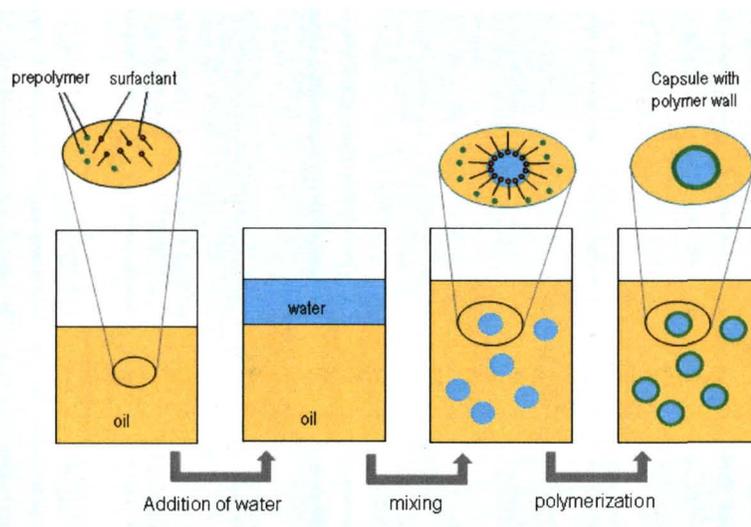
Figure 23. The interfacial polymerization process for water-core microcapsules.

Water-core microcapsule synthesis was found to be considerably more challenging than that of the oil-core until recently. In general, it is easier to make stable oil-in-water emulsions (Figure 24a)

18

because there are more options of surfactants to stabilize the oil-in-water emulsions. This is due to the type of intermolecular interactions such as columbic 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 dispersions 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 24b). However, it is possible to obtain water-in-oil emulsions that are kinetically stable.
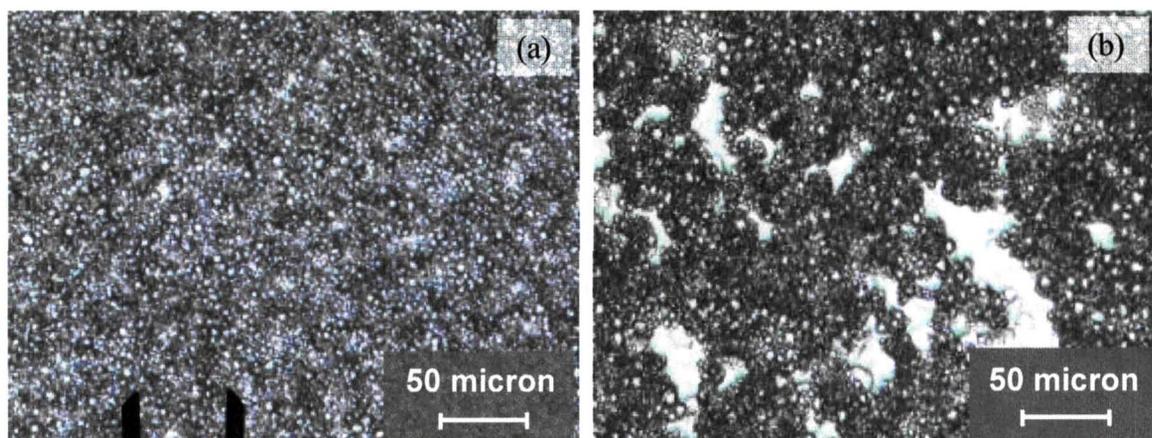
Figure 24. (a) Oil-in-water emulsion showing a homogenous size distribution and a good dispersion. (b) An early water-in-oil emulsion formula showing some clustering.

Initially, water-core microcapsules were formed through the interfacial reaction of water-in-oil emulsion, as shown in Figure 23. However, this process needed considerable improvement because, in addition to the difficulty encountered with the clustering of the emulsion, it also used a harmful solvent, toluene, as the oil phase. The water-in-oil emulsion was only stable when the water content was low (less than 10%), making it very difficult to adjust the microcapsule size. The wall forming materials are water insoluble, so they are introduced in the oil phase, which results in the addition of acid catalyst in the water phase, which can be a concern for coating applications. Since then, several formula changes have been made to obtain an optimized water-core microcapsule formula.

Water-core Indicator Microcapsule: Optimization

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 micron 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. This new emulsion formula solved the clustering (or dispersion) problem of the water-core microcapsules (Figure 25).

Another important improvement to the water-core microcapsule involved the modification of the capsule wall materials. Previously, solvent soluble pre-polymer 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 were 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 into 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 inside, 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-mercaptopropionate), PTT. 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 the acidic capsule content. The introduction of the wall formation materials into the dispersed water phase (as shown in Figure 26) solved several problems simultaneously.
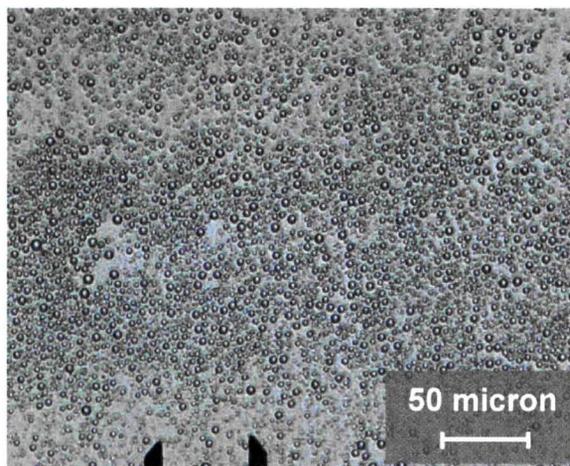

Figure 25. Water-core microcapsule with methyl myristate as the solvent for the oil phase.
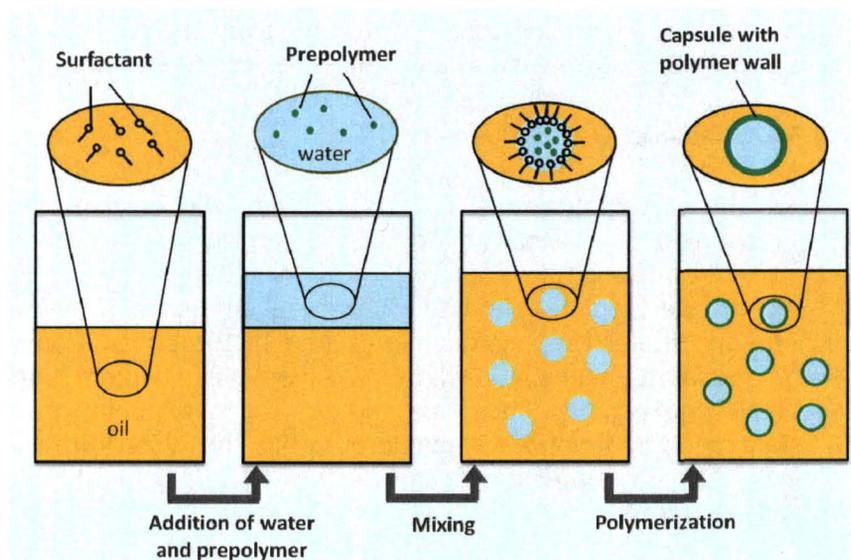

Figure 26. Interfacial polymerization process to synthesize water-core microcapsules, using water soluble prepolymer.

20

The formulation of water-core microcapsules using water soluble materials in their core is shown in Table 4 and their synthesis procedure is described in the schematic diagram shown in Figure 27. The oil phase is prepared by mixing methyl myristate and amide surfactant using a Powergen500 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 PTT. 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)
Water Phase	
water	40
melamine	3.0
formaldehyde (37%)	6.4
PTT	2
ethanol	10
indicator	2
Oil Phase (l)	
methyl myristate	160
amide surfactant	5
Catalyst	
stearic Acid	0.5
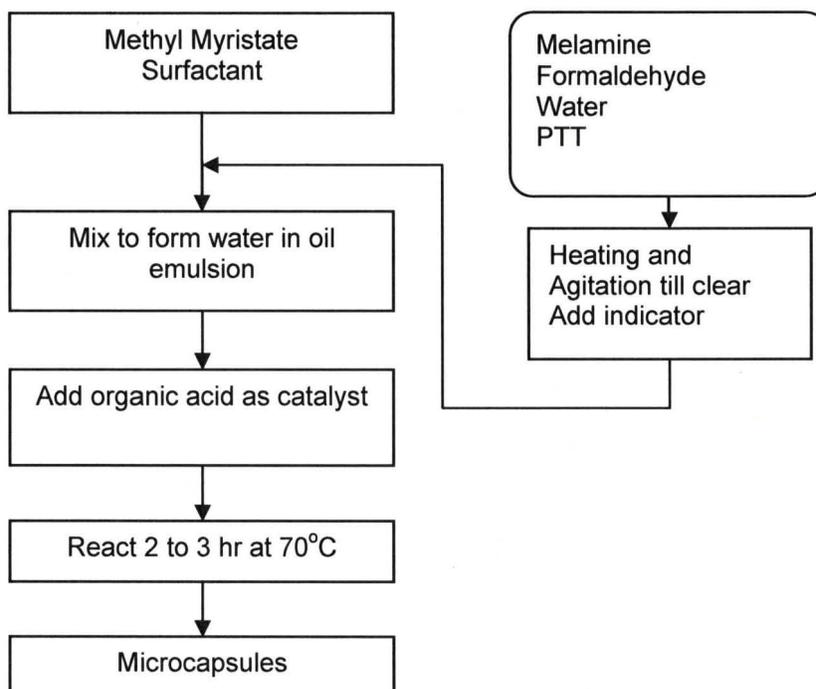
**Figure 27. Synthesis procedure for water-core microcapsules.**

21

Observations under the optical microscope showed that the emulsion was stable and that the water phase droplet size was homogenous. The following SEM images (Figure 28) show that capsules of a little less than 1micron were obtained and that many had the desirable spherical shape.
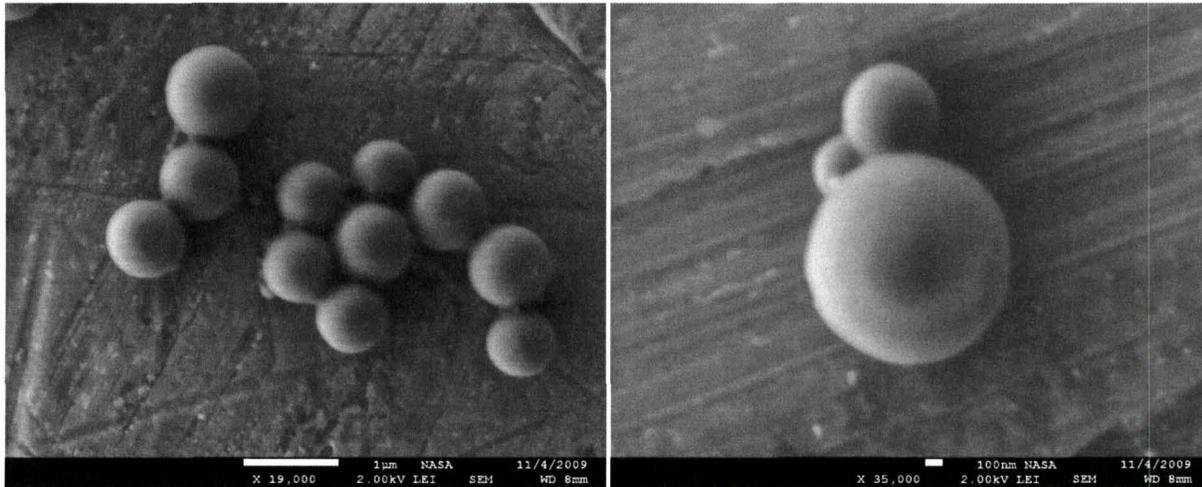
Figure 28. SEM images of the water-core microcapsules with phph.

Water-core Indicator Microcapsule: Testing

A study was performed to compare the corrosion detection functionality of the oil-core and water-core indicator microcapsules. Based on their starting formula, water-core microcapsules contain more indicator. Six round carbon steel coupons were prepared for corrosion evaluations and partially wrapped with copper tape in two different configurations. Agar solutions containing either oil-core or water-core phph microcapsules were poured over the coupons. The ability of the microcapsules to indicate corrosion, as indicated by the appearance of a fuchsia color on the copper tape, was observed over a 4-hour time period. Figure 29 displays pictures of the microcapsules indicating corrosion as a function of time. These pictures clearly show that the higher concentration indicator microcapsules provided earlier detection, as well as a more visible color change over the entire test period.
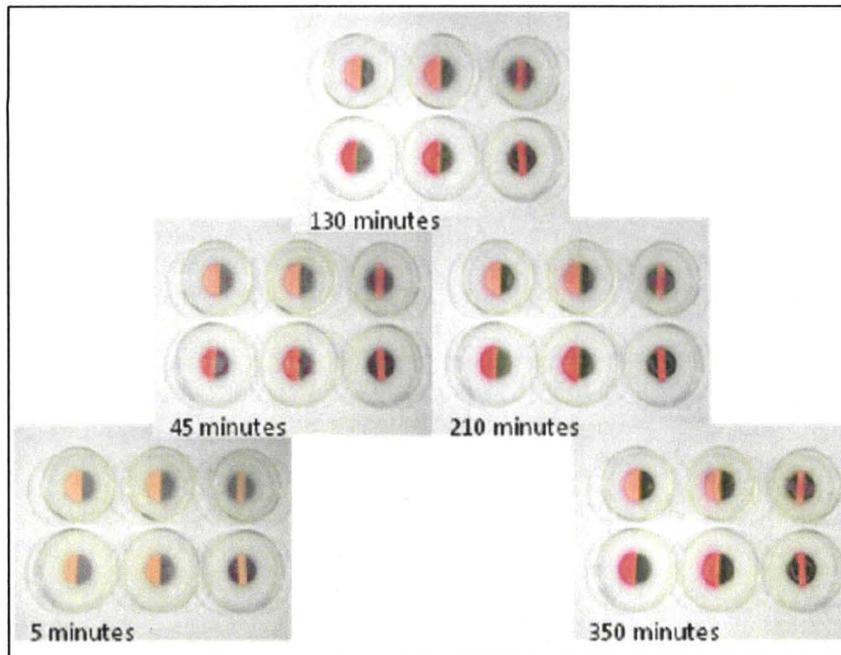
Figure 29. Corrosion indication test with phph oil-core microcapsule in Agar gel. The three samples in the top row contain oil-core microcapsules with lower concentration phph, while the three samples in the bottom row contain water-core microcapsule with higher concentration phph.

Indicator Microparticles

As mentioned above, the intensity of the indicator color change is largely determined by the amount of phph present. Since phph does not dissolve directly in the oil phase or the water phase, its concentration in the microcapsule core is not high enough to provide a color change of the desired intensity to detect corrosion. The phph concentration is about 2 wt% in the oil-core microcapsule and 5 wt% in the water-core microcapsule. In order to increase the amount of phph needed to get a more intense color change, a pH sensitive microparticle formulation was developed and optimized to increase the amount of incorporated phph up to 30 wt%.

A typical formula for pH sensitive microparticles with incorporated phph is shown in Table 5. The flow chart of the experimental procedure is shown in Figure 30. In Figure 31, an SEM image of phph microparticles with sizes of 1 to 2 μm.

Table 5. Microparticle formula with incorporated phph.

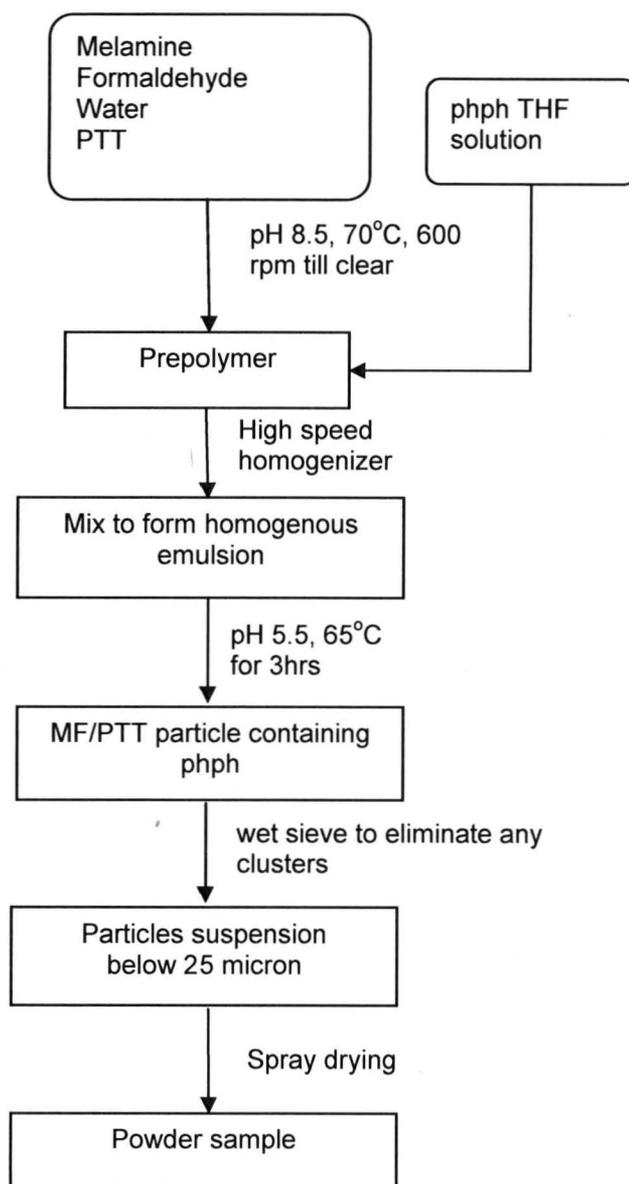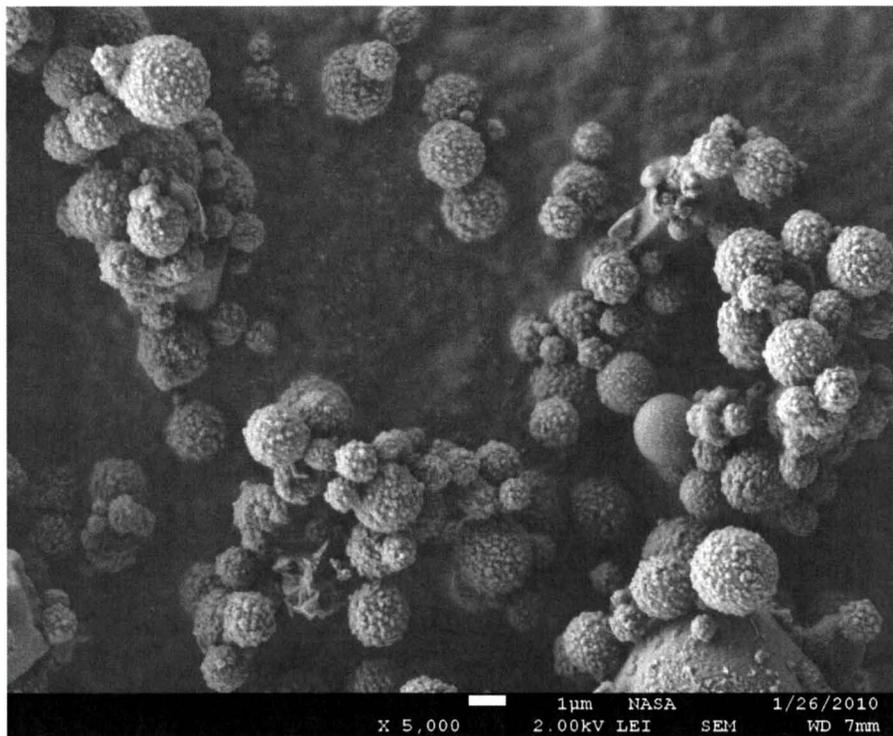| Reagent	Mass (g)
MFPTT resin	
Water	900
Melamine	45
Formaldehyde (37%)	96
PTT	32.5
Surfactant: SDS/Gum	3/3
phph Solution	
phph	50
THF	133
Catalyst	
PTSA	pH 5.5

**Figure 30. Synthesis process of pH sensitive microparticles with incorporated corrosion indicator phph.**

Figure 31. SEM image of phph indicator microparticles.

PROTOTYPE PAINT FORMULATION FOR CORROSION DETECTION

In order to develop a prototype paint formulation for corrosion indication, encapsulated phph was incorporated into different types of coating systems and tested for its effectiveness as a corrosion indicator. Urethane coatings were selected as potential candidates for a prototype corrosion indicating paint formulation. Encapsulated phph was incorporated into a clear urethane coating and its effectiveness as an early corrosion indicating coating as well as a hidden corrosion detecting coating was demonstrated experimentally. Detailed information of the test results follow.

Corrosion indication is one of the functions of the smart coating for corrosion detection, control, and self healing. This function was incorporated into coatings by encapsulating a corrosion indicator into pH sensitive microcapsules. Figure 32 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 in less than a 1 minute after immersion, which is considerably earlier than the 2 hours it takes for the typical color of rust to appear.
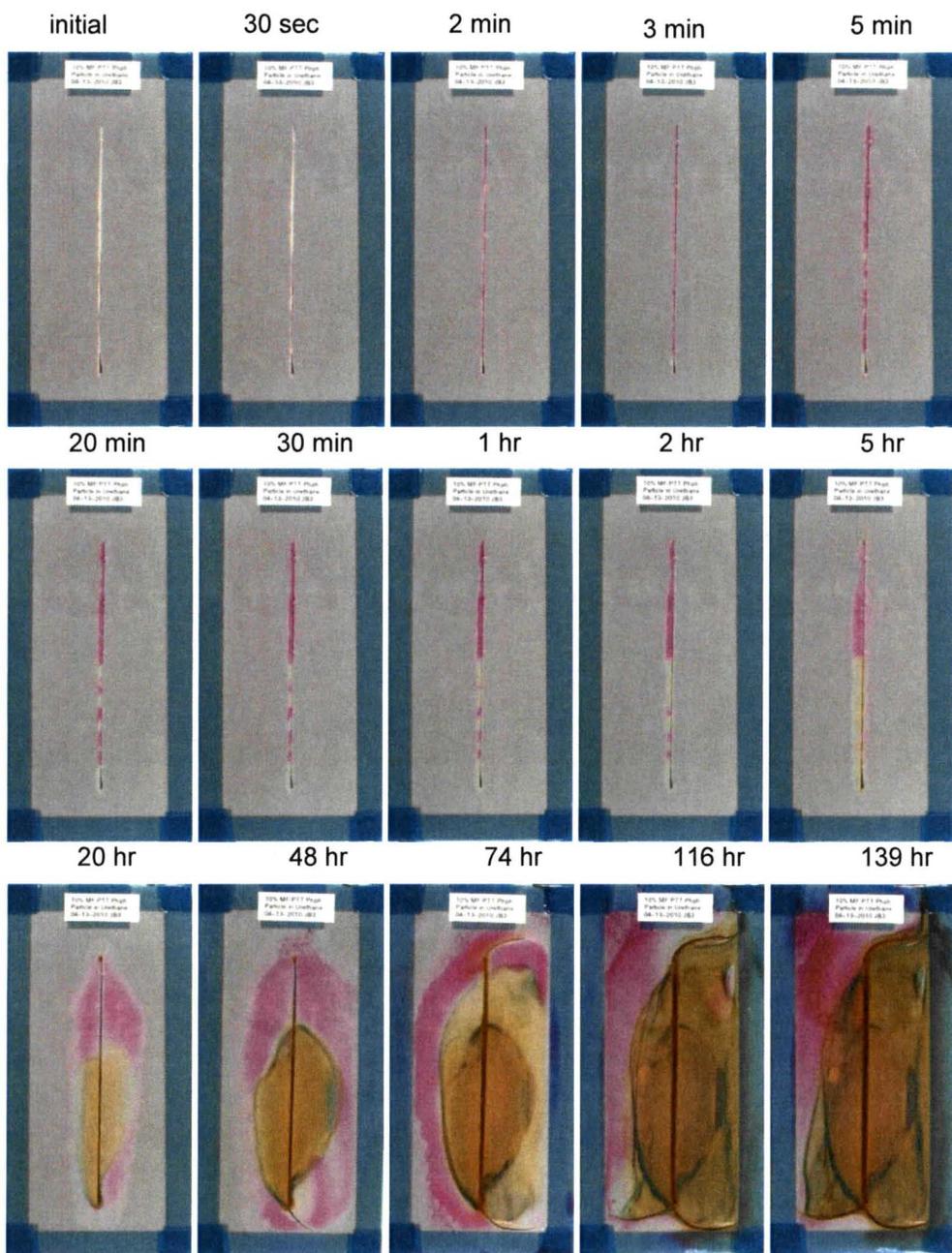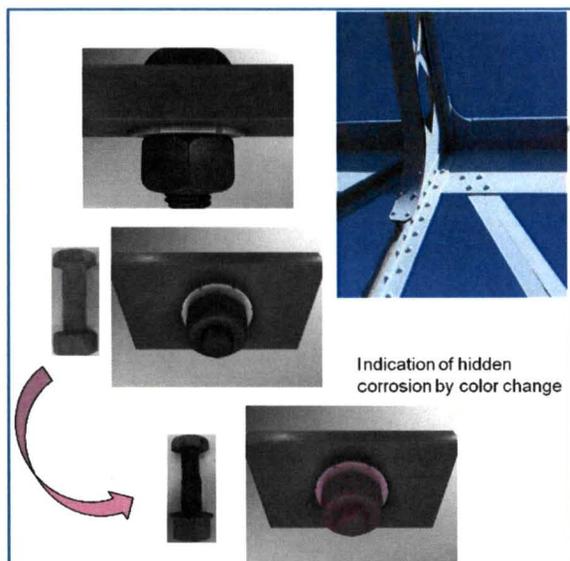
Figure 32. Corrosion indication test results.

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 on structural bolts is shown in Figure 34.

Bolts tend to corrode on the hidden shaft area before visible corrosion is seen on the bolt head or nut. Often, the head and nut are in pristine condition, even when significant corrosion has occurred on the shaft. There is no method to identify the degree of corrosion without removing the bolt from service. A coating that changes color on the bolt head or nut when corrosion starts would greatly facilitate the inspection process and increase the safety and reliability of the structure.

Figure 33. Pad 39B MLP-1: Bolt from Victaulic joint on center upper shield

Indication of hidden corrosion by color change

Figure 34. Conceptual illustration of hidden corrosion indication in structural bolts.

An experiment was designed to test the effectiveness of the encapsulated indicator to detect hidden corrosion when incorporated into a coating system. Several coating systems (Table 6) were prepared in order to find a coating system that would indicate crevice corrosion as can be expected to occur in a nut and bolt set up designed to duplicate the use of bolts to hold a structure. As can be seen in Figure 35., the epoxy/urethane coating system showed the ability of the coating to indicate hidden corrosion as evidenced by the appearance of the purple color.

Table 6. Coating systems used for hidden corrosion indication testing.

System number	Metal Substrate	Coating systems
1	Zinc galvanized nut and bolt	Clear urethane coating containing 10% phenolphthalein (phph) microcapsules.
2	Zinc galvanized nut and bolt	First coated with epoxy, then top coated with clear urethane containing 10% phph microcapsules.
3	Sand blasted nut and bolt.	The ends of the nut and bolt were coated with inorganic zinc coating; the entire nut and bolt was coated with urethane containing 10% phph microcapsules.
4	Sand blasted nut and bolt	The ends of the nut and bolt were coated with inorganic zinc coating. The entire nut and bolt was coated with epoxy and then top coated with a clear urethane containing 10% phph microcapsules.
5	Zinc galvanized nut and bolt	The ends of the nut and bolt were coated with urethane containing 10% phph microcapsules.
6	Zinc galvanized nut and bolt.	The ends of the nut and bolt were coated with epoxy and then top coated with urethane containing 10% phph microcapsules.

Figure 35. Indication of hidden corrosion after 600 hours of salt fog exposure.

SUMMARY

Various pH-sensitive microcapsules and microparticles containing corrosion indicators were synthesized through interfacial polymerization reactions in an emulsion. pH sensitive microparticles with corrosion indicator have also been developed using a modified *in situ* polymerization process as well as a spray drying process. 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.

A prototype smart coating for the autonomous detection of corrosion was prepared by blending pH-sensitive microcapsules and microparticles into commercially available coatings. Preliminary results from salt fog testing of panels, coated with commercially available coatings, in which the microcapsules and particles were incorporated, showed that pH sensitive microcapsules and microparticles can be used to detect corrosion before visible rust appears and to detect corrosion in hidden areas.

ACKNOWLEDGEMENTS

REFERENCES

1. W. L. Dunn, A. M. Yacout, "Corrosion Detection in Aircraft by X-ray Backscatter Methods," *Applied Radiation and Isotopes* 53, 4-5 (2000): p. 625.
2. M. Z. Silva, R. Gouyon, and F. Lepoutre, "Hidden Corrosion Detection in Aircraft Aluminum Structures Using Laser Ultrasonics and Wavelet Transform Signal Analysis, " *Ultrasonics,* 41, 4 (2003): p. 301.
3. J.H. Ali, W. B. Wang, P. P. Ho, R. R. Alfano, "Detection of Corrosion Beneath a Paint Layer by Use of Spectral Polarization Optical Imaging," *Optics Letters* 25,17 (2000): p.1303.
4. V. Agarwala, S. Ahmad, "Corrosion Detection and Monitoring – A Review," Proceedings of Corrosion 2000, paper no.271 (Houston, TX: NACE International, 2000).
5. J. Zhang and G. S. Frankel, "Corrosion-Sensing Behavior of an Acrylic-Based Coating System," *Corrosion* 55 (1999): p. 957.
6. R.E. Johnson and V.S. Agarwala, Fluorescence Based Chemical Sensors for Corrosion Detection, Corrosion1997, paper no. 304 (Houston, TX: NACE International, 1997).
7. R.E. Johnson and V.S. Agarwala, Using Fluorescent Compounds as Early Warning Detectors for Corrosion, *Materials Performance*, April 1994, pp.25-29.
8. G. S. Frankel, et al., Corrosion-Sensing Composition and Method of Use, US patent application 20030068824.
9. A. Kumar and L.D. Stephenson, "Smart Coatings," 23rd Army Science Conference, Orlando, Florida, December 2002, http://www.asc2002.com/summaries/a/AP-16.pdf
10. A. Augustyniak, J.Tsavalas, and W. Ming, "Early Detection of Steel Corrosion via "Turn-On" Fluorescence in Smart Epoxy Coatigs," *Applied Materals & Interfaces* 1,11 (2009): p. 2618.
11. U.R. Evans, *The Corrosion and Oxidation of Metals* (London, U.K.: Edward Arnold Pub. Ltd., 1960), p. 117.

12. H. S. Isaacs, G, Adzic, and C. S. Jeffcoate, "Visualizing Corrosion," *Corrosion* 56 (2000): p.971

13. O. B. Miled, D. Grosso, C. Sanchez, J. Livage, "An Optical Fibre pH Sensor Based on Dye Doped Mesostructured Silica," *Journal of Physics and Chemistry of Solids* 65, 10 (2004): p.1751.

14. M. P. Sibi and Z. Zong, "Determination of Corrosion on Aluminum Alloy under Protective Coatings Using Fluorescent Probes," *Progress in Organic Coatings* 47 (2003): p. 8.

15. D. E. Bryant, and D. Greenfield, "The Use of Fluorescent Probes for the Detection of Under-film Corrosion," *Progress in Organic Coatings* 57 (2006): p.416

16. M.G. Durrett, R. E. Johnson, and V. S. Agarwala, "ICI, Intelligent Corrosion Indicator, and its Use for the Early Detection of Corrosion on Aluminum Alloy Surfaces by Florescence," Corrosion 2000, Paper No. 00285 (Nashville, TN, 2000).

17. S-M. Li, H-R. Zhang, and J-H Liu, "Preparation and Performance of Fluorescent Sensing Coating for Monitoring Corrosion of Al Alloy 2024," *Transactions of Nonferrous Metals Society of China* 16 (2006): p. S159.

18. 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 (2000): p.111.

19. W. Li and L. M. Calle, "pH and Electrochemical Responsive Materials for Corrosion Control Applications", NACE Corrosion 2008, Paper 08214 (Nashville, TN, 2008).

20. L. M. Calle and W. Li, "Coatings and Methods for Corrosion Detection and/or Reduction," US Patent 7,790,225.

21. W. Li and L. M. Calle, "Controlled Release Microcapsules for Smart Coatings," NACE Corrosion 2007, Paper 07228 (Nashville, TN, 2007).

22. 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

23. http://en.wikipedia.org/wiki/PH_indicator